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# Exchange coupling in transition-metal ferromagnets

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The interatomic exchange integrals $J_{ij}$, associated with effective interactions between local magnetic moments at sites $i$ and $j$ in bcc Fe, fcc Co, and fcc Ni are calculated using the real-space linear-muffin-tin method within the atomic sphere approximation (LMTO-ASA). Our results are in excellent agreement with those obtained by $k$-space LMTO-ASA calculations.

Well-defined atomic moments in itinerant systems such as Fe, Co, and Ni exist over a rather wide range of temperatures. The magnitudes of such moments are fairly constant at low temperatures, although their directions may fluctuate, however slowly compared with typical hopping frequencies. In such a temperature range, the magnetic excitations in these systems can be described in terms of an effective Heisenberg model with interatomic exchange integrals that are calculable from first-principles spin-density-functional theory.[1–3] Exchange-coupled spin-fluctuation theories using an adiabatic approximation for the spin orientations have been recently revived to study the spin dynamics of itinerant ferromagnets at finite temperatures.[4,5] They develop original ideas of the late 1970s and 1980s,[6–10] expanding the applicability of the local moment picture, by avoiding the use of mean field theory and assumptions on the degree of short-range magnetic order.

Most of the first-principles methods for calculating interatomic exchange interactions in magnetic systems take advantage of the existence of translation symmetry, and determine the electronic structure of the material in the reciprocal space. However, there has been growing interest in magnetic structures lacking translational symmetry such as interfaces with steps and terraces of variable sizes, nanoparticles deposited on clean surfaces,[11] granular materials,[12] and nanoscopic metallic magnetic clusters encapsulated by a nonmagnetic material.[13] In fact, recent advances in experimental techniques have allowed a refined application to the growth of those heterostructures, and it is important for magnetic technology to have information about the magnetic interactions inside and between the constituent magnetic units. In the absence of translational symmetry it is much more convenient to describe the electronic structure of the system in real space. The real-space linear-muffin-tin method within the atomic sphere approximation (RS-LMTO-ASA) method has been devised to treat complex metallic structures with a large number of inequivalent atoms. It has been previously employed with success to examine substitutional and interstitial impurities in metallic hosts, as well as other defects in metals and metallic surfaces.[14] In the present work, we have used the theory developed in the literature,[1,2] and adapted it to the RS-LMTO-ASA method, in order to study the exchange coupling in magnetic metallic systems. However, before attempting to deal with composite structures, it is important to show that our approach produces results compatible with other methods.

Here, we calculate interatomic exchange integrals $J_{ij}$ between local magnetic moments at various sites $i$ and $j$ in bcc Fe, fcc Co, and Ni using the RS-LMTO-ASA approach and compare our results with those obtained by well established $k$-space LMTO-ASA calculations.[15,16] The RS-LMTO-ASA scheme follows the steps of the LMTO-ASA formalism, but uses the recursion method[17] to solve the eigenvalue problem directly in real space. It is a linear method and the solutions are accurate near a given energy $E_\nu$, usually taken at the center of gravity of the occupied bands. We work in the orthogonal representation of the LMTO-ASA formalism, and expand the Hamiltonian in terms of tight-binding (TB) parameters, neglecting terms of order $(E-E_\nu)^3$ and higher. The orthogonal Hamiltonian can then be written as[18]

$$H=E_\nu+\overline{h}-\overline{hoh}, \tag{1}$$

where

$$\overline{h}=\overline{C}-E_\nu+\overline{\Delta}^{1/2}\overline{S}\overline{\Delta}^{1/2}. \tag{2}$$

Here $\overline{h}$ is a Hermitian matrix, $\overline{C}$, $\overline{\Delta}$ and $\overline{o}$ are potential parameters of the tight-binding LMTO-ASA representation, and $\overline{S}$ is the structure constant in this representation. The matrix $\overline{S}$ connecting different sites decays exponentially with intersite distance, and $\overline{h}$ has a TB form. To solve the eigenvalue problem in real space, we consider a large cluster to simulate the system, and use the recursion method[17] with the Beer-Pettifor terminator[19] to complete the recursion chain. The method is rather general and may be employed to calculate any desired one-electron property. It yields on-site and intersite Green's functions; two recursion calculations are required to determine the intersite propagators. A more detailed description of the procedure in the context of RS-LMTO-ASA calculations can be found elsewhere.[20]

Under appropriate conditions, spin fluctuations in itinerant electron ferromagnets can be described in terms of a classical effective Heisenberg Hamiltonian $\mathcal{H} = -\Sigma'_{ij} J_{ij} \hat{e}_i \cdot \hat{e}_j$, where $\hat{e}_i$ is a unit vector indicating the direction of the moment at site *i*. The magnitudes of the moments have been folded into the pair interactions. In this context, the pair interactions $J_{ij}$ may be obtained from the energy necessary to perform infinitesimal rotations of opposite angles in the directions of the local magnetic moments at sites *i* and *j*, respectively. Using the force theorem and Lloyd's formula, expressions for $J_{ij}$ can be derived in terms of scattering path operators and matrices,[1,2] which are suitable for use in first-principle calculations based on spin-density-functional theory. A similar approach has been recently developed in the framework of the *k*-space TB-LMTO method.[16] Within the RS-LMTO-ASA scheme, it is more convenient to express $J_{ij}$ in terms of the true Green's functions, which have dimensions of the inverse of energy. Using the relation between true and auxiliary Green's functions[3,21] in the orthogonal representation, where the second derivative of the potential function is zero, we obtain

$$J_{ij} = \frac{\mathrm{Im\,Tr}}{4\pi} \int_{-\infty}^{E_F} dE [\delta_i(E) G_{ij}^{\uparrow\uparrow}(E) \delta_j(E) G_{ji}^{\downarrow\downarrow}(E)], \tag{3}$$

where the trace is over orbital indices, $G_{ij}^{\sigma\sigma}$ is the propagator for electrons with spin $\sigma$ between sites *i* and *j* in the ferromagnetic configuration, and $\delta_i$ is a diagonal matrix in orbital indices whose elements are

$$\delta_{li}(E) = \frac{C_{li}^{\downarrow}\Delta_{li}^{\uparrow} - C_{li}^{\uparrow}\Delta_{li}^{\downarrow} + (\Delta_{li}^{\downarrow} - \Delta_{li}^{\uparrow})E}{(\Delta_{li}^{\uparrow}\Delta_{li}^{\downarrow})^{\frac{1}{2}}}. \tag{4}$$

Here, $C_{li}^{\sigma}$ and $\Delta_{li}^{\sigma}$ are potential parameters at site *i* of the orthogonal LMTO-ASA representation,[18] and $l = 0$, 1, and 2, are associated with *s*, *p*, and *d* electrons.

The quantity $\delta_i(E)$ has units of energy and may be associated with an energy-dependent local exchange splitting at site *i*. We note that when $\Delta_i^{\uparrow} = \Delta_i^{\downarrow}$, the energy dependence of $\delta_i(E)$ disappears, and it reduces to $\delta_i = C_i^{\downarrow} - C_i^{\uparrow}$, which is the difference between the centers of the up-spin and down-spin bands. Such energy-independent exchange splittings are frequently used in parametrized TB calculations. Usually, it is assumed that the *d*-band exchange splitting $\delta_{di}$ satisfies the Stoner relation $\delta_{di} = m_i I_{di}$, where $m_i$ is the local magnetic moment at site *i*, and $I_{di}$ is associated with the effective Coulomb interaction between *d* electrons at the same site.[18] Because the spin splitting of *s*- and *p*-like states is very small compared to that of the *d*-like states, $\delta_{spi}$ is often set equal to zero.[10,22]

Using well established relations,[3,16,21] we can write the effective exchange interaction of the local moment at site 0 with all other moments $J_0 = \Sigma_{j \neq 0} J_{0j}$ as

$$J_0 = -\frac{\mathrm{Im\,Tr}}{4\pi} \int_{-\infty}^{E_F} dE \Big\{ \delta_0(E) G_{00}^{\uparrow\uparrow}(E) \delta_0(E) G_{00}^{\downarrow\downarrow}(E) + \delta_0(E) \times \Big[ \Delta_0^{\downarrow -1/2} \Delta_0^{\uparrow 1/2} G_{00}^{\uparrow\uparrow}(E) - \Delta_0^{\uparrow -\frac{1}{2}} \Delta_0^{\downarrow \frac{1}{2}} G_{00}^{\downarrow\downarrow}(E) \Big] \Big\}. \tag{5}$$

With Eqs. (3) and (5), one can obtain $J_{ij}$ and $J_0$ from first principles. All Green's functions and potential parameters involved are determined by the RS-LMTO-ASA method. The procedure described here is formulated entirely in real space and does not require the system to have translational symmetry. Therefore, it is suitable for determining exchange interactions in complex metallic structures such as clusters of magnetic atoms in metals and metallic surfaces.

We have employed such a procedure to obtain $J_{ij}$ and $J_0$ for Fe, Co, and Ni. Our calculations were performed using large clusters of $\approx 8000$ atoms built for the appropriate structure with the corresponding experimental lattice parameters. We have considered a basis with 9 orbitals per site (corresponding to *s*, *p*, and *d* electrons) and have used 30 levels of recursion. We performed scalar relativistic calculations within the local spin-density approximation (LSDA), with the exchange and correlation potential of von Barth and Hedin.[23] We have taken $\bar{h}$ to connect the first 12 neighbors of the fcc structure, and the 14 first and second neighbors of the bcc structure. Since in the second-order term $\bar{h}$ is applied twice, the Hamiltonian *H* in Eq. (1) connects many more sites. To test our numerical accuracy, we first consider a cluster of 13 Co atoms embedded in a nonpolarized Cu matrix. Values of $J_{ij}$ between all Co sites were calculated as well as the effective exchange interaction $J_0$ for the central Co atom and its 12 neighbors at the Co-Cu interface. The nonpolarized Cu atoms do not explicitly contribute to $J_0$, and the sum rule $J_0 = \Sigma_{j \neq 0} J_{0j}$ was verified both for the central Co and for its neighbors.

In Table I, we present results for the interatomic exchange interactions $J_{ij}$ in fcc Ni and Co. We fix a site *i* and consider different sites *j* along the directions indicated in the first column of the table. Results obtained by two different groups using *k*-space LMTO-ASA formalism[15,16] are also shown for comparison. Calculated values of the effective exchange interaction $J_0$ are given in the last line. In Table II, we present our results for $J_{ij}$ and $J_0$ in bcc Fe. Previous results obtained by *k*-space LMTO-ASA calculations are given in the last two columns of Table II. The *s*-*d*, *p*-*d*, and *d*-*d* contributions to $J_{ij}$ are also shown. Clearly, our calculated values of $J_{ij}$ and $J_0$ using the RS-LMTO-ASA method are in excellent agreement with those obtained using *k*-space approaches with similar LMTO-ASA Hamiltonians.[15,16] They are also consistent with plots of $J_{ij}$ as a function of intersite distances $R_{ij}$ published recently for these elements.[3] As expected by previous model calculations,[24] we have found that the decrease of $|J_{ij}|$ as a function of $R_{ij}$ is faster in fcc Ni and Co than in bcc Fe, where it exhibits a long-range oscillatory behavior. In the first columns of Table II, we show the *s*-*d*, *p*-*d*, and *d*-*d* contributions to $J_{ij}$ in bcc Fe. The other contributions are extremely small and are not shown. The exchange interactions in ferromagnetic transition metals are expected to be dominated by *d* electrons and the contributions of *s* and *p* orbitals are often neglected. Our results for $J_{ij}$ confirm such expectations. The *s*-*d* and *p*-*d* contributions are not completely negligible, but the *d*-*d* contributions to $J_{ij}$ are dominant and account for most of the effect.

In spite of the good agreement with previous *k*-space LMTO-ASA calculations, our results for $J_{ij}$ in bcc Fe differ from those obtained in real space by Spišák and Hafner.[25]

TABLE I. Results (in mRy) of real space and *k*-space (Refs. 15 and 16) LMTO-ASA calculations of $J_{ij}$ between the 10 first neighbors in ferromagnetic Ni and Co. Values of $J_0$ are also shown.

| | | fcc Ni | | | fcc Co | |
|---|---|---|---|---|---|---|
| Site | RS | Ref. 15 | Ref. 16 | RS | Ref. 15 | Ref. 16 |
| (110) | 0.206 | 0.210 | 0.204 | 1.00 | 1.02 | 1.07 |
| (200) | 0.014 | 0.000 | 0.003 | 0.091 | 0.084 | 0.110 |
| (211) | 0.032 | 0.026 | 0.025 | 0.126 | 0.118 | 0.116 |
| (220) | 0.012 | 0.011 | 0.010 | -0.118 | -0.110 | -0.086 |
| (310) | 0.005 | 0.036 | 0.004 | 0.026 | 0.027 | 0.027 |
| (222) | -0.001 | 0.000 | -0.004 | 0.041 | 0.047 | 0.048 |
| (321) | 0.007 | 0.007 | 0.007 | -0.021 | -0.022 | -0.022 |
| (400) | -0.001 | 0.000 | -0.001 | 0.016 | 0.015 | 0.013 |
| (330) | -0.012 | | -0.011 | 0.028 | | 0.028 |
| (411) | 0.000 | | 0.001 | 0.004 | | 0.008 |
| $J_0$ | 3.31 | 3.82 | 3.73 | 14.51 | 14.88 | 15.63 |

There is a factor of two difference between our definitions of $J_{ij}$, but this is a trivial factor that can easily be taken into account when comparing the results. One of the major differences is the relative importance of the *p*-*d* contributions to $J_{ij}$ compared to the *d*-*d* ones. Our calculations (see Table II) show that the former are, roughly, one order of magnitude smaller than the latter, whereas Spišák and Hafner report them as being of the same order. The reason for this discrepancy may be partially due to the approximate expression that they have used to calculate $J_{ij}$. Equation (7) in their paper, holds when the exchange splitting $\delta_i$ is constant, i.e., both energy and orbital independent. Then it can be taken outside both the integral in energy and the trace over orbitals that occur in Eq. (3). Their expression also holds when the exchange splitting is assumed constant for all *d* orbitals, and zero for *s* and *p* ones. However, in such a case, the trace in Eq. (3) is restricted to *d* orbitals only, and no explicit *sp*-*d* contributions to $J_{ij}$ are expected. The use of a constant exchange splitting $\delta_i = m_i I_{di}$ when calculating contributions of *sp* orbitals enhance their values considerably and may explain the large *sp*-*d* contributions they have reported.[25]

Finally, it is interesting to examine the effect of the explicit energy dependence of $\delta_i(E)$ in the calculations of $J_{ij}$. To investigate this effect, we split $\delta_i(E)$ into energy-independent and energy-dependent terms and evaluate their contributions separately. Using (4), we divide the integrand of (3) into three parts according to the energy dependence of the terms multiplying the Green's functions: the first is constant in energy and only involves the energy-independent term of the exchange splitting $\delta_i$, while the second and third parts are, respectively, linear and quadratic in energy and involve the energy-dependent term of $\delta_i$. In Table III, we show those contributions, together with the full values of $J_{ij}$, for some pairs of sites $ij$ in fcc Ni, fcc Co, and bcc Fe. The quadratic contribution is clearly negligible. The linear one is usually small, but may be important in some cases, such as for $J_{ij}$ between nearest neighbors in bcc Fe. The explicit energy dependence of $\delta_i$ in this case accounts for approximately one-third of the $J_{ij}$ value.

Summarizing, we have calculated from first-principles the effective exchange interactions $J_{ij}$ and $J_0$ for ferromagnetic fcc Co and Ni and bcc Fe within the RS-LMTO-ASA

TABLE II. Real-space results (in mRy) for the *s*-*p*, *p*-*d*, and *d*-*d* contributions, and the total $J_{ij}$ in bcc Fe. In the last two columns, *k*-space results for $J_{ij}$ are shown for comparison. Values of $J_0$ are shown in the last line.

| bcc Fe | | Real space(RS) | | | *k* space | |
|---|---|---|---|---|---|---|
| Site | *s*-*d* | *p*-*d* | *d*-*d* | Total | Ref. 15 | Ref. 16 |
| (111) | -0.047 | -0.089 | 1.33 | 1.20 | 1.24 | 1.45 |
| (200) | -0.001 | -0.064 | 0.760 | 0.692 | 0.646 | 0.793 |
| (220) | 0.001 | -0.007 | -0.024 | -0.030 | 0.007 | -0.023 |
| (311) | -0.003 | -0.004 | -0.091 | -0.100 | -0.108 | -0.109 |
| (222) | -0.001 | 0.007 | -0.077 | -0.068 | -0.071 | -0.136 |
| (400) | -0.003 | -0.004 | 0.049 | 0.042 | 0.035 | 0.053 |
| (331) | 0.000 | -0.001 | -0.001 | -0.001 | 0.002 | 0.000 |
| (420) | 0.000 | 0.000 | 0.014 | 0.014 | 0.014 | 0.014 |
| (422) | 0.000 | 0.000 | -0.020 | -0.020 | | -0.031 |
| (333) | 0.001 | -0.002 | 0.139 | 0.138 | 0.157 | 0.172 |
| (511) | 0.000 | 0.000 | 0.023 | 0.023 | | 0.013 |
| $J_0$ | | | | 11.03 | 12.38 | 13.58 |

TABLE III. Real-space results (in mRy) for $J_{ij}$ (total) in ferromagnetic Fe, Ni, and Co. Contributions coming from the constant (const.), linear term (linear), and quadratic term (quadr.) are also shown.

| | Site | Quadr. | Linear | Const. | Total |
|---|---|---|---|---|---|
| | (111) | 0.011 | 0.422 | 0.763 | 1.20 |
| Fe | (200) | 0.002 | -0.064 | 0.754 | 0.692 |
| | (220) | -0.002 | 0.020 | -0.048 | -0.030 |
| | (110) | 0.002 | 0.044 | -0.248 | -0.206 |
| Ni | (200) | 0.001 | -0.009 | 0.022 | 0.014 |
| | (211) | 0.000 | -0.009 | 0.041 | 0.032 |
| | (110) | 0.000 | -0.032 | 1.03 | 1.00 |
| Co | (200) | 0.001 | -0.042 | 0.131 | 0.091 |
| | (211) | 0.000 | -0.012 | 0.139 | 0.126 |

scheme. The procedure is entirely formulated in real space, and since it does not require the system to be periodic, it can be employed to study complex structures. Our results are in excellent agreement with those obtained using $k$-space LMTO-ASA formalism. The exchange splitting $\delta_i$ that appears in the expression of $J_{ij}$ is energy dependent. However, when the spin dependence of the potential parameter $\Delta_i$, associated with hopping, is neglected, $\delta_i$ becomes energy independent. Then for $d$ orbitals the relation $\delta_{di}=m_i I_{di}$, frequently used in parametrized calculations, is retrieved. We have also examined the effect of the explicit energy dependence of $\delta_i(E)$ in the calculations of $J_{ij}$. This effect is usually small, but may be important in some cases and neglecting the energy dependence of $\delta_i$ could lead to inaccurate values of $J_{ij}$. In contrast with previous orbital resolved calculation for bcc Fe,[25] we found that the contribution of $sp$ orbitals to $J_{ij}$ is roughly one order of magnitude smaller than that of $d$ orbitals. The large $sp$-$d$ contributions reported in Ref. 25 are probably due to the use of a simplified expression to calculate $J_{ij}$.

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