A new scheme to calculate the exchange tensor and its application to diluted magnetic semiconductors

H. Ebert and S. Mankovsky

Universität München, Dept. Chemie und Biochemie/Phys. Chemie, Butenandtstr. 5–13, D–81377 München, Germany

(Dated: December 5, 2008)

Abstract

A new scheme to calculate the exchange tensor $J_{ij}$ describing in a phenomenological way the anisotropic exchange coupling of two moments in a magnetically ordered system is presented. The ab-initio approach is based on spin-polarised relativistic multiple-scattering theory within the framework of spin-density functional theory. The scheme is applied to ferromagnetic CrTe as well as the diluted magnetic semiconductor (DMS) system Ga$_{1-x}$Mn$_x$As. In the later case the results show that there is a noticeable anisotropy in the exchange coupling present, although not as pronounced as suggested in recent theoretical investigations.

PACS numbers: Valid PACS appear here
I. INTRODUCTION

The mapping of the energy of a magnetic solid calculated from first principles for different magnetic configurations onto a Heisenberg Hamiltonian is nowadays a widely used concept that allows a number of interesting subsequent investigations. An example for this is the determination of the Curie temperature of a ferromagnet by means of Monte Carlo simulations using the calculated exchange coupling parameters \( J_{ij} \) as input (\( i \) and \( j \) are indices labeling the individual atomic sites) \[1\]. Apart from fitting the \( J_{ij} \)'s to the total energies obtained for different magnetic configurations one can use the energies of spin spirals as basis for such a mapping \[2\]. As an alternative one may use perturbation theory, that allow to calculate the \( J_{ij} \)'s directly. In fact the expression derived by Lichtenstein et al. \[3\] within the framework of non-relativistic multiple scattering theory is now successfully used for a wide range of materials \[4, 5, 6\].

Initiated among others by investigations on the magnetic ground state configuration of nano-scale systems, there is strongly growing interest in the interplay of exchange coupling and spin-orbit coupling \[7\]. Besides the magnetic anisotropy energy, the spin-orbit coupling gives rise to an anisotropic exchange coupling. Using again the above mentioned concept the isotropic exchange constants \( J_{ij} \) have to be replaced by a corresponding exchange coupling tensor \( \bar{J}_{ij} \). By generalising the approach of Lichtenstein et al. to a fully relativistic formulation, Udvardi et al. \[8\] could derive corresponding expressions for the elements of \( \bar{J}_{ij} \). Corresponding applications to thin films as well as to finite deposited clusters can be found in the literature \[8, 9\]. A disadvantage of the expressions worked out by Udvardi et al. \[8\] is that one has to use various magnetic configurations as a reference state to determine all elements of \( \bar{J}_{ij} \). In the following we present an alternative approach that can be derived in a rather transparent way and does not have that problem. As it is demonstrated both approaches give nevertheless results that are quite close to each other. As an application of our new scheme we present results for the exchange tensor \( \bar{J}_{ij} \) in ferromagnetic CrTe and in the diluted magnetic semiconductor (DMS) system Ga\(_{1-x}\)Mn\(_x\)As. The later will be discussed in relation to recent work of Timm and MacDonald \[10\] who used a tight-binding description of the system in contrast to the ab-initio approach employed here that is based on local spin density approximation (LSDA).
II. THEORETICAL APPROACH

Starting point of our derivation for $J_{ij}$ is the expression for the change in energy $\Delta E_{ij}$ of a system upon a perturbation taking place at sites $i$ and $j$. An expression for $\Delta E_{ij}$ was worked out by several authors [3, 11] within the framework of multiple scattering theory and making use of Lloyd’s formula. The derivation of this expression can straightforwardly be applied when working in the framework of spin-polarised relativistic multiple scattering or KKR [12] formalism. Adopting the convention for the corresponding electronic Green’s function as used by Dederichs and coworkers [13] its off-site part is given by:

$$G(\vec{r}_i, \vec{r}_j, E) = -ip\sum_{\Lambda\Lambda'} R^i_{\Lambda}(\vec{r}_i, E)G^{ij}_{\Lambda\Lambda'}(E)R^j_{\Lambda'}(\vec{r}_j, E), \quad (1)$$

where $G^{ij}_{\Lambda\Lambda'}(E)$ is the so-called structural Green’s function, $R^i_{\Lambda}$ is a regular solution to the single-site Dirac equation labeled by the combined quantum numbers $\Lambda$ ($\Lambda = (\kappa, \mu)$), with $\kappa$ and $\mu$ being the spin-orbit and magnetic quantum numbers [14] and $p$ is the electron momentum. The energy change $\Delta E_{ij}$ can then be written as [3, 11]

$$\Delta E_{ij} = -\frac{1}{\pi} \Im \int dE \text{Trace} \Delta t^{ij} G^{ij} \Delta t^{ji}, \quad (2)$$

where $\Delta t^{ij}$ is the change of the single-site $t$-matrix due to the perturbation $\Delta V^i(\vec{r})$ at site $i$ and the underline denotes matrices with respect to the quantum numbers $\Lambda$. To first order in $\Delta V^i(\vec{r})$ the change $\Delta t^{ij}$ is given by

$$\Delta t^{ij}_{\Lambda\Lambda'} = \int d^3r R^{ij}_{\Lambda'}(\vec{r}) \Delta V(\vec{r}) R^i_{\Lambda}(\vec{r}) = \Delta V^{(R)}_{\Lambda\Lambda'} \cdot \quad (3)$$

Using instead the convention for the Green’s function as used by Győrffy and coworkers [15] one may express $\Delta E_{ij}$ in terms of the scattering path operator $\tau^{ij}_{\Lambda\Lambda'}(E)$

$$\Delta E_{ij} = -\frac{1}{\pi} \Im \int dE \text{Trace} \Delta V^{(Z)}_{\Lambda\Lambda'} \tau^{ij} \Delta V^{(Z)}_{\Lambda\Lambda'} \tau^{ji}, \quad (4)$$

where use have been made of the relation $G^{ij} = (\tau^i)^{-1} \tau^{ij} (\tau^j)^{-1}$ for $i \neq j$ and the matrix elements $\Delta V^{(Z)}_{\Lambda\Lambda'}$ are to be evaluated using the alternative set of regular solutions $Z^i_{\Lambda}$ to the single-site Dirac equation [12, 15].
Changing the orientation of the spin magnetic moment \( \vec{m}_i \) within an atomic cell \( i \) and adopting the rigid spin approximation (RSA) \[16\] implies a corresponding change of the spin-dependent potential \( \beta \vec{\sigma} \vec{B}(\vec{r}) \) by:

\[
\Delta V(\vec{r}) = V_\vec{n}(\vec{r}) - V_{\vec{n}_0}(\vec{r}) = \beta \vec{\sigma}(\hat{n} - \hat{n}_0)B(\vec{r}) ,
\]

where \( \beta \) is one of the standard Dirac matrices and \( \vec{\sigma} \) is the vector of 4 \( \times \) 4-spin matrices \[16\]. In writing Eq. \((5)\) a collinear spin magnetisation within the cell has been assumed together with a change of its orientation from \( \hat{n}_0 \) to \( \hat{n} \). Accordingly, \( B(\vec{r}) \) corresponds to the difference of the spin-projected potential functions \( B(\vec{r}) = \frac{1}{2}(V^\uparrow(\vec{r}) - V^\downarrow(\vec{r})) \) \[12\]. This leads for the matrix elements \( \Delta V^{(Z)\alpha}_{\Lambda\Lambda'} \) to:

\[
\Delta V^{(Z)\alpha}_{\Lambda\Lambda'} = \sum_{\alpha=x,y,z} \Delta V^{(Z)\alpha\alpha}_{\Lambda\Lambda'} \Delta \alpha
\]

with

\[
\Delta V^{(Z)\alpha\alpha}_{\Lambda\Lambda'} = \int d^3 r Z^\alpha_{\Lambda}(\vec{r}) \beta \sigma_\alpha B(\vec{r}) Z^{\Lambda'}_{\Lambda'}(\vec{r}) .
\]

Comparison with the generalised Heisenberg Hamiltonian

\[
H_{ex} = -\frac{1}{2} \sum_{i,j} \hat{\epsilon}_i J_{ij} \hat{\epsilon}_j
\]

with \( \hat{\epsilon}_{i(j)} \) the orientation of the spin magnetic moment at site \( i(j) \) allows one to write for the elements of the exchange coupling tensor \( J_{ij} \)

\[
J^{\alpha_1\alpha_j}_{ij} = -\frac{1}{\pi} \Im \int dE \text{Trace}\Delta V^{(Z)\alpha_1\alpha_j}_{ij} \Delta V^{(Z)\alpha_j\alpha_1}_{ji} .
\]

The scheme outlined above has been implemented using the spin-polarised relativistic (SPR) version of multiple scattering theory \[12, 15\]. All calculations have been done within the framework of the local spin density approximation (LSDA) to spin density functional theory \[17\]. To represent the results for the exchange tensor \( J_{ij} \) we use the conventional decomposition of the corresponding Heisenberg Hamiltonian in Eq. \([8] \):
FIG. 1: Isotropic exchange interaction parameters $J_{ij}$ between Cr atoms at sites $i$ and $j$ in ferromagnetic CrTe as a function of the inter-atomic distance $R_{ij}$. The results based on the present approach (full symbols) are compared to results obtained using the approach of Udvardi et al. [8] (open symbols). Circles and squares represent the coupling of a Cr atom in layer 1 (Cr1) to another Cr atom in layer 1 (Cr1) or layer 2 (Cr2), respectively.

$$H_{ex} = -\frac{1}{2} \sum_{ij} \hat{e}_i J_{ij} \hat{e}_j - \frac{1}{2} \sum_{ij} \hat{e}_i J^S_{ij} \hat{e}_j$$

$$-\frac{1}{2} \sum_{ij} \vec{D}_{ij} [\hat{e}_i \times \hat{e}_j].$$

Here $J_{ij}$ is the isotropic exchange coupling constant, $J^S_{ij}$ is the traceless symmetric part of $J_{ij}$ and the antisymmetric part is represented by the Dzyaloshinski-Moriya (DM) vector $\vec{D}_{ij}$. It should be emphasized that isotropic in the context of $J_{ij}$ refers to spin-space and does not imply that there is no anisotropy in real space, i.e. $J_{ij}$ will in general not only depend on the distance $|\vec{R}_{ij}|$ between two sites but also on the orientation $\hat{R}_{ij}$ of the distance vector.

III. RESULTS AND DISCUSSION

To demonstrate the application of our approach we present in Figs. 1 and 2 results for the coupling parameters $J_{ij}$ and $\vec{D}_{ij}$ of the two inequivalent Cr atoms in ferromagnetic CrTe having the NiAs structure. The isotropic parameters $J_{ij}$ shown in Fig. 1 reflect dominating ferromagnetic coupling that is quite far reaching, i.e. slowly decaying. As one notes the
FIG. 2: Components of the Dzyaloshinski-Moriya interaction vector $\vec{D}_{ij}$ (from top to bottom: $x, y, z$) between Cr atoms at sites $i$ and $j$ in ferromagnetic CrTe as a function of the inter-atomic distance $R_{ij}$. The results based on the present approach (full circles) are compared to results obtained using the approach of Udvardi et al. [8] (open squares).
isotropic exchange coupling between a central Cr atom in layer 1 (denoted Cr1) to another Cr atom in layer 1 and 2 (denoted Cr1 and Cr2 and represented by squares and circles, respectively, in Fig. 1) is in the same order of magnitude. This means there is no remarkable spatial anisotropy imposed by the layered structure of the system for the isotropic coupling constant $J_{ij}$. The anisotropy of the exchange coupling is represented by $J^{S}_{ij}$ as well as by $\vec{D}_{ij}$. As $J^{S}_{ij}$ turns out to be quite small we show in Fig. 2 only the three components of the DM vector $\vec{D}_{ij}$. Many of the DM vector components are zero due to symmetry restrictions [18]. In particular one finds a non-zero DM vector $\vec{D}_{ij}$ only if the sites $i$ and $j$ belong to different sub-lattices Cr1 and Cr2. Due to the NiAs structure of the system the non-vanishing $x$- and $y$-components of the vector are of the same order of magnitude while the $z$-component is one order of magnitude larger. The different behaviour of the $x$-, $y$- and $z$-components reflects obviously to some extent the quasi-layered structure of the system (hexagonal Cr layers with Te-layers in between). However, the anisotropic exchange coupling is still about two orders of magnitude smaller than the isotropic one.

As the comparison of the results for $J_{ij}$ and $\vec{D}_{ij}$ obtained using the approach presented above and that of Udvardi et al. [8], respectively, in Figs. 1 and 2 demonstrates, both schemes give very similar results. This also holds for other systems studied so far with most pronounced differences occurring for the DM vector. It should be stressed, however, that the above scheme allows to determine $J_{ij}$ with respect to one common reference state; i.e. there is no need to use various reference states to get all tensor elements. This ensures that the results for the various elements are always consistent even when the choice of the reference state...
FIG. 4: Isotropic exchange interaction $J_{ij}$ between Mn atoms at sites $i$ and $j$ in Ga$_{1-x}$Mn$_x$As, scaled by the factor $(R_{ij}/\alpha)^2$, as a function of the inter-atomic distance $R_{ij}$. Results are given for 7 at.% Mn (full circles) and for 4 at.% Mn (open squares).

state influence the result, e.g. when the RSA is not fully justified.

To demonstrate that the DM interaction is indeed induced by spin-orbit coupling (SOC) we performed model calculations with the strength of SOC artificially increased by a factor of 2. While the isotropic exchange coupling constants $J_{ij}$ hardly changed, the DM vector components increased essentially by the same factor. This can be seen by comparing $D_{ij}^{\hat{z}}$ given in Fig. 3 with the results in Fig. 2 (top). Fig. 3 also shows that for this specific situation results based on the two approaches considered may differ in an appreciable way.

Figs. 4 and 5 show the results of an application of our approach to the diluted magnetic semiconductor system Ga$_{1-x}$Mn$_x$As. The isotropic exchange coupling (Fig. 4) and also its concentration dependence agrees quite well with the results of other authors [6], indicating in particular that the spin-orbit coupling accounted within the present work affects the isotropic exchange coupling only slightly. As mentioned above and as was noted by other authors [6, 19] there is a directional dependency for $J_{ij}$. This is demonstrated by Fig. 6 where results for the concentration $x = 0.04$ are given for $\hat{R}_{ij}$ along [001], [110], and [111] separately. As for the magnitude of $J_{ij}$, this spatial anisotropy of $J_{ij}$ is only slightly influenced by inclusion of SOC. In contrast to this SOC is ultimately responsible for the anisotropy in the exchange coupling represented by the DM vector shown in Fig. 5. In contrast to the CrTe system considered above the three components of the DM vectors are of the same order of magnitude as a consequence of the zincblende structure of Ga$_{1-x}$Mn$_x$As.
Although, it seems not possible to give a simple scaling behaviour of the magnitude of the exchange coupling parameters with respect to the inter-atomic distance $R_{ij}$, one notes that the components of $\vec{D}_{ij}$ decay less rapidly as $J_{ij}$ with increasing $R_{ij}$. This behaviour was also found for other systems and is in line with the findings of Timm and MacDonald [10]. However, our results for the isotropic as well as anisotropic exchange coupling constants differ quite appreciably from those obtained recently in a more phenomenological way by these authors. In particular the tensor elements representing anisotropic exchange are found to be around one order of magnitude smaller than given in the previous work. The anisotropy of the DM interaction is demonstrated in Fig. [7] for the component $D_{ij}^z$. As one notes $D_{ij}^z$ depends quite strongly in the direction $R_{ij}$. In particular one finds $D_{ij}^z$ to be zero e.g. for the [111] direction due to symmetry. Also because of the symmetry of the system one finds for each direction a symmetry-related one for which the sign of $D_{ij}^z$ is reversed.

The presence of a non-collinear ferromagnetic structure in Ga$_{1-x}$Mn$_x$As is assumed to be partially responsible for the missing of remanent magnetisation observed experimentally in annealed samples [20, 21, 22]. In particular, the remanent magnetisation in this DMS system can be noticeably increased in the presence of a rather small magnetic field. Such a behaviour could indeed be explained by the presence of non-collinear magnetism in the system [22].

The anisotropy of the exchange coupling in Ga$_{1-x}$Mn$_x$As was studied theoretically by various authors [10, 23, 24, 25] to find whether it can be responsible for the formation of a non-collinear ferromagnetic structure as a ground state in this DMS system. However, these investigations were based on phenomenological or semi-phenomenological approaches and the results obtained are rather controversial. In contrast to this, the present approach allows us to evaluate the elements of the exchange coupling tensor (in particular, its antisymmetric part representing the DM coupling) on the basis of ab-initio electronic structure calculations. As was demonstrated above, this leads indeed to a rather large value for the DM coupling in Ga$_{1-x}$Mn$_x$As, which is only about one order of magnitude smaller than for the isotropic exchange. As mentioned, this finding is in line with the results of Timm and MacDonald [10]. Obviously, the values for the DM coupling term cannot be considered as negligibly small, and as a consequence one cannot exclude a noticeable non-collinear ferromagnetic order in the system. To clarify this question corresponding Monte Carlo simulations based on the calculated exchange tensor will be performed.
IV. SUMMARY

A new scheme to calculate the exchange coupling tensor $J_{ij}$ has been presented that is based on ab-initio electronic structure calculations using spin-polarized fully relativistic multiple scattering theory and spin density functional theory. Application to ferromagnetic CrTe as well as to other systems demonstrates that the approach gives results for the exchange tensor elements very similar to those obtained using the approach of Udvardi et al. However, the new approach makes use of a unique reference state ensuring the internal consistency of the tensor elements. Application to the diluted magnetic semiconductor system Ga$_{1-x}$Mn$_x$As led to an isotropic exchange in full accordance with previous non-relativistic calculations that were also based on ab-initio electronic structure calculations. The results obtained for the anisotropic exchange coupling are in accordance with the data of Timm and MacDonald concerning the variation with distance. However, numerically the coupling constants obtained by the present ab-initio approach and the more phenomenological scheme of these authors differ in an appreciable way.

V. ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft within the Schwerpunktprogramm 1153, Schwerpunktprogramm 1136 as well as the Sonderforschungsbereich SFB 689.

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FIG. 5: Components of Dzyaloshinski-Moriya interaction vector $\vec{D}_{ij}$ (from top to bottom: $x, y, z$) between Mn atoms at sites $i$ and $j$ in Ga$_{1-x}$Mn$_x$As, scaled by the factor $(R_{ij}/a)^2$, as a function of the inter-atomic distance $R_{ij}$. Results are given for 7 at.% Mn (full circles) and for 4 at.% Mn (open squares).
FIG. 6: Scaled exchange interactions \((R_{ij}/a)^2J_{ij}\) in ferromagnetic Ga\(_{1-x}\)Mn\(_x\)As, \(x = 0.04\), as a function of the inter-atomic distance \(R_{ij}\) along different directions.

FIG. 7: Components of Dzyaloshinski-Moriya interaction \(\vec{D}_{ij}\) between Mn atoms at sites \(i\) and \(j\) in Ga\(_{1-x}\)Mn\(_x\)As, \(x = 0.04\), scaled by factor \((R_{ij}/a)^2\), as a function of the inter-atomic distance \(R_{ij}\) along different directions.