

Exchange interaction between J -multiplets

Naoya Iwahara and Liviu F. Chibotaru

Theory of Nanomaterials Group, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

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Analytical expressions for the exchange interaction between J -multiplets of interacting metallic centers are derived on the basis of a complete electronic model which includes the intrasite relativistic effects. A common belief that this interaction can be approximated by an isotropic form $\propto \mathbf{J}_1 \cdot \mathbf{J}_2$ (or $\propto \mathbf{J}_1 \cdot \mathbf{S}_2$ in the case of interaction with an isotropic spin) is found to be ungrounded. It is also shown that the often used “ $1/U$ approximation” for the description of the kinetic contribution of the exchange interaction is not valid in the case of J -multiplets. The developed theory can be used for microscopic description of exchange interaction in materials containing lanthanides, actinides and some transition metal ions.

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I. INTRODUCTION

Strong magnetic anisotropy induced by spin-orbit coupling on the metal sites is a key ingredient for a number of intriguing properties of magnetic materials, such as single-molecule magnet behavior [1, 2], magnetic multipole ordering [3], and various exotic electronic phases [4, 5]. If the spin-orbit coupling exceeds the crystal-field splitting of the ground term LS on the metal site, the latter acquires unquenched orbital momentum $\hat{\mathbf{L}}$ and the low-lying spectrum is well described as crystal-field split eigenstates of the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, where $\hat{\mathbf{S}}$ is the spin of the metallic term. This situation takes place in lanthanides [6], actinides [3] and some transition metal ions in a cubic symmetry environment [7, 8].

The exchange interaction between such split- J crystal-field levels (or groups of levels) is significantly more complicated than the exchange interaction between pure spin terms ($L = 0$) described by the Heisenberg Hamiltonian $\mathcal{J}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$. For the weak spin-orbit coupling, the discrepancy of the exchange Hamiltonian from the isotropic form was first pointed out by Stevens [9]. Later, the anisotropic exchange interaction was extensively developed by Moriya [10] based on the Anderson’s microscopic approach [11, 12]. In the case of the strong spin-orbit coupling, the exchange interaction including the higher order terms of $\hat{\mathbf{J}}$ was also phenomenologically treated since long time ago [13, 14]. The microscopic description was addressed for the first time by Elliott and Thorpe [15] for uranium oxides, and by Hartmann-Boutron [16] for transition metal compounds on the basis of simplified analysis based on so-called $1/\bar{U}$ approximation (\bar{U} is the average electron promotion energy between the sites). Recently, within the same approximation, the microscopic derivation of the exchange Hamiltonian between J -multiplets was completed by Santini *et al.* [3].

Despite this early evidence of complexity of exchange interaction between metal ions with unquenched orbital moments, it was repeatedly conjectured that the exchange interaction between fully degenerate J -shells, involving $(2J_1 + 1)$ and $(2J_2 + 1)$ angular momentum eigen-

states on the first and the second magnetic centers, respectively, is described by an isotropic exchange Hamiltonian written in terms of $\hat{\mathbf{J}}_i$ momenta:

$$\hat{H}_{\text{Heis}} = \mathcal{J}\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2. \quad (1)$$

Contrary to Heisenberg Hamiltonian for isotropic spins, there is no *a priori* justification for the Hamiltonian (1). Nevertheless, this form is often used for the description of interaction between lanthanides or actinides (or a similar form, $\propto \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{S}}_2$, in the case of their interaction with an isotropic spin), especially, in the last years [17–30]. One of the reasons that the simple bilinear form has been often used is that the large numbers of the phenomenological exchange parameters cannot be easily determined.

It is not clear, however, how important are “non-Heisenberg” terms in the actual J - J coupling, nor is the $1/\bar{U}$ approximation *a priori* justified for metal ions with unquenched orbital momenta. Both these questions can only be answered after a more complete derivation of exchange interaction between J multiplets on the basis of a reliable microscopic model. Besides, a microscopic description of J - J (J - S) exchange interaction is desirable due to a very large number of phenomenological parameters, in contrast to weakly-anisotropic spin systems containing only a few of them [31, 32]. Given that many microscopic electronic parameters describing individual magnetic centers and their interaction can be accurately derived via density functional theory [33] or *ab initio* calculations [34], a microscopically derived Hamiltonian for J multiplets can become a powerful tool for the investigation of exchange interaction in materials containing lanthanides, actinides and transition metal ions with unquenched orbital momentum. To this end the electronic Hamiltonians only need to be downfolded on the reduced manifold of low-lying states at the corresponding metal ions.

In this work, we derive analytically the exchange Hamiltonians for interacting J -multiplets and for interacting J -multiplet and isotropic spin, starting from a microscopic electronic Hamiltonian including the relativistic interactions on the metal sites. The obtained exchange parameters are expressed via electronic matrix

elements which can be derived from electronic structure calculations. The structure of the exchange Hamiltonian is discussed and the result is applied for the analysis of some systems with different geometries. Comparison with the predictions given by the Hamiltonian (1) and the simplified treatment on the basis of $1/\bar{U}$ approximation shows that both of them are not suitable approaches to describe the exchange interaction of ions with unquenched orbital momentum. Finally, the relative contributions to the kinetic exchange interaction from intermediate states is analyzed.

II. MICROSCOPIC DESCRIPTION OF INTERSITE INTERACTION

We derive the expression for the interaction between metal ions with unquenched orbital moments. The derivation is based on a complete electronic Hamiltonian, including all intrasite relativistic effects, and employs adequate approximations. The multipolar intersite interactions of electromagnetic type, such as the electric quadrupolar and magnetic dipolar interactions, have been described elsewhere [3, 14, 35, 36] and are not considered here. Their effect can be taken into account as additive contribution to the exchange parameters.

A. Electronic multiplets on sites

The nonrelativistic electronic state of an ion with partially filled nl shell (n is the main quantum number and l is the one-electron orbital angular momentum) corresponds to an LS -term characterized by the total orbital $\hat{\mathbf{L}}$ and spin $\hat{\mathbf{S}}$ angular momenta [37]. The eigenfunctions $\{|\alpha_{LS}LM_LSM_S\rangle\}$ are described by orbital and spin quantum numbers, L and S , and the projections of $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ on a given axis z , M_L and M_S , respectively; α_{LS} indicates the other quantum numbers. The $(2L+1)(2S+1)$ -fold degenerate term is further split by the spin-orbit interaction into J -multiplets which are eigenstates of the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. The corresponding eigenfunctions $\{|\alpha_JJM\rangle\}$ are characterized by quantum numbers of the total angular momentum J and its projection $M = -J, -J+1, \dots, J$ (α_J stands for other quantum numbers).

In general, the spin-orbit interaction mixes multiplets with the same J belonging to different LS terms (the so-called J - J mixing [36]). In the case when this mixing can be neglected, each J -multiplet is attributed to one LS -term and the corresponding wave functions become of the form $(\alpha_J = (\alpha_{LS}, L, S))$:

$$|\alpha_JJM\rangle = \sum_{M_L M_S} |\alpha_{LS}LM_LSM_S\rangle C_{LM_L SM_L}^{JM}, \quad (2)$$

where $C_{LM_L SM_L}^{JM}$ is the Clebsch-Gordan coefficient (A2) [38]. This is a good approximation, in particular, for

the ground J -multiplet of trivalent ions from the late lanthanides series, Ln^{3+} .

When the metal ions are embedded in complexes or crystals, their electronic structure is modified due to covalent and electrostatic interaction of the magnetic nl orbitals with the environment. In the case of f -metals the magnetic orbitals are usually strongly localized and the effect of the surrounding is relatively weak. For example, in the case of lanthanide, the intraionic bielectronic interaction leading to atomic terms separation is ca 5-7 eV and the spin-orbit splitting is ca 1 eV for lanthanide ions, thus exceeding several times the the crystal-field splitting, which is usually of the order of 0.1 eV [39]. In this situation the low-energy electronic states are well approximated as crystal-field split atomic J -multiplets. Due to the weak hybridization of the $4f$ orbitals with the surrounding, the Wannier functions of the corresponding magnetic orbitals practically coincide with the atomic $4f$ orbitals. Similar holds true for actinide ions although $5f$ orbitals are more delocalized than $4f$ orbitals.

On the other hand, the effect of the hybridization of d orbitals with the ligand orbitals is usually much stronger than in lanthanides and actinides resulting in a crystal-field splitting which often overcomes the atomic LS -term splitting. Therefore, the orbital angular momentum is generally not a good quantum number for nondegenerate ground state of embedded transition metal ions. Moreover this orbital angular momentum is quenched as a rule, $\langle \hat{\mathbf{L}} \rangle = 0$, in most compounds. The exception is the cubic environment, in which the d orbitals split into doubly degenerate e and triply degenerate t_2 levels. When the t_2 orbital are partially filled, the electronic state is characterized by the nonzero fictitious orbital angular momentum $\tilde{L} = 1$, which couples to the total spin of the site via spin-orbit coupling and gives molecular multiplets characterized by fictitious total angular momentum $\tilde{\mathbf{J}} = \tilde{\mathbf{L}} + \hat{\mathbf{S}}$ (see Ref. 8 for details).

B. Intersite interaction

The electronic Hamiltonian \hat{H} for electrons localized at two sites can be divided into the intrasite contributions \hat{H}_0^i ($i = 1, 2$), the intersite bielectronic \hat{H}'_{bi} and electron transfer \hat{H}_t parts:

$$\hat{H} = \sum_{i=1,2} \hat{H}_0^i + \hat{H}'_{bi} + \hat{H}_t. \quad (3)$$

The intrasite Hamiltonian for site i , \hat{H}_0^i , contains all effects discussed in Sec. II A such as the non-relativistic atomic terms, the spin-orbit term and other relativistic corrections, and the crystal-field. The eigenstate of \hat{H}_0^i is determined by the number of electrons N_i in magnetic orbitals and crystal-field level p , $|iN_i, p\rangle$. \hat{H}'_{bi} consists of intersite Coulomb interaction \hat{H}_{Coul} and direct exchange

(multipole) part \hat{H}_{DE} :

$$\hat{H}'_{\text{bi}} = \hat{H}_{\text{Coul}} + \hat{H}_{\text{DE}}, \quad (4)$$

$$\hat{H}_{\text{Coul}} = \sum_{mn\sigma\sigma'} U' \hat{n}_{1m\sigma} \hat{n}_{2n\sigma'}, \quad (5)$$

$$\hat{H}_{\text{DE}} = - \sum_{mm'n'\sigma\sigma'} V_{mm'n'n} \hat{c}_{1m\sigma}^\dagger \hat{c}_{1n\sigma'} \hat{c}_{2m'\sigma'}^\dagger \hat{c}_{2n'\sigma}, \quad (6)$$

where m, n indicate the projection of the orbital angular momentum l_i , σ is the projection of the electron spin momentum, $\hat{c}_{im\sigma}^\dagger$ ($\hat{c}_{im\sigma}$) is the electron creation (annihilation) operator in spin-orbital (m, σ) of site i ($= 1, 2$), $\hat{n}_{im\sigma} = \hat{c}_{im\sigma}^\dagger \hat{c}_{im\sigma}$, U' is the intersite electron repulsion, $V_{mm'n'n}$ is the intersite exchange integral,

$$V_{mm'n'n} = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{1m}^*(\mathbf{r}_1) \psi_{2m'}^*(\mathbf{r}_2) \times v(|\mathbf{r}_1 - \mathbf{r}_2|) \psi_{2n}(\mathbf{r}_1) \psi_{1n'}(\mathbf{r}_2), \quad (7)$$

ψ_{im} is the Wannier function at site i and component m , and $v(|\mathbf{r}_1 - \mathbf{r}_2|)$ is the two body interaction. Note that \hat{H}'_{bi} does not change the number of the electrons on each sites. The transfer Hamiltonian is written as

$$\hat{H}_t = \sum_{i \neq j} \sum_{mm'\sigma} t_{mm'}^{ij} \hat{c}_{im\sigma}^\dagger \hat{c}_{jm'\sigma}, \quad (8)$$

where $t_{mm'}^{ij}$ is the electron transfer parameter between orbitals m of site i and m' of j .

As discussed by Anderson [11, 12], the direct exchange parameter (7) and the transfer parameters are finite due to the delocalization of the magnetic orbital ψ_{im} on the ligand between metal sites (or the other magnetic site). The electron transfer parameter between metal sites is at least several times smaller than the intrasite electron repulsion. Thus, the electronic Hamiltonian \hat{H} (3) can be divided into zeroth order Hamiltonian

$$\hat{H}_0 = \sum_{i=1}^2 \hat{H}_0^i + \hat{H}_{\text{Coul}} \quad (9)$$

and small terms \hat{H}_{DE} and \hat{H}_t . For localized magnetic electrons, the latter can be treated in the first and the second order of perturbation theory, respectively [11, 12]. This is done here via a unitary transformation,

$$\hat{H}_{\text{eff}} = e^{-\hat{S}} \hat{H} e^{\hat{S}}, \quad (10)$$

removing \hat{H}_t from the initial Hamiltonian. Neglecting the terms higher than second order after the transfer parameters, we obtain the effective Hamiltonian acting on the ground J -multiplets on sites,

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \bar{H}. \quad (11)$$

In the unperturbed Hamiltonian (9), there are no terms which vary the numbers of the electrons. Then the electronic states can be written as follows:

$$|N_1, N_2, r\rangle = \sum_{p,q} |1N_1, p\rangle |2N_2, q\rangle C_{pq,r}^{N_1 N_2}, \quad (12)$$

where r indicates the eigenstate of the system and $C_{pq,r}^{N_1 N_2}$ is a coefficient. In the derivation of the effective Hamiltonian, we consider the truncated vector space \mathcal{B} of the electron configurations which include up to one electron transfer with respect to the numbers of the electrons in the ground electron configurations. Hereafter, N_i is used as the number of electrons on site i in the ground electron configurations. For simplicity, the numbers of electrons in the ground configurations will not be written explicitly, and the configurations s with $N_1 - 1$ and $N_2 + 1$ ($N_1 + 1$ and $N_2 - 1$) electrons on sites 1 and 2 are expressed by the type of the virtual electron transfer, $1 \rightarrow 2$ ($2 \rightarrow 1$). Therefore, \mathcal{B} is defined as follows:

$$\mathcal{B} = \{|r\rangle, |1 \rightarrow 2, s\rangle, |2 \rightarrow 1, s'\rangle\}. \quad (13)$$

The eigenenergies of the states $|r\rangle, |i \rightarrow j, s\rangle$ are denoted as E_r^0 and $E_s^{i \rightarrow j}$, respectively.

The exponent of the unitary operator $e^{\hat{S}}$ is given as

$$\hat{S} = \sum_{i \neq j} \sum_r \sum_s \left(\frac{\hat{P}_s^{i \rightarrow j} \hat{H}_t \hat{P}_r^0}{E_r^0 - E_s^{i \rightarrow j}} - \frac{\hat{P}_r^0 \hat{H}_t \hat{P}_s^{i \rightarrow j}}{E_r^0 - E_s^{i \rightarrow j}} \right), \quad (14)$$

where \hat{P}_r^0 and $\hat{P}_s^{i \rightarrow j}$ are the projection operators,

$$\hat{P}_r^0 = |r\rangle \langle r|, \quad (15)$$

$$\hat{P}_s^{i \rightarrow j} = |i \rightarrow j, s\rangle \langle i \rightarrow j, s|. \quad (16)$$

The exponent \hat{S} is chosen to fulfill the condition

$$[\hat{S}, \hat{H}_0 + \hat{H}_{\text{DE}}] = \hat{H}_t \quad (17)$$

within the space \mathcal{B} . The effective Hamiltonian (10) within $\mathcal{B}_0 = \{|r\rangle\}$ is obtained as

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \hat{H}_{\text{DE}} - \frac{1}{2} [\hat{S}, \hat{H}_t], \quad (18)$$

up to second order after \hat{H}_t . The second and the third terms in Eq. (18) correspond to \bar{H} defined above,

$$\bar{H} = \hat{H}_{\text{DE}} + \hat{H}_{\text{KE}}, \quad (19)$$

$$\hat{H}_{\text{KE}} = \frac{1}{2} \sum_{i \neq j} \sum_r \sum_s \frac{\hat{H}_t \hat{P}_s^{i \rightarrow j} \hat{H}_t \hat{P}_r^0}{E_r^0 - E_s^{i \rightarrow j}} + \text{H.c.} \quad (20)$$

Note that the terms $\hat{P}_s^{i \rightarrow j} \hat{H}_t \hat{P}_r^0 \hat{H}_t$ and $\hat{H}_t \hat{P}_r^0 \hat{H}_t \hat{P}_s^{i \rightarrow j}$ do not enter here because they map the states outside the domain \mathcal{B}_0 .

Neglecting the effects of the crystal-field splitting in the denominator of \hat{H}_{KE} , which is a reasonable approximation for our systems, the eigenstates r, s reduce to the sets of the J -multiplet states:

$$r \rightarrow (\alpha_1 J_1 M_1, \alpha_2 J_2 M_2), \quad (21)$$

$$s \rightarrow (\alpha_J J M, \alpha_{J'} J' M'), \quad (22)$$

where, J_i is the total angular momentum with the ground electron configuration, and J, J' are the total angular momenta for intermediate states arising from the transfer

of one electron between the sites. The kinetic exchange Hamiltonian becomes

$$\hat{H}_{\text{KE}} = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha_i J_i, \alpha_j J_j} \sum_{\alpha_j J, \alpha'_j J'} \frac{\hat{H}_t \hat{P}_{\alpha_j J, \alpha'_j J'}^{i \rightarrow j} \hat{H}_t \hat{P}_{\alpha_i J_i, \alpha_j J_j}^0}{E_{\alpha_i J_i, \alpha_j J_j}^0 - E_{\alpha_j J, \alpha'_j J'}^{i \rightarrow j}} + \text{H.c.}, \quad (23)$$

where the projection operators are

$$\hat{P}_{\alpha_i J_i, \alpha_j J_j}^0 = \hat{P}_{\alpha_i J_i}^{N_i} \hat{P}_{\alpha_j J_j}^{N_j}, \quad (24)$$

$$\hat{P}_{\alpha_j J, \alpha'_j J'}^{i \rightarrow j} = \hat{P}_{\alpha_j J}^{N_j-1} \hat{P}_{\alpha'_j J'}^{N_j+1}, \quad (25)$$

and $\hat{P}_{\alpha_j J}^N$ is the projection operator on site i ,

$$\hat{P}_{\alpha_j J}^N = \sum_{M=-J}^J |iN\alpha_j JM\rangle \langle iN\alpha_j JM|. \quad (26)$$

In the space of the ground J -multiplets on sites, $\mathcal{B}_J = \{|J_1 M_1, J_2 M_2\rangle : -J_i \leq M_i \leq J_i\}$, the kinetic exchange Hamiltonian reduces to

$$\hat{H}_{\text{KE}} = \sum_{i \neq j} \sum_{\alpha_j J, \alpha'_j J'} \frac{\hat{H}_t \hat{P}_{\alpha_j J, \alpha'_j J'}^{i \rightarrow j} \hat{H}_t}{E_{J_i, J_j}^0 - E_{\alpha_j J, \alpha'_j J'}^{i \rightarrow j}}. \quad (27)$$

Here, α_i of the ground J -multiplet is not written for the sake of simplicity and $\hat{P}_{\alpha_i J_i, \alpha_j J_j}^0$ is omitted because it is the unit operator within \mathcal{B}_J .

Substituting Eq. (8) into Eq. (27), we obtain

$$\hat{H}_{\text{KE}} = \sum_{i \neq j} \sum_{\alpha_j J} \sum_{\alpha'_j J'} \sum_{mn\sigma} \sum_{m'n'\sigma'} -t_{mm'}^{ij} t_{n'n}^{ji} \times \frac{\left(\hat{c}_{im\sigma}^\dagger \hat{P}_{\alpha_j J}^{N_j-1} \hat{c}_{in\sigma'} \right) \left(\hat{c}_{jm'\sigma} \hat{P}_{\alpha'_j J'}^{N_j+1} \hat{c}_{jn'\sigma'}^\dagger \right)}{U_{ij} + \Delta E_{\alpha_j J}^{N_j-1} + \Delta E_{\alpha'_j J'}^{N_j+1}}, \quad (28)$$

where U_{ij} is the smallest promotion energy for the electron transfer from site i to site j , and $\Delta E_{\alpha_j J}^N$ is the excitation energy from the ground intermediate state with N electrons. In the derivation of Eq. (28), we have not used the approximate form (2) for the J -multiplets in both the ground and the virtual states. The quantum number J for the virtual states fulfills the condition $|J_i - l_i - 1/2| \leq J \leq J_i + l_i + 1/2$. Although the crystal-field splitting is neglected, the multiplet structures of sites are completely retained in Eq. (28). Hence, important effects such as the Goodenough's mechanism [40] are included in the kinetic exchange Hamiltonian.

III. EXCHANGE HAMILTONIAN IN J -REPRESENTATION

The Hamiltonian \bar{H} (19) is transformed into tensor form with the use of irreducible (double) tensor technique [41], method of equivalent operator [8], and the form of J -multiplet state (2):

$$\bar{H} = \sum_{kqk'q'} \mathcal{J}_{kqk'q'} \frac{O_k^q(\hat{\mathbf{J}}_1) O_{k'}^{q'}(\hat{\mathbf{J}}_2)}{O_k^0(J_1) O_{k'}^0(J_2)}. \quad (29)$$

Here, $O_k^q(\hat{\mathbf{J}}_1)$ and $O_{k'}^{q'}(\hat{\mathbf{J}}_2)$ are Stevens operators [42] (see also Appendix A 3) whose ranks k and k' have to obey the relation $k + k' = \text{even}$ due to the invariance of the Hamiltonian with respect to time inversion [8] (see Appendix C), q and q' are component, and $O_k^0(J_1)$ and $O_{k'}^0(J_2)$ are the scalars obtained by replacing $\hat{\mathbf{J}}_i^2$ and \hat{J}_{iz} in $O_k^0(\hat{\mathbf{J}}_i)$ with eigenvalues $J_i(J_i + 1)$ and J_i , respectively ($i = 1, 2$). The exchange coupling constant $\mathcal{J}_{kqk'q'}$ is a sum of the direct exchange $\mathcal{J}_{kqk'q'}^{\text{DE}}$ and the kinetic $\mathcal{J}_{kqk'q'}^{\text{KE}}$ contributions [43]:

$$\mathcal{J}_{kqk'q'} = \mathcal{J}_{kqk'q'}^{\text{DE}} + \mathcal{J}_{kqk'q'}^{\text{KE}}. \quad (30)$$

The advantages of using the exchange Hamiltonian in the tensorial form is that with Eq. (29) it is easier (i) to obtain physical insight on the exchange interaction and (ii) to combine it with other terms such as crystal-field and Zeeman interaction included in \hat{H}_0 . The latter can be treated at *ab initio* level [32, 34].

A. Direct exchange interaction

The outline of the derivation for the direct exchange part in \bar{H} is given here, whereas details of the calculations are given in Appendix B 1. The direct product of the double tensors $\hat{c}_{im\sigma}^\dagger \hat{c}_{in\sigma'}$ appearing in \hat{H}_{DE} (6) is reduced as follows:

$$\hat{c}_{im\sigma}^\dagger \hat{c}_{in\sigma'} = (-1)^{l_i+n+\frac{1}{2}+\sigma'} \sum_{a\alpha b\beta} \left\{ \hat{c}_i^\dagger \otimes \bar{c}_i \right\}_{b\beta}^{a\alpha} \times C_{l_i m l_i - n}^{a\alpha} C_{\frac{1}{2} \sigma \frac{1}{2} - \sigma'}^{b\beta}, \quad (31)$$

where $\bar{c}_{in\sigma'} = (-1)^{l_i+n+\frac{1}{2}+\sigma'} \hat{c}_{i-n-\sigma'}$ (A16) is a double tensor (see Appendix A 2), the curly bracket $\{\hat{c}_i^\dagger \otimes \bar{c}_i\}_{b\beta}^{a\alpha}$ indicates the irreducible operator of ranks (a, b) and components (α, β) constructed from the product of two tensors, where the superscripts and subscripts are the orbital and spin parts, respectively. The irreducible tensor operator is replaced by the total angular momentum operator $\hat{\mathbf{J}}_i$ using the method of equivalent operator for double tensor (A26):

$$\left\{ \hat{c}_i^\dagger \otimes \bar{c}_i \right\}_{b\beta}^{a\alpha} = \sum_{kq} C_{a\alpha b\beta}^{kq} \mathcal{D}_{abk}^i \frac{O_k^q(\hat{\mathbf{J}}_i)}{O_k^0(J_i)}. \quad (32)$$

Here, \mathcal{D}_{abk}^i is a tensor with three indices a, b, k (B2). Note that when the method of equivalent operator (A26) is used, the form of $|JM\rangle$ (2) is assumed.

Substituting Eqs. (31), (32) into \hat{H}_{DE} (6), we obtain the tensor form of the direct exchange Hamiltonian. The exchange parameter \mathcal{J}^{DE} is obtained as

$$\mathcal{J}_{kqk'q'}^{\text{DE}} = - \sum_{aa'b} \nu_{kqk'q'}^{aa'b} \mathcal{D}_{abk}^1 \mathcal{D}_{a'bk'}^2, \quad (33)$$

where

$$\begin{aligned} \mathcal{V}_{kqk'q'}^{aa'b} &= \sum_{mn} \sum_{m'n'} \sum_{\alpha\alpha'\beta} (-1)^{l_1+l_2+n+n'-\beta} V_{mm'n'n} \\ &\times C_{l_1 m l_1 - n}^{\alpha\alpha} C_{\alpha\alpha\beta}^{kq} C_{l_2 m' l_2 - n'}^{\alpha'\alpha'} C_{\alpha'\alpha'b-\beta}^{k'q'}. \end{aligned} \quad (34)$$

B. Kinetic exchange interaction

The derivation of the kinetic exchange parameter \mathcal{J}^{KE} is similar to that of \mathcal{J}^{DE} . As in the previous case, only the outline of the derivation is given here and the details can be found in Appendix B2. In comparison with the direct exchange, the derivation of \mathcal{J}^{KE} is cumbersome because of the projection operator $\hat{P}_{i\alpha J}^N$ appearing in Eq. (28). The latter is reducible within the product group $SO(3) \otimes SU(2)$ where the creation \hat{c}^\dagger and annihilation \bar{c} (A16) operators are irreducible. Therefore, we first transform $\hat{P}_{i\alpha J}^N$ into the sum of the irreducible double tensors $\hat{P}_{i\alpha J a\alpha'\alpha'}^N$ (B11), and then the product such as $\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J a\alpha'\alpha'}^{N_i-1} \hat{c}_{in\sigma'}$ is reduced. The irreducible tensor operator $\{\hat{c}_i^\dagger \otimes \{\hat{P}_{i\alpha J a\alpha'}^{N_i-1} \otimes \bar{c}_i\}_d\}_{e\epsilon}^{c\gamma}$ is replaced by the total angular momentum $\hat{\mathbf{J}}_i$ using the method of the equivalent operator (A26), and finally we obtain the kinetic exchange parameter:

$$\begin{aligned} \mathcal{J}_{kqk'q'}^{\text{KE}} &= \sum_{fxx'} \sum_{\alpha J} \sum_{\alpha' J'} \frac{\{t \times t\}_{kqk'q'}^{fxx'} \mathcal{F}_{\alpha J}^1 \mathcal{G}_{\alpha' J'}^2}{U_{12} + \Delta E_{1\alpha J}^{N_1-1} + \Delta E_{2\alpha' J'}^{N_2+1}} \\ &+ \sum_{fxx'} \sum_{\alpha J} \sum_{\alpha' J'} \frac{\{t \times t\}_{kqk'q'}^{fxx'} \mathcal{G}_{\alpha J}^1 \mathcal{F}_{\alpha' J'}^2}{U_{21} + \Delta E_{1\alpha J}^{N_1+1} + \Delta E_{2\alpha' J'}^{N_2-1}}, \end{aligned} \quad (35)$$

where

$$\begin{aligned} \{t \times t\}_{kqk'q'}^{fxx'} &= (-1)^{l_1-l_2-f+q'} \sum_{mn} \sum_{m'n'} \sum_{\xi\xi'\phi} t_{mm'}^{12} t_{n'n}^{21} \\ &\times C_{l_1 n k q}^{x\xi} C_{f\phi l_1 m}^{x\xi} C_{l_2 - n' k' q'}^{x'\xi'} C_{f-\phi l_2 - m'}^{x'\xi'}. \end{aligned} \quad (36)$$

The range of variation of indices of the tensors described above, as well as in the subscripts of \mathcal{F} and \mathcal{G} is specified in Appendix B2. As in the case of the derivation of \mathcal{J}^{DE} , Eq. (2) is used. Because of this assumption, the quantum numbers of the intermediate multiplets contributing to \mathcal{J}^{KE} obey the relations: $|L_i - l_i| \leq L \leq L_i + l_i$, $|S_i - 1/2| \leq S \leq S_i + 1/2$, and $|J_i - l_i - 1/2| \leq J \leq J_i + l_i + 1/2$, where L, S, J without subscript i refer to the intermediate states [44].

C. Structure of the exchange Hamiltonian

The domains of variation of k and q characterize the structure of the Hamiltonian (29). The upper bound for

the rank k and k' in Eq. (29) is only determined by the electronic state of site 1 and 2, respectively [45]:

$$k_{\text{max}} = \min[2l_i + 1, 2J_i]. \quad (37)$$

Thus the maximum rank for f -electron system, f^N , is 7 for $N = 2-4$ and 7-13, $k_{\text{max}} = 5$ for $N = 1, 5$ and $k_{\text{max}} = 0$ for $N = 6$ [46].

On the other hand, the range of q is determined by the nonzero parameters describing the intersite interactions, $V_{mm'n'n}$ and $t_{mm'}^{12} t_{n'n}^{21}$. If Δ_{max} is the maximal difference of the indices corresponding to one site in the above parameters ($m - n$ for site 1 and $m' - n'$ for site 2) then the upper bound for q (q') is

$$q_{\text{max}} = \min[\Delta_{\text{max}} + 1, k_{\text{max}}]. \quad (38)$$

Note that terms with $-q_{\text{max}}$ will also be present in the Hamiltonian (29) due to the time reversal symmetry, implying the following range: $-q_{\text{max}} \leq q \leq q_{\text{max}}$.

The effective Hamiltonian (29) is further divided into the exchange \hat{H}_{ex} and the zero-field splitting parts. The latter is defined as comprising terms with either $k = 0$ or $k' = 0$.

D. Decomposition of \bar{H}

Knowledge of the domain of rank k (37) in the general exchange Hamiltonian (29) allows us to calculate $\mathcal{J}_{kqk'q'}$ by using the orthogonality of the Stevens operators:

$$\begin{aligned} \mathcal{J}_{kqk'q'} &= (-1)^{q+q'} \left(\frac{\Pi_{kk'}}{\Pi_{J_1 J_2}} C_{J_1 J_1 k 0}^{J_1 J_1} C_{J_2 J_2 k' 0}^{J_2 J_2} \right)^2 \\ &\times \text{Tr} \left[\hat{Q}_{k-qk'-q'} \bar{H} \right], \end{aligned} \quad (39)$$

where $\Pi_j = \sqrt{2j+1}$ and $\Pi_{jj'} = \Pi_j \Pi_{j'}$, the trace (Tr) is taken over the ground J -multiplets, and

$$\hat{Q}_{kqk'q'} = \frac{O_k^q(\hat{\mathbf{J}}_1) O_{k'}^{q'}(\hat{\mathbf{J}}_2)}{O_k^0(J_1) O_{k'}^0(J_2)}. \quad (40)$$

The form (39) for the exchange parameters offer some advantages for practical calculations. \bar{H} enters Eq. (39) in the form of the numerical matrices in the basis of the products of multiplet wave functions on sites, $|J_1 M_1, J_2 M_2\rangle$. The exchange parameters obtained by Eqs. (33), (35) and those calculated by the projection (39) have been compared with each other for some test examples.

IV. EXCHANGE INTERACTION BETWEEN J -MULTIPLY AND ISOTROPIC SPIN

When the orbital angular momentum is zero in the ground state term of one of the sites, the low-energy states of this site are characterized by the corresponding spin $\hat{\mathbf{S}}$. This situation is encountered in mixed

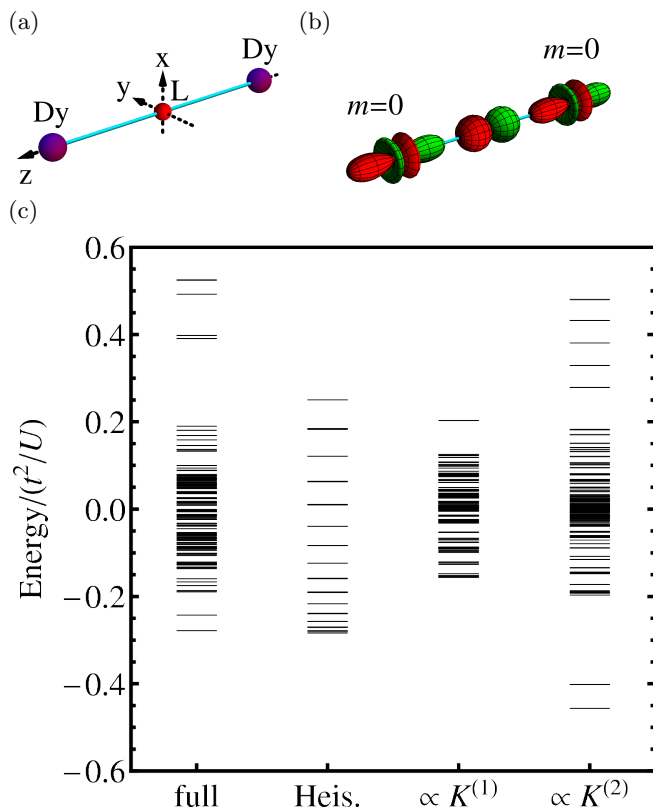


FIG. 1. (Color online) (a) Linearly bridged Dy dimer with one ligand atom (L). (b) Kinetic exchange interaction between $4f_{(5z^2-3r^2)_z}$ orbitals. (c) Calculated exchange spectrum with full \hat{H}_{ex} (43) and with its different contributions ($U \equiv U_{12} = U_{21} = 5$ eV). The excitation energies of the intermediate states entering Eq. (35) have been calculated *ab initio* (Sec. V A).

lanthanide-transition metal and lanthanide-radical complexes [1, 32, 47]. The exchange Hamiltonian between a J -multiplet and an isotropic spin is obtained in a similar way as Eq. (29):

$$\bar{H} = \sum_{kq} \mathcal{J}_{kq00} \frac{O_k^q(\hat{\mathbf{J}}_1) \hat{I}_2}{O_k^0(J_1)} + \sum_{kqq'} \mathcal{J}_{kq1q'} \frac{O_k^q(\hat{\mathbf{J}}_1) \hat{S}_{2q'}}{O_k^0(J_1) S_2}. \quad (41)$$

The expressions for exchange coupling constants are similar to Eqs. (33), (35) and are listed in Appendix D. Because of the lack of orbital degrees of freedom on site 2 ($l_2 = 0$), the rank k' of the spin operator does not exceed 1. Due to the time-reversal symmetry, k is even and odd for the first and the second terms in Eq. (41), respectively. As in the previous case, the former ($k' = 0$) is zero-field splitting term and the latter ($k' = 1$) is the exchange interaction.

V. EXAMPLES

We further consider some typical examples of J - J and J - S exchange interaction. Since the kinetic exchange interaction is usually much stronger than the direct exchange interaction [11, 12], we only take into account the former. In order to include the multiplet structure of intermediate states in Eq. (35), first we calculate *ab initio* the excitation energies of the virtual electron-transfer states. The calculated exchange levels are compared with those arising from the bilinear form (1) and corresponding to the $1/\bar{U}$ approximation.

A. Excitation energies of Dy^{2+} and Dy^{4+} ions

The excitation energies $\Delta E_{\alpha JJ}$ appearing in the denominator of the kinetic exchange Hamiltonian (28) are calculated *ab initio*. Since the effect of the crystal-field splitting in the intermediate states is negligible (Sec. II A), we used the energy levels of the free Ln^{2+} and Ln^{4+} ions. In this work, we only calculated the energies for $\text{Ln} = \text{Dy}$ that we will use in the following sections. Apart from the crystal-field splitting, there is totally symmetric electrostatic potential which only depends on the number of electrons and shifts uniformly the J -multiplet energies. This effect is absorbed in the minimum promotion energy U_{ij} in Eq. (35). The energies are calculated using the complete active space self-consistent field (CASSCF) and the restricted active space SCF state interaction (RASSI) methods with ANO-RCC QZP basis set [49]. With the CASSCF method, the LS -term energies are obtained, while with the RASSI method, the spin-orbit (J -multiplet) energy levels are calculated. For the CASSCF calculations, all $4f$ orbitals are included into the active space. The terms included in the RASSI mixing are 6P , 6F , 6H for Dy^{2+} and 7F , 5S , 5P , three 5D , two 5F , three 5G , two 5H , two 5I , 5K , 5L for Dy^{4+} . The excitation energies are tabulated in Table I.

There are several LS -terms which appear more than once, i.e., 5D , 5F , 5G , 5H , 5I terms of Dy^{4+} ion. These terms obtained by the CASSCF calculations are assigned to the symmetrized LS -states within the shell model, $|l^N \alpha_{LS} LSJM\rangle$, comparing the patterns of the *ab initio* and the model spin-orbit splittings of each LS -term. The symmetrized LS -states are constructed by using the coefficient of fractional parentage [48]. In the basis of symmetrized states, the matrix element of the spin-orbit

TABLE I. Excitation energies of Dy^{2+} and Dy^{4+} (meV). The number in the parenthesis indicates quantum number α_{LS} in the main text, where the enumeration follows Ref. 48.

Dy^{2+}			Dy^{4+}			Dy^{4+}				
LS -term	J	$\Delta E_{\alpha_J J}$	LS -term	J	$\Delta E_{\alpha_J J}$	LS -term	J	$\Delta E_{\alpha_J J}$		
5I	8	0.000	7F	6	0.000	${}^5H(2)$	4	8738.547		
	7	458.212		5	309.504		${}^5I(1)$	8	10579.798	
	6	859.148		4	508.583			7	10778.918	
	5	1202.808		${}^5D(1)$	4			13934.562	6	10917.180
	4	1489.190		${}^5D(2)$	4			7624.320	5	11003.924
5D	4	5667.150	${}^5D(3)$	4	3298.723	${}^5I(2)$	4	11049.978		
5F	5	2369.357	${}^5F(1)$	5	5838.268		8	5827.337		
	4	2655.740		4	5936.668		7	6035.414		
5G	6	3412.346	${}^5F(2)$	5	11206.930		5K	6	6173.415	
	5	3756.005		4	11118.121			5	6242.469	
	4	4042.388		${}^5G(1)$	6	6925.862		4	6261.863	
		5	7221.721		9	6516.513				
		4	7423.960		8	6766.583				
		6	4540.837		7	6935.080				
		5	4539.168		6	7051.111				
		${}^5G(2)$	4	4613.355	5L	5	7130.959			
			6	13458.495		10	4277.003			
			5	13323.410		9	4402.240			
		${}^5G(3)$	4	13191.767	${}^5H(2)$	8	4537.021			
			7	8096.483		7	4674.613			
			6	8392.826		6	4809.212			
			5	8603.858						

Hamiltonian $\hat{H}_{\text{so}} = \zeta \sum_{i=1}^N \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i$ ($\zeta > 0$) is given by

$$\begin{aligned}
& \langle l^{4l+2-N} \alpha_{LS} LSJM_J | \hat{H}_{\text{so}} | l^{4l+2-N} \alpha'_{LS} L'S'J'M'_J \rangle \\
&= -\delta_{LL'} \delta_{SS'} \delta_{JJ'} \delta_{M_J M'_J} \zeta \frac{\Pi_{LJ} \sqrt{l(l+1)}}{\sqrt{2}} \\
& \times \left\{ \begin{matrix} L & S & J \\ L & S & J \\ 1 & 1 & 0 \end{matrix} \right\} \langle l^N \alpha_{LS} LS || \{\hat{c}^\dagger \otimes \bar{c}\}_1^1 || l^N \alpha'_{LS} LS \rangle
\end{aligned} \tag{42}$$

for $N \leq 2l + 1$. Here, the curly bracket with 3×3 elements are the $9j$ symbol (A5). Therefore, the spin-orbit splitting is proportional to the reduced matrix element of operator $\{\hat{c}^\dagger \otimes \bar{c}\}_1^1$ [50].

B. Kinetic exchange through monoatomic bridge

As a simple example, consider an exchange-coupled Dy^{3+} dimer with axial bridging geometry (Fig. 1a). The largest transfer parameter (t) is expected between $f_{5z^3-3r^2z}$ ($m = 0$) orbitals because of their sigma bonding to the p_z orbital of the bridging ligand atom (Fig. 1b). Then, according to the rule (38), $q_{\text{max}} = 1$, while Eq. (36) gives $q = -q'$. The resulting form of the exchange

Hamiltonian \hat{H}_{ex} , after expanding the Stevens operators in Eq. (29), is

$$\hat{H}_{\text{ex}} = \hat{K}^{(1)} + \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \hat{K}^{(2)} + \hat{K}^{(2)} \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2, \tag{43}$$

$$\hat{K}^{(1)} = \sum_{k,k'=0}^7 \mathcal{K}_{kk'}^{(1)} \hat{J}_{1z}^k \hat{J}_{2z}^{k'}, \tag{44}$$

$$\hat{K}^{(2)} = \sum_{k,k'=1}^7 \mathcal{K}_{kk'}^{(2)} \hat{J}_{1z}^{k-1} \hat{J}_{2z}^{k'-1}, \tag{45}$$

where $k + k' = \text{even}$. We can see that, even in this simplest case, \hat{H}_{ex} does not reduce to the isotropic form (1) because Ising ($\propto \hat{K}^{(1)}$) and mixed Ising-Heisenberg ($\propto \hat{K}^{(2)}$) terms, both involving high powers of momentum projection operators of two sites. The parameters $\mathcal{K}_{kk'}^{(1)}, \mathcal{K}_{kk'}^{(2)}$ are tabulated in Table II. When the eigenvalue of \hat{J}_{iz} is large, the higher order terms are significantly enhanced and contribute to the exchange interaction rather than the bilinear term. As a result the exchange spectra calculated with the full Hamiltonian (43) and with its Heisenberg-type part (1) show large discrepancy between them (Fig. 1(c)). The discrepancy is also seen in their eigenstates. The difference between the exchange states of (43) with those of \hat{H}_{Heis} (1) is compared by expanding the former by the latter. The solution of \hat{H}_{Heis} for two

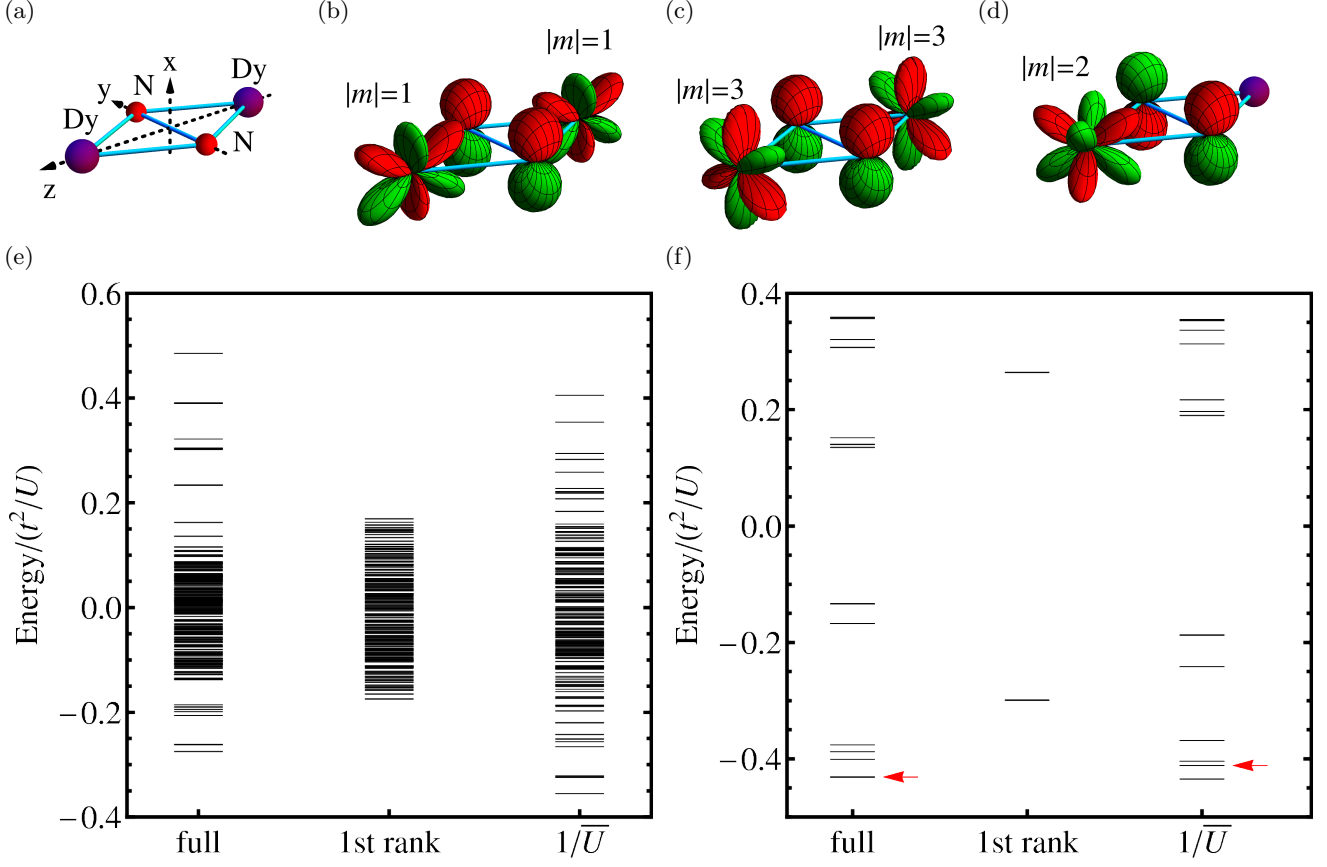


FIG. 2. (Color online) (a) Dy dimer bridged via N_2^{2-} anion (D_{2h} core symmetry). Large (purple) and small (red) balls are Dy and N, respectively. (b), (c) Kinetic exchange interaction between $4f_{(5z^2-r^2)x}$ orbitals and $4f_{x^3-3xy^2}$ orbitals, respectively, via the HOMO of N_2^{2-} . (d) Kinetic exchange interaction between the $4f_{xyz}$ orbital of Dy and the LUMO of N_2^{2-} . (e) Calculated exchange spectrum with full \hat{H}_{ex} and its first-rank contribution ($U \equiv U_{12} = U_{21} = 5$ eV), and in the $1/\bar{U}$ approximation for kinetic exchange pattern (b). (f) Calculated exchange spectrum with full \hat{H}_{ex} and its first-rank contribution ($U_{21} = 3$ eV), and in the $1/\bar{U}$ approximation for kinetic exchange pattern (d). The calculations in (e) and (f) involved exchange parameters (35) with excitation energies of the intermediate states on Dy evaluated *ab initio*. \bar{U} in the calculation within $1/\bar{U}$ approximation was chosen to reproduce the width of the spectrum for full \hat{H}_{ex} .

site system is given

$$|J_{12}M_{12}\rangle = \sum_{M_1, M_2} |J_1M_1, J_2M_2\rangle C_{J_1M_1, J_2M_2}^{J_{12}M_{12}}, \quad (46)$$

where J_{12} and M_{12} are the total angular momentum for the dimer and its projection. The low-energy exchange states of \hat{H}_{ex} (43) are written in the basis of $\{|J_{12}M_{12}\rangle\}$ as follows:

$$\begin{aligned} |\Psi_1, A_{1g}\rangle &\approx 0.574|0,0\rangle + 0.773|2,0\rangle + 0.190|4,0\rangle \\ &\quad - 0.160|6,0\rangle, \\ |\Psi_2, A_{1u}\rangle &\approx 0.846|1,0\rangle + 0.505|3,0\rangle - 0.161|7,0\rangle, \\ |\Psi_{3,4}, E_{1u}\rangle &\approx 0.352|1,\pm 1\rangle + 0.768|3,\pm 1\rangle + 0.522|5,\pm 1\rangle \\ &\quad + 0.107|7,\pm 1\rangle, \\ |\Psi_{5,6}, E_{1g}\rangle &\approx 0.636|2,\pm 1\rangle + 0.712|4,\pm 1\rangle + 0.294|6,\pm 1\rangle. \end{aligned}$$

Here, the irreducible representation Γ of $D_{\infty h}$ is used, and the states $|\Psi_i, \Gamma\rangle$ belong to the eigenvalues $E_{1,2} =$

-0.278523 , $E_{3,4,5,6} = -0.243015$, respectively, in the units of t^2/U_{12} . The low-energy exchange states are not necessarily mainly contributed by the ground state of the antiferromagnetic \hat{H}_{Heis} , $|J_{12}M_{12}\rangle = |0,0\rangle$. Therefore, we conclude that the Heisenberg form of the interaction is not adequate to describe the exchange interaction between J -multiplets.

C. Kinetic exchange through biatomic bridge

Consider the exchange interaction in the Dy^{3+} dimer bridged by the N_2^{n-} ($n = 2, 3$) anion (Fig. 2(a)) [51]. In the case of $n = 2$, $4f$ electrons of Dy^{3+} ions would transfer between the metal sites via the highest occupied molecular orbital (HOMO) of N_2^{2-} (Figs. 2(b),(c)). The HOMO overlaps with the $f_{(5z^2-r^2)x}$ ($|m| = 1$) and the $f_{x^3-3xy^2}$ ($|m| = 3$) metal orbitals, the former interaction

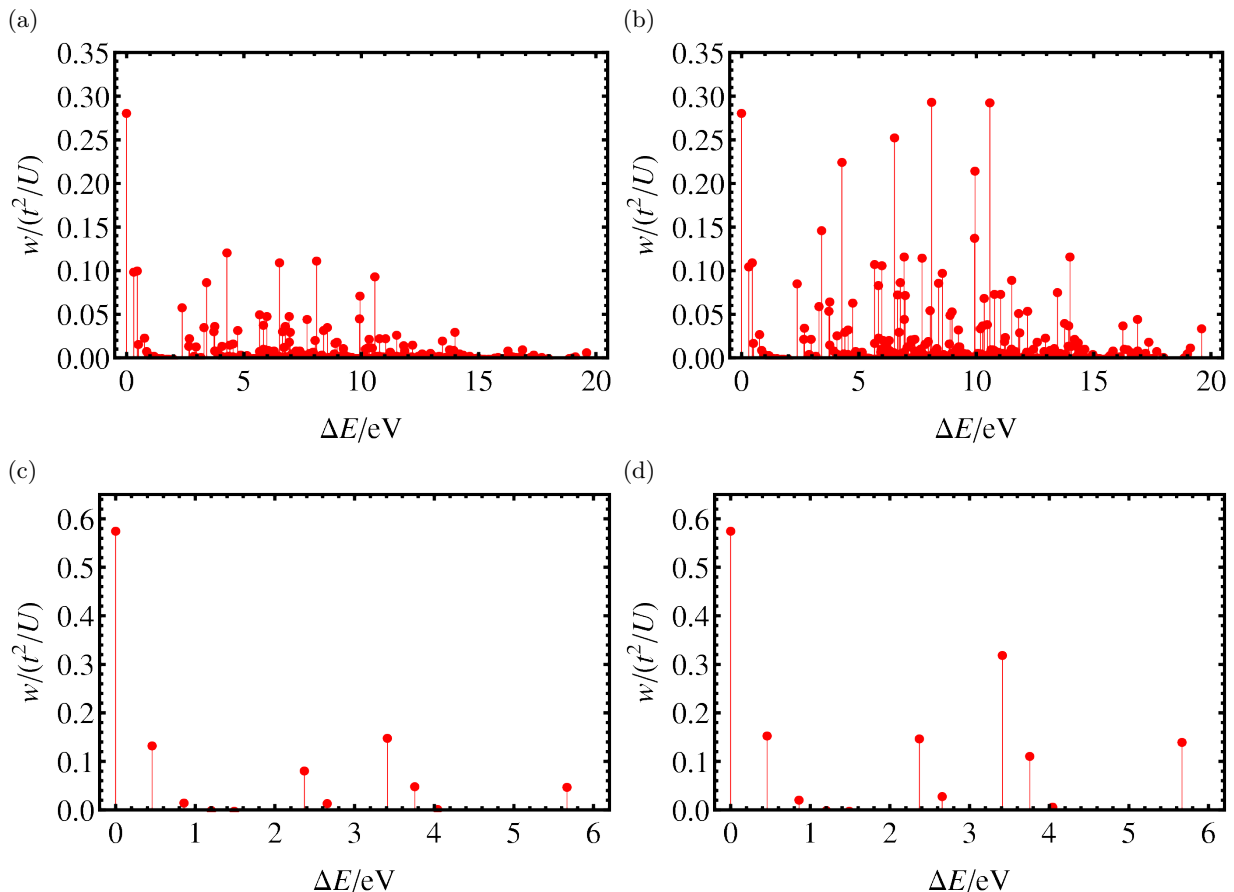


FIG. 3. The contributions from the intermediate states w corresponding to the excitation energy ΔE ($= \Delta E_{\alpha_J J}^N + \Delta E_{\alpha'_J J'}$) for (a) the full exchange interaction \hat{H}_{ex} and (b) the exchange within the $1/\bar{U}$ approximation $\hat{H}_{\text{ex}}^{1/\bar{U}}$ for Dy^{3+} dimer bridged by N_2^{2-} and for (c) the full exchange interaction and (d) the exchange within the $1/\bar{U}$ approximation for the Dy-radical system ($n = 3$). The units of w are t^2/U_{21} for (a), (c) and t^2/\bar{U} for (b), (d).

being dominant. Hence, we only consider the electron transfer between the orbitals with $|m| = 1$ (Fig. 2(b)). For them $\Delta_{\text{max}} = 2$ and we obtain according to Eq. (38) $q_{\text{max}} = 3$. Then \hat{H}_{ex} will include powers of $\hat{J}_{i\pm}$ ($= \hat{J}_{ix} \pm i\hat{J}_{iy}$) for each center up to third order.

Figure 2(e) shows the calculated exchange spectrum for full \hat{H}_{ex} , and its first-rank contribution, and for one single promotion energy \bar{U} ($1/\bar{U}$ approximation) [3, 15]. Although the first-rank contribution is bilinear in $\hat{J}_{i\gamma}$, it is not isotropic and the corresponding spectrum does not resemble the pattern of levels of Heisenberg-type Hamiltonian (1). Also the spectrum is quite different when the $1/\bar{U}$ approximation is applied. This approximation neglects the splitting of the LS -terms which exceeds several times the minimal electron promotion energy. As a result, the relative contributions to the exchange interaction from various intermediate states are significantly modified. In order to see the variation of the contributions from the intermediate states to the kinetic exchange interaction, we divide the kinetic exchange Hamiltonian

as follows:

$$\hat{H}_{\text{ex}} = \sum_{\alpha_J J} \sum_{\alpha'_J J'} \hat{h}_{\text{ex}}(\alpha_J J, \alpha'_J J'). \quad (47)$$

Here, $\hat{h}_{\text{ex}}(\alpha_J J, \alpha'_J J')$ indicates the term which only includes the contribution from the set of the intermediate states $(\alpha_J J, \alpha'_J J')$. The contribution from each such process can be measured by the width w of the eigenvalues of $\hat{h}_{\text{ex}}(\alpha_J J, \alpha'_J J')$. The widths w for the full exchange Hamiltonian \hat{H}_{ex} and those within $1/\bar{U}$ approximation are shown in Figure 3(a) and (b), respectively. In comparison with the contributions to the full Hamiltonian, those from the high energy states ($\Delta E \approx 5\text{-}10$ eV) are exaggerated in $\hat{H}_{\text{ex}}^{1/\bar{U}}$.

In the case of N_2^{3-} bridge, the main exchange coupling arises between the f_{xyz} orbital of Dy and the unpaired electron occupying the lowest unoccupied molecular orbital (LUMO) of N_2^{2-} (Fig. 2(d)). The LUMO level in N_2^{3-} has significantly higher energy compared to the orbital energy of $4f$ electrons in Dy^{3+} . On this reason and also due to a larger space distribution of the LUMO com-

TABLE II. $\mathcal{K}_{kk'}^{(1)}$ and $\mathcal{K}_{kk'}^{(2)}$.

$\mathcal{K}_{00}^{(1)}$	4.4458×10^{-3}	$\mathcal{K}_{11}^{(2)}$	2.2245×10^{-3}
$\mathcal{K}_{02}^{(1)}$	-3.7903×10^{-3}	$\mathcal{K}_{13}^{(2)}$	-3.2216×10^{-4}
$\mathcal{K}_{04}^{(1)}$	1.7181×10^{-4}	$\mathcal{K}_{15}^{(2)}$	1.5888×10^{-5}
$\mathcal{K}_{06}^{(1)}$	-1.7242×10^{-6}	$\mathcal{K}_{17}^{(2)}$	-1.8049×10^{-7}
$\mathcal{K}_{11}^{(1)}$	1.0908×10^{-2}	$\mathcal{K}_{22}^{(2)}$	4.8355×10^{-5}
$\mathcal{K}_{13}^{(1)}$	-1.1514×10^{-3}	$\mathcal{K}_{24}^{(2)}$	-4.6269×10^{-6}
$\mathcal{K}_{15}^{(1)}$	3.5361×10^{-5}	$\mathcal{K}_{26}^{(2)}$	7.4785×10^{-8}
$\mathcal{K}_{17}^{(1)}$	-2.9084×10^{-7}	$\mathcal{K}_{33}^{(2)}$	4.3815×10^{-5}
$\mathcal{K}_{22}^{(1)}$	2.9710×10^{-3}	$\mathcal{K}_{35}^{(2)}$	-2.1423×10^{-6}
$\mathcal{K}_{24}^{(1)}$	-1.3026×10^{-4}	$\mathcal{K}_{37}^{(2)}$	2.3716×10^{-8}
$\mathcal{K}_{26}^{(1)}$	1.2614×10^{-6}	$\mathcal{K}_{44}^{(2)}$	4.4502×10^{-7}
$\mathcal{K}_{33}^{(1)}$	1.1745×10^{-4}	$\mathcal{K}_{46}^{(2)}$	-7.2365×10^{-9}
$\mathcal{K}_{35}^{(1)}$	-3.3571×10^{-6}	$\mathcal{K}_{55}^{(2)}$	1.0531×10^{-7}
$\mathcal{K}_{37}^{(1)}$	2.6060×10^{-8}	$\mathcal{K}_{57}^{(2)}$	-1.1732×10^{-9}
$\mathcal{K}_{44}^{(1)}$	5.4544×10^{-6}	$\mathcal{K}_{66}^{(2)}$	1.1839×10^{-10}
$\mathcal{K}_{46}^{(1)}$	-4.9672×10^{-8}	$\mathcal{K}_{77}^{(2)}$	1.3155×10^{-11}
$\mathcal{K}_{55}^{(1)}$	7.4109×10^{-8}		
$\mathcal{K}_{57}^{(1)}$	-3.9138×10^{-10}		
$\mathcal{K}_{66}^{(1)}$	4.1115×10^{-10}		

pared to the $4f$ orbitals, the minimal electron promotion energy from N_2^{3-} to Dy^{3+} (U_{21}) is expected to be much smaller than in the opposite direction (U_{12}). Hence, we neglect the latter process. Given that the Dy orbitals involved in the electron transfer have $|m| = 2$, according to Eq. (38) $q_{\max} = 5$, the same for the maximal power of $\hat{J}_{1\pm}$ in the exchange Hamiltonian.

Figure 2(f) shows the exchange levels obtained for full \hat{H}_{ex} , its first-rank part, and for the $1/\bar{U}$ approximation. In the present case, the first-rank part of \hat{H}_{ex} coincides with Eq. (1), while the corresponding spectrum strongly differs from the full \hat{H}_{ex} indicating the importance of higher order terms. As in the previous example, the $1/\bar{U}$ approximation modifies the relative contributions to the exchange interaction from intermediate states (Fig. 3 (c),(d)) and induces, in particular, the interchange of the three-fold degenerate ground and the nondegenerate first excited states (marked with arrow in Fig. 2(f)) [52] [53]. Because of the difference in the nature of the exchange states, the magnetic properties predicted by the exchange states of the full Hamiltonian and the $1/\bar{U}$ approximation differ from each other.

There is another reason that the $1/\bar{U}$ approximation is not recommended: the Hund's rule coupling is completely neglected within this approximation, leading to the removal of the Goodenough's ferromagnetic exchange contribution [40] though the latter plays important role in many systems.

VI. CONCLUSION

The main results of the present work can be summarized as follows:

1. We derived the Hamiltonian of exchange interaction between J -multiplets (J - J) and between J -multiplet and isotropic spin (J - S) on the basis of a complete electronic Hamiltonian, including the intrasite relativistic effects. The exchange parameters are expressed via microscopic quantities which can be extracted from first principle calculations. Despite their microscopic character, the obtained expressions (33) and (35) are general (i) for arbitrary choice of quantization axes on two magnetic sites (which are not expected to coincide) and (ii) for various magnetic ions, which can be lanthanides, actinides, transition metal ions under special conditions or any their combinations. The only requirement is that the low-lying states on the sites are well approximated by crystal-field split eigenstates of a total angular momentum.
2. The structure of the J - J and J - S exchange Hamiltonian is clarified on the basis of derived exchange Hamiltonian. More specific, the maximal rank and the projections of the irreducible tensors appearing in the exchange Hamiltonian are elucidated.
3. The obtained form of the (kinetic) exchange Hamiltonian was analyzed for different geometries of the bridge. The relation between the geometry and the structure of the Hamiltonian was established.
4. On the basis of considered examples, we found that the exchange spectrum in systems with J - J and J - S interaction cannot be adequately described neither by exchange Hamiltonian of isotropic form (1) nor within the $1/\bar{U}$ approximation.
5. The contributions to the kinetic exchange Hamiltonian from the intermediate J -multiplets are analyzed. It is found that the $1/\bar{U}$ approximation exaggerates the terms from the excited states. Moreover, within the $1/\bar{U}$ approximation, the term splitting which is larger than the average U is neglected, leading to the wrong order of exchange levels.

In combination with *ab initio* and DFT extraction of microscopic electronic parameters, the microscopic exchange Hamiltonians derived in this work can become a powerful tool for the investigation of strongly anisotropic materials containing metal ions with unquenched orbital momentum.

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Appendix A: Theoretical tools

The transformation of the exchange Hamiltonian into the tensor form is done using the theory of angular momentum [38, 41, 54]. For the convenience of the readers, the tools necessary in the derivation are collected here.

1. Coupling of angular momenta

For the phase of the spherical harmonics $Y_j^m(\theta, \phi)$, we use the convention in Refs. 38 and 54. With this phase convention, the complex conjugation of Y_j^m is related to Y_j^{-m} as

$$[Y_j^m(\theta, \phi)]^* = (-1)^m Y_j^{-m}(\theta, \phi). \quad (\text{A1})$$

Here, the subscript j indicates the rank, the superscript m is the component, θ and ϕ are the spherical angular coordinates.

Consider two systems whose states are the eigenstates of the angular momentum, $|j_i m_i\rangle$ ($i = 1, 2$). The coupled state characterized by the total angular momentum can be constructed using the Clebsch-Gordan coefficients, $C_{j_1 m_1 j_2 m_2}^{j m}$:

$$|j m\rangle = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2\rangle C_{j_1 m_1 j_2 m_2}^{j m}. \quad (\text{A2})$$

The Clebsch-Gordan coefficients have following symmetry properties (Eqs. 8.4.3. (10), (11) in Ref. 38):

$$\begin{aligned} C_{j_1 m_1 j_2 m_2}^{j_3 m_3} &= (-1)^{j_1 + j_2 - j_3} C_{j_2 m_2 j_1 m_1}^{j_3 m_3} \\ &= (-1)^{j_1 - m_1} \frac{\Pi_{j_3}}{\Pi_{j_2}} C_{j_1 m_1 j_3 - m_3}^{j_2 - m_2} \\ &= (-1)^{j_1 - m_1} \frac{\Pi_{j_3}}{\Pi_{j_2}} C_{j_3 m_3 j_1 - m_1}^{j_2 m_2} \\ &= (-1)^{j_2 + m_2} \frac{\Pi_{j_3}}{\Pi_{j_1}} C_{j_3 - m_3 j_2 m_2}^{j_1 - m_1} \\ &= (-1)^{j_2 + m_2} \frac{\Pi_{j_3}}{\Pi_{j_1}} C_{j_2 - m_2 j_3 m_3}^{j_1 m_1} \\ &= (-1)^{j_1 + j_2 - j_3} C_{j_1 - m_1 j_2 - m_2}^{j_3 - m_3}, \end{aligned} \quad (\text{A3})$$

where $\Pi_j = \sqrt{2j+1}$.

Using the Clebsch-Gordan coefficients, the $6j$ and $9j$ symbols are defined as [38]

$$\delta_{jj'} \delta_{mm'} (-1)^{j_1 + j_2 + j_3 + j} \Pi_{j_1 j_2 j_3} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} = \sum_{m_i m_{ij}} C_{j_{12} m_{12} j_3 m_3}^{j m} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_1 m_1 j_2 m_2}^{j' m'} C_{j_2 m_2 j_3 m_3}^{j_{23} m_{23}}, \quad (\text{A4})$$

and

$$\delta_{jj'} \delta_{mm'} \Pi_{j_{12} j_{34} j_{13} j_{24}} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{matrix} \right\} = \sum_{m_i m_{ij}} C_{j_{12} m_{12} j_{34} m_{34}}^{j m} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_3 m_3 j_4 m_4}^{j_{34} m_{34}} C_{j_{13} m_{13} j_{24} m_{24}}^{j' m'} C_{j_1 m_1 j_3 m_3}^{j_{13} m_{13}} C_{j_2 m_2 j_4 m_4}^{j_{24} m_{24}}, \quad (\text{A5})$$

respectively. Here, $\sum_{m_i, m_{ij}}$ stands for the summation over all m_i and m_{ij} ($i, j = 1, 2, 3, 4$). The $6j$ symbol (A4) is symmetric with respect to the permutation of columns and the interchange of the upper and lower components of two columns (Eq. 9.4.2. (2) in Ref. 38).

From Eqs. (A4), (A5), we immediately obtain some formulae involving $6j$ or $9j$ symbol. Multiplying both sides of Eq. (A4) by $C_{j_1 m_1 j_2 m_2}^{j' m'}$ and summing over $j' m'$, we obtain (Eq. 8.7.3. (12) in Ref. 38)

$$(-1)^{j_1 + j_2 + j_3 + j} \Pi_{j_{12} j_{23}} C_{j_1 m_1 j_2 m_2}^{j m} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} = \sum_{m_2 m_3 m_{12}} C_{j_{12} m_{12} j_3 m_3}^{j m} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_2 m_2 j_3 m_3}^{j_{23} m_{23}}. \quad (\text{A6})$$

Similarly, multiplying both sides of Eq. (A4) by $C_{j_{12} m_{12} j_3 m_3}^{j m} C_{j_1 m_1 j_2 m_2}^{j' m'}$ and summing over $j m, j' m'$, we obtain (Eq. 8.7.3. (12) in Ref. 38)

$$\sum_{j m} (-1)^{j_1 + j_2 + j_3 + j} \Pi_{j_{12} j_{23}} C_{j_{12} m_{12} j_3 m_3}^{j m} C_{j_1 m_1 j_2 m_2}^{j m} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} = \sum_{m_2} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_2 m_2 j_3 m_3}^{j_{23} m_{23}}. \quad (\text{A7})$$

Multiplying both sides of Eq. (A5) by $C_{j_{13}m_{13}j_{24}m_{24}}^{j'm'}$ and summing over $j'm'$, we obtain similar formula involving five Clebsch-Gordan coefficients:

$$\Pi_{j_{12}j_{34}j_{13}j_{24}} C_{j_{13}m_{13}j_{24}m_{24}}^{jm} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = \sum_{m_i m_{ij}} C_{j_{12}m_{12}j_{34}m_{34}}^{jm} C_{j_1m_1j_2m_2}^{j_{12}m_{12}} C_{j_3m_3j_4m_4}^{j_{34}m_{34}} C_{j_1m_1j_3m_3}^{j_{13}m_{13}} C_{j_2m_2j_4m_4}^{j_{24}m_{24}}. \quad (\text{A8})$$

Multiplying both sides of Eq. (A5) by $C_{j_{12}m_{12}j_{34}m_{34}}^{jm} C_{j_{13}m_{13}j_{24}m_{24}}^{j'm'}$ and summing over $jm, j'm'$, we obtain a formula involving five Clebsch-Gordan coefficients (Eq. 8.7.4. (26) in Ref. 38):

$$\Pi_{j_{12}j_{34}j_{13}j_{24}} \sum_{jm} C_{j_{12}m_{12}j_{34}m_{34}}^{jm} C_{j_{13}m_{13}j_{24}m_{24}}^{jm} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = \sum_{m_i} C_{j_1m_1j_2m_2}^{j_{12}m_{12}} C_{j_3m_3j_4m_4}^{j_{34}m_{34}} C_{j_1m_1j_3m_3}^{j_{13}m_{13}} C_{j_2m_2j_4m_4}^{j_{24}m_{24}}. \quad (\text{A9})$$

2. Irreducible tensor operator

The irreducible tensor operator is defined as the operator \hat{T}_{kq} which transforms as spherical harmonics Y_k^q (A1) under $SO(3)$ rotations:

$$\hat{R}\hat{T}_{kq}\hat{R}^\dagger = \sum_{q'=-k}^k \hat{T}_{kq'} D_{q'q}^k(R), \quad (\text{A10})$$

where $D_{q'q}^k(R) = \langle Y_k^{q'} | \hat{R} | Y_k^q \rangle$ is the Wigner D -function [38], $R \in SO(3)$, and \hat{R} is the rotational operator for R . Since Eq. (A10) holds for any infinitesimal rotations, \hat{T}_{kq} satisfies

$$[\hat{J}_\mu, \hat{T}_{kq}] = \sqrt{k(k+1)} C_{kq1\mu}^{kq+\mu} \hat{T}_{kq+\mu}. \quad (\text{A11})$$

The matrix element of \hat{T}_{kq} with respect to the eigenstates of the angular momentum, $\{|JM\rangle\}$, is proportional to the Clebsch-Gordan coefficient (A2). The Wigner-Eckart theorem reads (Eq. 13.1.1. (2) in Ref. 38)

$$\langle JM' | \hat{T}_{kq} | JM \rangle = \frac{(-1)^{2k} \langle J || \hat{T}_k || J \rangle}{\Pi_J} C_{JMkq}^{JM'}. \quad (\text{A12})$$

One of the irreducible tensor operators is the spherical tensor operator $Y_k^q(\hat{\mathbf{J}})$ which is constructed replacing the coordinates in the spherical harmonics $Y_k^q(\mathbf{r}/r)$ by the total angular momentum operator ($\mathbf{r}/r \rightarrow \hat{\mathbf{J}}$) and averaging it over all possible permutations of $\hat{\mathbf{J}}$ operators [8]. For example, $\hat{J}_\mu \hat{J}_\nu$ is replaced by $(\hat{J}_\mu \hat{J}_\nu + \hat{J}_\nu \hat{J}_\mu)/2$.

When the system consists of two subsystems, double tensor [38, 41] is used. In this work, the subsystems are the orbital and the spin parts of the system. The orbital and spin subsystems transform as irreducible tensor within $SO(3)$ and $SU(2)$ operations, respectively. Thus, for the rotation of the system $R = R_1 R_2 \in SO(3) \otimes SU(2)$, where $R_1 \in SO(3)$ and $R_2 \in SU(2)$, the double tensor $\hat{T}_{k_2q_2}^{k_1q_1}$ of ranks k_1 and k_2 transform as

$$\hat{R}\hat{T}_{k_2q_2}^{k_1q_1}\hat{R}^\dagger = \sum_{q_1'=-k_1}^{k_1} \sum_{q_2'=-k_2}^{k_2} \hat{T}_{k_2q_2'}^{k_1q_1'} D_{q_1'q_1}^{k_1}(R_1) D_{q_2'q_2}^{k_2}(R_2), \quad (\text{A13})$$

and $\hat{T}_{k_2q_2}^{k_1q_1}$ fulfills

$$[\hat{L}_\mu, \hat{T}_{k_2q_2}^{k_1q_1}] = \sqrt{k_1(k_1+1)} C_{k_1q_11\mu}^{k_1q_1+\mu} \hat{T}_{k_2q_2}^{k_1q_1+\mu}, \quad (\text{A14})$$

$$[\hat{S}_\mu, \hat{T}_{k_2q_2}^{k_1q_1}] = \sqrt{k_2(k_2+1)} C_{k_2q_21\mu}^{k_2q_2+\mu} \hat{T}_{k_2q_2+\mu}^{k_1q_1}. \quad (\text{A15})$$

One of the double tensor operator is the electron creation operator in atomic spin-orbital (m, σ) , $\hat{c}_{im\sigma}^\dagger$. This is clear since $\hat{c}_{im\sigma}^\dagger$ creates the one-electron state which transforms as the product of the spherical harmonics, $|lm, \frac{1}{2}\sigma\rangle$. On the other hand, the annihilation operator $\hat{c}_{im\sigma}$ does not fulfill Eqs. (A14) and (A15), whereas $\bar{c}_{i-m-\sigma}$ defined below does [41]:

$$\hat{c}_{im\sigma} = (-1)^{l_i+m+\frac{1}{2}+\sigma} \bar{c}_{i-m-\sigma}. \quad (\text{A16})$$

Thus, $\bar{c}_{i-m-\sigma}$ instead of the annihilation operator is a double tensor.

3. Method of equivalent operator

Consider an irreducible tensor \hat{T}_{kq} of rank k and its argument q acting on the spin degrees of freedom. Replacing J in Eq. (A12) with S , we obtain an expression of the matrix element of \hat{T}_{kq} . On the other hand, the matrix element of the spherical tensor operator $Y_k^q(\hat{\mathbf{S}})$ is written as

$$\langle SM' | Y_k^q(\hat{\mathbf{S}}) | SM \rangle = \frac{(-1)^{2k} \langle S || Y_k(\hat{\mathbf{S}}) || S \rangle}{\Pi_S} C_{SMkq}^{SM'}, \quad (\text{A17})$$

where $\hat{\mathbf{S}}$ is an abstract spin operator. Comparing Eqs. (A12) and (A17), one finds the relation between tensor operators \hat{T}_{kq} and $Y_k^q(\hat{\mathbf{S}})$:

$$\langle SM' | \hat{T}_{kq} | SM \rangle = \frac{\langle S || \hat{T}_k || S \rangle}{\langle S || Y_k(\hat{\mathbf{S}}) || S \rangle} \langle SM' | Y_k^q(\hat{\mathbf{S}}) | SM \rangle. \quad (\text{A18})$$

This equation holds for any matrix element, and hence, in the space of $\{|SM\rangle\}$,

$$\hat{T}_{kq} = \frac{\langle S || \hat{T}_k || S \rangle}{\langle S || Y_k(\hat{\mathbf{S}}) || S \rangle} Y_k^q(\hat{\mathbf{S}}). \quad (\text{A19})$$

The reduced matrix element in the denominator is simplified using Eq. (A17) with $M = M' = S$ and $q = 0$,

$$\langle S || Y_k(\hat{\mathbf{S}}) || S \rangle = \frac{(-1)^{-2k} \Pi_S}{C_{SSk0}^{SS}} Y_k^0(S). \quad (\text{A20})$$

Consequently, \hat{T}_{kq} is expressed as

$$\hat{T}_{kq} = \frac{(-1)^{2k} \langle S || \hat{T}_k || S \rangle}{\Pi_S} C_{SSk0}^{SS} \frac{Y_k^q(\hat{\mathbf{S}})}{Y_k^0(S)}. \quad (\text{A21})$$

Eq. (A21) holds for

$$0 \leq k \leq 2S. \quad (\text{A22})$$

$Y_k^q(S)$ in the denominator of Eq. (A21) is the scalar obtained by substituting $\hat{\mathbf{S}}^2 = S(S+1)$ and $\hat{S}_z = S$ in the spherical harmonic tensor $Y_k^q(\hat{\mathbf{S}})$.

Now, we consider the case of double tensors $\hat{T}_{k'q'}$ of rank (k, k') . Assuming Eq. (2), it is transformed into the tensor form within the space of the ground J -multiplet, $\{|JM\rangle\}$. The matrix element of $\hat{T}_{k'q'}$ is

$$\begin{aligned} \langle JM' | \hat{T}_{k'q'}^{kq} | JM \rangle &= \sum_{M'_L M'_S} \sum_{M_L M_S} C_{LM'_L SM'_S}^{JM'} C_{LM_L SM_S}^{JM} \\ &\times \langle LM'_L SM'_S | \hat{T}_{k'q'}^{kq} | LM_L SM_S \rangle. \end{aligned} \quad (\text{A23})$$

The Wigner-Eckart theorem (A12) is applied to the orbital and the spin parts of the double tensor separately,

$$\begin{aligned} \langle JM' | \hat{T}_{k'q'}^{kq} | JM \rangle &= \frac{(-1)^{2k+2k'} \langle LS || \hat{T}_{k'} || LS \rangle}{\Pi_{LS}} \\ &\times \sum_{M'_L M'_S} \sum_{M_L M_S} C_{LM'_L SM'_S}^{JM'} C_{LM_L SM_S}^{JM} \\ &\times C_{LM_L kq}^{LM'_L} C_{SM_S k'q'}^{SM'_S}. \end{aligned} \quad (\text{A24})$$

Using Eq. (A9), the sum of the products of the Clebsch-Gordan coefficients reduces to the sum involving $9j$ symbol:

$$\begin{aligned} \langle JM' | \hat{T}_{k'q'}^{kq} | JM \rangle &= (-1)^{2k+2k'} \langle LS || \hat{T}_{k'} || LS \rangle \sum_{nm} \Pi_{Jn} \\ &\times C_{JMnm}^{JM'} C_{kqk'q'}^{mm} \begin{Bmatrix} L & S & J \\ L & S & J \\ k & k' & n \end{Bmatrix}, \end{aligned} \quad (\text{A25})$$

where n is the rank, m is its argument. The rest procedure is the same as the derivation of Eq. (A21). $C_{JMnm}^{JM'}$

is replaced by the matrix element of the irreducible tensor operator $Y_n^m(\hat{\mathbf{J}})$, and $\hat{T}_{k'q'}^{kq}$ within $\{|JM\rangle\}$ is expressed as

$$\begin{aligned} \hat{T}_{k'q'}^{kq} &= (-1)^{2k+2k'} \langle LS || \hat{T}_{k'} || LS \rangle \sum_{nm} \Pi_{Jn} \\ &\times C_{JJn0}^{JJ} C_{kqk'q'}^{nm} \begin{Bmatrix} L & S & J \\ L & S & J \\ k & k' & n \end{Bmatrix} \frac{Y_n^m(\hat{\mathbf{J}})}{Y_n^0(J)}. \end{aligned} \quad (\text{A26})$$

k, k' , and n in Eq. (A26) obey

$$\begin{aligned} 0 \leq k \leq 2L, \quad 0 \leq k' \leq 2S, \\ \max[|k - k'|, 0] \leq n \leq \min[k + k', 2J]. \end{aligned} \quad (\text{A27})$$

In the derivation of Eq. (A26) we used Eq. (2), while it is not mandatory. However, without using Eq. (2), the result will have a more complicated form.

In the previous works, the so-called Stevens operator $O_k^q(\hat{\mathbf{J}}) = A_{kq} Y_k^q(\hat{\mathbf{J}})$ has been used instead of Y_k^q where A_{kq} is a coefficient which depends on both k and q [42]. However, the original Stevens operator does neither obey Eq. (A11) nor the Wigner-Eckart theorem (A12). In order to use the Wigner-Eckart theorem, one can introduce such coefficient A_k that only depends on k and is independent from q [55, 56]. Furthermore, we write the Stevens operator in the form of $O_k^q(\hat{\mathbf{J}})/O_k^0(J)$ which is equal to $Y_k^q(\hat{\mathbf{J}})/Y_k^0(J)$. Since the constant A_k is canceled in this form, it is possible to apply the Wigner-Eckart theorem (A12):

$$\langle JM' | \frac{O_k^q(\hat{\mathbf{J}})}{O_k^0(J)} | JM \rangle = \frac{C_{JMkq}^{JM'}}{C_{JJk0}^{JJ}}. \quad (\text{A28})$$

In this article, we use the latter (see for example Eq. (A26)).

Appendix B: Derivation of the exchange Hamiltonian in J -representation

1. Direct exchange Hamiltonian

Detailed calculation of \mathcal{J}^{DE} is shown here. Applying the method of equivalent operator (A26), $\{\hat{c}_i^\dagger \otimes \bar{c}_i\}_{b\beta}^{\alpha\alpha}$ in Eq. (31) becomes

$$\begin{aligned} \left\{ \hat{c}_i^\dagger \otimes \bar{c}_i \right\}_{b\beta}^{\alpha\alpha} &= \sum_{kq} \Pi_{kJ_i} C_{J_i J_i k 0}^{J_i J_i} C_{\alpha\alpha b\beta}^{kq} \begin{Bmatrix} L_i & S_i & J_i \\ L_i & S_i & J_i \\ a & b & k \end{Bmatrix} \\ &\times (-1)^{2a+2b} \langle L_i S_i || \left\{ \hat{c}_i^\dagger \otimes \bar{c}_i \right\}_b^a || L_i S_i \rangle \\ &\times \frac{O_k^q(\hat{\mathbf{J}}_i)}{O_k^0(J_i)}. \end{aligned} \quad (\text{B1})$$

Introducing \mathcal{D}_{abk}^i defined by

$$\mathcal{D}_{abk}^i = \Pi_{k J_i} C_{J_i J_i k 0}^{J_i J_i} \begin{Bmatrix} L_i & S_i & J_i \\ L_i & S_i & J_i \\ a & b & k \end{Bmatrix} \times (-1)^{2a+2b} \langle L_i S_i || \{ \hat{c}_i^\dagger \otimes \bar{c}_i \}_b^a || L_i S_i \rangle, \quad (\text{B2})$$

Eq. (B1) reduces to Eq. (32).

Replace $\{ \hat{c}_i^\dagger \otimes \bar{c}_i \}_{b\beta}^{a\alpha}$ in Eq. (31) with Eq. (32),

$$\hat{c}_{im\sigma}^\dagger \hat{c}_{in\sigma'} = (-1)^{l_i+n+\frac{1}{2}+\sigma'} \sum_{a\alpha b\beta} \sum_{kq} C_{a\alpha b\beta}^{kq} \mathcal{D}_{abk}^i \times C_{l_i m l_i - n}^{a\alpha} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{b\beta} \frac{O_k^q(\hat{\mathbf{J}}_i)}{O_k^0(J_i)}. \quad (\text{B3})$$

Substituting Eq. (B3) in the direct exchange Hamiltonian (6),

$$\begin{aligned} \hat{H}_{\text{DE}} = & - \sum_{kq} \sum_{k'q'} \sum_{a\alpha b\beta} \sum_{a'\alpha' b'\beta'} \\ & \times \sum_{mnm'n'} V_{mm'n'n} (-1)^{l_1+n} (-1)^{l_2+n'} \\ & \times \sum_{\sigma\sigma'} (-1)^{\frac{1}{2}+\sigma'} (-1)^{\frac{1}{2}+\sigma} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{b\beta} C_{\frac{1}{2}\sigma' \frac{1}{2}-\sigma}^{b'\beta'} \\ & \times C_{a\alpha b\beta}^{kq} C_{l_1 m l_1 - n}^{a\alpha} C_{a'\alpha' b'\beta'}^{k'q'} C_{l_2 m' l_2 - n'}^{a'\alpha'} \\ & \times \mathcal{D}_{abk}^1 \mathcal{D}_{a'b'k'}^2 \frac{O_k^q(\hat{\mathbf{J}}_1) O_{k'}^{q'}(\hat{\mathbf{J}}_2)}{O_k^0(J_1) O_{k'}^0(J_2)}. \end{aligned} \quad (\text{B4})$$

Since $(-1)^{\frac{1}{2}+\sigma} = (-1)^{-\frac{1}{2}-\sigma}$, $(-1)^{\sigma'-\sigma} = (-1)^{-\beta}$, and $\sum_{\sigma\sigma'} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{b\beta} C_{\frac{1}{2}\sigma' \frac{1}{2}-\sigma}^{b'\beta'} = \delta_{bb'} \delta_{\beta, -\beta'}$, using Eq. (34),

$$\hat{H}_{\text{DE}} = - \sum_{kqk'q'} \sum_{aa'b'} V_{kqk'q'}^{aa'b'} \mathcal{D}_{abk}^1 \mathcal{D}_{a'b'k'}^2 \frac{O_k^q(\hat{\mathbf{J}}_1) O_{k'}^{q'}(\hat{\mathbf{J}}_2)}{O_k^0(J_1) O_{k'}^0(J_2)}. \quad (\text{B5})$$

The coefficient of the operators is Eq. (33).

The ranks for the orbital (a) and the spin (b) parts of $\{ \hat{c}_i^\dagger \otimes \bar{c}_i \}_{b\beta}^{a\alpha}$ are bounded by $2l_i$ and $2 \times 1/2$, respectively. Moreover, from the $9j$ symbol in Eq. (B1), $a \leq 2L_i$ and $b \leq 2S_i$ where L_i and S_i are the LS -term for the ground J -multiplet states, respectively. Thus, the ranges of ranks a, b are given as

$$0 \leq a \leq 2 \min[l_i, L_i], \quad 0 \leq b \leq 2 \min[1/2, S_i], \quad (\text{B6})$$

The maximum of b is 1 because $S_i \geq 1/2$ for the magnetic ions. For given (a, b) , k is at most $a + b$. Simultaneously k is less than or equal to $2J_i$ (B1). Therefore, the range of k is

$$0 \leq k \leq \min[2l_i + 1, 2L_i + 1, 2J_i]. \quad (\text{B7})$$

2. Kinetic exchange Hamiltonian

In the kinetic exchange Hamiltonian \hat{H}_{KE} , the operators appear as the form of $\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J}^{N_i-1} \hat{c}_{im'\sigma'}$ and $\hat{c}_{im\sigma} \hat{P}_{i\alpha J}^{N_i+1} \hat{c}_{im'\sigma'}^\dagger$. One should note that the projection operator $\hat{P}_{i\alpha J}^N$ is totally symmetric within $SO(3)$ group, whereas reducible within the $SO(3) \otimes SU(2)$ group. Thus, $\hat{P}_{i\alpha J}^N$ is reduced within $SO(3) \otimes SU(2)$ group in order to simultaneously treat it with the other double tensors. With the use of Eq. (2), the projection operator $\hat{P}_{i\alpha J}^N = \sum_M |iN\alpha J JM\rangle \langle iN\alpha J JM|$ is

$$\hat{P}_{i\alpha J}^N = \sum_M \sum_{M_L, M_S} \sum_{M'_L, M'_S} C_{LM_L SM_S}^{JM} C_{LM'_L SM'_S}^{JM} \times |iN\alpha_{LS} LM_L SM_S\rangle \langle iN\alpha_{LS} LM'_L SM'_S|. \quad (\text{B8})$$

Introducing the irreducible double tensor $\hat{P}_{i\alpha J a\alpha a'\alpha'}^N$ defined by

$$\hat{P}_{i\alpha J a\alpha a'\alpha'}^N = \sum_{m_L m_S} \sum_{m'_L m'_S} (-1)^{L+m'_L+S+m'_S} C_{m_L m_S}^{a\alpha} C_{m'_L m'_S}^{a'\alpha'} \times C_{S m_S S - m'_S}^{a'\alpha'} |L m_L S m_S\rangle \langle L m'_L S m'_S|, \quad (\text{B9})$$

the projection operator $\hat{P}_{i\alpha J}^N$ is written as

$$\begin{aligned} \hat{P}_{i\alpha J}^N = & \sum_M \sum_{m_L m_S} \sum_{m'_L m'_S} (-1)^{L+m'_L+S+m'_S} C_{m_L m_S}^{JM} \\ & \times C_{m'_L m'_S}^{JM} \sum_{a\alpha, a'\alpha'} C_{m_L m_S}^{a\alpha} C_{m'_L m'_S}^{a'\alpha'} \hat{P}_{i\alpha J a\alpha a'\alpha'}^N. \end{aligned} \quad (\text{B10})$$

Using the symmetry properties of the Clebsch-Gordan coefficients (A3) and the $6j$ symbol (A4),

$$\hat{P}_{i\alpha J}^N = \sum_{a\alpha} (-1)^{J-L-S+\alpha} \Pi_{JJ} \begin{Bmatrix} S & S & a \\ L & L & J \end{Bmatrix} \hat{P}_{i\alpha J a\alpha a-\alpha}^N, \quad (\text{B11})$$

The range of the rank a in Eq. (B11) is

$$0 \leq a \leq 2 \min[S, L], \quad (\text{B12})$$

and $-a \leq \alpha \leq a$. Substituting Eq. (B11) into $\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J}^{N_i-1} \hat{c}_{im'\sigma'} = (-1)^{l_i+n+\frac{1}{2}+\sigma'} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J}^{N_i-1} \bar{c}_{i-n-\sigma'}$,

$$\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J}^{N_i-1} \hat{c}_{im'\sigma'} = \sum_{a\alpha} (-1)^{J-L-S+\alpha} \Pi_{JJ} \begin{Bmatrix} S & S & a \\ L & L & J \end{Bmatrix} (-1)^{l_i+n+\frac{1}{2}+\sigma'} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha J a\alpha a-\alpha}^{N_i-1} \bar{c}_{i-n-\sigma'}. \quad (\text{B13})$$

The operator in Eq. (B13), $\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J a\alpha a-\alpha}^{N_i-1} \bar{c}_{i-n-\sigma'}$, is reduced as follows:

$$\begin{aligned} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J a\alpha a-\alpha}^{N_i-1} \bar{c}_{i-n-\sigma'} &= \sum_{b\beta d\delta} C_{a\alpha l_i-n}^{b\beta} C_{a-\alpha \frac{1}{2}-\sigma'}^{d\delta} \hat{c}_{im\sigma}^\dagger \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_{d\delta}^{b\beta} \\ &= \sum_{b\beta c\gamma d\delta e\epsilon} C_{a\alpha l_i-n}^{b\beta} C_{a-\alpha \frac{1}{2}-\sigma'}^{d\delta} C_{l_i m b \beta}^{c\gamma} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{e\epsilon} \left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_{e\epsilon}^{c\gamma}. \end{aligned} \quad (\text{B14})$$

Using Eqs. (A3) and (A7),

$$\begin{aligned} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J a\alpha a-\alpha}^{N_i-1} \bar{c}_{i-n-\sigma'} &= \sum_{b\beta c\gamma d\epsilon} C_{a\alpha l_i-n}^{b\beta} C_{l_i m b \beta}^{c\gamma} \sum_{f\phi} (-1)^{\frac{1}{2}+2a+\alpha+d+f} \Pi_{de} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ a & e & d \end{Bmatrix} \\ &\times C_{e\epsilon a\alpha}^{f\phi} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{f\phi} \left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_{e\epsilon}^{c\gamma}. \end{aligned} \quad (\text{B15})$$

Here, the ranges of the ranks b, c, d, e, f are

$$\begin{aligned} |a-l_i| \leq b \leq a+l_i, \quad |a-1/2| \leq d \leq a+1/2, \quad |b-l_i| \leq c \leq b+l_i, \\ |d-1/2| \leq e \leq d+1/2, \quad \max[|a-e|, 0] \leq f \leq \min[a+e, 2 \times 1/2]. \end{aligned} \quad (\text{B16})$$

and their arguments satisfy $-b \leq \beta \leq b$, $-d \leq \delta \leq d$, $-c \leq \gamma \leq c$, $-e \leq \epsilon \leq e$, $-f \leq \phi \leq f$, respectively. Note that f is at the largest 1. Substituting Eq. (B15) into Eq. (B13),

$$\begin{aligned} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J J}^{N_i-1} \hat{c}_{in\sigma'} &= (-1)^{l_i+n+\frac{1}{2}+\sigma'} (-1)^{J-L-S} \Pi_{JJ} \sum_{a\alpha b\beta c\gamma d\epsilon f\phi} (-1)^{\frac{1}{2}+d+f} \Pi_{de} \\ &\times \begin{Bmatrix} S & S & a \\ L & L & J \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ a & e & d \end{Bmatrix} C_{a\alpha l_i-n}^{b\beta} C_{l_i m b \beta}^{c\gamma} C_{e\epsilon a\alpha}^{f\phi} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{f\phi} \left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_{e\epsilon}^{c\gamma}. \end{aligned} \quad (\text{B17})$$

Similarly, the operator for the other site in \hat{H}_{KE} (28) becomes

$$\begin{aligned} \hat{c}_{jm'\sigma} \hat{P}_{j\alpha' J'}^{N_j+1} \hat{c}_{jn'\sigma'} &= (-1)^{l_j+m'+\frac{1}{2}+\sigma} (-1)^{J'-L'-S'} \Pi_{J'J'} \sum_{a\alpha b\beta c\gamma d\epsilon f\phi} (-1)^{-\frac{1}{2}+d} \Pi_{de} \\ &\times \begin{Bmatrix} S' & S' & a \\ L' & L' & J' \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ a & e & d \end{Bmatrix} C_{a\alpha l_j n'}^{b\beta} C_{l_j -m' b \beta}^{c\gamma} C_{e\epsilon a\alpha}^{f\phi} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{f-\phi} \left\{ \bar{c}_j \otimes \left\{ \hat{P}_{j\alpha' J' aa}^{N_j+1} \otimes \hat{c}_j^\dagger \right\}_d^b \right\}_{e\epsilon}^{c\gamma}. \end{aligned} \quad (\text{B18})$$

The operators in Eq. (B17) is written in terms of the total angular momentum using the method of equivalent operator. Applying Eq. (A26) to the irreducible tensor, $\left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_{e\epsilon}^{c\gamma}$ in Eq. (B17),

$$\begin{aligned} \hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J J}^{N_i-1} \hat{c}_{in\sigma'} &= (-1)^{l_i+n+\frac{1}{2}+\sigma'} (-1)^{J-L-S} \sum_{a\alpha b\beta c\gamma d\epsilon f\phi} (-1)^{\frac{1}{2}+d+f} \Pi_{JJde} \\ &\times \begin{Bmatrix} S & S & a \\ L & L & J \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ a & e & d \end{Bmatrix} C_{a\alpha l_i-n}^{b\beta} C_{l_i m b \beta}^{c\gamma} C_{e\epsilon a\alpha}^{f\phi} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{f\phi} \sum_{kq} \Pi_{J_i k} C_{J_i J_i k 0}^{J_i J_i} C_{c\gamma e\epsilon}^{kq} \begin{Bmatrix} L_i & S_i & J_i \\ L_i & S_i & J_i \\ c & e & k \end{Bmatrix} \\ &\times (-1)^{2c+2e} \langle L_i S_i \| \left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha_J aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_e^c \| L_i S_i \rangle \frac{O_k^q(\hat{\mathbf{J}}_i)}{O_k^0(J_i)}. \end{aligned} \quad (\text{B19})$$

From Eq. (A27), c, e , and k satisfy additional conditions:

$$0 \leq c \leq 2L_i, \quad 0 \leq e \leq 2S_i, \quad \max[|c-e|, 0] \leq k \leq \min[c+e, 2J_i]. \quad (\text{B20})$$

The Clebsch-Gordan coefficients are replaced by the sum involving $9j$ symbol (A9):

$$\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha_J J}^{N_i-1} \hat{c}_{in\sigma'} = (-1)^{l_i+\frac{1}{2}+\sigma'} \sum_{f\phi} \sum_{kq} \sum_{x\xi} (-1)^{2f} C_{l_i n k q}^{x\xi} C_{f\phi l_i m}^{x\xi} C_{\frac{1}{2}\sigma \frac{1}{2}-\sigma'}^{f\phi} \mathcal{F}_{\alpha_J J f x k}^i \frac{O_k^q(\hat{\mathbf{J}}_i)}{O_k^0(J_i)}. \quad (\text{B21})$$

Similarly,

$$\hat{c}_{jm'\sigma} \hat{P}_{j\alpha'_j J'}^{N_j+1} \hat{c}_{jn'\sigma'}^\dagger = (-1)^{l_j+\frac{1}{2}+\sigma+m'+n'} \sum_{f\phi} \sum_{kq} \sum_{x\xi} (-1)^{-1+f} C_{l_j-n'kq}^{x\xi} C_{f\phi l_j-m'}^{x\xi} C_{\frac{1}{2}\sigma-\frac{1}{2}\sigma'}^{f-\phi} \mathcal{G}_{\alpha'_j J' f x k}^j \frac{O_k^q(\hat{\mathbf{J}}_j)}{O_k^0(J_j)}. \quad (\text{B22})$$

Here, $\mathcal{F}_{\alpha'_j J' f x k}^i$ in Eq. (B21) is defined by

$$\begin{aligned} \mathcal{F}_{\alpha'_j J' f x k}^i &= \sum_{abcde} (-1)^{J-L-S+\frac{1}{2}+b+c+d-k} \Pi_{JJkkJ_i bcdef} C_{J_i J_i k 0}^{J_i J_i} \begin{Bmatrix} S & S & a \\ L & L & J \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & f \\ a & e & d \end{Bmatrix} \begin{Bmatrix} a & b & l_i \\ e & c & k \\ f & l_i & x \end{Bmatrix} \begin{Bmatrix} L_i & S_i & J_i \\ L_i & S_i & J_i \\ c & e & k \end{Bmatrix} \\ &\times (-1)^{2c+2e} \langle L_i S_i \| \left\{ \hat{c}_i^\dagger \otimes \left\{ \hat{P}_{i\alpha'_j aa}^{N_i-1} \otimes \bar{c}_i \right\}_d^b \right\}_e^c \| L_i S_i \rangle, \end{aligned} \quad (\text{B23})$$

and $\mathcal{G}_{\alpha'_j J' f x k}^j$ is obtained by replacing the reduced matrix element in Eq. (B23) by $\langle L_i S_i \| \{ \bar{c}_i \otimes \{ \hat{P}_{i\alpha'_j aa}^{N_i+1} \otimes \hat{c}_i^\dagger \}_d^b \}_e^c \| L_i S_i \rangle$. The ranges of x and its component ξ are

$$|f - l_i| \leq x \leq f + l_i, \quad (\text{B24})$$

and $-x \leq \xi \leq x$, respectively.

Substituting Eqs. (B21) and (B22) into \hat{H}_{KE} (28), and first summing over σ and σ' , the operator part of the numerator becomes

$$\begin{aligned} \sum_{\sigma\sigma'} \left(\hat{c}_{im\sigma}^\dagger \hat{P}_{i\alpha'_j J}^{N_i-1} \hat{c}_{in\sigma'} \right) \left(\hat{c}_{jm'\sigma} \hat{P}_{j\alpha'_j J'}^{N_j+1} \hat{c}_{jn'\sigma'}^\dagger \right) &= - \sum_{f\phi} \sum_{kq} \sum_{x\xi} \sum_{k'q'} \sum_{x'\xi'} (-1)^{l_i-l_j-f+q'} \mathcal{F}_{\alpha'_j J' f x k}^i \mathcal{G}_{\alpha'_j J' f x' k'}^j \\ &\times C_{l_i n k q}^{x\xi} C_{f\phi l_i m}^{x\xi} C_{l_j-n'k'q'}^{x'\xi'} C_{f-\phi l_j-m'}^{x'\xi'} \frac{O_k^q(\hat{\mathbf{J}}_i) O_{k'}^{q'}(\hat{\mathbf{J}}_j)}{O_k^0(J_i) O_{k'}^0(J_j)}. \end{aligned} \quad (\text{B25})$$

The kinetic exchange Hamiltonian (28) is

$$\begin{aligned} \hat{H}_{\text{KE}} &= \sum_{i \neq j} \sum_{kq} \sum_{k'q'} \sum_{f x x'} \sum_{\alpha'_j J} \sum_{\alpha'_j J'} \frac{\sum_{mn} \sum_{m'n'} \sum_{\xi\xi'} \phi (-1)^{l_i-l_j-f+q'} t_{mm'}^{ij} t_{n'n}^{ji} C_{l_i n k q}^{x\xi} C_{f\phi l_i m}^{x\xi} C_{l_j-n'k'q'}^{x'\xi'} C_{f-\phi l_j-m'}^{x'\xi'}}{U_{ij} + \Delta E_{i\alpha'_j J}^{N_i-1} + \Delta E_{j\alpha'_j J'}^{N_j+1}} \\ &\times \mathcal{F}_{\alpha'_j J' f x k}^i \mathcal{G}_{\alpha'_j J' f x' k'}^j \frac{O_k^q(\hat{\mathbf{J}}_i) O_{k'}^{q'}(\hat{\mathbf{J}}_j)}{O_k^0(J_i) O_{k'}^0(J_j)}. \end{aligned} \quad (\text{B26})$$

The numerator is replaced by $\{t \times t\}_{kqk'q'}^{fxx'}$ (36), and we obtain Eq. (35).

The range of k in Eqs. (B21) and (B22) is $k \leq \min[c + e, 2J_i, x + l_i]$ from Eqs. (B12), (B16), and (B23). Since $0 \leq f \leq 1$, $c + e \leq 2a + 2l_i + 1$, and $x \leq l_i + 1$, the range of k becomes

$$0 \leq k \leq \min[2l_i + 1, 2J_i]. \quad (\text{B27})$$

The range of q is restricted by the transfer parameter as well as the maximal k (k_{max}). Considering the conservation law for the arguments of Clebsch-Gordan coefficients in Eq. (36), $q = \phi + m + n$, and $|\phi| \leq 1$,

$$|q| \leq \min[k_{\text{max}}, 2m_{\text{max}} + 1], \quad (\text{B28})$$

where $m_{\text{max}} (\geq 0)$ is the maximum projection of the magnetic orbital that contributes to the electron transfer.

Appendix C: Property of $\mathcal{J}_{kqk'q'}$

By using the Hermiticity of \bar{H} (29) and

$$\left[O_k^q(\hat{\mathbf{J}}) \right]^\dagger = (-1)^{-q} O_k^{-q}(\hat{\mathbf{J}}), \quad (\text{C1})$$

we obtain

$$(-1)^{-q-q'} (\mathcal{J}_{kqk'q'})^* = \mathcal{J}_{k-qq'-q'}. \quad (\text{C2})$$

On the other hand, using the time-reversal symmetry of \bar{H} and

$$\theta O_k^q(\hat{\mathbf{J}}) \theta^{-1} = \left[O_k^q(-\hat{\mathbf{J}}) \right]^* = (-1)^{k-q} O_k^{-q}(\hat{\mathbf{J}}), \quad (\text{C3})$$

where θ is time-reversal operator [8], we obtain

$$(-1)^{k+k'-q-q'} (\mathcal{J}_{kqk'q'})^* = \mathcal{J}_{k-qq'-q'}. \quad (\text{C4})$$

Comparing Eq. (C2) and Eq. (C4),

$$(-1)^{k+k'} = 1. \quad (\text{C5})$$

Therefore, both of k and k' are even or odd.

Appendix D: Exchange Hamiltonians for J -multiplet interacting with isotropic spin

The exchange Hamiltonian between J -multiplet and isotropic spin is obtained replacing orbital angular momentum of the spin site ($i = 2$) with zero. When the spin state consists of some nondegenerate molecular orbitals, the orbital indices r are introduced.

1. Direct exchange Hamiltonian

Since $l_2 = 0$ and $L_2 = 0$, $J_2 = S_2$, $a' = 0$, $b = k'$, and the $9j$ symbol in $\mathcal{D}_{a'b k'}^2$ (B2) reduces to $1/\Pi_{S_2 S_2 k'}$. Therefore, $\mathcal{D}_{a'b k'}^2$ becomes

$$\tilde{\mathcal{D}}_{rr'k'}^2 = C_{S_2 S_2 k' 0}^{S_2 S_2} \frac{(-1)^{2k'} \langle S_2 \| \{ \hat{c}_{2r}^\dagger \otimes \bar{c}_{2r'} \}_{k'} \| S_2 \rangle}{\Pi_{S_2}}. \quad (\text{D1})$$

Here, a' and b are omitted for simplicity, and the molecular orbital index r is introduced. On the other hand, $\mathcal{V}_{kqk'q'}^{arr'}$ is

$$\mathcal{V}_{kqk'q'}^{arr'} = \sum_{mn} \sum_{\alpha} (-1)^{l_1+n-q'} V_{mrr'n} C_{l_1 m l_1 - n}^{a\alpha} C_{a\alpha k' - q'}^{kq}, \quad (\text{D2})$$

where, $m' = n' = 0$, $\alpha' = 0$, and $q' = -\beta$ are used. The direct exchange parameter between J -multiplet and isotropic spin is given by

$$\mathcal{J}_{kqk'q'}^{\text{DE}} = - \sum_a \sum_r \mathcal{V}_{kqk'q'}^{arr'} \mathcal{D}_{ak'k}^1 \tilde{\mathcal{D}}_{rr'k'}^2. \quad (\text{D3})$$

From Eq. (B7), the rank for the spin site k' is 0 or 1.

2. Kinetic exchange Hamiltonian

Since $l_2 = 0$ and $L_2 = 0$, $J_2 = S_2$, $a' = b' = c' = 0$, $x' = f$, $e' = k'$ and $d' = 1/2$ from the $6j$ and the $9j$ symbols in \mathcal{F} (B23). The values of the $6j$ and the $9j$ symbols are $(-1)^{2S'}/\Pi_{S'}$, $(-1)^{1+k'}/\Pi_{f\frac{1}{2}}$, $\delta_{fk'}/\Pi_{k'k'}$, and

$1/S_2 S_2 k'$, respectively. Thus, $\mathcal{F}_{\alpha_j J f x k}^2$ becomes

$$\tilde{\mathcal{F}}_{\alpha_S r r' k'}^2 = (-1)^{2S} \frac{\Pi_S}{\Pi_{S_2}} C_{S_2 S_2 k' 0}^{S_2 S_2} (-1)^{2k'} \times \langle S_2 \| \{ \hat{c}_{2r}^\dagger \otimes \hat{P}_{2\alpha_S 0}^{N_2-1} \bar{c}_{2r'} \}_{k'} \| S_2 \rangle. \quad (\text{D4})$$

Here, the rank for the orbital part in the double tensor projection operator is removed, $\hat{P}_{2\alpha_S 0}^{N_2-1}$ is irreducible tensor form which acts on spin state:

$$\hat{P}_{2\alpha_S a\alpha}^N = \sum_{m_S m'_S} (-1)^{S+m'_S} C_{S m_S S - m'_S}^{a\alpha} |S m_S\rangle \langle S m'_S|. \quad (\text{D5})$$

$\tilde{\mathcal{G}}_{\alpha_S r r' k'}^2$ is obtained by replacing $\langle S_2 \| \{ \hat{c}_{2r}^\dagger \otimes \hat{P}_{2\alpha_S 0}^{N_2-1} \bar{c}_{2r'} \}_{k'} \| S_2 \rangle$ with $\langle S_2 \| \{ \bar{c}_{2r} \otimes \hat{P}_{2\alpha_S 0}^{N_2+1} \hat{c}_{2r'}^\dagger \}_{k'} \| S_2 \rangle$. On the other hand, $\{t \times t\}_{kqk'q'}^{fxx'}$ (36) reduces to

$$\{t \times t\}_{kqk'q'}^{xrr'} = (-1)^{l_1 - k' + q'} \sum_{mm'} \sum_{\xi} t_{mr}^{12} t_{r'm'}^{21} \times C_{l_1 m' k q}^{x\xi} C_{k' - q' l_1 m}^{x\xi}. \quad (\text{D6})$$

Therefore, the kinetic exchange coupling parameter is obtained as

$$\mathcal{J}_{kqk'q'}^{\text{KE}} = \sum_{xrr'} \sum_{\alpha_j J \alpha'_S S'} \frac{\{t \times t\}_{kqk'q'}^{xrr'} \mathcal{F}_{\alpha_j J k' x k}^1 \tilde{\mathcal{G}}_{\alpha'_S r r' k'}^2}{U_{12} + \Delta E_{1\alpha_j J}^{N_1-1} + \Delta E_{2\alpha'_S S'}^{N_2+1}} + \sum_{xrr'} \sum_{\alpha_j J \alpha'_S S'} \frac{\{t \times t\}_{kqk'q'}^{xrr'} \mathcal{G}_{\alpha_j J k' x k}^1 \tilde{\mathcal{F}}_{\alpha'_S r r' k'}^2}{U_{21} + \Delta E_{1\alpha_j J}^{N_1+1} + \Delta E_{2\alpha'_S S'}^{N_2-1}}. \quad (\text{D7})$$

From Eq. (B27), the rank for the spin site k' is 0 or 1.

Appendix E: Reduced matrix elements of the creation operators

In order to calculate the exchange interaction parameters, the reduced matrix elements in Eqs. (B2), (B23) must be evaluated. In the direct exchange interaction (33), there appear $(-1)^{2a+2b} \langle L_i S_i \| \{ c_i^\dagger \otimes \bar{c}_i \}_b^a \| L_i S_i \rangle$ and $(-1)^{2a+2b} \langle L_j S_j \| \{ \bar{c}_j \otimes \hat{c}_j^\dagger \}_b^a \| L_j S_j \rangle$. However, note that the irreducible tensor operators are the same type as V^{11} used for the calculations of the spin-orbit coupling [50]. On the other hand, for the calculations of the kinetic exchange interactions (35), $(-1)^{2c+2e} \langle L_i S_i \| \{ c_i^\dagger \otimes \{ \hat{P}_{i\alpha_j a a}^{N_i-1} \otimes \bar{c}_i \}_d^b \}_e^c \| L_i S_i \rangle$ and $(-1)^{2c+2e} \langle L_j S_j \| \{ \bar{c}_j \otimes \{ \hat{P}_{j\alpha_j a a}^{N_j+1} \otimes \hat{c}_j^\dagger \}_d^b \}_e^c \| L_j S_j \rangle$ have to be evaluated. By straightforward calculations, the former is

TABLE III. Reduced matrix elements of the creation operator for the ground 6H -term of Dy^{3+} .

Γ	$(-1)^{2(l+1/2)}\langle f^9, {}^6H \hat{c}^\dagger f^8, \Gamma\rangle/\Pi_{LS}$	Γ	$(-1)^{2(l+1/2)}\langle f^9, {}^6H \hat{c}^\dagger f^8, \Gamma\rangle/\Pi_{LS}$	Γ	$(-1)^{2(l+1/2)}\langle f^{10}, \Gamma \hat{c}^\dagger f^9, {}^6H\rangle/\Pi_{LS}$
7F	$\sqrt{\frac{7}{3}}$	${}^5G(2)$	$-\frac{1}{7}\sqrt{\frac{65}{11}}$	5D	$-2\sqrt{\frac{11}{35}}$
${}^5D(1)$	$-\frac{1}{3}\sqrt{\frac{10}{7}}$	${}^5G(3)$	$\frac{3}{7}\sqrt{\frac{3}{2}}$	5F	$\sqrt{\frac{33}{35}}$
${}^5D(2)$	$-\frac{2\sqrt{5}}{21}$	${}^5H(2)$	-1	5G	$-\sqrt{\frac{13}{7}}$
${}^5D(3)$	$\frac{3}{7}\sqrt{\frac{15}{11}}$	${}^5I(1)$	$\frac{1}{3}\sqrt{\frac{91}{11}}$	5I	$\sqrt{\frac{14}{5}}$
${}^5F(1)$	$-\frac{1}{\sqrt{6}}$	${}^5I(2)$	$\frac{1}{3}\sqrt{\frac{26}{11}}$		
${}^5F(2)$	$-\sqrt{\frac{3}{22}}$	5K	$-\sqrt{\frac{15}{11}}$		
${}^5G(1)$	$-\sqrt{\frac{65}{154}}$	5L	$\sqrt{\frac{17}{11}}$		

$$\begin{aligned}
& \frac{\Pi_{L_i S_i}}{C_{L_i M_L c \gamma}^{L_i M'_L} C_{S_i M_S e \epsilon}^{S_i M'_S}} \left| \frac{(-1)^{2(l_i+1/2)} \langle l_i^{N_i}, L_i S_i | \hat{c}_i^\dagger | l_i^{N_i-1}, \alpha LS \rangle}{\Pi_{L_i S_i}} \right|^2 \\
& \times \sum_{mn} \sum_{\alpha\beta} \sum_{N_L N'_L} (-1)^{l_i+n+L+N_L} C_{l_i m \beta}^{c\gamma} C_{\alpha l_i - n}^{b\beta} C_{L N'_L L - N_L}^{a\alpha} C_{L_i M'_L l_i m}^{L N'_L} C_{L_i M_L l_i n}^{L N_L} \\
& \times \sum_{\sigma\sigma'} \sum_{\alpha'\delta} \sum_{N_S N'_S} (-1)^{\frac{1}{2}+\sigma'+S+N_S} C_{\frac{1}{2}\sigma\delta}^{e\epsilon} C_{\alpha\alpha'\frac{1}{2}-\sigma'}^{d\delta} C_{S N'_S S - N_S}^{a\alpha'} C_{S_i M'_S \frac{1}{2}m}^{S N'_S} C_{S_i M_S \frac{1}{2}n}^{S N_S}, \quad (E1)
\end{aligned}$$

and the latter is

$$\begin{aligned}
& \frac{\Pi_{L_j S_j}}{C_{L_j M_L c \gamma}^{L_j M'_L} C_{S_j M_S e \epsilon}^{S_j M'_S}} \left| \frac{(-1)^{2(l_j+1/2)} \langle l_j^{N_j+1}, \alpha LS | \hat{c}_j^\dagger | l_j^{N_j}, L_j S_j \rangle}{\Pi_{LS}} \right|^2 \\
& \times \sum_{mn} \sum_{\alpha\beta} \sum_{N_L N'_L} (-1)^{l_j+m+L+N_L} C_{l_j - m \beta}^{c\gamma} C_{\alpha\alpha l_j n}^{b\beta} C_{L N'_L L - N_L}^{a\alpha} C_{L_j M'_L l_j m}^{L N'_L} C_{L_j M_L l_j n}^{L N_L} \\
& \times \sum_{\sigma\sigma'} \sum_{\alpha'\delta} \sum_{N_S N'_S} (-1)^{\frac{1}{2}+\sigma+S+N_S} C_{\frac{1}{2}-\sigma\delta}^{e\epsilon} C_{\alpha\alpha'\frac{1}{2}\sigma'}^{d\delta} C_{S N'_S S - N_S}^{a\alpha'} C_{S_j M'_S \frac{1}{2}m}^{S N'_S} C_{S_j M_S \frac{1}{2}n}^{S N_S}. \quad (E2)
\end{aligned}$$

Here, the components $M_L, M'_L, M_S, M'_S, \gamma, \epsilon$ are chosen so that $C_{L_i M_L c \gamma}^{L_i M'_L} C_{S_i M_S e \epsilon}^{S_i M'_S} \neq 0$ is satisfied. For the calculations of the equations, the reduced matrix elements of the creation operators, $\hat{c}_{i\sigma}^\dagger$, are necessary. They are calculated as [41]

$$\begin{aligned}
& \frac{(-1)^{2(l+1/2)} \langle f^N \alpha LS | \hat{c}^\dagger | f^{N-1} \alpha' L' S' \rangle}{\Pi_{LS}} \\
& = \sqrt{N} \langle f^N \alpha LS | \{ f^{N-1}(\alpha' L' S') f LS \}, \quad (E3)
\end{aligned}$$

where $\langle f^N \alpha LS | \{ f^{N-1}(\alpha' L' S') f LS \}$ is the coefficient of fractional parentage, which is tabulated in Ref. 48. The reduced matrix elements of \hat{c}^\dagger necessary for the present examples are shown in Table III.

Appendix F: Exchange states of N_2^{2-} bridged Dy^{3+} dimer

The difference between the eigenstates of the full exchange Hamiltonian $\hat{H}_{\text{ex}}, |\Psi_i, \Gamma\rangle$, and those of the Heisenberg type Hamiltonian (1), $|J_{12} M_{12}\rangle$, are compared as in the case of the linear system. The low-energy states are, in the basis of $\{|J_{12} M_{12}\rangle\}$ (46),

$$\begin{aligned}
|\Psi_1, b_{1u}\rangle &\approx 0.767|1, 0\rangle + 0.493|3, 0\rangle + 0.108(|3, -2\rangle + |3, 2\rangle) + 0.345|5, 0\rangle + 0.118|7, 0\rangle, \\
|\Psi_2, a_g\rangle &\approx 0.552|0, 0\rangle + 0.661|2, 0\rangle + 0.400|4, 0\rangle + 0.250|6, 0\rangle, \\
|\Psi_3, b_{2g}\rangle &\approx 0.586(-|2, -1\rangle + |2, 1\rangle) - 0.260(-|4, -1\rangle + |4, 1\rangle) + 0.256(-|4, -3\rangle + |4, 3\rangle) + 0.108(-|8, -1\rangle + |8, 1\rangle), \\
|\Psi_4, b_{3u}\rangle &\approx -0.545(-|1, -1\rangle + |1, 1\rangle) - 0.158(-|3, -1\rangle + |3, 1\rangle) - 0.161(-|3, -3\rangle + |3, 3\rangle) + 0.293(-|5, -1\rangle + |5, 1\rangle) \\
&\quad - 0.218(-|5, -3\rangle + |5, 3\rangle) - 0.129(-|7, -1\rangle + |7, 1\rangle), \\
|\Psi_5, b_{1u}\rangle &\approx -0.285|1, 0\rangle + 0.680|3, 0\rangle - 0.448(|3, -2\rangle + |3, 2\rangle), \\
|\Psi_6, a_g\rangle &\approx 0.446|0, 0\rangle - 0.331|2, 0\rangle + 0.347(|2, -2\rangle + |2, 2\rangle) - 0.460|4, 0\rangle + 0.255(|4, -2\rangle + |4, 2\rangle) + 0.181|6, 0\rangle \\
&\quad - 0.155(|6, -2\rangle + |6, 2\rangle).
\end{aligned}$$

Here, the irreducible representation Γ of D_{2h} symmetry is used. The exchange states belong to the eigenvalues $E_1 = -0.274979$, $E_2 = -0.274977$, $E_3 = -0.262325$, $E_4 = -0.262299$, $E_5 = -0.260815$, $E_6 = -0.260805$, respectively. As in the axial system, the low-energy states are not well described by \hat{H}_{Heis} . Within the $1/\bar{U}$ approximation, the low-energy states become

$$\begin{aligned}
|\Psi_1^{1/\bar{U}}, a_g\rangle &= 0.509|0, 0\rangle + 0.696|2, 0\rangle + 0.434|4, 0\rangle + 0.222|6, 0\rangle, \\
|\Psi_2^{1/\bar{U}}, b_{1u}\rangle &= 0.740|1, 0\rangle + 0.559|3, 0\rangle + 0.330|5, 0\rangle + 0.115|7, 0\rangle, \\
|\Psi_3^{1/\bar{U}}, b_{3u}\rangle &= 0.554(-|1, -1\rangle + |1, 1\rangle) + 0.205(-|3, -1\rangle + |3, 1\rangle) + 0.193(-|3, -3\rangle + |3, 3\rangle) - 0.234(-|5, -1\rangle + |5, 1\rangle) \\
&\quad + 0.220(-|5, -3\rangle + |5, 3\rangle), \\
|\Psi_4^{1/\bar{U}}, b_{2g}\rangle &= 0.608(-|2, -1\rangle + |2, 1\rangle) - 0.188(-|4, -1\rangle + |4, 1\rangle) + 0.279(-|4, -3\rangle + |4, 3\rangle), \\
|\Psi_5^{1/\bar{U}}, a_g\rangle &= 0.489|0, 0\rangle - 0.263|2, 0\rangle - 0.374(-|2, -2\rangle + |2, 2\rangle) - 0.430|4, 0\rangle - 0.265(-|4, -2\rangle + |4, 2\rangle) + 0.141|6, 0\rangle \\
&\quad + 0.127(-|6, -2\rangle + |6, 2\rangle) - 0.103(-|6, -4\rangle + |6, 4\rangle), \\
|\Psi_6^{1/\bar{U}}, b_{1u}\rangle &= 0.351|1, 0\rangle - 0.618|3, 0\rangle + 0.471(|3, -2\rangle + |3, 2\rangle) + 0.109(|5, -4\rangle + |5, 4\rangle).
\end{aligned}$$

The exchange states $|\Psi_i^{1/\bar{U}}\rangle$ are also ordered as the increase of the energy. Some levels are interchanged due to

the $1/\bar{U}$ approximation. $|\Psi_i\rangle$ and $|\Psi_i^{1/\bar{U}}\rangle$ with the same representation quantitatively differ from each other.

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