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Antisymmetric double exchange and zero-field splittings in mixed-valence clusters

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Abstract

The effect of an antisymmetric double exchange (AS DE) interaction in the mixed-valence (MV) dimeric d^n-d^{n+1} and trimeric $d^n-d^n-d^{n+1}$ clusters of orbitally non-degenerate ions is considered. In the dimeric clusters, strong isotropic Anderson–Hasegawa (AH) DE and Heisenberg exchange interactions ($t-J$ model) form isotropic DE states $E_{\pm}{}^0$(S). In the MV dimers, the Moriya spin-flop hopping, which is determined by the spin-orbit coupling, is described by the effective Hamiltonian of an AS DE interaction $\mathbf{H}_{\mathrm{ASDE}}=2i\mathbf{K}_{ab}\mathbf{T}_{ab}(\mathbf{S}_b-\mathbf{S}_a)$, where $\mathbf{K}_{ab}=-\mathbf{K}_a$ is a real AS vector coefficient, $\mathbf{T}_{ab}$ is the isotropic transfer operator. The operator H_{ASDE} has a form of the spin-transfer interaction. Analytical expressions for the matrix elements of HASDE were obtained for $\mathrm{d}^{\mathrm{n}}-\mathrm{d}^{\mathrm{n}+1}$ clusters. The AS DE matrix elements depend on the projection M of S. AS DE mixes the AH DE states E_+^0(S) and E_-^0(S) with the same S of the different parity. The AS DE coupling and the Dzialoshinsky–Moriya (DM) AS exchange ($\mathbf{H}_{\mathrm{DM}}=\mathbf{G}_{ab}[\mathbf{S}_a\times\mathbf{S}_b]$) mix the AH states with different S of the same parity. AS DE forms the effective spin S'. In the d^1-d^2 and d^9-d^8 clusters, the AS DE contributions to the zero-field splitting (ZFS) parameters are different for the AH high-spin states $E_+(3/2)$ and $E_-(3/2)$. An AS DE leads to non-collinear orientation of spins in the MV pair and anisotropy of g-factors. An anisotropic DE contributes to ZFS. In the trimeric MV clusters, the isotropic DE forms the isotropic trigonal ${}^{2S+1}\Gamma$ terms, $\Gamma=A_1, A_2, E$. The AS DE results in the new effect: the linear fine splittings Δ of the degenerate ${}^{2S+1}E$ DE terms. The fine splittings Δ are proportional to the AS DE parameter $K_Z=(K_{ab}^Z+K_{bc}^Z+K_{ca}^Z)/3$ of the MV trimer. The vector of the AS DE interaction K_Z is directed along the trigonal Z-axis of the MV trimer. The AS DE mixes the ${}^{2S+1}A_1$ and ${}^{2S+1}A_2$, ${}^{2S+1}E$ and ${}^{2S+1}E$ DE terms ($\Delta S=0$, 1). In the trimeric MV clusters with high individual spins s_i, the AS DE and DM AS exchange mixing of the DE levels ${}^{2S+1}\Gamma$ determines the contributions of the second order to the ZFS parameters D_S, which are different for the A_i and E DE terms. For the [Cu(II)Cu$_2$(I)] delocalized cluster, the AS DE ZFS $\Delta=2K_Z\sqrt{3}$of the ground ${}^2E$ DE term determines strong anisotropy of the Zeeman splittings, anisotropy of g-factors ($g_Z\neq 0$, $g_{X,Y}=0$) and magnetic properties.

Keywords: Antisymmetric double exchange; Mixed-valence clusters; Zero-field splitting

1. Introduction

The mixed-valence (MV) clusters of transition metal ions are attracting considerable attention as single-molecular magnets, models for investigation of magnetism at the mesoscopic scale [1–4] and the active centers of ferredoxins and enzymes. In the MV clusters of paramagnetic ions, the double exchange (DE) [5,6] and the Heisenberg exchange (HE) interaction $\mathbf{H}_0=\Sigma J_{ij}\mathbf{S}_i\mathbf{S}_j$ forms the cluster states. The Anderson–Hasegawa (AH) [6] DE interaction (the hopping of the extra electron between d^n and d^{n+1} ions in the MV pair) results in the spin-dependent resonance splittings $E_{\pm}^0(S)=\pm(S+1/2)t_0/(2s_0+1)$, where S is the total spin, $s_0=S(d^n)$, t_0 is the one-electron transfer (ET) integral. In the dimeric MV systems, the states of the AH DE plus HE interactions ($t-J$ model) $E_{\pm}^0(S)=\pm(S+1/2)t_0/(2s_0+1)+J[S(S+1)-3/4]$ are isotropic. The AH DE coupling does not mix the states with different S and also the $E_+^0(S)$ and $E_-^0(S)$ DE states of different parity with the same S. Strong AH DE results in the ferromagnetic ground state $S_{\mathrm{gr}}=S_{\max}$. The isotropic AH DE in dimers was investigated in detail (see review articles [7–9] and references therein). Strong isotropic DE interaction $t=$

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1350 cm^{-1} was found experimentally in the [Fe(II)Fe(III)] cluster in the $[Fe_2(OH)_3(tmtacu)_2]^{2+}$ complex [10,11]. The concept of the DE (spin-dependent ET) in the MV pair is widely used in magnetism of the MV compounds, particularly DE magnets, in the theory of the MV metal clusters in inorganic chemistry and bioinorganic chemistry of iron–sulfur proteins.

The DE concept was developed for trimeric [12–15], tetrameric [16,17] and more complicated clusters [17] (see [7–9]) as well as for the MV dimers of orbitally degenerate ions [18]. Theoretical investigations of DE between the three ions in the MV trimers [12–14,19–29] demonstrate a variety of different types of magnetic behavior. The resulting non-ferromagnetic DE ground state was found experimentally in the MV Ni trimer in [30]. The DE coupling in one MV pair determines the magnetic properties, Mössbauer and EPR spectra of the [3Fe4S] clusters in ferredoxins and model systems [15,8,19,31–34,29].

The migration of the extra electron (hole) among the three ions in the trigonal trimer forms the resulting isotropic trigonal DE terms $^{2S+1}\Gamma$ (A_1, A_2, and E) [13]. The spin dependence of the DE parameters is determined by the 9-j symbols [12,13]. The trigonal DE states are accidentally degenerate in the t–J model. The DE exchange does not mix different $^{2S+1}$ Γ DE terms of trimer.

Usually the spin-orbit coupling (SOC) is not considered in the theory of the DE between orbitally non-degenerate ions. However, the consideration of only isotropic DE is not enough for description of zero-field splittings (ZFS) of the DE levels, magnetic anisotropy and anisotropy of the EPR spectra. The consideration of ZFS and anisotropy requires the taking SOC into account in the theory of the DE.

The taking SOC into account [35,36] in the theory of the exchange between two identical orbitally non-degenerate d^n ions results in the Dzialoshinsky–Moriya (DM) [35–37] antisymmetric (AS) exchange interaction $\mathbf{H}_{DM} = \Sigma_{ij}\mathbf{G}_{ij}[\mathbf{S}_i \times \mathbf{S}_j]$, where $\mathbf{G}_{ij} = -\mathbf{G}_{ji}$ is an AS DM vector coefficient. The virtual vector transfer (spin-flop hopping) [36] in the Cu(II)–Cu(II) system determines the DM AS parameter and anisotropic (AN) interaction. The microscopic theory of the DM AS exchange and symmetric AN exchange between monovalent ions is widely used in magnetism and was further developed in Refs. [38–48] for insulating cuprates.

The SOC for the transfer of hole between the neighboring sites in doped La_2CuO_4 was considered in Refs. [42,46]. An extension of the t–J model includes the spin-orbit hopping term and AN term [42]. The model [42] is restricted by the systems of the hole transfer in the Cu(II) matrix ($S_i = 1/2$) and does not consider the high-spin systems and polynuclear clusters.

The SOC effect in the DE model and origin of ZFS of the DE levels are considered in this work for dimeric $[d^n - d^{n+1}]$ and trimeric $[d^n - d^n - d^{n+1}]$ clusters. The taking SOC into account in the theory of the Anderson–Hasegawa DE leads to antisymmetric double exchange (AS DE) interaction [53,54]. The AS DE contributes to the second-order ZFS parameters $D_S(^{2S+1}\Gamma)$ of the $^{2S+1}\Gamma_i$ DE terms, S > 1/2. AS DE determines anisotropy of the Zeeman splitting, magnetic moment and EPR spectra. In the MV trimers, AS DE splits linearly the trigonal DE ^{2S+1}E-terms.

2. Spin-orbit coupling in the d^1–d^0, d^9–d^{10} clusters with double exchange (ET)

In the Moriya theory [35,36] of the AN superexchange, the one electron Hamiltonian of the inter-ion virtual transfer between Cu(II) ions was written in conventional terms of annihilation and creation operators

$$\begin{aligned}\mathbf{H}^0_{ab} = {} & t_{ab}[a^+_\uparrow b_\uparrow + a^+_\downarrow b_\downarrow + a_\uparrow b^+_\uparrow + a_\downarrow b^+_\downarrow] \\ & + C^z_{ab}[a^+_\uparrow b_\downarrow - a^+_\downarrow b_\downarrow + a_\uparrow b^+_\uparrow - a_\downarrow b^+_\downarrow] \\ & + C^-_{ab}[a^+_\uparrow b_\downarrow + a_\uparrow b^+_\downarrow] + C^+_{ab}[a^+_\downarrow b_\uparrow + a_\downarrow b^+_\downarrow]\end{aligned} \tag{1}$$

$t_{ab} = \langle \varphi_a || \varphi_b \rangle$ are the standard isotropic inter-center one-ET integrals without SOC. The first term in Eq. (1) is the convenient transfer (DE) term for the t–J models. The AS vector transfer integrals $\mathbf{C}_{ab}(\mathbf{C}^v_{ab} = -\mathbf{C}^v_{ba})$, which are connected with the SO coupling, were determined in Ref. [36]

$$\begin{aligned}& \langle \varphi_a(m_a = \pm 1/2)|H_{ab}|\varphi_b(m_b = \pm 1/2)\rangle = t_{ab}(\varphi) \pm C^\pm_{ab}, \\ & \langle \bar{\varphi}_a || \varphi_b \rangle = C^+_{ab}, \qquad \langle \varphi_a || \bar{\varphi}_b \rangle = C^-_{ab}, \\ & \langle \varphi_b(\pm 1/2) || \varphi_a(\pm 1/2) \rangle = t_{ab}(\varphi) \pm C^z_{ab}, \\ & \langle \bar{\varphi}_b || \varphi_a \rangle = C^+_{ba}, \qquad \langle \varphi_b || \bar{\varphi}_a \rangle = C^-_{ba}\end{aligned} \tag{2}$$

$\vec{C}^\pm_{ab}(C^x_{ab} \pm iC^y_{ab})$. The basis wave functions are $\varphi_{a\uparrow} = \varphi_a(m = 1/2) = \varphi_a$ and $\varphi_{a\uparrow} = \varphi_\downarrow(m = -1/2) = \vec{\varphi}_a$ [36]. The vector transfer parameters $\mathbf{C}_{ij}$ are pure imaginary. These spin-flop hopping terms determine the DM AS exchange constants $\mathbf{G}_{ij} = 2i\mathbf{C}_{ij}\mathbf{J}/t$ and AN exchange contribution $\mathbf{\Gamma}_{ij}$ in the pseudodipolar AN term $\mathbf{S}_i\mathbf{\Gamma}_{ij}\mathbf{S}_j$ [36] in the theory of superexchange between Cu(II) ions.

By using the Hamiltonian (Eq. (1)) for consideration of ET in the d^1–d^0 MV cluster, we obtain the matrix of ET ($d^1 - d^0 \rightleftarrows d^1 - d^0$) in the model (Eq. (1)) in the form

$$\begin{bmatrix} \bar{\varphi}_{a_\downarrow} & \varphi_{a_\uparrow} & \bar{\varphi}_{b_\downarrow} & \varphi_{b_\uparrow} \\ 0 & 0 & t_{ab} - C^z_{ab} & C^+_{ab} \\ 0 & 0 & C^-_{ab} & t_{ab} + C^z_{ab} \\ t_{ab} - C^z_{ba} & C^+_{ab} & 0 & 0 \\ C^-_{ba} & t_{ab} + C^z_{ba} & 0 & 0 \end{bmatrix} \tag{3}$$

To compare with the model (Eqs. (1) and (3)), we will consider first the SOC effect in ET (DE) in the case of the d^1–d^0 dimer (Ti^{3+}–Ti^{4+} and V^{4+}–V^{5+} pair).

The microscopic calculation of DE plus SOC for the MV dimer d^1-d^0 includes the formation of the renormalized ground state by the SOC admixture of the excited crystal field (CF) states ψ_m into the ground state φ_0 of the d_a^1 (d_b^1) ion of the d^1-d^0(d^0-d^1) pair in the localizations $d_a^1-d_b^0$ ($|a^*b\rangle$) and $d_a^0-d_b^1$ ($|ab^*\rangle$). These renormalized ground states φ_a are used then for calculations of DE (resonance interaction).

For the d^1-d^0 MV dimer, the Hamiltonian of the pair $\hat{H}_{12}=\hat{H}_{a*b}+\hat{H}_{ab*}+\hat{V}_{12}$ is the sum of the single-site terms for the localizations $|a^*b\rangle$ and $|ab^*\rangle$ and inter-ion interaction $\hat{V}_{12}$ of the direct type (Coulomb interaction) or indirect interaction through the ligand bridge. The single-site Hamiltonian for the d_α^1 ion includes the CF Hamiltonian HCF [49,50] for the 3d-electron and SOC $H_{LS}^a=\lambda_a L_a S_a$. In the case of the $|a^*b\rangle$ localization, the d^0 ion on the center b has a closed d-shell. The local octahedral CF with tetragonal distortion forms the orbitally non-degenerate ground $\zeta_a^0=d_{xy}^a$ state of the d_0^1 ion. The excited CF states $\xi_a=(d_{yz})_a$, $\eta_a=(d_{zx})_a$, $u_a=(d_{3z^2-r^2})_a$ and $v_a=(d_{x-y^2})_a$ are separated by the CF intervals $\varepsilon_\xi^a,\varepsilon_\eta^a,\varepsilon_u^a$ and ε_v^a, respectively [49,50]. SOC admixes the excited CF states ψ_m into the ground ζ_a^0 state. The non-zero SOC matrix elements for the t and e orbitals are represented in Refs. [49,50]. In the first order perturbation, the renormalized ground state functions for the center a have the form

$$\zeta_{\alpha\uparrow}=[\zeta_{\alpha\uparrow}^0+i\gamma_v^\alpha v_{\alpha\uparrow}-\gamma_\xi^\alpha\xi_{\alpha\downarrow}-i\gamma_\eta^\alpha\eta_{\alpha\downarrow}]/\sqrt{n_0},$$

$$\zeta_{\alpha\downarrow}=[\zeta_{\alpha\downarrow}^0-i\gamma_v^\alpha v_{\alpha\downarrow}+\gamma_\xi^\alpha\xi_{\alpha\uparrow}-i\gamma_\eta^\alpha\eta_{\alpha\uparrow}]/\sqrt{n_0} \qquad (4)$$

where d-orbital functions refer to the local Cartesian frame and

$$\gamma_v^\alpha=\lambda/\varepsilon_v^\alpha, \qquad \gamma_\xi^\alpha=\lambda/2\varepsilon_\xi^\alpha, \qquad \gamma_\eta^\alpha=\lambda/2\varepsilon_\eta^\alpha \qquad (5)$$

$n_0 I_0=1+\gamma_v^2+\gamma_\xi^2+\gamma_\eta^2$. The localized states $|a^*b\rangle(d_a^1-d_b^0)$ and $|ab^*\rangle(d_a^0-d_b^1)$ have the same energy. For the delocalized d^1-d^0 pair with $S=1/2$, the only active interaction $\hat{V}_{12}$ is the ET (double exchange). The DE interaction leads to the resonance splitting. The matrix elements of the DE coupling depend on the projection M of spin S

$$\langle\Phi_{a*b}(S=1/2,\ M=\pm1/2)|\hat{V}_{12}|\Phi_{ab*}(1/2,\ \pm1/2)\rangle$$
$$=t_{ab}(\zeta)\pm iK_{ab}^z \qquad (6)$$

where the isotropic transfer integral has the form

$$t_{ab}=[t_{ab}^0(\zeta)+t'_{ab}]/n_0, \qquad t'_{ab}=[\gamma_v^2 t_v+\gamma_\xi^2 t_\xi+\gamma_\eta^2 t_\eta] \qquad (7)$$

The $t_{ab}^0(\zeta)=\langle\zeta_a^0|\hat{V}_{12}|\zeta_b^0\rangle=t_\zeta$ term is the standard integral of ET in the ground state without SOC. The t'_{ab} term is the contribution to t_{ab} of the transfer in the excited states due to the SOC admixture. In the real vector transfer parameter

$$K_{ab}^z=[\gamma_v^b t_{ab}(\zeta_a^0,\ v_b)-\gamma_v^a t_{ab}(v_a,\ \zeta_b^0)]/n_0 \qquad (8)$$

$t_{\alpha\beta}(\zeta_\alpha^0,\ v_\beta)=\langle\zeta_\alpha^0|\hat{V}_{12}|v_\beta\rangle$ is the transfer integral between the ground orbital ζ_a^0 state on the center $\alpha(=a[b])$ and the excited v_β state on the center $\beta(=b[a])$. In the resonance representation $\psi_\pm(S)=[\Phi_{a*b}(S)\pm\Phi_{ab*}(S)]/\sqrt{2}$, the matrix of the DE plus the SOC for the d^1-d^0 MV dimer has the form:

$$\begin{bmatrix} \overline{\Psi}_+ & \Psi_+ & \overline{\Psi}_- & \Psi_- \\ t_{ab} & 0 & iK_{ab}^z & -iK_{ab}^+ \\ 0 & t_{ab} & iK_{ab}^- & -iK_{ab}^z \\ -iK_{ab}^\pm & -iK_{ab}^+ & -t_{ab} & 0 \\ iK_{ab}^- & iK_{ab}^z & 0 & -t_{ab} \end{bmatrix} \qquad (9)$$

where $t_{ab}=t_{ab}(\zeta)$, $\quad K_{ab}^\pm=K_{ab}^\eta\pm iK_{ab}^\zeta=K_{ab}^y\pm iK_{ab}^x$,

$$K_{ab}^\eta=[\gamma_\eta^a t_{ab}(\eta_a,\ \zeta_b^0)-\gamma_\eta^b t_{ab}(\zeta_b^0,\ \eta_b)]/n_0,$$

$$K_{ab}^\xi=[\gamma_\xi^a t_{ab}(\zeta_a,\xi_b^0)-\gamma_\xi^b t_{ab}(\xi_b^0,\zeta_b)]/n_0 \qquad (10)$$

The real vector transfer coefficients $\mathbf{K}_{ab}$ are AS: $\mathbf{K}_{ab}=-\mathbf{K}_{ba}(C_{ab}^z=iK_{ab}^z,\quad C_{ab}^\pm=iK_{ab}^\pm)$. The diagonal terms $\pm t_{ab}(\zeta)$ coincide with the result of the Anderson–Hasegawa equation $E_\pm^0(S)=\pm(S+1/2)t_\zeta/(2s_0+1)$. The SOC mixing of the isotropic AH DE states $E_+(S)$ and $E_-(S)$ is described by the non-diagonal AS DE terms K_{ab}^v in Eq. (10). The DE+SOC splitting for the d^1-d^0 cluster has the form

$$E_x(S,\ M)=\pm\sqrt{t^2+\mathbf{K}^2}, \qquad (11)$$

where $t=t_\zeta$ and $K^2=K_z^2+K_x^2+K_y^2$, $\sqrt{t^2+\mathbf{K}^2}$ is the effective transfer parameter.

The transfer integrals between the ground state and excited states $t_{\alpha\beta}(\varphi_\alpha^0,\psi_\beta)\neq0$ due to the tilt of the distorted octahedra ML_6 on the small angle θ ($\theta\ll1$) [36,46,39–42]. The tilting results in a small ($\sim\theta$) admixture of the ξ and η orbitals to the ground ζ orbital. In the case of the $|a^*b\rangle$ localization, the local CF 3d orbitals $(\zeta'_a)_{qr}$, ξ'_a, η'_a, u'_a, v'_a may be written in the common xyz-coordination system in the form [42,46] ($\theta_1=\theta/\sqrt{2}$):

$$(\zeta'_a)_{qr}=\zeta_a-\theta_1(\xi_a+\eta_a), \qquad v'_a=v_a+\theta_1(\xi_a-\eta_a),$$
$$u'_a=u_a+\theta_1\sqrt{3}(\xi_a+\eta_a),$$
$$\xi'_a=\xi_a-\theta_1(v_a+\sqrt{3}u_a-\zeta_a), \qquad (12)$$
$$\eta'_a=\eta_a-\theta_1(-v_a+\sqrt{3u_a}-\zeta_a)$$

In the case of the $|ab^*\rangle$ localization, θ should be changed to $-\theta$ in φ_b. The non-zero transfer integrals ($\sim\theta$) between the ground state ζ'_a and excited ψ'_b states have a form

$$t_{ab}(\zeta'_a,\xi'_b)=-\theta_1[t_{ab}(\zeta)+t_{ab}(\xi)],\ \ t_{ab}(\zeta'_a,\ \eta'_b)$$
$$=-\theta_1[t_{ab}(\zeta)+t_{ab}(\eta)] \qquad (13)$$

The corresponding transfer integrals between the ground state ζ'_b and excited ψ'_a state have the opposite sign: $t_{ab}(\zeta'_b,\ \xi'_a)=-t_{ab}(\zeta'_b,\ \xi'_b)$, $t_{ab}(\zeta'_b,\ \eta'_a)=-t_{ab}(\zeta'_a,$

η'_b) [36]. The $t_{\alpha\beta}(\varphi^0_\alpha,\ \psi_\beta)$ transfer integrals were calculated for the Cu(II)–Cu(II) pairs in [36,40–48]. The components of an AS vector transfer (DE) parameter K^k_{ab} in Eqs. (8) and (10) in the d^1-d^0 MV pair are the following [53]:

$$K^x_{ab} = -K^\xi_{ab} = \frac{\lambda\theta}{2\varepsilon_\xi}(t_\zeta + t_\xi),$$
$$K^y_{ab} = -K^\eta_{ab} = \frac{\lambda\theta}{2\varepsilon\eta}(t_v + t_\eta), \qquad K^z_{ab} = 0 \tag{14}$$

$|K^x_{ab}| = |K^y_{ab}|$ in the case of the tetragonal distortion with $\varepsilon_\xi = \varepsilon_\eta,\ t_\xi = t_\eta$. $|K^x_{ab}| \neq |K^y_{ab}|$ in the case of the low-symmetry distortion. The resonance splitting in the DE+SOC model $E_\pm = \pm\sqrt{t^2_{ab} + K^2_x + K^2_y}$ depends on the effective transfer parameter $t_{\text{eff}} = \sqrt{t^2_{ab} + K^2_x + K^2_y}$.

The estimations of the vector transfer parameters $|\mathbf{C}_{\text{ab}}|(=|\mathbf{K}_{\text{ab}}|)$ were obtained by Moriya [36] $|C_{ab}|/t_{ab} = K_{ab}/t_{ab} \sim \Delta g/g$, where Δg is a deviation from the g-value of a free electron. The AS $\mathbf{K}_{ab}$ vector DE parameters may be the quantities of the order of 1–5% of the DE parameter t_{ab}.

In the case of the hole-transfer in the $Cu^{2+}-Cu^{+}(d^9-d^{10})$ pair, the tilting of the CuL_6 octahedra results in a small ($\sim\theta$) admixture of the ξ and η orbitals to the ground v_0 orbital [36,42]. The components of the AS DE parameter $\vec{K}^i_{ab}$ are the following [42,53]:

$$K^x_{ab} = -K^\xi_{ab} = -[\gamma^b_\xi t_{ab}(v^0_a,\ \xi'_b) - \gamma^a_\xi t_{ab}(v^0_b,\ \xi'_a)]$$
$$= -\frac{\lambda\theta}{2\Delta_\xi}(t_v + t_\xi),$$

$$K^y_{ab} = -K^\eta_{ab} = -[\gamma^b_\eta t_{ab}(v^0_a,\ \eta'_b) - \gamma^a_\eta t_{ab}(v^0_b,\ \eta'_a)]$$
$$= -\frac{\lambda\theta}{2\Delta_\eta}(t_v + t_\eta),$$

$$K^z_{ab} = 0 \tag{15}$$

where $\Delta_\psi = \Delta[E_{\text{CF}}(\psi) - E_{gr}(v_0)], \psi = \xi,\ \eta$. An AN interaction $H'_{\text{AN}}\Sigma_{ij}\mathbf{S}_i\mathbf{\Gamma}_{ij}\mathbf{S}_j$ [42] with symmetric AN parameter

$$\mathbf{\Gamma}_{\text{ij}} = \frac{4}{U}[\mathbf{C}_{\text{ij}}\mathbf{C}_{\text{ji}} + \mathbf{C}_{\text{ji}}\mathbf{C}_{\text{ij}} + 1(\mathbf{C}_{\text{ij}}\mathbf{C}_{\text{ji}})]$$
$$= \frac{J}{t^2}[\mathbf{C}_{\text{ij}}\mathbf{C}_{\text{ji}} + \mathbf{C}_{\text{ji}}\mathbf{C}_{\text{ij}} + 1(\mathbf{C}_{\text{ij}}\mathbf{C}_{\text{ji}})] \tag{16}$$

is not active in the $Cu^{2+}-Cu^{+}(d^9-d^{10})$ pair with the total spin $S = 1/2$ and $J = 0$.

3. Antisymmetric double exchange in the d^9-d^8 (d^1-d^2) cluster

The calculations of DE plus SOC in the d^n-d^{n+1} MV dimers with the high-spin ions ($S_i \geq 1/2$) we consider on an example of the d^9-d^8 (d^1-d^2)[$S_a = 1/2,\ S_b = 1;\ S = 1/2,\ 3/2$] cluster. In the spin representation, the Hamiltonian of the system has the form $\hat{H}_{12} = \hat{H}^e_{a*b} + \hat{H}^e_{ab*} + \hat{V}_{ab}$, where $\hat{H}^e_{a*b}(H^e_{ab*})$ is the Hamiltonian in the $|a*b\rangle(|ab*\rangle)$ localization, and $\hat{V}_{ab}$ is the DE operator. The Hamiltonian $H^{\text{e}}_{a*b} = H_{\text{HE}} + H_{\text{DM}} + H_{\text{AN}} + H^0_{\text{ZFS}}$ of the localized $d^2_a-d^1_b$, clusters includes the Hamiltonian of isotropic HE $H_{\text{HE}} = 2J_{ab}\mathbf{S}_{\text{a}}\mathbf{S}_b$, an AS DM exchange $H_{\text{DM}} = \mathbf{G}_{\text{ab}}[\mathbf{S}_{\text{a}} \times \mathbf{S}_{\text{b}}]$; an AN exchange $H_{\text{AN}} = \mathbf{S}_{\text{a}}\mathbf{\Gamma}_{\text{ab}}\mathbf{S}_{\text{b}}$, where $\mathbf{\Gamma}_{ab} = \mathbf{\Gamma}_{ba}$ is symmetric tensor. The Hamiltonian H^e_{a*b} includes also the standard operator of the local (individual) ZFS [49–51] for ion α with $S_\alpha > 1/2$

$$H^\alpha_{\text{ZFS}} = D_a[S^2_{az} - S_a(S_a + 1)/3] + E_a(S^2_{ax} - S^2_{ay}) \tag{17}$$

where D_α and E_α are the individual ZFS parameters of the localized α ion.

In the case of the localized clusters with strong HE ($J \gg |\mathbf{G}_{\text{ab}} > \mathbf{\Gamma}_{\text{ab}},\ J \gg D_\alpha,\ E_\alpha$), all AN interactions of the intra-ion and inter-ion type result in the second-order ZFS of the states with $S > 1/2$. The symmetric AN tensor $\mathbf{S\Gamma S}$ may be represented in the standard form of ZFS operator [51]

$$\hat{H}_{\text{ZFS}} = \Gamma_{xx}\hat{S}^2_x + \Gamma_{yy}\hat{S}^2_y + \Gamma_{zz}\hat{S}^2_z$$
$$= D_S\left[\hat{S}^2_z - \frac{1}{3}S(S+1)\right] + E_S(\hat{S}^2_x - \hat{S}^2_y) \tag{18}$$

where $D_S = \Gamma_{zz} - (\Gamma_{xx} + \Gamma_{yy})/2$, $E = (\Gamma_{xx} - \Gamma_{yy})/2$ and S is the effective spin. In the effective ZFS Hamiltonian (Eq. (18)) of the pair, the effective ZFS parameters D_S, E_S include the AN intra-ion and inter-ion contributions. We suppose, for simplicity, that both $|a*b\rangle$ and $|ab*\rangle$ configurations are characterized by the same exchange parameters J, G_{ab}, Γ_{ab} and also by the same corresponding CF parameters ε_φ the SOC constants λ and ZFS parameters for individual ions.

For consideration in the model Hamiltonian (Eq. (1)), we shall treat the $d^8_{\text{a}}-d^9_{\text{b}}$ cluster as the hole equivalent $d^2_a-d^1_b$ system. For the pair of ions in distorted octahedral local coordination, the localized determinant wave functions $\Phi_{a*b}(S,\ M)$ $\{\Phi_{ab*}(S,\ M)\}$ for example, for the $d^8_a-d^9_b$ $\{d^9_a-d^8_b\}$ cluster have the form $\Phi_{a*b}(S = 3/2,\quad M = 3/2) = |\text{u}_{\text{a}}\text{v}_{\text{a}}\text{u}_{\text{b}}|, \Phi_{\text{ab}*}(3/2,\quad 3/2) = |\text{u}_{\text{a}}\text{v}_{\text{b}}\text{u}_{\text{b}}|$. By using the Moriya Hamiltonian (Eq. (1)), the determinant wave functions and correlation $\vec{C}_{ij} = i\vec{K}_{ij}$, we obtain the DE matrix elements between the localized states $\Phi_{a*b}(S,\ M)$ and $\Phi_{ab*}(\vec{S},\ \vec{M})$ with the same total spin $S = S$

$$
\begin{aligned}
&\langle\Phi_{a*b}(3/2,\ \pm 3/2)|H^0_{ab}|\Phi_{ab*}(3/2,\ \pm 3/2)\rangle = t_\mathrm{v} \pm iK^z_{ab},\\
&\langle\Phi_{a*b}(3/2,\ \pm 1/2)|H^0_{ab}|\Phi_{ab*}(3/2,\ \pm 1/2)\rangle = t_\mathrm{v} \pm iK^z_\mathrm{ab}/3,\\
&\langle\Phi_{a*b}(1/2,\ \pm 1/2)|H^0_{ab}|\Phi_{ab*}(1/2,\ \pm 1/2)\rangle\\
&\quad = t_\mathrm{v}/2 \pm 5iK^z_\mathrm{ab}/6\\
&\langle\Phi_{a*b}(3/2,\ \pm 3/2)|H^0_{ab}|\Phi_{ab*}(3/2,\ \pm 1/2)\rangle = iK_\mp/\sqrt{3},\\
&\langle\Phi_{a*b}(3/2,\ \pm 1/2)\|\Phi_{ab*}(3/2, \mp 1/2)\rangle = 2iK_\mp/3,\\
&\langle\Phi_{a*b}(1/2,\ \pm 1/2)\|\Phi_{ab*}(1/2,\ \mp 1/2)\rangle = 5iK_\pm/6.
\end{aligned}
\tag{19a}
$$

The AS DE matrix elements of the mixing of the $S=1/2$ and $S=3/2$ states are the following:

$$
\begin{aligned}
&\langle\Phi_{a*b}(3/2,\ \pm 1/2)\|\Phi_{ab*}(1/2,\ \pm 1/2)\rangle = -i\sqrt{2}K_Z/3,\\
&\langle\Phi_{a*b}(3/2,\ \pm 3/2)\|\Phi_{ab*}(1/2,\ \mp 1/2)\rangle = iK_\mp/\sqrt{6},\\
&\langle\Phi_{a*b}(3/2,\ \mp 3/2)\|\Phi_{ab*}(1/2,\ \mp 1/2)\rangle\\
&\quad = \mp iK_\pm/3\sqrt{2}
\end{aligned}
\tag{19b}
$$

where $t = t_\mathrm{v}$, $K_\kappa = K^\kappa_{ab}$. The isotropic transfer contributions ($\sim t_v$) to Eq. (19a) do not depend on the projection M and are described by the AH [6] DE term $(S+1/2)t_v/(2S_0+1)$. The K^κ_{ab} terms in Eq. (19a) represent the AS DE contributions ($K^\kappa_{ab} = -K^\kappa_{ba}$). The AS DE matrix elements depend on M. The matrix of the Anderson–Hasegawa DE, HE, ZFS and AS DE for the $d^9_a - d^8_a$ ($d^1_a - d^2_b$) MV cluster is represented in Ref. [53].

In the localized clusters, the DM AS exchange $\mathbf{H}_\mathrm{DM} = \Sigma_{ij}\mathbf{G}_{ij}[\mathbf{S}_i \times \mathbf{S}_j]$, mixes the localized states with different total spin S [53].

In the resonance representation $\Psi_\pm(S,\ M)$, the states of the t–J model ($E^0_\pm(1/2) = \pm t/2$) and ($E^0_\pm(3/2) = 3J \pm t$) are represented on (Fig. 1(b)). The AN interactions Eq. (18) splits the $S=3/2$ levels: $\Delta = 2D_\mathrm{S}$ (Fig. 1(c)). The axial ZFS parameter D_S of the localized cluster includes the contributions of the individual ZFS terms (Eq. (17)), axial AN exchange and AS DM exchange.

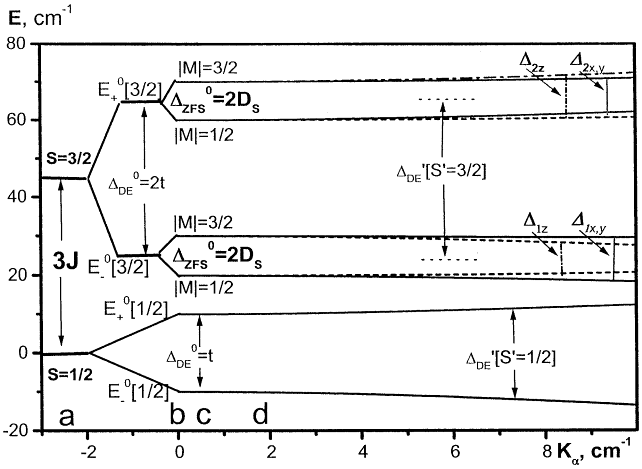

Fig. 1. An AS DE in the d^8-d^9 (d^2-d^1) MV cluster with the AH DE, HE ($t-J$ model) and initial ZFS $\Delta^0_\mathrm{ZFS} = 2D_\mathrm{S}$. (a) The Heisenberg levels, (b) the levels of the Anderson–Hasegawa plus HE ($t-J$) model, (c) initial ZFS of the S = 3/2 levels of the t–J model, (d) the dependence on the AS DE coupling [53]. Solid lines: $K_\alpha = K_z$, $K_{x,y} = 0$, dashed lines: $K_\alpha = K_{x,y}$, $K_z = 0$.

The AS DE (terms $\sim K^\kappa_{ab}$) mixes the states of different localization with the same total spin S: $\Phi_{a*b}(S=3/2)$ with $\Phi_{ab*}(3/2)$, and $\Phi_{a*b}(1/2)$ with $\Phi_{ab*}(1/2)$ (Eqs. (19a) and (19b)). In the resonance representation $\Psi_\pm(S,\ M)$, an AS DE mixes the AH DE states $\Psi_+(3/2)[E^0_+(3/2) = t+3J]$ and $\Psi_-(3/2)[E^0_-(3/2) = -t+3J]$ of different parity with the same total spin $S=3/2$. The AS DE mixes also the Anderson–Hasegawa DE states $\Psi_+(1/2)[E^0_+(1/2) = t/2]$ and $\Psi_-(1/2)[E^0_-(1/2) = -t/2]$ with the same total spin $S=1/2$. The AS DE mixing of the AH states with the same S depends on M. The DE energy intervals between the exchange–resonance AH DE levels $\mathrm{E}^0_\pm(S,\ M)$ essentially exceed the non-diagonal matrix elements ($\sim K_{ab}$) of the AS DE mixing of the $S=3/2$ and $S=1/2$ levels since $t > J \gg K_{ab}$.

The AS DE terms ($\sim K^\kappa_{ab}$) mixes also the states of different localization with different total spin S: $\Phi_{a*b}(S=3/2)$ with $\Phi_{ab*}(1/2)$, and $\Phi_{a*b}(1/2)$ with $\Phi_{ab*}(3/2)$ (Eq. (19b)). In the resonance $\Psi_\pm(S,\ M)$ representation, AS DE (and DM AS exchange) mixes the Anderson–Hasegawa DE states $E_+(3/2)$ [$E_-(3/2)$] with $E_+(1/2)[E_-(1/2)]$ of the same parity with different S. The AS DE mixing of the AH states with different S depends on M. The AS DE contribution to the mixing of the DE levels with different S is stronger than the DM AS exchange contribution since $K_{ab} \gg G_{ab}$, $K_{ab} \sim t(\Delta g/g)$), $G_{ab} \sim J(\Delta g/g)$), $t >> J$. In comparison with the DM AS exchange, which mixes the localized states with different total spins S [53], an AS DE in the delocalized system mixes the AH states $E^0_+(S)$ and $E^0_-(S)$ of the different parity with the same S, and also the AH states with different S with the same parity.

In the case $J=0$. $D_\mathrm{S}=0$ for the d^8-d^9 (d^2-d^1) cluster, we obtain the four states $E_\pm(S'=3/2) = \pm t_\mathrm{K}$, $E_\pm(S'=1/2) = \pm t_\mathrm{K}/2$, which are characterized by the effective DE (transfer) parameters to $t_\mathrm{K} = \sqrt{t^2+\mathbf{K}^2}$.

As it follows from the group-theoretical analysis [52] and the effective Hamiltonian method [49–51], the levels with $S=3/2$ of the MV d^n-d^{n+1} cluster must be split in the second order on SOC in the low-symmetric CF. The Hamiltonian of the zero-filed splitting has a standard form Eq. (18) [49–51]. The individual d^8-ion (Ni^{2+}) with $S=1$ is characterized by large ZFS: $\Delta_\mathrm{ZFS}(d^8) = 2D_0 = 2$–$4\ \mathrm{cm}^{-1}$. The ZFS of the individual Ni^{2+}-ion is a result of the combined effect of a noncubic CF and SOC in the second order of perturbation [49–51]. The ZFS parameter D_0 of the Ni^{2+}-ion is proportional to $\lambda^2(1/\varepsilon_\xi - 1/\varepsilon_\zeta)$ ZFS of the individual d^8-ion essentially contributes to ZFS $\Delta^0_\mathrm{ZFS}(S=3/2) = 2D_\mathrm{S}$ of the $S=3/2$ cluster state of the d^8-d^9 pair, where $D_\mathrm{S} = D_0 + \Gamma$. The symmetric AN exchange coupling in the localized d^8-d^9 pair ($H_\mathrm{AN} = \Gamma_1(S_{ax}S_{bx} + S_{ay}S_{by}) + \Gamma_2 S_{az}S_{bz}$, $\Gamma_1 =$

$\Gamma_{xx} = \Gamma_{yy}$, $\Gamma_2 = \Gamma_{zz}$) contributes to the axial AN parameter $\Gamma = (\Gamma_2 - \Gamma_1)/3$.

Fig. 1 demonstrates the action of the AS DE on the fine splittings of the levels of the d^9-d^8 (d^1-d^2) system with the AH DE, Heisenberg exchange and an initial axial ZFS $2D_0$ of the localized $S = 3/2$ level, $t = 20$, $J = 15$, $D_S = 5$ cm^{-1} [53]. The AH DE splits the HE levels $S = 3/2$ and $S = 1/2$ (Fig. 1a) on the $t-J$ AH DE levels $E^0_\pm(S = 3/2)$ and $E^0_\pm(S = 1/2)$ (Fig. 1). The ZFS operator $H_{ZFS} = D_S[S_z^2 - S(S+1)/3]$ splits the DE $E^0_\pm(S = 3/2)$ levels on the Kramers doublets $|M| = 3/2$ and $|M| = 1/2$ (Fig. 1c). The AS DE leads to modification of ZFS of the high-spin states. The ZFSs are different for the $E_+(S' = 3/2)$ and $E_-(S' = 3/2)$ states:

$$\Delta^{=}_{ZFS}[E_1(3/2)] = 2(D_S + \delta^{\pm}_K) \tag{20}$$

where the AS DE contributions to ZFS have a form:

$$\delta^{\pm}_k = [\delta^{\pm}_z - (\delta^{\pm}_x + \delta^{\pm}_y)/2], \quad \delta^{\pm}_\chi = 4K^2_\chi J/3t(t \pm 6J) \tag{21}$$

$\chi = x, y, z$. Since the intervals between the mixed AH levels are different in the $t-J$ model: $\Delta_{t-J}(E_\pm(S = 3/2), E_\pm(S = 1/2)) = t/2 \pm 3J$, the repulsion between the $E_-(S' = 3/2)$ and $E_-(S' = 1/2)$ levels is stronger than between the $E_+(S' = 3/2)$ and $E_+(S' = 1/2)$ levels. As a result, the AS DE contribution δ^-_K($E_-(3/2)$) to ZFS of the $E_-(3/2)$ state is larger than AS DE contribution $\delta^+_K[E_+(3/2)]$ to ZFS of the $E_+(3/2)$ state. The mixing of different spins by AS DE essentially contributes to the fine splitting. The AS DE contribution to ZFS is different for the cases $K_z \neq 0$, $K_{x,y} \neq 0$ and $K_{x,y} \neq 0$, $K_z = 0$ (Fig. 1d) [53]. The AS DE contributions $\delta^\pm_K$ to ZFS are proportional to $K^2J/t(t \pm 6J)$ in accordance with the estimate K^2J/t^2 for the symmetric AN parameters (Eq. (16)). This ZFS of the resonance AH DE states $E_\pm(S' = 3/2)$ disappears when $J = 0$.

The DM AS exchange mixing of levels results in the modification of the ZFS parameters $\delta^\pm_\chi$ (Eq. (20)): $\delta^\pm_\chi = \delta^\pm_\chi - \omega^\pm_\chi$, where $\omega^\pm_\chi = G_\chi(4K_\chi \pm 3G_\chi)/6(t \pm 6J)$ [53].

The AS DE results in an increase of the effective DE splittings (Fig. 1d). In the case $K_z \neq 0$, $K_{x,y} = 0$, $t \gg K$, the DE splittings have the form ($\rho = J/t$):

$$\begin{aligned}
&\Delta'_{DE} = [S' = 1/2] \simeq (\mathrm{t} + \tau_{1K}),\\
&\Delta'_{DE} = [S' = 3/2] = 2(t + \tau_{2k});\\
&\tau_{1K} = (K_z^2/2t)[(1 - 100\rho^2)/(1 - 36\rho^2)],\\
&\tau_{2K} = (K_z^2/2t)[(1 - 20\rho^2)/(1 - 36\rho^2)].
\end{aligned} \tag{22}$$

The AS DE contributions τ_{iK} to the AH DE parameter t are different for the $S' = 3/2$ and $S' = 1/2$ states. The AS DE coupling leads to contribution $\Delta'_J = -4K_z^2J/(t^2 - 36\mathrm{J}^2)$ to the HE interval $\Delta_\mathrm{J} = 3J$.

For the d^9-d^8 (d^1-d^2) cluster with the AH DE plus HE and AS DE, the dependence of the DE levels on the HE parameter J is represented on Fig. 2 ($t = 20$ cm^{-1}, $K_z = 10$ cm^{-1}, $K_{x,y} = 0$) for the model with $D_S = 0$, $E_S = 0$, $G_{ab} = 0$. The dashed lines represent the $t-J$ levels of the pure Anderson–Hasegawa DE plus HE model. The AS DE splittings of the states $E_-(S' = 3/2)_{J=0}$ take place both in the case of an antiferromagnetic HE ($J < 0$, $S_{gr} = S_{min}$) and ferromagnetic exchange ($J < 0$, $S_{gr} = S_{max}$). In the case of strong J, the levels are characterized by the total spin S. The external sublevels $E^{\Pi}_\pm(S' = 3/2)$ with the maximal effective DE splitting $2t_K$ depend linear on J. The ZFS for the $E_-(S' = 3/2)$ $\{E_+(S' = 3/2)\}$ state is $\delta_{1K} = \delta^-_K(E_-(3/2)) = 8K_z^2J/3t(t - 6J)$, $\{\delta_{2K} = \delta^+_K(E_-(3/2)) = 8K_z^2J/3t(t + 6J)\}$ $J > 0$ and δ_{2K} for $J < 0$. The AS DE mixes the states characterized by S. The strong repulsion of the levels takes place in the areas of the crossing of the AH levels of the $t-J$ model Fig. 2.

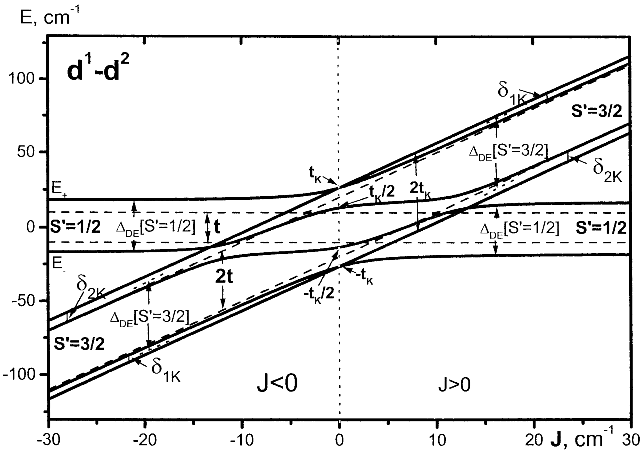

Fig. 2. The dependence of the energy levels $E_\pm(S)$ on the HE parameter J in the d^8-d^9 (d^2-d^1) system with the Anderson–Hasegawa DE ($t = 20$ cm^{-1}), HE and AS DE ($K_z = 10$ cm^{-1}, $K_{x,y} = 0$)—solid lines. The dashed lines—the levels of the $t-J$ model ($\mathbf{K} = 0$).

4. Operator of antisymmetric double exchange

For dimeric MV d^n-d^{n+1} clusters in the $t-J$ model, the Moriya vector transfer operator Eq. (1) may be represented in the form of the effective Hamiltonian. This effective Hamiltonian of the AS DE has the following form

$$H_{ASDE} = 2i\mathbf{K}_{ab}\mathbf{T}_{ab}(\mathbf{S}_b - \mathbf{S}_a), \tag{23}$$

where $\mathbf{K}_{ab}$ is an AS ($\mathbf{K}_{ab} = -\mathbf{K}_{ba}$) vector coefficient, $\hat{\mathbf{T}}_{ab}$ is the transfer operator, S_b, S_a are spins of the ions of the d^n-d^{n+1} pair [53]. The effective AS DE Hamiltonian Eq. (23) describes the spin-transfer interaction. The operator Eq. (23) of the AS DE is Hermitian and invariant relative to the time inversion operation. The matrix elements of the second-order perturbation operator H_{ASDE} between the states of different localization have the form

$$\begin{aligned}&\langle\Phi_{a*b}(S,M)|H_{\mathrm{ASDE}}|\Phi_{ab*}(S,M)\rangle\\&\quad=2i\mathbf{K}_{ab}\langle\Phi_{a*b}(S,M)|\hat{\mathbf{T}}_{ab}|\Phi_{ab*}(S,M)\rangle\\&\qquad\times\langle\Phi_{ab*}(S,M)|(\mathbf{S}_b-\mathbf{S}_a)|\Phi_{ab*}(S,M)\rangle\end{aligned}\qquad(24)$$

The isotropic transfer operator $\hat{\mathbf{T}}_{ab}$ acts between the states of different localization with the same S and M. The spin operator $(\mathbf{S}_b-\mathbf{S}_a)$ is active in the spin space of the states of the same localization.

In the case of the states with the same S ($S=S$), the first multiplier in Eq. (24) represents the Anderson–Hasegawa DE contribution $\langle\Phi_{a*b}(S,M)|\hat{\mathbf{T}}_{ab}|\Phi_{ab*}(S,M)\rangle=[(S+1/2)/(2S_a+1)]$. The matrix elements of the κ component of the spin operator $(\mathbf{S}_b-\mathbf{S}_a)$ depend on the difference $[S_\mathrm{b}(S_\mathrm{b}+1)-S_\mathrm{a}(S_\mathrm{a}+1)]$ [53]. The matrix elements of the AS DE operator Eq. (23) between the states of different localization with $S=S$, $M=M$ depend on projection M of S:

$$\begin{aligned}&\langle\Phi_{a*b}(S,M)|H_{\mathrm{ASDE}}|\Phi_{ab*}(S,M)\rangle\\&\quad=iK^z_{ab}\left(\frac{2S+1}{2S_a+1}\right)\frac{[S_b(S_b+1)-S_a(S_a+1)]}{S(S+1)}M\end{aligned}\qquad(25)$$

The mixing of the Anderson–Hasegawa DE states with different total spin S ($S'\neq S$), which was obtained in the model Hamiltonian Eq. (1), may be described by the effective operator of the AS DE mixing $H'_{\mathrm{ASDE}}=2i\mathbf{K}_{ab}\mathbf{T}'_{ab}(\mathbf{S}_b-\mathbf{S}_a)$. The matrix elements $\langle\Phi_{a*b}(S,M)|H'_{\mathrm{ASDE}}|\Phi_{ab*}(S,M)\rangle$ in this case ($S'\neq S$) have the form of Eq. (24), where the matrix elements of the transfer operator $\mathbf{T}'_{ab}$, are the following:

$$\langle\Phi_{a*b}(S,M)|\mathbf{T}'_{ab}|\Phi_{ab*}(S,M)\rangle=(2S_a+1)/2\qquad(26)$$

For the states with $S'\neq S$, the AS DE interaction matrix elements of the spin mixing in Eq. (26) are represented in [53].

In the case $K_{x,y}\neq 0$, the AS DE Eq. (23) results in non-collinear orientation of spins $\mathbf{S}_a$ and $\mathbf{S}_b$ of the MV $\mathrm{d}^n-\mathrm{d}^{n+1}$ dimer, which were oriented in parallel by the isotropic Anderson–Hasegawa DE interaction.

For the MV $\mathrm{d}^2-\mathrm{d}^3$ cluster. The AS DE contributions to ZFS parameter D_S is different for the $\mathrm{E}_+(\mathrm{S}'=5/2)$ and $\mathrm{E}_-(\mathrm{S}'=5/2)$ states: $D_S^{\pm}(5/2)=D_S+\delta_K^{\pm}(5/2)$, $\delta_K^{\pm}(5/2)=2K_z^2J/t(t\pm 15J)$ [53].

5. AS DE anisotropy of g-factor in the MV $\mathrm{d}^1-\mathrm{d}^0$ cluster

For the MV $\mathrm{d}^1-\mathrm{d}^0$ cluster ($\mathrm{S}=1/2$) in the AH DE plus AS DE ($K_{x,y,z}\neq 0$) model, the Zeeman interaction $\mathrm{H_z}=\mathrm{g_0}\beta\mathbf{SH}$ ($\mathrm{g_0}$ is g-factor of the localized system) forms the Zeeman levels in the parallel (z) and perpendicular (x) orientations

$$E^{\pm}_\alpha=\pm\{t^2+K^2+h^2_\alpha\pm 2h_\alpha[t^2+K^2_\alpha]^{1/2}\}^{1/2}\qquad(27)$$

where $\alpha=x,\ z$; $h_\alpha=\mathrm{g_0}H_\alpha/2$. In the case $K=0$, the Zeeman splitting is isotropic $\pm(t\pm h_\alpha)$. The AS DE contribution to the g-factors has the form:

$$g_\alpha=g_0\{(t^2+K^2_\alpha)/(t^2+K^2)\}^{1/2}\qquad(28)$$

In the case $K_{x,y}\neq 0$, $K_z=0$, we obtain an anisotropy of g-factors ($\mathrm{g_z}<\mathrm{g_x}$) induced by AS DE.

6. The crystal field splitting and anisotropic double exchange in the MV $\mathrm{d}^9-\mathrm{d}^8$ cluster

In the $\mathrm{d}^8-\mathrm{d}^9$ MV cluster, the detailed consideration of the CF splittings and the SOC admixture of the $^3\mathrm{T}_2$ and $^1\mathrm{T}_2$ excited terms to the ground $^3\mathrm{A}_2$ state of the high-spin d^8-ion results in the modification of the AS DE parameters and DM AS exchange constant [53]. The AS DE parameters $\mathrm{K}^\kappa_{\mathrm{ab}}$ are different for the states with different total spin S and for the 3/2–1/2 AS DE mixing terms.

The SOC admixture to the ground $^3\mathrm{A}_2$ state of the $^3\mathrm{T}_2$ and $^1\mathrm{T}_2$ excited terms of the d^8-ion (with the tetragonal splitting) leads to AN DE splitting of the DE levels in the MV dimeric cluster of orbitally non-degenerate ions. The AN DE inter-ion interaction $\mathrm{H}'_{\mathrm{AN}}=\mathbf{T}_{\mathrm{ab}}\mathbf{S}_{\mathrm{a}}\boldsymbol{\Gamma}'_{\mathrm{ab}}\mathbf{S}_{\mathrm{b}}$ results in an axial ZFS of the $E_\pm(3/2)$ AH levels, which may be described by the AN DE effective Hamiltonian

$$H_{\mathrm{ANDE}}=\Gamma'(3/2)\mathbf{T}_{ab}[S^2_z-S(S+1)/3]\qquad(29)$$

where $\mathbf{T}_{\mathrm{ab}}$ is the AH transfer operator ($\langle\Phi_\pm(3/2)|\mathbf{T}_{\mathrm{ab}}|\Phi_\pm(3/2)\rangle=\pm 1$), $\Gamma'(3/2)$ is the AN DE parameter of the easy-axis two-ion anisotropy [53]. The $\Gamma'(3/2)$ AN DE parameter is proportional to the $t_\alpha(\gamma_{1\alpha}-\gamma_{2\alpha})^2$ and $(t_\alpha-t_\mathrm{v})(\gamma^2_{1\alpha}-\gamma^2_{2\alpha})$ terms, where the $\gamma_{1\alpha}$ and $\gamma_{2\alpha}$ coefficients determine the SOC admixture of the α components of the $^3\mathrm{T}_2$ and $^1\mathrm{T}_2$ excited terms, respectively [53]. The $\Gamma'(3/2)$ AN DE parameter is proportional to the transfer integral t_α, i.e. depends on an anisotropy of the ET (DE). The $\Gamma'(3/2)$ parameter of the AN DE splitting of the DE states with $\mathrm{S}>1$ does not depend on θ and J. In comparison, the AS DE contribution to the second order ZFS parameter is proportional to $\mathrm{K}^2\mathrm{J}/t(t\pm 6J)$ (Eq. (21)). The $\Gamma'(3/2)$ contribution to ZFS may be the value of the order of magnitude 0.1–1 cm^{-1} since $t_\alpha\sim 10^3$–10^4 cm^{-1}. The axial AN DE contributions to ZFS are different for the $E_\pm(3/2)$ levels: $2[D_S{}^{\pm}\Gamma'(3/2)]$. The AN DE in the clusters of orbitally degenerate ions was considered in Ref. [18].

7. Antisymmetric double exchange in the MV [$d^9-d^{10}-d^{10}$]([$d^1-d^0-d^0$] trimer

We consider first the AS DE coupling in the [$Cu^{2+}-Cu^{+}-Cu^{+}$]([$d^9-d^{10}-d^{10}$]) trimers with the hole transfer. The ground orbital of the Cu(II) ion is $\varphi_\alpha=(v_0)_\alpha$. The isotropic DE interaction in this trigonal trimer forms the DE states, which are characterized by IR $\Gamma=A_1$ and E of the D_3 group symmetry of the cluster with the migration of the extra hole among the three ions [13]. The A-type wave function represents the symmetrical combination of the three localized states: $\Phi(A)=[|a^*bc\rangle+|ab^*c\rangle+|abc^*\rangle]/\sqrt{3}\{\Phi(^2A_1)=(\varphi_a+\varphi_b+\varphi_c)/\sqrt{3}\}$. For the twofold degenerate E-state we obtain $\Phi(E_x)=[|ab^*c\rangle-|abc^*\rangle]/\sqrt{2}$, $\Phi(E_y)=[2|a^*bc\rangle-|ab^*c\rangle-|abc^*\rangle]/\sqrt{6}\{\Phi(^2E_x)=(\varphi_b-\varphi_c)/\sqrt{2}$, $\Phi(^2E_y)=(2\varphi_a-\varphi_b-\varphi_c)/\sqrt{6}\}$. The system has the same energy in all localizations.

The Moriya transfer Hamiltonian has the following form for the MV trimer

$$\mathbf{H}_t=\sum_{\alpha,\beta=a,b,c}\{t_{\alpha\beta}[\alpha_\uparrow^+\beta_\uparrow+\alpha_\downarrow^+\beta_\downarrow]+iK_{\alpha\beta}^{\pm}[\alpha_\uparrow^+\beta_\downarrow-\alpha_\downarrow^+\beta_\downarrow]$$
$$+iK_{\alpha\beta}^{+}\alpha_\downarrow^+\beta_\uparrow+iK_{\alpha\beta}^{-}\alpha_\uparrow^+\beta_\downarrow\} \qquad (30)$$

For the trigonal cluster (the D_3 group of symmetry) the isotropic DE parameters t arc symmetric $t_{ab}=t_{ba}$, $t_{ac}=t_{ca}$, $t_{bc}=t_{cb}$, $t_{ab}=t_{bc}=t_{ac}=t$. The $\Phi(^2A_1)$ and $\Phi(^2E)$ wave functions diagonalize the DE coupling (t terms) in Eq. (30) without SOC ($\mathbf{K}_{\alpha\beta}=0$): $E(^2A_1)=2t$, $E(^2E)=-t$. The DE interaction does not depend on M. In the case of positive DE parameter t, the migration of the extra hole in the delocalized [$Cu^{4/3+}-Cu^{+}-Cu^{+}$] cluster forms the trigonal fourfold degenerate ^2E DE term.

As it follows from the group-theoretical consideration [52], the trigonal orbitally degenerate ^2E term must be split by SOC into two Kramers doublets in according with the expansion $E\times D^{(1/2)}=(\bar{A}_1+\bar{A}_2)+\bar{E}$, where $\bar{A}_1$, $\bar{A}_2$, $\bar{E}$ are IR of the double group D_3. The extra degeneracy of the DE ground state ^2E is the result of the lack of SOC in the theory of DE in trimers. The effective Hamiltonian of the SOC for the ^2E term of the trigonal group has a form [49]:

$$H_{eff}=\Delta T(A_{2g})S_Z \qquad (31)$$

$T(A_{2g})$ is the orbital operator in the trigonal base $u_\pm=(u_x\pm u_y)/\sqrt{2}$ [49] which transforms like the base of IR A_{2g} of the trigonal D_3 group. The effective SOC Hamiltonian Eq. (31) results in the splitting of the ^2E term

$$E[u_\pm(M=\pm1/2)]-E[u_\pm(M=\mp1/2)]=\Delta \qquad (32)$$

into two Kramers sublevels $^2E[u_\pm(\pm1/2)]$ and $^2E[u_\pm(\mp1/2)]$. The splitting is linear on SOC. In that way, the group-theoretical consideration and the effective Hamiltonian method show that the ground state ^2E DE term of the trigonal MV cluster must be split linearly by SOC into two Kramers doublets [54].

For finding this splitting we will consider the isotropic t-terms and vector transfer AS DE terms $K_{\alpha\beta}^{\kappa}$, ($K_{\alpha\beta}^{v}=-K_{\beta\alpha}^{v}$) in the Hamiltonian Eq. (30). The trigonal symmetry of the trimer results in the equivalence of the pair AS DE interactions: $|K_{ab}^{v}|=|K_{bc}^{v}|=|K_{ac}^{v}|$. For the $d^9-d^{10}-d^{10}$ cluster, the operator of the AS DE may be represented in the form $H_{ASDE}=2i\Sigma_{\alpha,\beta}\mathbf{K}_{\alpha\beta}\mathbf{T}_{\alpha\beta}(\mathbf{S}_\beta-\mathbf{S}_\alpha)$, where $\alpha\beta=ab$, bc, ca, $\mathbf{T}_{\alpha\beta}$ is the isotropic transfer operator for the $\alpha\beta$ pair.

The eigenvalue of the $^2A_1$ DE term $E(^2A_1)=2t$ does not depend on the AS DE parameter $\mathbf{K}_{\alpha\beta}$. For the ^2E DE term, the matrix of the Moriya Hamiltonian Eq. (30) results in the AS DE splitting $E_\pm=-t\pm\sqrt{}(3(K_x^2+K_y^2+K_z^2))$ in the trigonal representation $\Phi_\pm$. The cluster AS DE parameters K_κ have a form

$$K_Z=(K_{ab}^Z+K_{bc}^Z+K_{ca}^Z)/\sqrt{3},$$
$$K_\pm=(K_{ab}^\pm+K_{bc}^\pm+K_{ca}^\pm)/\sqrt{3} \qquad (33)$$

The cyclic condition $K_{ab}^{v}=K_{bc}^{v}=K_{ca}^{v}$ is fulfilled for the pair contributions to the cluster AS DE parameter. In the case $K_x=K_y=0$, the AS DE splitting of the ^2E DE term has the form

$$E[^2E_\pm(\pm1/2)]=-t+K_z\sqrt{3},$$
$$E[^2E_\pm(\mp1/2)]=-t-K_z\sqrt{3} \qquad (34)$$

In the delocalized $Cu^{4/3+}{}^{-}-Cu^{4/3+}-Cu^{4/3+}$ cluster, the AS DE splitting of the ^2E DE term $E[^2E_\pm(\pm1/2)]-E[^2E_\pm(\mp1/2)]=2K_Z\sqrt{3}$ is linear on the AS DE parameter K_Z. In the case $K_x=K_y=0$, the result Eq. (34) coincides with the result of the effective Hamiltonian Eq. (31) with $\Delta=2K_Z\sqrt{3}$. The K_Z component of the AS DE interaction in the MV trimer plays the role of the spin-orbital coupling of S with the orbital moment operator of the $T(A_{2g})$ type in the effective Hamiltonian Eq. (31).

The AS DE coupling does not mix the DE A_1 and E terms with the same $S=1/2$ since the K_Z component of the AS DE operator transforms as IR A_2 of the trigonal group.

For the microscopic consideration of the AS DE in the [$Cu^{2+}-Cu^{+}-Cu^{+}$] cluster, we suppose the octahedral coordination of each Cu ion with the tetragonal distortion, which forms the ground v d-orbital for the Cu^{2+}-ion. The renormalized SOC-admixed ground state wave functions for the Cu(II) ion localized on the center α have the form

$$v_\alpha(m=\pm1/2)=v_\alpha^0(\pm1/2)-i\gamma_\xi\xi_a'(\mp1/2)$$
$$\pm\gamma_n\eta_\alpha'(\mp1/2)\pm i\gamma_\zeta\zeta_a'(\pm1/2) \qquad (35)$$

where d-orbital functions refer to the local (a, b, c) Cartesian frame, $\gamma_\zeta=\lambda/\Delta_\zeta$, $\gamma_\psi=\lambda/2\Delta_\psi$, $\psi=\xi,\eta$, and α a(b) {c} for the |a*bc⟩ (ab*c⟩) {abc*⟩} localization. We will consider the trimer with the local z_α-axis of each octahedra oriented on the center of the trimer with the small tilt θ from the plain of the trimer. Using the v_α d-orbitals Eq. (36), we obtain the matrix elements of the resonance coupling $V_{\alpha\beta}$ between the three localizations [54]:

$$\begin{aligned}
&\langle\Phi_{a*bc}(S=1/2,\ \ M=\pm1/2)|V_{ab}|\Phi_{ab*c}(1/2,\ \ \pm1/2)\rangle\\
&\quad = t_{\mathrm{v}} \pm iK^{\zeta}_{ab},\\
&\langle\Phi_{a*bc}(1/2,\ \ \mp1/2)|V_{ab}|\Phi_{ab*c}(1/2,\ \ \pm1/2)\rangle\\
&\quad = i(K^{\xi}_{ab} \mp iK^{\eta}_{ab}),\\
&\langle\Phi_{ab*c}(1/2,\ \ \pm1/2)|V_{bc}|\Phi_{abc*}(1/2,\ \ \pm1/2)\rangle = t_{\mathrm{v}} \pm iK^{\zeta}_{bc},\\
&\langle\Phi_{abc*}(1/2,\ \ \pm1/2)|V_{ac}|\Phi_{a*bc}(1/2,\ \ \pm1/2)\rangle\\
&\quad = t_{\mathrm{v}} \pm iK^{\zeta}_{ca}
\end{aligned} \tag{36}$$

The components of the real AS DE parameters $K^{\kappa}_{\alpha\beta}$ for the pair αβ (= ab, bc, ca) have a form ($\psi = \xi$, η)

$$\begin{aligned}
K^{\Psi}_{\alpha\beta} &= \gamma_\Psi[\langle \mathrm{v}^0_\beta||\Psi_\alpha\rangle - \langle \mathrm{v}^0_\alpha||\Psi_\beta\rangle],\ \ K^{\zeta}_{\alpha\beta}\\
&= \gamma_\zeta[\langle \mathrm{v}^0_\alpha||\zeta_\beta\rangle - \langle \mathrm{v}^0_\beta||\zeta_\alpha\rangle]
\end{aligned} \tag{37}$$

The comparison of the results Eqs. (37) and (38) of the microscopic calculation with the results of the Moriya model Hamiltonian Eq. (31) shows that the AS DE parameters $K^{Z}_{\alpha\beta}$, $K^{\pm}_{\alpha\beta}$ of the Hamiltonian Eq. (31) may be represented through the microscopic parameters $K^{Z}_{\alpha\beta}$; $K^{Z}_{\alpha\beta} = K^{\zeta}_{\alpha\beta}$; $K^{\pm}_{\alpha\beta} = K^{\xi}_{\alpha\beta} \pm iK^{\eta}_{\alpha\beta}$. The transfer integrals between the ground orbital state $\mathrm{v}^0_\alpha[\mathrm{v}^0_\beta]$ on the center α [β] and the excited CF state $\phi_\alpha[\phi_\beta]$ ($\phi = \xi, \eta, \zeta$) on the center [α] are different from zero due to the relative tilt of the distorted octahedra in the MV trimer.

In the MV trimer with the local z_α-axes of octahedra directed on the shifted up ($\theta \ll 1$) center of the trimer, the local 3d-orbitals of the Cu^{2+} ion localized on the center *a* may be written in the common (cluster) XYZ-coordination system (φ_A) in the form

$$\begin{aligned}
&\mathrm{v}_{\mathrm{a}} = \mathrm{v}_{\mathrm{A}}/2 - \sqrt{3}u_{\mathrm{A}}/2 - \theta\xi_A,\\
&u_{\mathrm{a}} = -u_{\mathrm{A}}/2 - \sqrt{3}\mathrm{v}_{\mathrm{A}}/2 - \theta\sqrt{3}\xi_{\mathrm{A}},\\
&\xi_{\mathrm{a}} = -\xi_{\mathrm{A}} + \theta(\mathrm{v}_{\mathrm{A}} + \sqrt{3}u_{\mathrm{A}}),\\
&\eta_{\mathrm{a}} = -\zeta_{\mathrm{A}} + \theta\eta_{\mathrm{A}},\ \ \zeta_{\mathrm{a}} = \eta_{\mathrm{A}} + \theta\zeta_{\mathrm{A}}
\end{aligned} \tag{38}$$

In the case of the localization of the extra hole on the centers β = b, c, the local d-orbitals have the following form in the common coordination system [54]:

$$\begin{aligned}
&\mathrm{v}_\beta = -\mathrm{v}_j/4 - \sqrt{3}u_j/2 \mp \sqrt{3}\zeta_j/4 \pm \theta(\sqrt{3}\eta_j \pm \xi_j)/2,\\
&u_\beta = \sqrt{3}\mathrm{v}_j/4 - u_j/2 \pm 3\zeta_j/4 \pm \theta\sqrt{3}(\sqrt{3}\eta_j \pm \xi_j)/2,\\
&\xi_\beta = \xi_j/2 \pm \sqrt{3}\eta_j/2 + \theta(\sqrt{3}u_j - \mathrm{v}_j/2 \mp \sqrt{3}\zeta_j/2),\\
&\eta_\beta = \zeta_j/2 \mp \sqrt{3}v_j/2 - \theta(\eta_j \mp \sqrt{3}\xi_j)/2,\\
&\zeta_\beta = -\eta_j/2 \pm \sqrt{3}\xi_j/2 - \theta(\zeta_j \mp \sqrt{3}\mathrm{v}_j)/2
\end{aligned} \tag{39}$$

where the upper (lower) signs in the right part of Eq. (39) correspond to the β = b, j = B (β = c, j = C) indexes.

The isotropic DE parameters in the cluster coordinate system have a form $t_{\alpha\beta}(\mathrm{v}) = \langle \mathrm{v}_\alpha||\mathrm{v}_\beta\rangle = (6t_{\mathrm{u}} - t_{\mathrm{v}})/8$, αβ = ab, bc, ac and $t_{\mathrm{v}} = t_\zeta$, $t_\xi = t_\eta$ for the trigonal trimer.

By using Eqs. (38) and (39), we obtain the following non-zero transfer integral between the ground v^0_α and excited ψ_β states in the MV pair of the trigonal trimer:

$$\begin{aligned}
&\langle \mathrm{v}^0_\alpha||\zeta_\beta\rangle = -\langle \mathrm{v}^0_\beta||\zeta_\alpha\rangle = \theta\sqrt{3}(t_{\mathrm{v}} - 2t_\xi)/4,\\
&\langle \mathrm{v}^0_\alpha||\xi_\beta\rangle = \langle \mathrm{v}^0_\beta||\xi_\alpha\rangle = -\theta(6t_{\mathrm{u}} + 2t_\xi + t_{\mathrm{v}})/4,\\
&\langle \mathrm{v}^0_\alpha||\eta_\beta\rangle = -\langle \mathrm{v}^0_\beta||\eta_\alpha\rangle = -\sqrt{3}t_{\mathrm{v}}
\end{aligned} \tag{40}$$

αβ = ab, bc, ca. The transfer integrals Eq. (40) [54] essentially differ from the transfer integrals for the MV dimer due to the strong tilt of the octahedra in the trimer. The components $K^{\kappa}_{\alpha\beta}$ of the vector coefficient of the AS DE in the trimer (αβ = ab, bc, ca) have a form:

$$\begin{aligned}
&K^{\zeta}_{\alpha\beta} = \theta\gamma_\zeta\sqrt{3}(t_{\mathrm{v}} - 2t_\xi)/2, \qquad K^{\eta}_{\alpha\beta} = -\gamma_\eta\sqrt{3}t_{\mathrm{v}}/2,\\
&K^{\xi}_{\alpha\beta} = 0
\end{aligned} \tag{41}$$

For the monomeric d^9 ion, the γ_ζ and $\gamma_\eta = \gamma_\xi$ parameters determine the deviation of the g-factors of the Cu^{2+} ion from the value $g_0 = 2.00$ due to SOC: $\Delta g_{||} = 4g_0\gamma_\zeta$, $\Delta g_\perp = g_0\gamma_\xi$ [51]. The estimation of the $K^{\kappa}_{\alpha\beta}$ components of the AS DE vector may be obtained as $K^{\zeta}_{\alpha\beta} = \theta\Delta g_{||}\sqrt{}3(t_{\mathrm{v}} - 2t_\xi)/16$, $K^{\eta}_{\alpha\beta} = \Delta g_\perp\gamma_\eta\sqrt{}3t_{\mathrm{v}}/4$.

The $K^{\zeta}_{\alpha\beta}$ components of the AS DE vector in the αβ pair are directed perpendicular to the plane of the trimer along the trigonal *Z*-axis of the cluster $K^{Z}_{ab} = K^{\zeta}_{ab}$, $K^{Z}_{bc} = K^{\zeta}_{bc}$, $K^{Z}_{ca} = K^{\zeta}_{ca}$, $K^{Z}_{ab} = K^{Z}_{bc} = K^{Z}_{ca}$. The calculations of the ‘in plane’ components of the $\mathbf{K}_{\alpha\beta}$ AS DE vector coefficients show that $K^{\xi}_{ab} = 0$ and the K^{η}_{ab} components are directed along the **αβ** vector for the each pair and $|K^{\eta}_{ab}| = |K^{\eta}_{bc}| = |K^{\eta}_{ca}|$. The pair vectors $\mathbf{K}_{\alpha\beta}$ contribute to the cluster **K** parameter as a sum $\mathbf{K} = (\mathbf{K}_{ab} + \mathbf{K}_{bc} + \mathbf{K}_{ca})/3$. The cluster K_X and K_Y parameters are equal to zero due to the trigonal symmetry and the cyclic conditions. In that way, the vector of the AS DE coupling of the trigonal trimer

$$\begin{aligned}
&K_Z = (K^{Z}_{ab} + K^{Z}_{bc} + K^{Z}_{ca})/3 = \theta\gamma_\zeta\sqrt{3}(t_{\mathrm{v}} - 2t_\xi)/2,\\
&K_X = K_Y = 0
\end{aligned} \tag{42}$$

is directed alone the trigonal *Z*-axis of the cluster. The $K_Z \neq 0$, $K_Z \sim \lambda$, $K_X = K_Y = 0$ condition confirms the effective Hamiltonian Eq. (31) results.

The AS DE splitting and the vector parameters Eq. (42) in the MV trimer is essentially different from the AS DE contributions in the MV dimers [53]. In the MV dimer, AS DE contributes in the second order to the ZFS parameters (Eq. (21)). In the trigonal trimer, the splitting of the ground ^2E term is determined only by the AS DE interaction. The splitting Δ is linear on the AS DE parameter K_Z, which allows one to find the AS DE parameter experimentally from the magnetic and EPR measurements.

By using the intrinsic parameters $\lambda = 829$ cm^{-1} and $\varepsilon_\zeta = 12\,300$ cm^{-1} for the Cu^{2+} ion and, for example t = 10^4 cm^{-1}, θ = 0.01–0.1 we can estimate the AS DE parameter as $K_Z \sim 5–50$ cm^{-1} and $\Delta(=2K_Z\sqrt{3}) > 10$ cm^{-1}.

8. Anisotropy of the cluster *g*-factors and magnetic moment induced by the AS double exchange in the MV trimer

We will include the Zeeman interaction $H_Z = \Sigma g_\alpha \beta \mathbf{S}_\alpha \mathbf{H}$ with isotropic local g-factors $g_\alpha = g_0$ for consideration of the AS DE effect in the Zeeman splitting and magnetic anisotropy. The Zeeman splitting and g-factor are isotropic for the exited $^2A_1$ DE term of the delocalized [Cu^{2+}–Cu^{+}–Cu^{+}] trimer. For the ground ^2E DE term, the Zeeman splitting has the form $E = -t \pm \sqrt{(\sqrt{3}K_Z \pm h_Z)^2 + h_X^2 + h_Y^2}$ where $h\alpha = g_0\beta H_\alpha/2$. In the external magnetic field $H = H_Z$ parallel to the trigonal axis Z of the cluster, the Zeeman splittings of the AS DE sublevels $E_\pm(\pm 1/2)$ and $E_\pm(\mp 1/2)$ are linear (Fig. 3):

$$E^{\|}_{1,2} = -t + \sqrt{3}K_Z \pm h_Z, \quad E^{\|}_{1,2} = -t - \sqrt{3}K_Z \pm h_Z \tag{43}$$

In the case of the external field $H = H_X$ in the plain of the cluster, the Zeeman splitting

$$E^{\perp}_{1,2} = -t + \sqrt{3K_Z^2 + h_X^2}, \quad E^{\perp}_{3,4} = -t - \sqrt{3K_Z^2 + h_X^2} \tag{44}$$

depend non-linearly on the magnetic field and $E^{\perp}_{1,2} = -t + \sqrt{3}K_Z + h_X^2/2\sqrt{3}K_Z$, $E^{\perp}_{3,4} = -t - \sqrt{3}K_Z - h_X^2/2\sqrt{3}K_Z$ by assuming that $h_Z \ll K_Z$ (Fig. 3(b)). In the considered model, the g-factors are strongly anisotropic ($g_{\|} = g_0$, $g_\perp = 0$) for the Kramers sublevels of the ground ^2E DE term [54].

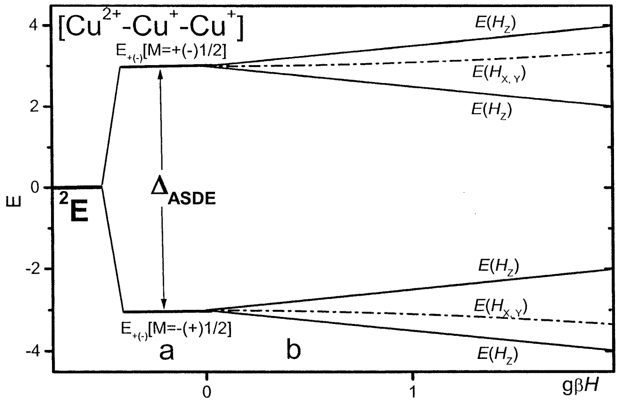

Fig. 3. (a) The AS DE splitting $\Delta_{\mathrm{ASDE}} = 2K_Z\sqrt{3}$ of the DE trigonal ^{2}E ground state of the delocalized [Cu(II)Cu$_2$(I)] MV cluster. (b) The Zeeman splittings of the $E_\pm(\pm 1/2)$ and $E_\pm(\mp 1/2)$ Kramers doublets of the trigonal ^2E term in the external magnetic field $H = H_Z$ (solid lines) parallel to the trigonal Z-axis and $H = H_X$ (dash-doted lines) in the plain of the trimeric cluster.

Strong anisotropy of the Zeeman splitting of the ground E term results in an anisotropy of the magnetic susceptibility χ (or effective magnetic moment $\mu_{\mathrm{eff}} = \sqrt{3\chi kT/N}$) of the cluster in the ground state [54]. In the small magnetic field $H = H_Z$, $h \ll kT$ the magnetic susceptibility $\chi_{\|}$ is described by the Curie law $\chi_{\|} = C/T$ due to linear field dependence for $H = H_Z$. The non-linear field dependence in the perpendicular magnetic field $H = H_X$ results in an essential deviation of $\chi_\perp$ from the Curie law: $\chi_\perp = (Ck/\sqrt{3}K_Z)th(\sqrt{3}K_Z/kT)$ for kT, $h_X \ll K_Z$.

In the case of the relatively small AS DE splitting of the ground ^2E DE term ($\Delta \sim 1–5$ cm^{-1}), the AS DE coupling constant may be found from the maximum in the low temperature heat capacity c(T), which is determined by the AS DE interval $\Delta = 2K_Z\sqrt{3}$.

9. The AS double exchange in the [d^n–d^n–d$^{n\pm1}$] MV clusters

The MV clusters [d^n–d^n–d$^{n\pm1}$] with $n = 1, 2\ldots$ demonstrate new AS DE effects, which can not be considered in the simple MV [d^9–d^{10}–d^{10}] ([d^1–d^0–d^0]) cluster with $S = 1/2$: the AS DE mixing of the trigonal DE levels with different S. In the [d^9–d^9–d^{10}] ([d^1–d^1–d^0]) MV cluster with the migrating hole, the total spin is $S =$ O, 1. In this case, the inter-ion interactions in the localized system include the HE $\mathbf{H}_{\mathrm{HE}} = \Sigma J_{\alpha\beta}\mathbf{S}_\alpha\mathbf{S}_\beta$ and DM exchange $\mathbf{H}_{\mathrm{DM}} = \Sigma \mathbf{G}_{\alpha\beta}[\mathbf{S}_\alpha \times \mathbf{S}_\beta]$ between two ions with $s_j = 1/2$. The isotropic DE and HE (t–J model) form the isotropic DE terms $^3A_2$, ^3E;$^1A_1$, ^1E: $E[^3A_2] = t+2J$, $E[^3E] = -t+2J$; $E[^1A_1] = 2t$, $E[^1E] = -t$ [13]. Since the K_X and K_Y components of the AS DE interaction are equal to zero in the trigonal MV trimer (Eq. (42)), the transfer Hamiltonian Eq. (31) has the only Z components of the spin-flop hopping for the trigonal MV trimer

$$\mathbf{H}_1^Z = \sum_{\alpha,\beta=a,b,c} \{t_{\alpha\beta}[\alpha_\uparrow^+\beta_\uparrow + \alpha_\downarrow^+\beta_\downarrow] + iK^z_{\alpha\beta}[\alpha_\uparrow^+\beta_\downarrow - \alpha_\downarrow^+\beta_\downarrow]\} \tag{45}$$

The Z component of the AS DE spin-transfer interaction

$$\mathbf{H}^Z_{\mathrm{ASDE}} = 2i\sum_{\alpha,\beta} K^Z_{\alpha\beta}\mathbf{T}_{\alpha\beta}(S^Z_\beta - S^Z_\alpha) \tag{46}$$

is the spin equivalent of the operator Eq. (45) for the considered cluster.

The AS DE coupling mixes the ${}^3A_2$ and ${}^1A_1$ trigonal DE terms. The AS DE mixing $\langle\Phi({}^3A_2,\ M=0)|H_1^Z|\Phi({}^1A_1,\ M=0)\rangle=-2iK_Z$ of the ${}^3A_2$ and ${}^1A_1$ DE terms is determined by the cluster AS DE parameter $K_Z=(K_{ab}^Z+K_{bc}^Z+K_{ca}^Z)/3$ The DM AS exchange mixes the $S=1$ and $S=0$ localized levels of the trimer in each localized state, for example, $\langle\psi_{a*bc}(1{,}0)|H_{\mathrm{DM}}^Z|\psi_{a*bc}(0{,}0)\rangle=-iG_{bc}^Z/2$. In the delocalized MV cluster, the both AS DE and DM AS exchange contribute to the SOC mixing of the terms ${}^3A_1$ and ${}^1A_1$

$$\langle\Phi({}^3A_2,0)|H_1^Z+H_{\mathrm{DM}}^Z|\Phi({}^1A_1,0)\rangle=-2i(K_Z+G_Z/4),$$

$$G_Z=(G_{ab}^Z+G_{ba}^Z+G_{ca}^Z)/3$$

The effective ZFS Hamiltonian $H_{\mathrm{ZFS}}=D_{\mathrm{S}}[S_Z^2-S(S+1)/3]$ [49–51] describes ZFS $2\mathrm{D}_{\mathrm{S}}$ of the $S=1$ states of the trigonal cluster in the second order on SOC. The local contributions to ZFS are zero ($s_i=1/2$).

The second order contribution of the AS DE and DM AS exchange to the ZFS parameter $D_0({}^3A_2)$ of the ${}^3A_2$ trigonal DE term (due to the mixing with the ${}^1A_1$ singlet) has a form $D_0({}^3A_2)=2(K_Z+G_Z/4)^2/(2t-J)$. The AS DE contribution to ZFS is essentially stronger than the pure DM AS exchange contribution since $K_Z\sim\Delta(g/g)t$, $G_Z\sim\Delta(g/g)J$ and $t\ll J$.

For the orbitally degenerate ${}^3E$ DE term, the AS DE results in the linear AS DE fine splitting of the ${}^3E$ term $E_\pm[M=\pm1]=t+2J+\sqrt{3K_Z}$, $E_\mp[M=\pm1]=t+2J-\sqrt{3K_Z}$, and in the second order contribution to the $D_0({}^3E)$ ZFS parameter of the ${}^3E$ term $D_0({}^3E)=-(K_Z-G_Z/2)^2/2(t+J)$ [54].

The DE states ${}^3E$ and ${}^1E$ are not mixed with the ${}^3A_2$ and ${}^1A_1$ terms by the AS DE and DM AS exchange.

The AS DE effect in the MV trimers with high individual spins was considered in Ref. [54]. In all MV trimers, only the AS DE coupling determines the linear fine splittings of the ${}^{2S+1}E$ DE terms with maximal total spin S $[\varepsilon_1({}^{2S_{\max}+1}E_\pm,M)=\pm K_ZM\sqrt{3}/S_{\max}]$. For the ${}^{2S+1}E$ terms with non-maximal total spin S (spin-frustrated levels), both AS DE and DM AS exchange determine the linear splittings, since AS couplings mix the S states with different intermediate spins [54]. The AS DE contribution to the linear fine splittings Δ dominates since $K_Z\ll G_Z$. The AS DE coupling mixes the ${}^{2S+1}A_1$ and ${}^{2S+1}A_2$, ${}^{2S+1}E$ and ${}^{2S+1}E$ DE terms $\Delta S=0{,}1$. The AS DE does not mix the A and E terms and also the same A_i terms since the operator of the AS DE interaction transforms on the A_{2g} representation of the trigonal D_3 group [54]. In the trimeric clusters with high individual spin S_i, both AS DE and DM AS exchange are active: the DM AS exchange mixes the localized S levels and the AS DE mixes the DE terms of the delocalized trimer. The AS DE plus DM AS exchange mixing of the DE levels ${}^{2S+1}\Gamma$ with different S and also the mixing of the ${}^{2S+1}\Gamma_i$ terms with different intermediate spins S_{ij} determine the AS contributions to the cluster ZFS parameters D_S. The AS DE contributions to the second order ZFS parameters D_S in trimers are stronger than the DM ASE contributions since $K_Z\gg G_Z$, $K_Z/G_Z=t/J$. The AS DE contributions are different for different ${}^{2S+1}A_i$ and ${}^{2S+1}E$ terms. In general, the AS DE contributions to the cluster ZFS parameters $D_S({}^{2S+1}\Gamma_i)$ has the form $\vec{D}_S({}^{2S+1}\Gamma_i)=\Sigma[(mK_Z+nG_Z)^2/(pt+qJ)]$.

10. Conclusion

An AS DE coupling was considered for the MV dimeric $\mathrm{d}^n-\mathrm{d}^{n+1}$ and trimeric $\mathrm{d}^n-\mathrm{d}^{n+1}-\mathrm{d}^{n+1}$ clusters.

10.1. Dimeric MV clusters

Strong Anderson–Hasegawa DE and HE interactions ($t-J$ model) form isotropic exchange-resonance states $E_\pm^0(S)$ characterized by the total spin S and parity.

The SOC in the $\mathrm{d}^n-\mathrm{d}^{n+1}$ clusters in the $t-J$ model may be represented in the form of the effective AS DE Hamiltonian $H_{\mathrm{ASDE}}=2i\mathbf{K}_{ab}\mathbf{T}_{ab}(\mathbf{S}_b-\mathbf{S}_a)$(Eq. (23)) where $\mathbf{K}_{ab}$ is the real AS ($\mathbf{K}_{ab}=-\mathbf{K}_{ba}$) vector coefficient, $\hat{\mathbf{T}}_{ab}$ is the isotropic transfer operator. The AS DE Hamiltonian has a form of the spin-transfer interaction. The Eqs. (24)–(26) describe the analytical solutions of the AS DE Hamiltonian Eq. (23) for the MV dimers. The matrix elements of the AS DE interaction depend on the projection M of total spin. The AS DE leads to non-collinear orientation of spins.

10.1.1. The $d^1-d^0(d^9-d^{10})$ clusters

An AS DE mixes the isotropic AH resonance states $E_+^0(S=\frac{1}{2})$ and $\mathrm{E}_-^0(\frac{1}{2})$ and forms the effective spin $S'=\frac{1}{2}$ The resonance splitting $E_\pm^0(S'=\frac{1}{2})=\pm\sqrt{t^2+\mathbf{K}_{ab}^2}$ is characterized by the effective DE parameter $t_{\mathrm{eff}}=\sqrt{t^2+\mathbf{K}_{ab}^2}$. The vector of the AS DE in the MV dimer is directed perpendicular to the Z-axis of the dimer. The AS DE admixture of the excited crystal field states results in the modification of the DE (transfer) parameter t. AS DE results in an anisotropy of g-factors.

10.1.2. The $d^8-d^9(d^2-d^1)$ cluster

An AS DE mixes the Anderson–Hasegawa DE states $E_+^0(S)$ and $E_-^0(S)$ of different parity with the same total spin S ($S=3/2$ or $\frac{1}{2}$). The AS DE and DM AS exchange mix the AH states $E_\pm^0(3/2)$ and $E_\pm^0(\frac{1}{2})$ of the same parity with different total spin S, $\Delta S=1$. For the MV $\mathrm{d}^8-\mathrm{d}^9(\mathrm{d}^1-\mathrm{d}^2)$ cluster with an initial ZFS $2\mathrm{D}_{\mathrm{S}}$ of the $E_\pm^0$(3/

2) states ($H^0_{\mathrm{ZFS}} = D_S[S_Z^2 - S((S+1)/3]$) the AS DE contributes to the resulting ZFSs of the high-spin ($S = 3/2$) states. The AS DE contributions $\delta_K^{\pm}(3/2)$ to the ZFS parameters D_S are different for the $E_+(3/2)$ and $E_-(3/2)$ states $\Delta^{\pm}_{\mathrm{ZFS}}[E_\pm(3/2)] = 2[D_S + \delta_K^{\pm}(3/2)]$. The AS DE contributions $\delta_K^{\pm}(3/2)$ are proportional to $K^2J/t(t \pm 6J)$. The AS DE contributions to ZFS are anisotropic.

The taking into account the DM AS exchange mixing of the localized levels with different total spin S results in the modification of the $\delta_\chi^{\pm}$ part of the ZFS parameters D_S:$\tilde{\delta}_\chi^{\pm} = \delta_\chi^{\pm} - \omega_\chi^{\pm}$, where $\omega_\chi^{\pm} = G_\chi(4K_\chi \pm 3G_\chi)/6(t \pm 6J)$. The contribution of AS DE to the ZFS parameters in the delocalized MV system is stronger than the DM AS exchange contribution since $K_K \gg G_K$.

In the MV $\mathrm{d}^n - \mathrm{d}^{n+1}$ dimers with the Anderson–Hasegawa DE and HE inter-ion coupling, an AS DE $\mathbf{H}_{\mathrm{ASDE}} = 2i\mathbf{K}_{ab}\widehat{\mathbf{T}}_{ab}(\mathbf{S}_b - \mathbf{S}_c)$ plays the role analogous to the role of the DM AS exchange $\mathbf{H}_{\mathrm{DM}} = \mathbf{G}_{ab}(\mathbf{S}_a \times \mathbf{S}_b)$ in the mono-valent $\mathrm{d}^n - \mathrm{d}^n$ pair with the HE inter-ion coupling.

10.2. Trimeric MV clusters

The AS DE results in the linear fine splittings Δ of the isotropic degenerate ${}^{2S+1}E$ DE terms. The splittings Δ are proportional to the AS DE parameter $K_Z = (K_{ab}^Z + K_{bc}^Z + K_{ca}^Z)/3$ of the MV trimer. The vector of the AS DE interaction K_Z is directed along the trigonal Z-axis of the trigonal MV cluster. Only AS DE mixes the ${}^{2S+1}A_1$ and ${}^{2S+1}A_2$, ${}^{2S+1}E$ and ${}^{2S+1}E$ DE terms with the same total spin S. The AS DE and DM AS exchange mix the ${}^{2S+1}A_1$ and ${}^{2S+1}A_2$, ${}^{2S+1}E$ and ${}^{2S+1}E$ DE terms with different S. AS DE does not mix the A and E terms and also the same A_i terms. In trimeric MV clusters with high-spins S_i, the AS DE and DM AS exchange mixing of the DE levels ${}^{2S+1}\Gamma$ with different total spin S ($\Delta S = 1$) determines the contributions to the second order ZFS trigonal D_{S} parameters ($H_{\mathrm{ZFS}} = D_s[S_Z^2 - S(S+1)/3]$). The AS DE contributions to the ZFS parameters D_S are different for the A_i and E terms. For the delocalized [Cu(II)Cu$_2$(I)] MV cluster, the AS DE splitting $\Delta = 2K_Z\sqrt{3}$ of the ground ${}^2E$ DE term determines strong anisotropy of the Zeeman splitting, anisotropy of g-factors and magnetic properties.

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