

## Dmitry Zakharov (Autor) Exchange and Relaxation in Spin Chains



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# 1. Introduction

The effective dimensionality and electron correlations determine the properties of interacting electron systems. Furthermore, correlation effects increase as the number of effective dimensions decreases: for example, in three-dimensional metallic systems, the low-energy electronic states behave as Fermi liquid quasiparticles, whereas in one dimension, even weak interactions break the quasiparticles into collective excitations. The concept of a Luttinger liquid [Tomonaga'50, Luttinger'63] has recently been established as vital to our understanding of the behavior of one-dimensional quantum systems. This concept has led to a number of theoretical breakthroughs, in particular, this theory characterizes the low-energy excitation spectrum as consisting entirely of *independent* spin and charge density fluctuations. Over the last decade its descriptive power has been confirmed experimentally, when high quality quantum wires have been fabricated displaying all characteristic Luttinger liquid properties [Bockrath'99, Ishii'03].

The variety of exotic ground states, new phases of matter and quantum effects dominating thermal fluctuations are only some of the phenomena that the low-dimensional systems offer to enrich solid state physics. Moreover, the theoretical treatment is sufficiently simplified in a reduced dimension allowing to solve many theoretical models exactly. For more than 30 years the experimental realization of (quasi-)low-dimensional compounds is not a real problem anymore: anisotropy of exchange coupling obtained in organic spin systems reaches the values of  $10^4$ :1 [Dietz'71]. It has also to be mentioned that the huge fundamental work made in the field of low-dimensional systems is of great importance in three-dimensional systems as well. One of the recent examples is given by the three-dimensional cubic system  $Tl_2Ru_2O_7$  which has been supposed to evolve into a one-dimensional spin-one system with a spin gap below T = 120 K [Lee'06]. The appearance of the gap was predicted by Haldane in 1983 as an inherent property of integer spin chain systems [Haldane'83]. But low-dimensional systems are not only interesting from a fundamental physics point-of-view. They offer unique opportunities for practical applications, for example building of quantum computers, high-capacious data-storage elements and superconductors. Therefore, understanding the properties of low-dimensional spin systems is one of the central problems in quantum magnetism.

Nevertheless, despite the fact that the field of low-dimensional magnetism developed into one of the most active areas of today's solid state physics, the number of unexplained phenomena tends to increase with time. Their understanding needs a more detailed study of the physics underlying these phenomena. In this thesis we will characterize the spin relaxation mechanisms in one-dimensional spin systems using the electron spin resonance spectroscopy. This technique allows to directly access the spin of interest and gain information on its relaxation processes and, in particular, on the exchange interaction with its neighbors. The systems chosen for the present study are all structurally different but reveal a clear one-dimensional character in their magnetic properties. In spite of structural differences, we will show the close similarity of their relaxation behavior and identify the dominant sources of spin relaxation common in all compounds.

Two of the systems investigated are the members of the sodium-vanadium bronze series  $Na_x V_2 O_5$  which acquired a paradigmatic status. The possibility to tune the vanadium valence between  $V^{4+}$  ( $3d^1$ ) and  $V^{5+}$  ( $3d^0$ ) allows the realization of a variety of spin-1/2 systems with strong quantum effects. Moreover, the rich structural chemistry of these systems, where the V ions can occur in pyramidal, tetrahedral, or octahedral coordination, gives rise to the formation of very interesting chain-like and ladder-like structures.  $\beta$ -Na<sub>1/3</sub>V<sub>2</sub>O<sub>5</sub> which shows a metal-to-insulator transition and superconductivity under pressure is only one member of this series. This study focuses on two other compounds with higher Na concentration:  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub> and  $\eta$ -Na<sub>9/7</sub>V<sub>2</sub>O<sub>5</sub>. The former system reveals charge ordering phenomena [Grenier'02] and has been intensively studied during the last decade. The latter one came only recently into the focus of interest and we will show that its ground state can be understood in terms of exotic spin objects.

Strictly speaking, both of these systems are not ideal spin chains.  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub> represents a prototypical two-leg spin-ladder system, and  $\eta$ -Na<sub>9/7</sub>V<sub>2</sub>O<sub>5</sub> can be described as a zigzag-like chain. In order to make this study more conclusive, a linear spin chain compound, TiOCl, was considered as well. The properties of this system are even more exciting. TiOCl exhibits a spin-Peierls-like dimerization [Pytte'74] with the highest transition temperature known at the moment [Shaz'05] and undergoes a metal-to-insulator transition under pressure [Kuntscher'06]. Furthermore, electron doped TiOCl has been suggested to exhibit unconventional superconductivity with a  $T_{\rm C}$  of about room temperature [Craco'06].

The course of this thesis is the following: First, we give an introduction to the microscopical theory of superexchange in Chapter 2, including the generalized schemas of the Dzyaloshinsky-Moriya and the pseudodipolar exchange. In Chapter 3, we briefly review the properties of low-dimensional systems necessary for the following analysis. The basic ideas of electron spin resonance spectroscopy in concentrated spin systems are given in Chapter 4. In the following Chapters we consider three spin-chain systems:  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub>, where the spin relaxation can be explained by only one type of exchange interaction is treated first, in Chapter 5. The next Chapter deals with the more involved situation in TiOC1. Chapter 7 treats then the  $\eta$ -Na<sub>9/7</sub>V<sub>2</sub>O<sub>5</sub> system. The electron spin resonance data in this compound are even richer in features, but are crucial in determining the nature of the low-temperature ground state. Chapter 8 is devoted to conclusions. It is followed finally by an Appendix which contains the explicit derivation of exchange constants in terms of a perturbation theory.

## 2. Microscopic Theory of Superexchange

Exchange interaction, the major source of magnetic ordering in solids, constitutes the head stone of the theory of magnetism. The concept of exchange coupling arose in 1927 with the Heitler-London theory of the chemical bonds [Heitler'27], and was at once applied by Heisenberg [Heisenberg'28] to the theory of ferromagnetism. The Heisenberg model of exchange interaction became the foundation for most of the current theoretical treatments of cooperative magnetic phenomena. The principal feature of this model is the assumption that the interaction  $\mathcal{H}_{iso}$  between two magnetic atoms a and b in a crystal can be expressed as  $\mathcal{H}_{iso} = J(\mathbf{S}_a \cdot \mathbf{S}_b)$ , where J is an exchange integral and  $\mathbf{S}_{\alpha}$  is the spin operator for the respective atom. Obviously, the sign and magnitude of J are extremely important in determining the transition temperatures, the magnetic structures, and indeed practically all of the fundamental magnetic properties of a crystal. But this model does not account for any anisotropic effects.

Generally, the exchange interaction

$$\mathcal{H}_{\text{ex}} = \sum_{ij} J_{ij} S_{a,i} S_{b,j} \qquad \left(i, j = \{x, y, z\}\right)$$
(2.1)

contains two anisotropic terms as well

$$\mathcal{H}_{\text{ex}} = J(\mathbf{S}_a \cdot \mathbf{S}_b) + \frac{1}{2} \sum_{ij} D_{ij} \left( S_{a,i} S_{b,j} + S_{a,j} S_{b,i} \right) + \left( \mathbf{d} \cdot \left[ \mathbf{S}_a \times \mathbf{S}_b \right] \right).$$
(2.2)

The second term describes the symmetric anisotropic exchange and the third term – the Dzyaloshinsky-Moriya (antisymmetric) interaction. Both of them are considerably smaller than the isotropic Heisenberg exchange (the first term), but have a profound impact on the magnetic properties of crystals. Among others, they produce canted spin arrangements and can even lead to phase transitions in the systems of lower dimension, as for instance the Berezinsky-Kosterlitz-Thouless transition in two-dimensional lattice. Moreover, the anisotropic parts of exchange interaction seem to be the origin of magnetism-induced ferroelectricity. A particular importance they get in spin-1/2 systems, where they represent the only one source of anisotropy.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> (i) Double exchange interaction which cannot be written using spin variables is beyond the scope of this work and will only be mentioned briefly in chapter 2.2.5.

<sup>(</sup>ii) In case  $\mathbf{S} > 1/2$ , this equation may only be the leading term of a series expansion with respect to the total spin operators  $\mathbf{S}_a$  and  $\mathbf{S}_b$ , in which higher terms such as biquadratic  $(S_{a,i}S_{b,j})^2$  occur.

In spite of the remarkable success in the general theory of cooperative phenomena, any rigorous treatment of exchange interactions in three-dimensional systems lies behind the classical statistical theory. But the difficulties of quantum-mechanical treatment can be overcome in a lower dimension: The recent field-theory calculation of the spin-1/2 quantum antiferromagnetic chain by Oshikawa and Affleck [Oshikawa'02] gives an unique opportunity to study the exchange interactions in spin chain compounds using the rigorous theoretical basis. On the other hand, the large isotropic exchange  $(J/k_{\rm B} \sim 10^2 \text{ K})$ characteristic for one-dimensional spin systems serves as a background for comparatively small anisotropic contributions and makes it difficult to access them by means of magnetic susceptibility or by inelastic neutron scattering. But the spin-spin relaxation, measured by the electron spin resonance spectroscopy, is driven primarily by the local fields produced by the anisotropic parts only. That makes the electron spin resonance an ideal tool to study these fine effects.

One of the main purposes of this thesis is to investigate the influence of the exchange interaction on the spin relaxation in low-dimensional systems both from the experimental and the theoretical side. In this chapter we will discuss a theoretical approach, which allows to estimate their magnitude microscopically and allows in the most ocular (and correct) way to deal with the exchange interactions.

## 2.1. Exchange Mechanisms

Spin exchange correlations may only occur if the wave functions of the electron of interest have a non negligible overlap. In case of direct overlap of the orbitals of neighboring magnetic ions one speaks about *direct exchange*.

#### 2.1.1. Direct Exchange Interaction

The Hamiltonian of direct exchange between the ions a and b has generally the form [Eremin'72]

$$\mathcal{H}_{\rm dir} = -\frac{1}{2} \left( \mathcal{HP} + \mathcal{PH} \right) + \frac{1}{2} \left( \sum \mathcal{H} |\psi_1 \psi_2\rangle \langle \psi_1 \psi_2 | \mathcal{P} + \sum \mathcal{P} |\psi_1 \psi_2\rangle \langle \psi_1 \psi_2 | \mathcal{H} \right).$$
(2.3)

$$J = \frac{1}{3} \sum_{i} J_{ii}, \quad D_{ij} = J_{ij}^{\text{sym}} - J\delta_{ij}, \qquad J_{ij}^{\text{sym}} = \frac{1}{2} (J_{ij} + J_{ji});$$
  
$$d_x = \frac{1}{2} J_{yz}^{\text{asym}}, \quad d_y = \frac{1}{2} J_{zx}^{\text{asym}}, \quad d_z = \frac{1}{2} J_{xy}^{\text{asym}}, \quad J_{ij}^{\text{asym}} = \frac{1}{2} (J_{ij} - J_{ji}).$$

Theoretical [Anderson'59, Gondaira'66] as well as experimental [Harris'63] estimates of this contribution give the value, which is two orders of magnitude smaller than the bilinear part (2.1). In this work we will concern only S = 1/2 systems for which this expression is fully correct. The quantities entering into Eq. (2.2) are

Here  $|\psi_1\psi_2\rangle \equiv |\psi_1\rangle|\psi_2\rangle$  means the product of the wave functions of interacting electrons, the permutation operator  $\mathcal{P} = \sum_{ij} \mathcal{P}_{ij}$  interchanges two electrons *i* and *j*. Let us discuss the case of one electron on each site (see Fig. 2.1). The total Hamiltonian then reads

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Z_a e^2}{r_{a1}} - \frac{Z_b e^2}{r_{b2}} - \frac{Z_b e^2}{r_{b1}} - \frac{Z_a e^2}{r_{a2}} + \frac{e^2}{r_{12}}.$$
 (2.4)



Figure 2.1.: Schematical representation of two interacting electrons 1 and 2 belonging to the ions a and b, respectively.

In terms of spin operators the Hamiltonian of direct exchange between two electrons in the states  $\eta$  and  $\zeta$  reads

$$\mathcal{H}_{\rm dir}^{\eta\zeta} = J_{\eta\zeta}^{\rm dir} \left[ \frac{1}{2} + 2 \left( \mathbf{s}_{\eta} \cdot \mathbf{s}_{\zeta} \right) \right], \tag{2.5}$$

where the parameter  $J_{\eta\zeta}^{\text{dir}}$  is determined by [Schastnev'75]

$$J_{\eta\zeta}^{\text{dir}} = -\langle \eta_1 \zeta_2 | \frac{e^2}{r_{12}} | \eta_2 \zeta_1 \rangle + 2 \operatorname{Re} \langle \eta | \zeta \rangle \langle \eta | \frac{p^2}{2m} | \zeta \rangle -$$

$$- | \langle \eta | \zeta \rangle |^2 \left[ \varepsilon_\eta + \varepsilon_\zeta - \langle \eta | U_2 | \eta \rangle - \langle \zeta | U_1 | \zeta \rangle + \langle \eta_1 \zeta_2 | \frac{e^2}{r_{12}} | \eta_1 \zeta_2 \rangle \right].$$

$$(2.6)$$

 $S_{\eta\zeta} \equiv \langle \eta | \zeta \rangle$  represents the overlap integral.  $U_1$  and  $U_2$  are the Coulomb energies of electrons in the field of the other atoms,  $\varepsilon_{\eta}$  and  $\varepsilon_{\zeta}$  – the Hartree-Fock energies of the electrons in the states  $\eta$  and  $\zeta$ , respectively:

$$U_{2} = -\frac{Z_{b}e^{2}}{r_{b1}} + \langle \zeta_{2} | \frac{e^{2}}{r_{12}} | \zeta_{2} \rangle, \qquad \varepsilon_{\eta} | \eta_{1} \rangle \equiv \left( \frac{p_{1}^{2}}{2m} - \frac{Z_{a}e^{2}}{r_{a1}} \right) | \eta_{1} \rangle.$$
(2.7)

The first term in Eq. (2.6) represents the *potential exchange* as introduced by Anderson [Anderson'59]. It is always negative and favors a *ferromagnetic* spin alignment. Detailed calculations show [Freeman'61, Freeman'62] that  $J_{\eta\zeta}^{\text{dir}}$  is negative only in case of zero overlap of the neighboring orbitals  $S_{\eta\zeta} = 0$ , otherwise the last two terms in Eq. (2.6) will dominate and lead to an antiferromagnetic coupling.



Figure 2.2.: Channel model of exchange interaction [Eremin'77]. The exchange coupling of each pair of spins  $J_{\alpha\alpha'}$  is supposed to be mutually independent that allows their algebraical summation (2.9).

The microscopical expression (2.6) corresponds to the exchange between a pair of spins. In case of several electrons on one site the exchange operator is usually approximated by the sum of individual exchange integrals  $J_{\eta\zeta}^{\text{dir}}$  depicted in Fig. 2.2:  $\mathcal{H}_{\text{dir}} = \sum \mathcal{H}_{\text{dir}}^{\eta\zeta}$ . For detailed discussion of this 'channel model' we refer to [Eremin'77, Eremin'80]. Here we will consider only the case of interacting ions in the ground state what is usually the case in magnetic resonance measurements. According to Hund's rule they possess the maximal spin value  $\mathbf{s}_{\eta} = \frac{1}{2S_a} \mathbf{S}_a$ ,  $\mathbf{s}_{\zeta} = \frac{1}{2S_b} \mathbf{S}_b$ , and, hence, the spin dependent part of the Hamiltonian of direct exchange reads

$$\mathcal{H}_{\rm dir} = J^{\rm dir} \left( \mathbf{S}_a \cdot \mathbf{S}_b \right), \tag{2.8}$$

where the effective exchange integral is given by

$$J^{\rm dir} = \frac{1}{2S_a S_b} \sum_{\eta \zeta} J^{\rm dir}_{\eta \zeta}.$$
 (2.9)

The exchange integral (2.9) scales with the overlap squared and decreases exponentially with the distance r between the spins. Therefore, direct exchange plays a large role only for radicals [Musin'76] and in case of 90° metal-ligand-metal exchange geometry. For 3*d*-ions it becomes negligible already at  $r \sim 2.7 - 3$  Å. In practice, magnetic ions aand b are always separated by diamagnetic ions c, so that no appreciable direct overlap is to be expected in this case. That led Kramers [Kramers'34] to propose that a strong admixture of the cation's and intermediate anion's wave functions could be invoked to couple the cations *indirectly*.

#### 2.1.2. Indirect Exchange Mechanisms

It is tempting to assume, by analogy with the case of direct exchange, that exchange coupling in case of three-center system a - c - b will be proportional to the product of the overlap integrals  $J_{\eta\zeta} \propto S_{\eta\kappa}^2 S_{\kappa\zeta}^2$  ( $\kappa$  is the state of the intermediate diamagnetic ion c). This contribution referred as Yamashita-Kondo's mechanism is nevertheless only marginal because the overlap integrals  $S_{\eta\kappa}$  are usually small compared to the covalency parameters (i. e. hopping integrals  $t_{\eta\kappa}$ , see Eq. A.17).

The hopping integrals  $t_{\eta\kappa}$  characterize the kinetic energy of electrons or their desire to delocalize. Whenever their repulsion predominates and prevents metallic conduction, the tendency to delocalize can gain energy by spreading electrons into nonorthogonal overlapping orbitals, naturally leading to the antiferromagnetic spin ordering. This problem was first considered by Kramers who developed a unique method of handling configuration interactions [Kramers'34]. The idea by Kramers is displayed in Fig. 2.3(i). The excited configuration in which an electron has been removed from the nonmagnetic center c and placed on a leaves an unpaired spin on c and b leading to a spin coupling due to the direct overlap of these charge densities. The magnitude of this type of indirect exchange can be estimated as  $J_{\eta\zeta} \propto t_{\eta\kappa}^2 S_{\kappa\zeta}^2$ .

Twenty years later Pratt [Pratt'55] could show that such polarization effects cannot produce the actual antiferromagnetic spin-ordering and proposed another scheme shown in Fig. 2.3(ii): two electrons of the diamagnetic ion are simultaneously transferred to the magnetic ions providing an antiferromagnetic coupling. An attempt to compare the effectiveness of all possible mechanisms of superexchange was made by Yamashita and Kondo [Yamashita'58], but it was not possible to single out the most efficient one. In 1959, Anderson [Anderson'59] simplified and unified the various mechanisms giving rise to superexchange interaction. He showed that the superexchange mechanism, where the ionic configuration  $a^+b^-$  is obtained (see Fig. 2.4), strongly dominates all others. On the one hand, the energy of this ionic state is higher than the energy of the unperturbed state by an amount  $U = \Delta_{ab}$ , corresponding to the average electrostatic repulsion energy for two electrons on the same site. On the other hand, the system gains kinetic energy  $J_{\eta\zeta} \propto t_{\eta\kappa}^2 t_{\kappa\zeta}^2$ . This delocalization stabilizes the singlet configuration, because the two



Figure 2.3.: Schematic representation of the indirect exchange between two magnetic ions a and b via a diamagnetic ion c proposed by (i) Kramers in 1934 [Kramers'34] and (ii) Pratt in 1955 [Pratt'55]. The green arrows denote the virtual hoppings of electrons. Numeration corresponds to the sequence of the electron transfers.

electrons at site b must necessarily pair up. Anderson's approach to the theory of superexchange interactions has become classical and will be considered in more detail in the next section.

## 2.2. Isotropic Exchange Interaction

The following consideration generalizes Anderson's approach [Anderson'59] by accounting directly for the states of an intermediate ion. It is based on the method of canonical transformations which allows in a natural way to derive the constants of exchange interactions using a perturbation theory. The detailed description of this method can be found in appendix A. Here we will only use the results of these calculations, which are needed to discuss the underlying physical processes.

First, let us introduce some notations:  $a_{\eta}^{+}(a_{\eta'})$  and  $b_{\zeta}^{+}(b_{\zeta'})$  are the creation (annihilation) operators of electrons on the magnetic ions,  $c_{\kappa}^{+}(c_{\kappa'})$  – on the intervening diamagnetic ions. With  $\eta, \varphi, \xi$  we denote the orbital and spin states of the magnetic ion a $[\eta \equiv (n_{\eta}l_{\eta}m_{\eta}s_{\eta})]$  and with  $\zeta, \theta, \lambda$  the corresponding states of the magnetic ion b. The letters  $\kappa, \rho$  signify the one-electron states of the diamagnetic ion c.

### 2.2.1. Classical Concept: Antiferromagnetic Spin Ordering

The most effective mechanism of the isotropic superexchange between two magnetic ions a and b via the intervening ion c as first described by Anderson [Anderson'59] is illustrated in Fig. 2.4. By counting the involved electronic hopping processes, it becomes evident that this mechanism corresponds to the forth order of perturbation theory with respect to the energy of the electron hoppings.



Figure 2.4.: Schematic representation of the "superexchange" between two magnetic ions a and b via a diamagnetic ion c proposed by Anderson [Anderson'59]. The green arrows denote the virtual hoppings of electrons. The Greek letters denote the orbital states of an electron on the corresponding ion.

Consequently, this process can be described by the Hamiltonian (A.22), which is derived in the appendix. Here, we add a factor of two to this Hamiltonian

$$\mathcal{H}_{\rm kin} = 2 \cdot \frac{t_{\eta\rho} t_{\rho\zeta} t_{\zeta\kappa} t_{\kappa\eta}}{\Delta_{ac}^2 \Delta_{ab}} \left( -\frac{1}{2} + 2(\mathbf{s}_{\eta} \cdot \mathbf{s}_{\zeta}) \right), \qquad (2.10)$$

because we also take into account the electron transfer from site *a* to site *b*. Moreover,  $t_{\eta\rho}$  denotes the *hopping (transfer) integral* between the orbital states  $\eta$  and  $\rho$ ,  $\Delta_{ab} \sim U$ and  $\Delta_{ac}$  are the electron transfer energies from ion *a* to the cation *b* and to the anion *c*, respectively. The expression (2.10) represents the *kinetic exchange* in Anderson's notation and was considered to be intrinsically *antiferromagnetic*. This type of exchange constitutes an *isotropic* antiferromagnetic exchange interaction

$$\mathcal{H}_{\rm iso}^{\eta\zeta} = J_{\eta\zeta} \left( \mathbf{s}_{\eta} \cdot \mathbf{s}_{\zeta} \right) \longrightarrow \mathcal{H}_{\rm iso} = J \left( \mathbf{S}_a \cdot \mathbf{S}_b \right), \tag{2.11}$$

where the constant of isotropic exchange is given by

$$J_{\eta\zeta} = 4 \cdot \frac{t_{\eta\rho} t_{\rho\zeta} t_{\zeta\kappa} t_{\kappa\eta}}{\Delta_{ac}^2 \Delta_{ab}} \quad \text{and} \quad J = \frac{1}{4S_a S_b} \sum_{\eta\zeta} J_{\eta\zeta}.$$
 (2.12)

The direct exchange (2.8) is also isotropic, but negligible as compared to the kinetic exchange because of the large distance between the interacting ions. It is worth noting, that the isotropic exchange is strongly antiferromagnetic only in case of 180° bond geometry (all three ions are lying on a straight line). The deviations of the bond angle  $\theta$  from 180° can be described by introducing geometrical factors like, for example,  $t(\theta) \propto -t_{\sigma}\cos\theta - t_{\pi}\sin\theta$ . As we will discuss in the following, competition and quantum-interference effects between different exchange paths can occur in some cases and can lead to a strong *ferromagnetic* coupling of spins [Bencini'90, Krug'02].

#### 2.2.2. Ferromagnetic Superexchange

Following Anderson, ferromagnetic coupling can be obtained considering two major processes: (i) potential exchange and (ii) transfer of the electron to the unoccupied orbital of the neighboring ion. The indirect potential exchange is, as a matter of fact, of the same nature as the corresponding direct process. It describes the electrostatic energy of the system as a spin-spin interaction in the basis of one-electron wave functions. Anderson's treatment allows to separate the part of the interaction containing the spreading of the orbitals of the *d*-electrons into the neighboring ions by the modification of the local wave functions. The exchange effect then appears as a consequence of the direct overlap of the new longer-ranging orbitals. But this process only plays a minor role compared to the following one.

The second mechanism is shown schematically on the left side of Fig. 2.5. This is a fifth-order effect of transfer together with the internal exchange coupling  $V_{mm'}^{(1)} = J_H$  (see