

Ni-Ni ion pair excitation transfer in D_{3h} symmetry

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Abstract The mechanisms contributing to excitation transfer are examined for Ni-Ni ion pairs in order to explain the delocalized character of electronic excitations observed in CsNiF₃. Using both first- and second-order perturbation theory and from symmetry arguments, the kind of interactions giving matrix elements between states connecting different sites for the position of the excitation are discussed.

1. Introduction

A large amount of papers has been published dealing with the analysis the low energy levels in CsNiF₃, considered as one of the most typical one-dimensional (1D) ferromagnets. This 1D behavior in the magnetic order has been observed between $T_N = 2.6$ K and 40 K¹. However, information about the first optically excited state is scarce. Recently, measurements of fluorescence after selective excitation ($3\sim 2\text{-}3T_2$ transition in the notation for states of isolated $P4i_2+$ ions) were performed at temperatures between 1.3 K and 20 K, in the presence of an external magnetic field from 0 to 5 K G. From these results it was concluded that fast transfer exists between Ni ions in the 1D chain, until the excitation is trapped at the end of a segment of equal Ni ions, in a slower process.

In CsNiF₃ each Ni ion is surrounded by six F ions, in a distorted octahedron of D_{3h} symmetry. In our analysis we will consider a pair of Ni first neighbors, where

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each distorted octahedron has a triangular base in common with the following one. The symmetry of the pair is D_{3h} , having a reflection plane perpendicular to the triangular axis. (Fig. 1).

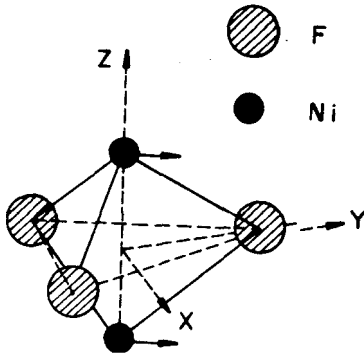


Fig. 1 - Schematic representation of two neighbouring Ni ions in CsNiF_3 showing the D_{3h} symmetry of the pair.

An isolated Ni ion ($3d^8 - ^3F$) in an octahedral field has an orbital singlet 3A_2 (or $t_{2g}^6 e_g^2$ in a strong field scheme), as the ground state and the first excited state is $^3T_{2g}$ (or $t_{2g}^5 e_g^3$). We use the electron-hole equivalence in what follows.

To describe the intersite transfer we assume as usual, that the effective model Hamiltonian appropriate for the system can be written as

$$H = \sum_{\alpha} H_{\alpha} + \sum_{\alpha\beta} H_{\alpha\beta} \quad (1)$$

where H_{α} is the Hamiltonian of an ion at site α , and $H_{\alpha\beta}$ represents the interionic interactions.

The delocalized excited state can be described as a kind of tight-binding Frenkel exciton⁴, in which the excitation "jumps" between sites while the number of electrons in each ion is conserved.

We indicate by ψ_{α} a multielectron state in which a particular ion α is in one of its excited states e_{α} , while the rest of them are in the ground state f_{γ} . (We assume the ground state to be orbitally non-degenerate). Taking ψ_{α} as the

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antisymmetrized product of one-ion wave functions, we put $|\psi_\alpha\rangle = |e_\alpha\{f_\gamma\}\rangle$ where $\{f_\gamma\}$ is a set of occupied one-electron states which will be taken as “passive” within the problem under consideration (as a sort of frozen core).

The exciton state can be written as

$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{\alpha} \exp(-i\vec{k}\cdot\vec{R}_\alpha) |\psi_\alpha\rangle$$

where N is the number of ions, \vec{k} a wave sector, and \vec{R}_α is the position vector from the origin to site α .

The matrix elements of the Hamiltonian (1) can be expressed in this basis as

$$H(k) = \langle \psi_k | \sum_{\alpha\beta} H_{\alpha\beta} | \psi_k \rangle = \frac{1}{N} \sum_{\alpha\beta} \exp(i\vec{k}\cdot\vec{r}_{\alpha\beta}) h_{\alpha\beta}$$

with $\vec{r}_{\alpha\beta} = \vec{R}_\alpha - \vec{R}_\beta$ and $h_{\alpha\beta} = \langle \psi_\alpha | H_{\alpha\beta} | \psi_\beta \rangle$; $h_{\alpha\beta}$ represents the effective energy transfer matrix element in which we are interested.

2. The Many-electron states

In order to examine the effective energy transfer operator we will use an analysis which is based on the theory of magnetic interactions in insulators as described in ref. 5. We use the nomenclature as in ref. 6 where the theory of coupled Cr^{3+} pairs is treated in a similar form.

Although our study will be based on symmetry considerations, i.e. the electron states transforming irreducibly under the symmetry operations of the group coresponding to the system, it seems appropriate to give a brief account of the scheme to follow in order to built up the effective Hamiltonian.

Let us assume that we have at our disposal a set of symmetry-adapted one-electron states. These can be used to build up properly antisymmetrized many-electron states which can also be classified according with the symmetry of the system. Starting from these many-electron states an effective operator over a given manifold can be constructed as

$$\mathcal{H}_{\text{eff}} = P_n \tilde{\mathcal{H}} P_n$$

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where P_n is the projection operator over the selected functional subspace and

$$\tilde{\mathcal{H}} = \left\{ \mathcal{H} - \sum_{n'} \frac{\mathcal{H} P_{n'} \mathcal{H}}{\Delta n'} + \dots \right\}.$$

Based on these many-electron states it is possible to set up a perturbational scheme to correct them or alternatively to allow a form for \mathcal{H} which includes these corrections.

Up to second order in the real Hamiltonian \mathcal{H} , \mathcal{H}_{eff} can be written as

$$\mathcal{H}_{\text{eff}} = P_n \left\{ \mathcal{H} - \sum_n \frac{\mathcal{H} P_{n'} \mathcal{H}}{\Delta n} + \dots \right\} P_n$$

where \mathcal{H} contains in **principle** all the microscopic interactions which are considered relevant for the problem under consideration. As far as its **convergence** properties are concerned, this perturbative procedure rests heavily on the proper selection of the states, rather than on seeking a way to **separate** \mathcal{H} into some unperturbed \mathcal{H}_0 plus a perturbation \mathcal{H}' as it is more commonly practiced.

The model is **based** mainly on symmetry considerations, where the wave functions are defined by their transformation **properties** under the symmetry operations of the group corresponding to the ion pairs.

Now suppose that we have already **classified** the states forming P_n according to their symmetry properties as will be shortly described. The effective Hamiltonian within that manifold can then be written as

$$\mathcal{H}'_{\text{eff}} = \sum_{n, n'} |{}^n \Gamma_{\gamma k} \rangle \langle {}^{n'} \Gamma_{\gamma k} | A_{\gamma k}^{nn'} \quad (2)$$

where ${}^n \Gamma_{\gamma k}$ is a function transforming as the component k of irreducible **representation** Γ_{γ} and n distinguishes between repeated **representations** of the same kind. Naturally this Hamiltonian should be invariant under the operations of D_{3h} . The number of parameters in this effective theory is given by the non-vanishing ${}^{nn'} A_{\alpha k}$ and **follows** the symmetry of the system. Thus the externals $|{}^n \Gamma_{\gamma k} \rangle \langle {}^{n'} \Gamma_{\gamma k} |$ are only reflecting the symmetry behavior of the states with no **reference** to their

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internal structure, while the whole information about the proposed structure for the many-electron states, will be contained in the parameters $A_{\gamma k}^{nn'}$ through

$$A_{\gamma k}^{nn'} = \left\langle {}^n \Gamma_{\gamma k} | \mathcal{M} - \sum_n \frac{\mathcal{M} P_n \mathcal{M}}{\Delta_n} | {}^{n'} \Gamma_{\gamma k} \right\rangle$$

We start constructing the functions of the Ni-Ni pairs by defining first the one-electron functions as shown in table 1.

Table 1 - One-electron orbital wave function transformation properties in D_{3h} .

1 electron orbital		E	C_3^0	σ_v^0	σ_h^0	Transforms as
$ A\rangle$	$ A\rangle$	$ A\rangle$	$ A\rangle$	$ a\rangle$	$ 0\rangle$	$ 0\rangle$
$ B\rangle$	$ B\rangle$	$\omega B\rangle$	$ C\rangle$	$ b\rangle$	$\cos\theta 2\rangle - \text{sen}\theta 1\rangle$	$\cos\theta 2\rangle - \text{sen}\theta 1\rangle$
$ C\rangle$	$ C\rangle$	$\omega^2 B\rangle$	$ B\rangle$	$ c\rangle$	$\cos\theta 2\rangle + \text{sen}\theta 1\rangle$	$\cos\theta 2\rangle + \text{sen}\theta 1\rangle$
$ D\rangle$	$ D\rangle$	$\omega D\rangle$	$ E\rangle$	$ d\rangle$	$\text{sen}\theta 2\rangle + \cos\theta 1\rangle$	$\text{sen}\theta 2\rangle + \cos\theta 1\rangle$
$ E\rangle$	$ E\rangle$	$\omega^2 D\rangle$	$ B\rangle$	$ e\rangle$	$\text{sen}\theta 2\rangle - \cos\theta 1\rangle$	$\text{sen}\theta 2\rangle - \cos\theta 1\rangle$

$w = \exp(2\pi i/3)$ $\cos\theta = \sqrt{2/3}$

$|M_L\rangle \equiv$ eigenfunction of angular momentum $L = 2, M_L$

The operations considered are: C_3^0 , a rotation of 120° around the trigonal axis 0, σ_v^0 , a reflection by a plane containing the c axis, and σ_h^0 , a reflection by a plane perpendicular to c containing the three F ions. The index o indicates that they operate on the orbital part, while s will indicate operators acting on the spin part. The last column, in table 1, serves as a definition of the wave functions for those electrons of the second Ni of the pair. In this way we avoid ambiguities in the definition of the direction of coordinates in each site. We indicate with lowercase characters the one-electron orbitals obtained by operating with σ_h^0 on the orbitals of the first Ni, written with capital letter

$$|a\rangle = \sigma_h^0 |A\rangle$$

We will label the many-electron one-ion ground-state functions as θ_1, θ_0 and θ_{-1} (see table 2) to distinguish the M_s value for the components of the orbital

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singlet and the first excited state wave functions ψ_{AM_s} , ψ_{BM_s} , ψ_{CM_s} , where the first sub-index indicates the transformation **properties** of the orbital part.

Table 2 - Single-ion determinantal functions (spin-orbit not included) excited states corresponding to $M_s = 1$.

$$|\psi_A^1\rangle = \frac{1}{\sqrt{2}}(\bar{E}^+ \bar{B}^+ + \bar{D}^+ \bar{C}^+)$$

$$|\psi_B^1\rangle = \frac{1}{\sqrt{2}}(\bar{D}^+ \bar{A}^+ + \bar{E}^+ \bar{C}^+)$$

$$|\psi_C^1\rangle = \frac{1}{\sqrt{2}}(\bar{E}^+ \bar{A}^+ + \bar{D}^+ \bar{B}^+)$$

$$|\psi_{AM_s}\rangle > \psi_A \quad \text{transforms as } A, M_s = 1, 0, -1$$

Including spin orbit coupling:

ground state

$$|\phi_1\rangle = (\bar{D}^+ \bar{E}^+)$$

$$|\phi_0\rangle = (\bar{D}^+ \bar{E}^- + \bar{D}^- \bar{E}^+)$$

$$|\phi_{-1}\rangle = (\bar{D}^- \bar{E}^-)$$

relevant excited states

$$|\Phi_D\rangle = \frac{1}{\sqrt{3}}|\psi_{C^1}\rangle + \frac{1}{\sqrt{3}}(|\psi_{A^{-1}}\rangle + |\psi_{B^{-1}}\rangle)$$

$$|\Phi_E\rangle = \frac{1}{\sqrt{3}}|\psi_{B^{-1}}\rangle - \frac{1}{\sqrt{3}}(|\psi_{A^1}\rangle - |\psi_{C^0}\rangle)$$

Thus, we have 3 functions for the ground state and 9 for the excited state making a total of 54 functions for the pair with one excited ion. For the excited states we shall keep only those corresponding to the lowest energy after the spin orbit interaction and the trigonal distortion of the crystal field have been considered (Φ_D and Φ_E).

For the wave functions of the pair we shall take the antisymmetrized product of the functions of each ion which already are antisymmetrized products of one-electron states. If (A, D) indicates the determinantal state of one ion at site a and (a, b) is the same for an ion at site β , the function of the pair is represented by (A, D, a, b) and the antisymmetry is guaranteed.

Now we can write the functions of the pair. Defining

$$U_i^! = \frac{1}{2}(U_i + \sigma_h U_i) \quad \text{such that} \quad \sigma_h U_i^! = U_i^!$$

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$$U^n_i = \frac{1}{2}(U_i - \sigma_h U_i) \quad \text{such that} \quad \sigma_h U^n_i = -U^n_i$$

where U_1

$$U_1 = |\Phi_D(\alpha)\Phi_1(\beta) \rangle$$

$$U_2 = |\Phi_D(\alpha)\Phi_{-1}(\beta) \rangle$$

$$U_3 = |\Phi_D(\alpha)\Phi_0(\beta) \rangle$$

$$U_4 = |\Phi_E(\alpha)\Phi_1(\beta) \rangle$$

$$U_5 = |\Phi_E(\alpha)\Phi_{-1}(\beta) \rangle$$

$$U_6 = |\Phi_E(\alpha)\Phi_0(\beta) \rangle$$

These functions transform as shown in table 3.

Table 3 - Transformation properties of the functions U^i and U^n under symmetry operations of D_{3h} group.

	Representation	Degeneracy
$U^i_1 + U^i_5$	Γ_1	1
$U^i_1 - U^i_5$	Γ_2	1
U^i_2, U^i_4	$I\Gamma_6$	2
U^i_3, U^i_6	$II\Gamma_6$	2
$U^n_1 + U^n_5$	Γ_4	1
$U^n_1 - U^n_5$	Γ_3	1
U^n_2, U^n_4	$I\Gamma_5$	2
U^n_3, U^n_6	$II\Gamma_5$	2

The functions U^i and U^n have the correct transformation properties but they are not necessarily eigenstates.

The interactions we are interested in, can be represented by the effective Hamiltonian of eq. (1) operating on the subspace of the family functions U^i_i, U^n_i . Note that functions differing in parity under σ_h , will never mix.

Using the functions of table 3 the unperturbed Hamiltonian \mathcal{H}_0 is defined as to have those functions as eigenstates

$$\mathcal{H}_0 = \sum_n \bar{E}_n P_n$$

where P_n is the projection operator on the family of sublevels we are concerned with, and E_n is the mean value of energy for the family. This Hamiltonian \mathcal{H}_0 has the **symmetry** properties of H

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At this stage it must be pointed out that eq. (2) gives the overall effective Hamiltonian for the coupled pair according with symmetry requirements although not **all the terms involved in the products $|\sup{n}\Gamma_{\gamma k}\rangle \langle \sup{n'}\Gamma_{\gamma k}|$ will represent two-site excitation transfers.**

These can be recognized after decomposing the functions $|\sup{n}\Gamma_{\gamma k}\rangle$ into their uncoupled components as given in tables 3 and 2.

Thus the calculation of $\sup{nn'}A_{\gamma k}$ includes matrix elements such as:

$$\langle U'_i | H | U'_j \rangle = \langle U_i | H | U_j \rangle + \langle U_i | H \sigma_h | U_i \rangle$$

and

$$\langle U^n_i | H | U^n_j \rangle = \langle U_i | H | U_i \rangle - \langle U_i | H \sigma_h | U_i \rangle$$

Notice that H commutes with σ_h .

Here the second term $\langle U_i | H \sigma_h | U_i \rangle$ contains the matrix elements we are **looking for, i.e.**, those meaning transfer of an excitation from one ion to its neighbors, namely

$$\langle \Phi_1(\alpha) \Phi_D(\beta) | | \Phi_D(\alpha) \Phi_1(\beta) \rangle$$

Integrals such as $\langle \Phi_1(\alpha) \Phi_D(\beta) | | \Phi_i(\alpha) \Phi_E(\beta) \rangle$ represent intraionic **excitation** (at **site β**) and they will not be considered.

We are now in a position to examine what are the microscopic **mechanisms** contributing to the effective parameters by going into the perturbative treatment described in ref. 5.

As usual, we **separate** the microscopic Hamiltonian as a sum of: **one-electron** spin independent operators h_i (kinetic energy for **example**); **one-electron** spin-dependent operators h_i^s , (as the spin orbit interaction); **two-electron** spin-independent operators g_{ij} , (as **electron-electron** interaction); and **two-electron** spin-dependent operators g_{ij}^s , (as dipolar spin interactions).

3. First order perturbation theory

In first order perturbation theory, one-electron operators as h , and h_i^s **can** not contribute to the excitation transfer, which involves simultaneous **changes** in the

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states of two electrons, one for each ion of the pair. Only g_{ij} and g_{ij}^s must be considered. The first g_{ij} , being spin-independent, connects states with the same total M_s . The resulting integrals are of the type

$$\begin{aligned} (A d | g_{ij} | D a) &= \int \int d\tau_1 d\tau_2 A^*(r_1) D(r_1) d^*(r_2) a(r_2) g_{ij} \\ &\quad - \int \int d\tau_1 d\tau_2 A^*(r_1) a(r_1) d^*(r_2) D(r_2) g_{ij} \end{aligned}$$

When the operator is e^2/r_{12} , the first integral is **Coulomb-like**, and represents the electrostatic interaction of two charge distributions at sites a and β as given by the excitation process. The second is an exchange integral (direct exchange). It depends on the overlap of electronic wave functions centered at different sites. Some overlap can be expected for functions with a maximum of charge density along the **axis joining** the two ions of the pair, c . They are invariant for **rotations** around c and **thus** transform like A (or a). Matrix elements like $(D a || d A)$ (like $\sigma\pi$ bonding) should be more **important** than those like $(D b || d B)$ (as $\pi\pi$ bonding). Notice that g_{ij} **has** matrix elements relating states differing in one **electron** too, which are not of interest in our case.

The same kind of matrix elements appears for spin-dependent **two-electron** operators g_{ij}^s , but adding in **this** case matrix elements between functions with different M_s . An example of this kind of contributions is provided by the spin dipole-dipole interaction. Because of the r_{12}^3 denominators these integrals are expected to be much smaller than the Coulomb and exchange discussed before.

The **existence** of both kinds of integrals implies that an ion can oscillate **between** the ground and excited states, interchanging energy with one of the first neighbors, as well as exchanging energy accompanied by spin-flip process **respectively**.

Several final states are possible. The excited state includes spin up and down (spin orbit interaction **was** already included) and we can have final state with different spin on the ground state. For **example** $(A^+ \bar{d} || D^+ \bar{a})$. This means that excitation can be transferred with or without changing the spin on the ground state.

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4. Second order perturbation theory

Operator $h : h$

In the second-order perturbation theory those operators can connect states differing in two electron states, for example

$$\frac{(Ad|h|Dd)(Dd|h|Da)}{E_d - E_a} + \frac{(Ad|h|Aa)(Aa|h|Da)}{E_A - E_D}$$

Both terms are always together and cancel each other because $E_d - E_a = (E_A - E_D)$ if the ions and their environment are identical.

Elements like

$$\frac{(Ad|h|Dd)(Dd|h|Db)}{E_d - E_a} + \frac{(Ad|h|Ab)(Ab|h|Db)}{E_A - E_D}$$

such that the occupied orbital changes from one ion to the other, will not cancel but the energy levels being quasi degenerate, their contribution may be small.

The intermediate state can be one in which one electron is transferred from one ion to the other, the denominator U is always positive. Where U is the repulsion between two electrons on the same ion. They are essentially equivalent to Anderson's exchange⁷ mechanism which are sometimes referred to as kinetic exchange. They are for example

$$\frac{(Ad|h|ad)(ad|h|aD)}{U} + \frac{(Ad|h|AD)(AD|h|aD)}{U}$$

As these come in second order the intermediate state will be higher in energy and consequently these contributions can be negative and they may even cancel other contributions.

Operators $h : h, h, : h,$

The same matrix elements are expected, only the restrictions on M_s change.

Here are involved the so-called antisymmetric and anisotropic exchange⁵.

Operators $g:g$

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Now a lot of intermediate **states** are possible, even those including **vacant** states, and ligant **vacant** states. They are of the form

$$\frac{(Da|g|e_1e_2 \times e_1e_2|g|Ad)}{\Delta(e_1e_2 : Ad)}$$

where e_1, e_2 indicates vacant states.

This contribution can be positive as well as negative, depending on the energy denominators and they can **include** processes involving intermediate states in which ligand orbitals participate.

5. Conclusion

Using almost exclusively the symmetry properties of the system (Ni-Ni ion pair) we examined the energy transfer matrix elements allowed and what **kind of interactions** are able to participate on the process.

Mechanisms as Coulomb and exchange interaction (in first and **second** order perturbation theory), kinetic exchange, spin orbit and dipolar interaction (in **second** order perturbation theory), can contribute but **normally** they are expected to be small. As usually happens, at least for the low energy states, the strongest effect might arise from processes involving ligand orbitals in **second-order** perturbation theory. However, as the signs of different contributions can be **opposite** we can expect that the effective parameters for intersite energy transfer can be **very** small, as their numerical **value will** arise from a **delicate** balance of the **mechanisms** we have examined.

Experimentally it was concluded in ref. (3) that the excited state is delocalized, with a dispersion 1 cm^{-1} and the time of excitation transfer **along** a chain of normal Ni ions is less than $1 \mu\text{s}$, in agreement, at least qualitatively with our conclusion, **i.e.**, the diffusion exists but the exciton has a small dispersion.

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Resumo

Examinamos os mecanismos que contribuem para a transferência de excitação para os pares de íons Ni-Ni com a finalidade de explicar o caráter delocalizado das excitações eletrônicas observadas em CsNiF_3 . Discutimos os tipos de interações que dão elementos de matriz não nulos entre estados que conectam diferentes sítios para a posição de excitação, usando teoria de perturbações de primeira e segunda ordem e partindo de argumentos de simetria.