

Microscopic Approach to the Pseudo-Spin- $1/2$ Hamiltonian for Kramers Doublets in Exchange Coupled Co(II) Pairs

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Received August 22, 2002

The microscopic theory of the magnetically anisotropic effective pseudo-spin- $1/2$ Hamiltonian for a pair of Co²⁺ ions is reported. In the framework of the second-order perturbation approach, the analytical expressions are found for the components of the tensor of the exchange interaction, g -tensor, and the factor in the temperature independent paramagnetic contribution. The parameters of the Hamiltonian are expressed in terms of the basic intra- and intercenter parameters of the pair, namely, the spin–orbit coupling constant, orbital reduction factor, exchange integral, and low symmetry crystal field parameters including axial and rhombic terms.

1. Introduction

The study of the factors governing the magnetic anisotropy in transition metal complexes is directly related to the problem of the rational design of new single molecular magnets. In this view, the systems comprising ions with unquenched orbital angular momenta seem to be quite attractive. Among them, the exchange coupled polynuclear compounds of cobalt(II) ions are especially interesting as the systems exhibiting strong orbital contributions to the magnetic moments and thus strong magnetic anisotropy. This orbital magnetism arises from the ground orbital triplet 4T_1 of each cobalt(II) ion in a surrounding cubic crystal.

From the theoretical point of view, the problem of the magnetic exchange in cobalt(II) clusters is a hard nut to crack for magnetochemistry. Most of the works dealing with the magnetic properties of cobalt complexes have been performed in the framework of the Lines theory^{1,2} proposed more than 30 years ago. Lines developed an approximate

approach to the problem of the magnetic exchange in which the low-lying levels of individual ions (Kramers doublets) stabilized by the relatively strong spin–orbit coupling are treated exactly while the excited states are taken into account using the molecular field approximation. This theory deals with the situation when the cobalt ions are in a perfect octahedral ligand field and, hence, no magnetic anisotropy is imposed. Recently, axial distortions of the octahedral surrounding of cobalt ions were taken into account.^{3,4} This study is based on the exact solution^{5,6} of the energy matrix for the monomer that involves both spin–orbit coupling and axial distortion while the exchange interaction is considered only for the lowest doublets. The results obtained in this way are valid in the limit of weak exchange interaction as compared to the axial zero-field splitting. The method provides better results than the Lines theory for strongly distorted systems while in the case of small distortions the isotropic Lines model proves to be preferable for the description of the magnetic data. Finally, an approach⁷ based

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on the application of the irreducible tensor operator technique allowed the advance to the exact diagonalization of the Hamiltonian that includes spin–orbit coupling, axial and rhombic distortions, exchange, and Zeeman interactions. Providing more precise results, this method is, at the same time, more limited by the number of cobalt ions than the Lines theory due to the very big size of the matrices.

All mentioned considerations are based on the assumption that the exchange interaction between cobalt ions has the Heisenberg form, $\mathbf{H}_{\text{ex}} = -2JS_{\text{A}}S_{\text{B}}$, S_{A} and S_{B} being the real spins of the ions ($S_{\text{A}} = S_{\text{B}} = 3/2$). Although this simple form of the exchange may not always be entirely adequate for the orbitally degenerate ions, it has been successfully used in description of the numerous cobalt(II) cluster compounds.^{3,4,7,8} So, in the present study, we will use this approximation.

This discussion relates to the approaches that explicitly involve the basic intracenter and intercenter interactions in cobalt clusters. From this point of view, one can say that all these approaches are microscopic. On the other hand, there is another approach that deals with the phenomenological effective Hamiltonians describing the interaction between the low-lying Kramers doublets (pseudo-spin- $1/2$ formalism).⁹ Such types of Hamiltonians are widely used for the description of the magnetic anisotropy of cobalt(II) complexes at low temperatures when only the ground Kramers doublets are populated^{10–14} and are the only tool to treat extended systems. The main disadvantage of the phenomenological approach (dealing solely with the symmetry arguments) is a large number of unknown parameters, namely, the components of J - and g -tensors and the parameters describing the temperature independent paramagnetic contribution (TIP). This may lead to the overparametrization of the theory, so the fit to the experimental data is often artificial and the meaning of these effective exchange parameters is obscure. From this standpoint, it seems to be useful to find a relationship between the set of phenomenological parameters and the inherent parameters of the system, namely, the spin–orbit coupling parameter, axial and rhombic distortion parameters, orbital reduction factor, and intercenter exchange integral. To our knowledge, till now no attempts have been made to combine the microscopic theory with the pseudo-spin- $1/2$ formalism in cobalt clusters. In the present paper, we aimed to find the effective Hamiltonian for a binuclear

Kramers doublet system using the microscopic background. Under some approximations, we derive the analytical expressions for the components of the tensor of the exchange interaction, g -tensor, and parameter describing the TIP.

2. The Model

Spin–orbit coupling splits the ground 4T_1 term of Co(II) ion in a perfect octahedral ligand field into the doublet $J = 1/2(\Gamma_6)$, quartet $J = 3/2(\Gamma_8)$, and sextet $J = 5/2(\Gamma_7 + \Gamma_8)$ states with the energies $-5/2ka\lambda$, $-ka\lambda$, and $3/2ka\lambda$, respectively. Here, λ is the spin–orbit coupling parameter, k is the orbital reduction factor, a is introduced to distinguish between the orbital angular momentum operator in T_1 and P bases ($\mathbf{L}(T_1) = a\mathbf{L}(P)$, for Co(II) ion $a = -3/2$ in the weak crystal field limit⁵). The corresponding eigenvectors for Kramers doublet and for the excited quartet and sextet can be found using the Clebsch–Gordan decomposition:

$$\Phi(JM_J) = \sum_{M_L M_S} C_{1M_L 3/2M_S}^{JM_J} |1M_L\rangle |3/2M_S\rangle \quad (1)$$

The ground state is Kramers doublet that is well separated from the first excited quartet state (the gap $3/2ka\lambda$ is on the order of 300–400 cm^{-1}). In most cases, this splitting exceeds significantly intercenter exchange and also Zeeman interaction. This allows us to consider the low-lying energy levels of two exchange coupled Co(II) ions as the result of the interaction within two Kramers doublets and describe this interaction by a pseudo-spin- $1/2$ -Hamiltonian.

We will consider the situation when the octahedral ligand surroundings of Co(II) ions are slightly distorted and the energy splittings due to the noncubic components of the crystal field are smaller than those produced by spin–orbit coupling. Under this condition, the full Hamiltonian of the Co(II) pair can be split into the nonperturbed Hamiltonian \mathbf{H}_0 involving spin–orbit coupling, and the perturbation \mathbf{V} that includes exchange and Zeeman interactions and low-symmetry crystal field terms

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V} \quad (2)$$

where

$$\mathbf{H}_0 = \kappa a \lambda \sum_{j=A,B} \mathbf{L}_j \mathbf{S}_j \quad (2)$$

$$\mathbf{V} = -2JS_{\text{A}}S_{\text{B}} + \sum_{j=A,B} [D(\mathbf{L}_Z^j)^2 - 2/3] + E(\mathbf{L}_X^j)^2 - \mathbf{L}_Y^j + \beta \mathbf{H}(ak\mathbf{L}_j + g_e \mathbf{S}_j) \quad (3)$$

In eq 3, the isotropic Heisenberg form of the exchange interaction between the real spins $3/2$ is assumed. The Hamiltonian, eq 2, operates within the total space

$$\Psi_{J_A J_B}(M_{J_A} M_{J_B}) \equiv \Phi_A(J_A M_{J_A}) \Phi_B(J_B M_{J_B}) \quad (4)$$

In order to pass from the initial Hamiltonian to the effective pseudo-spin- $1/2$ -Hamiltonian operating within the restricted space of the direct product of the ground Kramers

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doublets, one can apply the second-order perturbation theory for the degenerate level. Then, the effective pseudo-spin-1/2 Hamiltonian can be presented as

$$\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{eff}}^{(1)} + \mathbf{H}_{\text{eff}}^{(2)} \quad (5)$$

where $\mathbf{H}_{\text{eff}}^{(1)}$ and $\mathbf{H}_{\text{eff}}^{(2)}$ are the first- and second-order terms defined as

$$\langle \Psi_{1/2,1/2}(M_{JA}, M_{JB}) | \mathbf{H}_{\text{eff}}^{(1)} | \Psi_{1/2,1/2}(M'_{JA}, M'_{JB}) \rangle = \langle \Psi_{1/2,1/2}(M_{JA}, M_{JB}) | \mathbf{V} | \Psi_{1/2,1/2}(M'_{JA}, M'_{JB}) \rangle \quad (6)$$

$$\langle \Psi_{1/2,1/2}(M_{JA}, M_{JB}) | \mathbf{H}_{\text{eff}}^{(2)} | \Psi_{1/2,1/2}(M'_{JA}, M'_{JB}) \rangle = - \sum_{J_A J_B \Delta_{J_A J_B} M''_{JA} M''_{JB}} \frac{1}{\Delta_{J_A J_B} M''_{JA} M''_{JB}} \langle \Psi_{1/2,1/2}(M_{JA}, M_{JB}) | \mathbf{V} | \Psi_{J_A J_B}(M''_{JA}, M''_{JB}) \rangle \times \langle \Psi_{1/2,1/2}(M'_{JA}, M'_{JB}) | \mathbf{V} | \Psi_{J_A J_B}(M''_{JA}, M''_{JB}) \rangle^* \quad (7)$$

where $\Delta_{J_A J_B} \equiv E_{J_A J_B} - E_{1/2,1/2}$ are the energy gaps between the ground and excited eigenvalues of \mathbf{H}_0 .

In order to find the matrix of $\mathbf{H}_{\text{eff}}^{(1)}$, one should calculate the matrices of spin and orbital angular momentum operators in the basis $\Phi_j(1/2, 1/2)$, $\Phi_j(1/2, -1/2)$ ($j = A, B$). One can find direct relations between these matrixes ($S_x^j, S_y^j, S_z^j, L_x^j, L_y^j, L_z^j$) and the spin-1/2 matrixes s^j (see refs 1 and 9) and arrive at the equation for $\mathbf{H}_{\text{eff}}^{(1)}$:

$$\mathbf{H}_{\text{eff}}^{(1)} = -\frac{50}{9} J s_A s_B + g_0 \beta (s_A + s_B) \mathbf{H} \quad (8)$$

where

$$g_0 = \frac{1}{3}(5g_e - 2ak) \quad (9)$$

Equations 8 and 9 coincide with the results of Lines.¹ As already noticed by this author, these equations do not provide a satisfactory description of the magnetic properties of Co(II) dimers even at low temperatures due to the neglecting of the mixture of the ground states with the excited ones by the exchange and Zeeman interactions. Moreover, this Hamiltonian does not carry any magnetic anisotropy because the distortion terms are not operative in the first-order approximation. This mixing can be taken into account in our second-order perturbation scheme, so we proceed to calculate the term $\mathbf{H}_{\text{eff}}^{(2)}$.

The second-order perturbation theory allows us to express the matrix of $\mathbf{H}_{\text{eff}}^{(2)}$ in terms of energy separations between the ground state and the relevant excited states (as a function of $ka\lambda$) and the parameters J , D , and E (see Supporting Information for a detailed deduction). Taking into account the relations between the matrix of $\mathbf{H}_{\text{eff}}^{(2)}$ and the direct products of spin-1/2 matrixes and the expression derived for $\mathbf{H}_{\text{eff}}^{(2)}$ (eq 6), one arrives at the following final expression for the effective pseudo-spin-1/2 Hamiltonian:

$$\mathbf{H}_{\text{eff}} = \sum_{\alpha=X,Y,Z} [-2J_\alpha s_\alpha^A s_\alpha^B + g_\alpha \beta (s_\alpha^A + s_\alpha^B) H_\alpha - \Lambda_\alpha \beta^2 H_\alpha^2] \quad (10)$$

The parameters of this Hamiltonian are given by

$$J_Z = \frac{25}{9} J + \frac{20}{81ka\lambda} (15J^2 - 4JD)$$

$$J_X = \frac{25}{9} J + \frac{20}{81ka\lambda} [15J^2 + 2J(D - 3E)]$$

$$J_Y = \frac{25}{9} J + \frac{20}{81ka\lambda} [15J^2 + 2J(D + 3E)] \quad (11)$$

$$g_Z = g_0 - \frac{8}{81ka\lambda} (25J - 3D)(ak - g_e)$$

$$g_X = g_0 - \frac{4}{81ka\lambda} [50J + 3(D - 3E)](ak - g_e)$$

$$g_Y = g_0 - \frac{4}{81ka\lambda} [50J + 3(D + 3E)](ak - g_e) \quad (12)$$

$$\Lambda_X = \Lambda_Y = \Lambda_Z = \frac{20}{27ka\lambda} (ak - g_e)^2 \quad (13)$$

Equations 10–13 are the main results of this paper.

3. Concluding Remarks

In summary, we have derived the effective pseudo-spin-1/2 Hamiltonian for a pair of Co²⁺ ions. The parameters of this Hamiltonian are found as the functions of the basic parameters of the system, namely, the spin-orbit coupling parameter, low symmetry crystal field parameters including axial and rhombic terms, orbital reduction factor, and intercenter exchange integral. The inclusion of the second order mixing with the excited states results in the appearance of the new terms in the exchange parameters and the principal values of g -tensor. The additional terms in g containing D and E arise, as usual, from one-center contributions and account for the anisotropy of the system. Provided $E = 0$, the magnetic anisotropy is axial, while terms containing E lead to the rhombic anisotropy. The second-order terms also contain magnetically isotropic contributions depending on the ratio $J/ka\lambda$. These terms are especially important for the appropriate estimation of g -factors and describe the influence of bicenter interactions on these parameters. The results show a significant deviation of the molecular g -factors from g -factors of the monomeric moieties. The anisotropy of the effective exchange parameters (in general, triaxial) appears to be due to the combined effect of the true isotropic exchange and low symmetry crystal fields. It is to be noted that these parameters also contain isotropic contributions. We have also found contributions associated with TIP. In the adopted approximation, the TIP proves to be isotropic and independent of the parameters J , D , and E . It is simply twice the value for the octahedral monomeric unit. Anisotropy in the TIP terms (depending on J , D , and E) is expected to appear within the higher-order perturbation theory.

Note that in the present form this theory is not directly applicable to the case of strongly distorted systems when our perturbation scheme fails. In this case, the low symmetry crystal field terms should be included in the zeroth-order Hamiltonian, while the perturbation involves exchange and

Zeeman terms. In this approximation, the parameters of the effective Hamiltonian calculated up to the first order will depend on D and E , the procedure for the case of axially distorted systems was outlined in ref 9. At the same time, an important effect of the exchange mixing of spin-orbital multiplets was not taken into account in this scheme. The present theory includes this effect, and within adopted approximation we found simple and transparent analytical expressions for the parameters. We believe that these results provide clear insight on the origin of the magnetic anisotropy in cobalt clusters.

We leave outside of this short paper a rather complicated question of the applicability of the isotropic exchange model in the case of orbitally degenerate ions. Our study of the exchange interaction in the presence of degeneracy^{15–19}

showed that the anisotropic exchange terms can play an important role. More comprehensive study of the exchange interaction in cobalt clusters based on the theory developed in refs 15–19 could elucidate the role of the exchange anisotropy in the effective interaction within Kramers doublets. This work is under way.

Acknowledgment. Financial support from the European Network on Molecular Nanomagnets, INTAS (Project 2000-0651), the Spanish Ministerio de Ciencia y Tecnología (Grant MAT 2001-3507), the Generalidad Valenciana (Grant GV01-312), and the Supreme Council on Science and Technological Development of Moldova (Grant N111) is highly appreciated. A.V.P. thanks the NATO Scientific Committee whose financial support made possible his stay at the University of Valencia. B.S.Ts. thanks the Spanish Ministerio de Educación, Cultura y Deporte, for a visiting professor grant. J.M.C.-J. thanks the Spanish Ministerio de Ciencia y Tecnología for a RyC contract.

Supporting Information Available: Additional mathematical details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0259686

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