Exchange interaction between \(J\)-multiplets

Naoya Iwashara and Liviu F. Chibotaru

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

(Dated: March 10, 2015)

Analytical expressions for the exchange interaction between \(J\)-multiplets of interacting metallic centers are derived on the basis of a complete electronic model. 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.

PACS numbers: 75.30.Et 71.70.Ej 75.50.Xx

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 \(\mathbf{L}\) and the low-lying spectrum is well described as crystal-field split eigenstates of the total angular momentum \(J = L + S\), where \(S\) is the spin of the metallic term. This situation takes place in lanthanides, actinides and some transition metal ions in a cubic symmetry environment[6][7]. 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 \(\mathbf{J}_1 \cdot \mathbf{S}_2\)[8][9]. It was however conjectured long time ago that the exchange interaction between fully degenerate \(J\)-shells, involving \((2J_1+1)\) and \((2J_2+1)\) angular momentum eigenstates on the first and the second magnetic centers, respectively, is described by a similar isotropic exchange Hamiltonian written in terms of \(\mathbf{J}_i\) momenta:

\[
\hat{H}_{\text{Heis}} = J \mathbf{J}_1 \cdot \mathbf{J}_2.
\]  

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, \(\propto \mathbf{J}_1 \cdot \mathbf{S}_2\), in the case of their interaction with an isotropic spin), especially, in the last years[10][23]. On the basis of simplified analysis based on so-called 1/\(U\) approximation[3] it has been pointed out that the \(J-J\) exchange Hamiltonian is not of the simple bilinear form [3]. It is not clear, however, how important are “non-Heisenberg” terms in the actual \(J-J\) coupling, nor is the 1/\(U\) approximation a priori justified for metal ions with unquenched orbital momenta. Both these questions can only be answered after a decent 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[24][25].

Given that many microscopic electronic parameters describing individual magnetic centers and their interaction can be accurately derived via density functional theory[26] or \(ab\) initio calculations[27], 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 complete electronic model. The obtained exchange parameters are expressed via electronic matrix elements which can be derived from electronic structure calculations. Comparison with the predictions given by the Hamiltonian [1] and the simplified treatment on the basis of 1/\(U\) approximation shows that both of them are not suitable approaches to describe the exchange interaction of ions with unquenched orbital momentum.

Microscopic description of intersite interaction.— The electronic Hamiltonian \(\hat{H}\) for a localized system can be divided into the \(0\) the intrasite contributions \(\hat{H}_0\) \((i=1,2)\), the intersite bielectronic \(\hat{H}_{\text{bi}}\) and electron transfer \(\hat{H}_t\) parts. \(\hat{H}_0\) contains all intrasite interactions including relativistic effects. \(\hat{H}_{\text{bi}}\) consists of intersite Coulomb interaction \(\hat{H}_{\text{Coul}}\) and direct exchange (multipole) part \(\hat{H}_{\text{DE}}\). \(\hat{H}\) can be divided into zeroth order Hamiltonian \(H_0 = 2 \sum_{i=1}^{2} \hat{H}_0 + \hat{H}_{\text{Coul}}\) and the terms \(\hat{H}_{\text{DE}}\) and \(\hat{H}_t\). For localized magnetic electrons, the latter terms can be treated in the first and the second order of perturbation theory, respectively[28]. This is done here via a unitary transformation 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,
\[ \hat{H}_{\text{eff}} = \hat{H}_0 + \hat{H} \] The last term \( \hat{H} \) consists of direct exchange \( \hat{H}_{\text{DE}} \) and the kinetic \( \hat{H}_{\text{KE}} \) parts:

\[ \hat{H}_{\text{DE}} = - \sum_{mn\sigma\sigma'} V_{mn'n'n} \hat{c}_{1m\sigma}^{\dagger} \hat{c}_{1n\sigma'} \hat{c}_{2m'n'} \hat{c}_{2n'\sigma'}, \]

\[ \hat{H}_{\text{KE}} = \sum_{i\neq j} \sum_{\mu} \sum_{\nu'J'} \sum_{m'n'} \sum_{\mu\sigma'_{J-1}} \sum_{\mu'\sigma'_{J+1}} U_{ij} - \Delta E_{ij\mu J} - \Delta E_{ij\mu'J'} \]

where \( m \) and \( \sigma \) are the projections of orbital \( (l_i) \) and spin angular momenta, respectively, \( \hat{c}_{1m\sigma}^{\dagger} \) is the electron creation (annihilation) operator in the orbital shell \( l_i \) of site \( i \) \((i=1,2)\), \( V_{mn'n'n} \) is the intersite bielectronic integral of exchange type and \( t_{mn}^{ij} \) is the intersite electron transfer parameter. \( \mu J \) indicates the intermediate state with total angular momentum \( J \) and \( \hat{T}_{ij\mu J}^{N+1} \) is the projection operator into the \( \mu J \) states with \( N \pm 1 \) electrons at site \( i \). \( U_{ij} \) is the minimum promotion energy for the electron transfer from site \( i \) to site \( j \), and \( \Delta E_{ij\mu J}^{N \pm 1} \) is the excitation energy from the ground multiplet into \( \mu J \) one on the site \( i \). In this derivation, the effects of the crystal-field splitting and the \( j-j \) mixing in the intermediate states \( \mu J \) are neglected because they are weaker than the multiplet splitting. Thus, each \( J \)-multiplet arises from one \( LS \)-term, \( \mu = (\alpha, L, S) \):

\[ |\mu J M \rangle = \sum_{M_L, M_S} |\alpha L M_L S M_S \rangle C^{JM}_{L M_L S M_S}, \]

where \( C^{JM}_{L M_L S M_S} \) is Clebsch-Gordan coefficient. This is a good approximation, in particular, for the ground \( J \)-multiplet.

**Exchange Hamiltonian in \( J \)-representation.**—The Hamiltonian \( \hat{H} \) is transformed into tensor form with the use of irreducible (double) tensor technique \[30\] and of method of equivalent operator \[31\]:

\[ \hat{H} = \sum_{kqk'q'} \mathcal{J}_{kqk'q'} O^{J_1}_{k}(\hat{J}_1) O^{J_2}_{k}(\hat{J}_2) \]

\[ \mathcal{J}_{kqk'q'} = \frac{O^{J_1}_{k}(\hat{J}_1) O^{J_2}_{k}(\hat{J}_2)}{O^{J_1}_{k}(\hat{J}_1) O^{J_2}_{k}(\hat{J}_2)}. \]

Here, \( O^{J_1}_{k}(\hat{J}_1) \) and \( O^{J_2}_{k}(\hat{J}_2) \) are Stevens operators 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 \[31\]. 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 \[32\].

The direct exchange parameter is obtained as

\[ \mathcal{J}_{kqk'q'}^{\text{DE}} = - \sum_{aa'b} V_{aa'b}^{kqk'q'} D_{abk}^{J_1} D_{a'bk'}^{J_2}. \]
and \( G_{\mu,\nu}^{f} \) is obtained by replacing the reduced matrix element in Eq. (11) by \( \langle L_i S_i | c_i \otimes \{ F_{\mu,\nu}^{N_i+1} \otimes c_i^\dagger \} d | L_i S_i \rangle \). The range of variation of indices of these tensors, as well as in the subscripts of \( F \) and \( G \) is specified in [29]. In the above equations, \( L, S, J \) refer to the intermediate states. The quantum numbers of the multiplets contributing to \( F^{\text{KE}} \) 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 \(|J_i - l_i - 1/2| \leq J \leq J_i + l_i + 1/2\) [33].

The domains of variation of \( k \) and \( q \) characterize the structure of the Hamiltonian [5]. The upper bound for the rank \( k \) and \( k' \) in Eq. (5) is only determined by the electronic state of the site 1 and 2, respectively:

\[
k_{\text{max}} = \min[2l_i + 1, 2J_i].
\]

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 \( N = 6 \).

On the other hand, the range of \( q \) for each allowed rank \( k \) is determined by the nonzero parameters describing the intersite interactions, \( V_{mm' n' n} \) and \( t_{m n}^{f} \). If \( \Delta_{\text{max}} \) is the maximal difference of the indices corresponding to one site in the above parameters \((m - n \text{ for site 1 and } m' - n' \text{ for the site 2})\) then the upper bound for \( q \) \((q')\) is

\[
q_{\text{max}} = \min[\Delta_{\text{max}} + 1, k].
\]

Note that terms with \(-q_{\text{max}}\) will also be present in the Hamiltonian [5] due to the time reversal symmetry, implying the following range: \(-q_{\text{max}} \leq q \leq q_{\text{max}}\).

The effective Hamiltonian [5] is further divided into the exchange \( \tilde{H}_{\text{ex}} \) and the zero-field splitting parts. The latter is defined as comprising terms of \( \tilde{H} \) with either \( k = 0 \) or \( k' = 0 \).

**Exchange interaction between \( J \)-multiplet and isotropic spin.**— When the orbital angular momentum is zero in ground state term of on of the sites, the low-energy states are characterized by the corresponding spin, \( \mathbf{S} \). This situation is encountered in mixed lanthanide-transition metal and lanthanide-radical complexes [11,25,34]. The exchange Hamiltonian between a \( J \)-multiplet and an isotropic spin is obtained in a similar way as Eq. (6):

\[
\tilde{H} = \sum_{kq} J_{kq00} O_k^0(\mathbf{J}_1) \mathbf{I}_2 + \sum_{kq'd} J_{kq1q'} O_k^1(\mathbf{J}_1) \mathbf{S}_{2q'},
\]

where \( O^0 \) and \( O^1 \) are the Stevens operators [5].

The expressions for exchange coupling constants are similar to Eqs. (6), (9) and are listed in [29]. 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. (14), respectively. As in the previous case, the former \((k' = 0)\) is zero-field splitting term and the latter \((k' = 1)\) is the exchange interaction.

**Kinetic exchange through monoatomic bridge.**— As a simple example, consider an exchange-coupled Dy\(^{3+}\) dimer with axial bridging geometry (Fig. 1b). The largest transfer parameter \((t)\) is expected between \( f_{5z^2-3z^2} \) \((m = 0)\) orbitals because of their sigma bonding to the \( p_z \) orbital of the bridging ligand atom (Fig. 1b). Then, according to the rule (13), \( q_{\text{max}} = 1 \), while Eq. (10) gives \( q = -q' \). The resulting form of \( \tilde{H}_{\text{ex}} \), after expanding the Stevens operators in [5], is

\[
\tilde{H}_{\text{ex}} = \tilde{K}^{(1)} + \tilde{K}^{(2)} = 4 \tilde{K}^{(1)} \mathbf{J}_1 \cdot \mathbf{J}_2,
\]

where \( k + k' \) is even. We can see that, even in this simplest case, \( \tilde{H}_{\text{ex}} \) does not reduce to the isotropic form (1) because Ising \((\propto \tilde{K}^{(1)})\) and mixed Ising-Heisenberg \((\propto \tilde{K}^{(2)})\) terms, both involving high powers of momentum projection operators of two sites. As a result the ex-
(a) Dy dimer bridged via $N_2^-$ anion ($D_{2h}$ core symmetry). Large (purple) and small (red) balls are Dy and N, respectively. (b), (c) Superexchange interaction between $4f_{(5z^2-r^2)x}$ and $4f_{x^3-3xy^2}$ orbitals, respectively, via the HOMO of $N_2^-$. (d) Superexchange interaction between the $4f_{xyz}$ orbital of Dy and the LUMO of $N_2^-$. (e) Calculated exchange spectrum with full $\hat{H}_{ex}$ and its first-rank contribution ($\bar{U} \equiv U_{12} = U_{21} = 5\, eV$), and in the $1/U$ approximation for superexchange pattern (b). (f) Calculated exchange spectrum with full $\hat{H}_{ex}$ and its first-rank contribution ($\bar{U}_{21} = 3\, eV$), and in the $1/U$ approximation for superexchange pattern (d). The calculations in (e) and (f) involved exchange parameters (9) with excitation energies of the intermediate states on Dy evaluated \textit{ab initio} [29]. $\bar{U}$ in the calculation within $1/U$ approximation was chosen to reproduce the width of the spectrum for full $\hat{H}_{ex}$.

FIG. 2. (Color online) (a) Dy dimer bridged via $N_2^-$ anion ($D_{2h}$ core symmetry). Large (purple) and small (red) balls are Dy and N, respectively. (b), (c) Superexchange interaction between $4f_{(5z^2-r^2)x}$ and $4f_{x^3-3xy^2}$ orbitals, respectively, via the HOMO of $N_2^-$. (d) Superexchange interaction between the $4f_{xyz}$ orbital of Dy and the LUMO of $N_2^-$. (e) Calculated exchange spectrum with full $\hat{H}_{ex}$ and its first-rank contribution ($\bar{U} \equiv U_{12} = U_{21} = 5\, eV$), and in the $1/U$ approximation for superexchange pattern (b). (f) Calculated exchange spectrum with full $\hat{H}_{ex}$ and its first-rank contribution ($\bar{U}_{21} = 3\, eV$), and in the $1/U$ approximation for superexchange pattern (d). The calculations in (e) and (f) involved exchange parameters (9) with excitation energies of the intermediate states on Dy evaluated \textit{ab initio} [29]. $\bar{U}$ in the calculation within $1/U$ approximation was chosen to reproduce the width of the spectrum for full $\hat{H}_{ex}$.

Kinetic exchange through biatomic bridge.—Consider the exchange interaction in the Dy$^{3+}$ dimer bridged by the $N_2^-$ ($n = 2, 3$) anion (Fig. 2(a)) [35]. 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 $N_2^-$ (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 being dominant. Hence, we only consider the electron transfer between the orbitals with $|m| = 1$ (Fig. 2(b)). For them $\Delta_{max} = 2$ and we obtain according to Eq. (13) $q_{max} = 3$. Then $\hat{H}_{ex}$ will include powers of $\hat{J}_{\pm}$ ($= \hat{J}_{ix} \pm i\hat{J}_{iy}$) 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 $\bar{U}$ ($1/U$ approximation) [3, 8]. Although the first-rank contribution is bilinear in $\hat{J}_{\alpha}$, the corresponding spectrum does not resemble the pattern of levels of Heisenberg-type Hamiltonian (1). Also the spectrum is quite different when the $1/U$ 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 is significantly modified (Fig. S1 [29]).

In the case of $N_2^-$ 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 $N_2^-$. (Fig. 2(d)). The LUMO orbital in $N_2^-$ 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-
pared to the 4f orbitals, the minimal electron promotion energy from N_{3}^{2−} 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. (15), q_{max} = 5 for large k, the same for the maximal power of J_{1+} in the exchange Hamiltonian. Figure 2(e) shows the exchange levels obtained for exact H_{ex}, its first-rank part, and for the 1/U approximation. In the present case, the first-rank component of H_{ex} coincides with Eq. (1), while the corresponding spectrum strongly differs from the full H_{ex} indicating the importance of higher order terms. As in the previous example, the 1/U approximation modifies the relative contributions to the exchange interaction from intermediate states 29 and induces, in particular, the change of the ground state (marked with arrow in Fig. 2(f)).

Conclusion.— We derived the Hamiltonian of exchange interaction between J-multiplet and between J-multiplet and isotropic spin on the basis of a complete electronic model. The exchange parameters are expressed via microscopic quantities which can be extracted from first principle calculations. Despite their microscopic character, the obtained expressions are general (i) for arbitrary choice of quantization axes 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 momentum. On the basis of several examples we found that the exchange spectrum in systems with J-J and J-S interaction cannot be adequately described neither by isotropic exchange Hamiltonian nor within 1/U approximation. Given these reasons, 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.

N. I. would like to acknowledge the financial support from the Fonds Wetenschappelijk Onderzoek- Vlaanderen (FWO) and the GOA grant from KU Leuven. We thank Liviu Ungur for his help with ab initio calculations.

[1] D. Gatteschi, R. Sessoli, and J. Villain, Molecular Nanomagnets (Oxford University Press, Oxford, 2006).
[2] R. Layfield and M. Murugesu, eds., Lanthanides and Actinides in Molecular Magnetism (Wiley, New Jersey, 2015).
[3] P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander, Rev. Mod. Phys. 81, 807 (2009).
[4] W. W. Lukens, N. Magnani, and C. H. Booth, Inorg. Chem. 51, 10105 (2012).
[5] S. I. Klokishner, S. M. Ostrovsky, O. S. Reu, A. V. Palii, P. L. Tregenna-Piggott, T. Brock-Nannestad, J. Bendix, and H. Mutka, J. Phys. Chem. C 113, 8573 (2009).
[6] S. Klokishner and O. Reu, Chem. Phys. Lett. 552, 130 (2012).
[7] D. Gatteschi, R. Sessoli, and J. Villain, Molecular Nanomagnets (Oxford University Press, Oxford, 2006).
and the exchange states of the model complexes.

[30] B. R. Judd, *Second Quantization and Atomic Spectroscopy* (The Johns Hopkins Press, Baltimore, 1967).

[31] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Claredon Press, Oxford, 1970).

[32] For interacting lanthanide ions, one should add also the contribution from magnetic dipolar interaction, which is of known first-rank form: \(-g_i^1\mu_i^n R_{i2}^2(J_1 \cdot n_2 - 3(J_2 \cdot n_2))\), where \(g_i\) is the Landé g factor.

[33] The correctness of Eqs. (9 - 11) was checked numerically by comparing the resulting exchange spectrum with the one predicted by Eq. (3).

[34] S. Demir, I.-R. Jeon, J. R. Long, and T. D. Harris, Coord. Chem. Rev. (2014), http://dx.doi.org/10.1016/j.ccr.2014.10.012.

[35] J. D. Rinehart, M. Fang, W. J. Evans, and J. R. Long, Nat. Chem., 3, 538 (2011).

**Supplemental Material**

for

“Exchange interaction between J-multplets”

**MICROSCOPIC DERIVATION OF AN EFFECTIVE INTERACTION HAMILTONIAN BETWEEN MAGNETIC CENTERS**

The model Hamiltonian \(\hat{H}\) for the localized system with two sites consists of the intrasite Hamiltonian \(\hat{H}_0\), the intersite bielectronic interaction \(\hat{H}_{bi}\), and the electron transfer Hamiltonian \(\hat{H}_t\). \(\hat{H}_{bi}\) includes all the important interactions such as the bielectronic, the spin-orbit and other relativistic effects, crystal-field. The eigenstate of the on-site Hamiltonian \(\hat{H}_0\) is determined by the number of electrons \(N\) and crystal-field level \(p\), \([n_i, p]\).

The intersite bielectronic interaction \(\hat{H}_{bi}\) has the Coulomb \(\hat{H}_{Coul}\) and the direct exchange \(\hat{H}_{DE}\) [2] terms [31][32]:

\[
\hat{H}_{bi} = \hat{H}_{Coul} + \hat{H}_{DE},
\]

(81)

\[
\hat{H}_{Coul} = \sum_{m\sigma} U^i \hat{n}_{1m\sigma} \hat{n}_{2m\sigma},
\]

(82)

\[
\hat{H}_{DE} = -\sum_{m\sigma} V_{mm'n'n} \hat{c}_{1m\sigma}^\dagger \hat{c}_{1m\sigma} \hat{c}_{2n'\sigma}^\dagger \hat{c}_{2n'\sigma},
\]

(83)

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

\[
V_{mm'n'n} = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*_{1m'}(\mathbf{r}_1) \psi_{2m'}(\mathbf{r}_2) \times v(\mathbf{r}_1 - \mathbf{r}_2) \psi_{2n'}(\mathbf{r}_1) \psi_{1n'}(\mathbf{r}_2),
\]

(84)

and \(v(\mathbf{r}_1 - \mathbf{r}_2)\) is the two body interaction. \(\hat{H}_{bi}\) does not change the number of the electrons on each sites.

In the case of the lanthanide system, the magnetic orbital is localized in comparison with actinide and transition metal compounds. The strengths of the bielectronic \((\approx 5-7 \text{ eV})\) and the spin-orbit splitting \((\approx 1 \text{ eV})\) are at least several times larger than the crystal field splitting \((\approx 0.1 \text{ eV})\) and electron transfer \((\approx 0.1 \text{ eV})\).

[33] [55] Thus, \(\hat{H}_t\) is treated as the perturbation to the unperturbed Hamiltonian, \(\hat{H}_0 + \hat{H}_{DE} = \sum_{i=1}^2 \hat{H}_0^i + \hat{H}_{bi}^i\).

In the unperturbed Hamiltonian, there is no term which vary the numbers of the electrons, the electronic states is written as

\[
|N_1, N_2, r\rangle = \sum_{p,q} |1N_1, p\rangle |2N_2, q\rangle C_{pq;r}^{N_1 N_2},
\]

(85)

where \(r\) indicates the eigenstate of the system, \(C_{pq;r}^{N_1 N_2}\) is a coefficient.

The effective Hamiltonian \(\hat{H}_{eff}\) for the low-energy states is derived performing the unitary transformation of the model Hamiltonian, \(\hat{H}_{eff} = e^{-\hat{S}} \hat{H} e^{\hat{S}}\). In the derivation of the effective Hamiltonian, we consider the truncated vector space \(\mathcal{M}\) of the electron configurations which includes up to one electron transfer \((N_1 \pm 1)\) with respect to the numbers of the electrons in the ground electron configurations. \(\mathcal{M} = \{ |N_1, N_2, r\rangle, |N_1 - 1, N_2 + 1, \pm 1, \pm 1\rangle, |N_1 + 1, N_2 - 1, \pm 1\rangle\}\). For simplicity, the space is written as

\[
\mathcal{M} = \{|r\rangle, |1 \rightarrow 2, s\rangle, |2 \rightarrow 1, s'\rangle\},
\]

(86)

where \(i \rightarrow j (i, j = 1, 2)\) indicates the electron transfer with respect to the ground configuration, and the numbers of electrons in the ground configuration are omit. The eigenstates \(|r\rangle, |i \rightarrow j, s\rangle\) in \(\mathcal{M}\) belong to the eigenenergies \(E_0^0\) and \(E_0^{i \rightarrow j}\) of the unperturbed Hamiltonian, respectively.

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

\[
\hat{S} = \sum_{i \neq j} \sum_r \sum_s \left( \hat{P}^{i \rightarrow j}_r \hat{H}_0^i \hat{P}^{i \rightarrow j}_r - \hat{P}^{0}_r \hat{H}_t \hat{P}^{i \rightarrow j}_r \right) \left( E^0_r - E^{i \rightarrow j}_s \right) \left( E^0_r - E^{i \rightarrow j}_s \right),
\]

(87)

where \(\hat{P}^{0}_r\) and \(\hat{P}^{i \rightarrow j}_r\) are the projection operators. The exponent \(\hat{S}\) is chosen to fulfill

\[
[\hat{S}, \hat{H}_0 + \hat{H}_{DE}] = \hat{H}_t
\]

(88)

within the space \(\mathcal{M}\). The effective Hamiltonian within the space of \(\mathcal{M}_0 = \{|r\rangle\}\) is

\[
\hat{H}_{eff} = \hat{H}_0 + \hat{H}_{DE} - \frac{1}{2} [\hat{S}, \hat{H}_t].
\]

(89)

Here, the terms up to second order after \(\hat{H}_t\) is left and the higher terms are neglected. The second and the third terms correspond to \(\hat{H}\) in the main text,

\[
\hat{H} = \hat{H}_{DE} + \hat{H}_{KE},
\]

(90)

\[
\hat{H}_{KE} = \frac{1}{2} \sum_{i \neq j} \sum_r \sum_s \left( \hat{H}_t \hat{P}^{i \rightarrow j}_r \hat{H}_t \hat{P}^{i \rightarrow j}_r - \frac{\hat{P}^{0}_r \hat{H}_t \hat{P}^{i \rightarrow j}_r \hat{H}_t}{E^0_r - E^{i \rightarrow j}_s} + \frac{\hat{P}^{0}_r \hat{H}_t \hat{P}^{i \rightarrow j}_r \hat{H}_t}{E^0_r - E^{i \rightarrow j}_s} \right).
\]

(91)
Note that the terms such as \( \hat{P}_s^{i\rightarrow j} \hat{H}_t \hat{P}_s^{0} \hat{H}_t \) are neglected because they are zero in \( \mathcal{M}_0 \).

Neglecting the effects of the crystal field splitting and direct exchange in the denominator of \( \hat{H}_{KE} \), the eigenstates \( r,s \) reduce to the sets of the \( J \)-multiplet states:

\[
  r \rightarrow (J_1, J_2), \quad s \rightarrow (\mu J, \nu J'),
\]

(\( \text{S12} \))

where, \( J_i \) is the total angular momentum with the ground electron configuration, and \( J, J' \) and \( \mu, \nu \) are the total angular momenta and the other quantum numbers for intermediate states, respectively. The kinetic exchange Hamiltonian becomes

\[
\hat{H}_{KE}^r_s = \frac{1}{2} \sum_{i \neq j} \sum_{\mu \lambda \nu \lambda'} \sum_{i \mu \lambda \nu \lambda'} \left( \frac{\hat{H}_t \hat{P}_s^{i\rightarrow j} \hat{H}_t \hat{P}_s^{0} \hat{H}_t}{E_{ij} - E_{i\mu \lambda \nu \lambda'}^{i\rightarrow j}} + \frac{\hat{P}_s^{i\rightarrow j} \hat{P}_s^{0} \hat{H}_t}{E_{ij} - E_{i\mu \lambda \nu \lambda'}^{i\rightarrow j}} \right).
\]

(S13)

In the space of the ground \( J \)-multiplets, \( \mathcal{M}_J = \{ |J_1M_1|J_2M_2 : -J_i \leq M_i \leq J_i \} \),

\[
\hat{H}_{KE} = \sum_{i \neq j} \sum_{\mu \lambda \nu \lambda'} \frac{\hat{H}_t \hat{P}_s^{i\rightarrow j} \hat{H}_t}{E_{ij} - E_{i\mu \lambda \nu \lambda'}^{i\rightarrow j}}.
\]

(S14)

Here, \( \hat{P}_s^{0} \) is omitted because it is the unit operator in \( \mathcal{M}_J \).

Substituting the explicit form of the transfer Hamiltonian,

\[
\hat{H}_t = \sum_{i \neq j} \sum_{\mu \lambda \nu \lambda'} t_{ij}^{\mu \lambda \nu \lambda'} \hat{e}_{i \mu \lambda \nu \lambda'} \hat{e}_{j \mu \lambda \nu \lambda'},
\]

(S15)

into Eq. (S14), we obtain

\[
\hat{H}_{KE} = \sum_{i \neq j} \sum_{\mu \lambda \nu \lambda'} \sum_{\mu \lambda \nu \lambda'} \sum_{\mu \lambda \nu \lambda'} \sum_{\mu \lambda \nu \lambda'} -t_{ij}^{\mu \lambda \nu \lambda'} \frac{\hat{P}_s^{N} \hat{e}_{i \mu \lambda \nu \lambda'}}{U_{ij} + \Delta E_{ij}^{N_{i\mu \lambda \nu \lambda'}}} \frac{\hat{P}_s^{N_{i\mu \lambda \nu \lambda'}} \hat{e}_{j \mu \lambda \nu \lambda'}}{U_{ij} + \Delta E_{ij}^{N_{i\mu \lambda \nu \lambda'}}}.
\]

(S16)

where \( t_{ij}^{\mu \lambda \nu \lambda'} \) is the transfer parameter, \( U_{ij} \) is the smallest promotion energy for the electron transfer from site \( i \) to site \( j \), \( \Delta E_{ij}^{N_{i\mu \lambda \nu \lambda'}} \) is the excitation energy from the ground intermediate state with \( N \) electrons, and \( \hat{P}_s^{N_{i\mu \lambda \nu \lambda'}} \) is the projection operator to the \( J \)-multiplet, \( (\mu J) \), of site \( i \):

\[
\hat{P}_s^{N_{i\mu \lambda \nu \lambda'}} = \sum_{M=-J}^{J} |iN_{\mu}JM\rangle \langle iN_{\mu}JM|.
\]

(S17)

**INTERACTION HAMILTONIAN IN J-REPRESENTATION**

The exchange Hamiltonian is transformed into tensor form. This is done using the reduction of the reducible operators, the method of equivalent operator (see for example Ref. S3), and the form of \( J \)-multiplet state (Eq. (4) in the main text).

The creation and annihilation operators, \( c_{i \mu \lambda \nu \lambda'}^{\dagger} \) and \( \hat{c}_{i \mu \lambda \nu \lambda'} \) transform as irreducible double tensor of \( SO(3) \otimes SU(2) \) group. \( \text{S6} \) \( \text{S7} \)

In the effective Hamiltonian \( \hat{H}_t \), these operators appear as a form of the products. For example, \( \hat{c}_{i \mu \lambda \nu \lambda'} \hat{c}_{i \mu \lambda \nu \lambda'} \) in \( \hat{H}_{DE} \). Since such products are not irreducible, they are reduced.

The irreducible double tensors \( \hat{A}_{\mu \lambda \nu \lambda'}^\gamma \) are transformed into the tensor form within the space of the ground \( J \)-multiplet, \( \{ |JM\rangle \} \), using the method of the equivalent operator and the form of the \( J \)-multiplet (Eq. (4) in the main text):

\[
\hat{A}_{\mu \lambda \nu \lambda'}^\gamma = (-1)^{2\epsilon + 2c} \langle L_iS_i||\hat{A}_{\mu \lambda \nu \lambda'}^\gamma||L_iS_i\rangle \sum_{kq} \Pi_{kq} J_k \times C_{J_i,j_k}^{J_i,j_{k0}} c_{q} \langle L_i S_i J_k | L_i S_i J_k | c c \rangle \frac{O_{q}^{\gamma}(J_k)}{O_{q}^{\gamma}(J_k)}. \]

(S18)

Here, the superscript and the subscript of \( \hat{A}_{\mu \lambda \nu \lambda'}^\gamma \) express the rank \((c,c)\) and the components \((\gamma,\gamma)\) of the orbital and the spin parts, respectively. \( J \) is the total angular momentum, \( L_i, S_i, J_i \) are the magnitude of the orbital, the spin, and the total angular momenta of the ground \( J \)-multiplet, respectively. \( O_{q}^{\gamma}(J_k) \) is the irreducible tensor operator of rank \( k \) and argument \( q \) (Stevens operator), \( C_{J_i,j_k}^{J_i,j_{k0}} \) is Clebsch-Gordan coefficient. \( \text{S7} \)

\( \langle L_iS_i||\hat{A}_{\mu \lambda \nu \lambda'}^\gamma||L_iS_i\rangle \) is the reduced matrix element of \( \hat{A}_{\mu \lambda \nu \lambda'}^\gamma \), \( \Pi_{kq} \) is the reduced matrix element of \( \hat{A}_{\mu \lambda \nu \lambda'}^\gamma \), \( \Pi_{kq} = \sqrt{J_k + 1} \), and \( \Pi_{kq} = \Pi_{kq} \). In the derivation of Eq. (S18), formula 8.7.4. (26) in Ref. S7 is used. The irreducible tensor operator \( O_{q}^{\gamma}(J_k) \) is constructed replacing the coordinates in the spherical harmonics \( Y_{kq}^{\gamma}(r/|r|) \) by the total angular momentum operator \( (r/|r| \rightarrow J) \) and summing over all possible permutations of \( J \) operators, where \( r \) is the Cartesian coordinate. \( O_{q}^{\gamma}(J) \) in the denominator of Eq. (S18) is the scalar obtained by substituting \( J^2 = J(J + 1) \) and \( Jz = J_z \) in \( O_{q}^{\gamma}(J) \). \( Y_{kq}^{\gamma} \) may be multiplied by a constant \( C_{k} \) which only depends on the rank \( k \). However, each \( O_{q}^{\gamma}(J) \) is divided by \( O_{q}^{\gamma}(J) \) in Eq. (S18), and the choice of the constant is not important here. The form \( O_{q}^{\gamma}(J)/O_{q}^{\gamma}(J) \) is taken because it is useful to apply the Wigner-Eckart theorem S7:

\[
\langle JM'\rangle \frac{O_{q}^{\gamma}(J)}{O_{q}^{\gamma}(J)} |JM\rangle = \frac{C_{J_{Mkq}}^{JM'} C_{J_{Mkq}}^{J_{Mkq}}}{C_{J_{Mkq}}^{J_{Mkq}}}. \]

(S19)
Direct exchange Hamiltonian

The direct product of the double tensors $c_{i}^\dagger c_{i\sigma}$ appearing in $H_{DE}$ is reduced as follows:

$$c_{i}^\dagger c_{i\sigma} = c_{i\alpha}^\dagger (-1)^{l_i+n+\frac{1}{2}+\sigma} \hat{c}_{i-n-\sigma}$$

$$= (-1)^{l_i+n+\frac{1}{2}+\sigma} \sum_{a b \beta} \left\{ \hat{c}_{i}^\dagger \otimes \hat{c}_{i} \right\}_{a b \beta}^{\alpha}$$

$$\times C_{i a b \beta}^{\alpha} C_{a b \beta}^{\alpha} \hat{c}_{i-n-\sigma},$$  \hspace{1cm} (S20)

where the curly bracket indicates the irreducible operator of ranks $(a, b)$ and components $(\alpha, \beta)$ constructed from the product of the creation and the annihilation operators. Using Eq. (S18) and formula 8.7.4. (26) in Ref. S7, we obtain the direct exchange part of Eq. (5) in the main text.

Kinetic exchange Hamiltonian

In the kinetic exchange Hamiltonian $\hat{H}_{KE}$, the operators appear as the form of $c_{i}^\dagger c_{i\sigma} \hat{P}_{i\mu J}^{N_{i}} c_{i\sigma}^\dag$ and $\hat{P}_{i\mu J}^{N_{i}} c_{i\sigma}^\dag c_{i\sigma}^\dagger$. One should note that the projection operator $\hat{P}_{i\mu J}^{N_{i}}$ is totally symmetric within SO(3) group, whereas reducible within the $SO(3) \otimes SU(2)$ group. Thus, $\hat{P}_{i\mu J}^{N_{i}}$ 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. (4) in the main text, the projection operator $\hat{P}_{i\mu J}^{N_{i}}$ is transformed into the double tensor:

$$\hat{P}_{i\mu J}^{N_{i}} = \sum_{\alpha} (-1)^{J-L+S+\alpha} \Pi_{JJ} \left\{ S S a \right\} \hat{P}_{i\mu a a a-\alpha},$$  \hspace{1cm} (S24)

where double tensor $\hat{P}_{i\mu a a a-\alpha}$ is defined by

$$\hat{P}_{i\mu a a a-\alpha} = \sum_{m L m S m_{S} m_{L}} (-1)^{L+m_{S}+S+m_{S} S} C_{L S L m_{L}}^{\alpha}$$

$$\times \sum_{j} \left\{ \hat{c}_{i}^\dagger \otimes \hat{c}_{i} \right\}_{j}^{\alpha} \Pi_{j j}$$

$$\times \frac{O_{j}^{\alpha}(J)}{O_{j}^{\alpha}(J)}$$  \hspace{1cm} (S21)

and the range of the rank $a$ in Eq. (S24) is

$$0 \leq a \leq 2 \min|S, L|, \hspace{1cm} (S26)$$

and $-a \leq \alpha \leq a$. In the derivation of Eq. (S24), the definition of the $6j$ symbol (Eq. 9.1. (5) in Ref. S7) is used. Substituting Eq. (S24) into $\hat{c}_{i}^\dagger c_{i\sigma} \hat{P}_{i\mu J}^{N_{i}} c_{i\sigma}^\dagger$, we obtain the direct exchange part of Eq. (5) in the main text.

$$\hat{c}_{i}^\dagger c_{i\sigma} \hat{P}_{i\mu J}^{N_{i}} c_{i\sigma}^\dagger = (-1)^{l_{i}+n+\frac{1}{2}+\sigma} \hat{c}_{i\sigma}^\dagger \hat{P}_{i\mu J}^{N_{i}} \hat{c}_{i-n-\sigma}$$

$$= \sum_{a} (-1)^{J-L+S+a} \Pi_{JJ} \left\{ S S a \right\} \hat{P}_{i\mu a a a-\alpha}$$

$$\times (-1)^{l_{i}+n+\frac{1}{2}+\sigma} \hat{c}_{i\sigma} \hat{P}_{i\mu a a a-\alpha} \hat{c}_{i-n-\sigma},$$  \hspace{1cm} (S27)

where the curly bracket indicates the irreducible operator of ranks $(a, b)$ and components $(\alpha, \beta)$ constructed from the product of the creation and the annihilation operators.
\[
\hat{c}_{i_{\alpha}a}^{\dagger} \hat{P}_{ij\sigma}^{-1} \hat{c}_{i_{\sigma}a} = \sum_{b_{\beta \delta}d} C_{a_{\alpha}a_{\beta}d}^{b_{\beta}d} \left( \hat{P}_{ij\alpha}^{-1} \otimes \hat{c}_{i_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}} = \sum_{b_{\beta \gamma}c_{\sigma \delta}d} C_{a_{\alpha}a_{\beta}d}^{b_{\beta}d} \left( \hat{P}_{ij\gamma}^{-1} \otimes \hat{c}_{i_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

Similarly, the other part in Eq. (S16) becomes

\[
\hat{c}_{j_{\alpha}a}^{\dagger} \hat{P}_{ji\sigma}^{-1} \hat{c}_{j_{\sigma}a} = \sum_{b_{\beta \delta}d} C_{a_{\alpha}a_{\beta}d}^{b_{\beta}d} \left( \hat{P}_{ji\alpha}^{-1} \otimes \hat{c}_{j_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

The ranges of the ranks \(b, c, d, e, f\) are

\[
\begin{align*}
|a - l_i| &\leq b \leq a + l_i, & |a - 1/2| &\leq d \leq a + 1/2, & |b - l_i| &\leq c \leq b + l_i, \\
|d - 1/2| &\leq e \leq d + 1/2, & \text{max} |a - e|, 0 &\leq f \leq \text{min} |a + e, 2 \times 1/2|.
\end{align*}
\]

and their arguments satisfy \(-b \leq \beta \leq b, -d \leq \delta \leq d, -e \leq \gamma \leq c, -e \leq \epsilon \leq e, -f \leq \phi \leq f\), respectively. Note that \(f\) is at the largest angle. In the last transformation, we used the symmetry properties of the Clebsch-Gordan coefficient and formula 8.7.3. (12) in Ref. S7. Substituting Eq. (S28) into Eq. (S27),

\[
\hat{c}_{i_{\alpha}a}^{\dagger} \hat{P}_{ij\sigma}^{-1} \hat{c}_{i_{\sigma}a} = \left(-1\right)^{l_i + 1/2} \hat{P}_{ij\sigma}^{-1} \hat{c}_{i_{\sigma}a} = \sum_{a_{\alpha}a_{\beta}d} \left(-1\right)^{l_i + 1/2 - d - f} \left< S L L J \right| \left| S S a \right>^{a a} \left< \frac{1}{2} \frac{1}{2} ight|^{f} \left< \frac{1}{2} a _{\epsilon} d \right|^{b_{\beta}d} \left( \hat{P}_{ij\alpha}^{-1} \otimes \hat{c}_{i_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

Similarly, the other part in Eq. (S16) becomes

\[
\hat{c}_{j_{\alpha}a}^{\dagger} \hat{P}_{ji\sigma}^{-1} \hat{c}_{j_{\sigma}a} = \sum_{a_{\alpha}a_{\beta}d} \left(-1\right)^{l_j + 1/2} \hat{P}_{ji\alpha}^{-1} \hat{c}_{j_{\sigma}a} = \sum_{a_{\alpha}a_{\beta}d} \left(-1\right)^{l_j + 1/2 - d - f} \left< S L L J \right| \left| S S a \right>^{a a} \left< \frac{1}{2} \frac{1}{2} ight|^{f} \left< \frac{1}{2} a _{\epsilon} d \right|^{b_{\beta}d} \left( \hat{P}_{ji\alpha}^{-1} \otimes \hat{c}_{j_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

The operators in Eqs. (S30) and (S31) are written in terms of the total angular momentum using the method of equivalent operator. Applying Eq. (S18) to the operator parts \(\left\{ \hat{c}_{i_{\sigma}a}^{\dagger} \left( \hat{P}_{ij\alpha}^{-1} \otimes \hat{c}_{i_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}} \right\}_{ee}\) in Eq. (S30) and \(\left\{ \hat{c}_{j_{\sigma}a}^{\dagger} \left( \hat{P}_{ji\alpha}^{-1} \otimes \hat{c}_{j_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}} \right\}_{ee}\) in Eq. (S31), and using the symmetry of the Clebsch-Gordan coefficients and formula 8.7.4. (20) in Ref. S7, we obtain

\[
\hat{c}_{i_{\alpha}a}^{\dagger} \hat{P}_{ij\sigma}^{-1} \hat{c}_{i_{\sigma}a} = \sum_{a_{\alpha}a_{\beta}d} \left< S L L J \right| \left| S S a \right>^{a a} \left< \frac{1}{2} \frac{1}{2} ight|^{f} \left< \frac{1}{2} a _{\epsilon} d \right|^{b_{\beta}d} \left( \hat{P}_{ij\alpha}^{-1} \otimes \hat{c}_{i_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

and

\[
\hat{c}_{j_{\alpha}a}^{\dagger} \hat{P}_{ji\sigma}^{-1} \hat{c}_{j_{\sigma}a} = \sum_{a_{\alpha}a_{\beta}d} \left< S L L J \right| \left| S S a \right>^{a a} \left< \frac{1}{2} \frac{1}{2} ight|^{f} \left< \frac{1}{2} a _{\epsilon} d \right|^{b_{\beta}d} \left( \hat{P}_{ji\alpha}^{-1} \otimes \hat{c}_{j_{\sigma}a} \right)_{d_{\delta}}^{b_{\beta}}
\]

The ranges of \(x\) and its component \(\xi\) are

\[
|f - l_i| \leq x \leq f + l_i,
\]

and \(-x \leq \xi \leq x\), respectively.
Using Eqs. (S26), (S29), (S34), the constraint \( k \leq \min[2J_i, c+e] \) in Eqs. (S32) and (S33), the maximal range of \( k \) becomes
\[
0 \leq k \leq \min[2J_i + 1, 2J_i]. \tag{S35}
\]
Here, \( \max[c+e] = 2a + 2J_i + 1 \) and \( 0 \leq f \leq 1 \) is used. From Eqs. (S32) and (S33), we also obtain the relation of \( c, e, k \):
\[
(-1)^{c+e+k} = 1. \tag{S36}
\]
In the case of \( q \), the range is also restricted by the transfer parameter. Considering the conservation law for the arguments of Clebsch-Gordan coefficients, \( q = \phi + m + n \), and \( |\phi| \leq 1 \),
\[
|q| \leq \min[k, 2m_{\text{max}} + 1], \tag{S37}
\]
where \( m_{\text{max}}(\geq 0) \) is the maximum projection of the magnetic orbital that contributes to the electron transfer. In Eqs. (S32), (S33), the nonzero terms satisfy simultaneously Eqs. (S20), (S29), (S34), (S35), (S36).
Substituting Eqs. (S32) and (S33) into \( \tilde{H}_{\text{KE}} \) (S10), we obtain Eq. (7).

Decomposition of \( \tilde{H} \)

Now we know the form of the general exchange Hamiltonian (5) and the domain of rank \( k \); it is possible to calculate \( \mathcal{J}_{kqk'}q' \) by using the orthogonality of the Stevens operator,
\[
\mathcal{J}_{kqk'}q' = (-1)^{n+q'} \left( \frac{\Pi_{kk'} \{ C_{J_1J_1} \Pi_{J_1J_2} C_{J_2J_2} \}^2}{\Pi_{J_1J_2}} \right) \times \text{Tr} \left[ \hat{Q}_{kqk'-q} \hat{H} \right], \tag{S38}
\]
where the trace (Tr) is taken over the ground \( J \)-multiplets, and
\[
\hat{Q}_{kqk'}q' = \frac{O_k^0(\hat{J}_1)O_{k'}^0(\hat{J}_2)}{O_k^0(\hat{J}_1)O_{k'}^0(\hat{J}_2)}. \tag{S39}
\]
The kinetic exchange parameters obtained by Eq. (7) in the main text and those by the projection, (S38), are compared with each other for some examples.

EXCHANGE HAMILTONIANS FOR \( J \)-MULTIPELT 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 a few nondegenerate molecular orbitals, the orbital indices \( r \) are introduced.

Direct exchange Hamiltonian

The direct exchange interaction becomes
\[
\mathcal{J}_{kqk'}q' = -\sum_a \sum_{rr'} \mathcal{V}_{aak'k} \hat{D}_{aak'k}^2 \hat{D}_{rr'}^{2k'k}, \tag{S40}
\]

Kinetic exchange Hamiltonian

The kinetic exchange coupling constant is obtained as
\[
\mathcal{J}_{kqk'}q' = \sum_{rr'} \sum_{\mu \nu} \sum_{\mu S} \left\{ \langle t \times t \rangle_{kk'q'} \mathcal{F}_{\mu \nu \mu S} \hat{G}_{\mu \nu \mu S}^2 \hat{G}_{\nu S \nu S}^2 \hat{G}_{\nu S \nu S}^2 \right\}
\times \left[ U_{12} + \Delta E_{\mu \nu S}^1 + \Delta E_{\nu S}^1 \frac{(-1)^{2k'} \langle S_2 \rangle}{\Pi_S} \langle \hat{c}_{2r} \otimes \hat{c}_{2r} \rangle_{k'} \langle S_2 \rangle \right], \tag{S41}
\]
and
\[
\hat{D}_{rr'}^{2k'k} = C_{aSaS_2k'0}^{-1} \langle S_2 \rangle \langle \hat{c}_{2r} \otimes \hat{c}_{2r} \rangle_{k'} \langle S_2 \rangle \tag{S42}
\]

 Reduced Matrix Elements of the Creation Operators

In order to calculate the exchange interaction parameters, the reduced matrix elements must be evaluated. For the kinetic exchange interactions, \( \langle L_r S_1 \rangle \{ \hat{c}_i^\dagger \otimes \hat{P}_{\nu \nu a}^{N_1} \otimes \hat{c}_i \}_{d} \| L_S S_2 \rangle \) and \( \langle L_r S_1 \rangle \{ \hat{c}_j \otimes \hat{P}_{\nu \nu a}^{N_1} \otimes \hat{c}_j \}_{d} \| L_S S_2 \rangle \). By straightforward calculations,
The components $M_L, M'_L, M_S, M'_S, \gamma, \epsilon$ are chosen so that they give $C_{L,M_L,C}^{i,M'_L}C_{S,M'_S}^{i,m}$ different from zero. Now, we need the reduced matrix element of the creation operators, $\hat{c}_{\imath m\alpha}^{\dagger}$, which are calculated as \[ (S6) \]

by using the c.f.p. \[ (S8) \] comparing the patterns of the spin-orbit splitting of each $LS$-term. In the basis of the spin-orbit Hamiltonian $H_{so} = \zeta \sum_{i=1}^{N} l_i \cdot s_i$ ($\zeta > 0$) is given as

$$\langle l^{\mu+2-N} \alpha L S J M J | \hat{H}_{so} | l^{\mu+2-N} \alpha' L' S' J' M' J' \rangle$$

$$= \delta_{LL'} \delta_{SS'} \delta_{JJ'} \delta_{M M'} \zeta \frac{\Pi_{ij} \sqrt{l(l+1)}}{2\sqrt{3}}$$

where $\langle l^{\mu} \alpha L S J | l^{\mu} \alpha' L' S' J' \rangle$ is the coefficient of fractional parentage (c.f.p.). The c.f.p.’s are obtained from the table in Ref. \[ SS \] The reduced matrix elements necessary for the present examples are tabulated below (Table \[ S1 \]).

**EXCITATION ENERGIES OF Dy$^{2+}$ AND Dy$^{4+}$**

The excitation energies $\Delta E_{\mu J}$ appearing in the denominator of the kinetic exchange Hamiltonian are calculated \textit{ab initio}. Since the effect of the crystal field splitting in the intermediate states is negligible, (its magnitude is the third order of smallness, $\ell^2/U \cdot \Delta E_{\ell\ell}/U$ ($\Delta E_{\ell\ell}/U \lesssim 0.01$) we used the energy levels of the free Dy$^{2+}$ and Dy$^{4+}$ ions are calculated using CASSCF and RASSI methods with ANO-RCC QZP basis set. \[ S9 \] For the CASSCF calculations, all 4f orbitals are included into the active space. There are several $LS$-terms which appear more than once ($^5 D, ^5 F, ^5 G, ^5 H, ^5 I$ of Dy$^{2+}$). These terms obtained by the CASSCF calculations are assigned to the symmetrized states constructed

The parameters $k_{kk'}^{(1)}$, $k_{kk'}^{(2)}$ of the exchange Hamiltonian for the linear Dy complex [Eqs. (11)-(13) in the main text] are tabulated in Table \[ S3 \] When $J_{12}$ is close
to 15/2, the higher order terms significantly contribute to the exchange interaction rather than the bilinear term. The difference between the present exchange states with those of the Heisenberg type Hamiltonian, $\hat{H}_{\text{Heis}} = J_1 \mathbf{J}_i \cdot \mathbf{J}_j$ (Eq. (1) in the main text), is compared by expanding the former by the latter. The solution of $\hat{H}_{\text{Heis}}$ for two site system is given [Eq. (1)]

$$|J, M\rangle = \sum_{M_i, M_j} |J_i M_i, J_j M_j\rangle \mathcal{C}_{J_i M_i, J_j M_j}^{JM}.$$  \hfill (S50)

The low-energy exchange states of $\hat{H}_{\text{ex}}$ are in the basis of $\{|J, M\rangle\}$, 

$$|\Psi_1, A_{1g}\rangle \approx 0.574|0, 0\rangle + 0.773|2, 0\rangle + 0.190|4, 0\rangle - 0.160|6, 0\rangle,$$

$$|\Psi_2, A_{1u}\rangle \approx 0.846|1, 0\rangle + 0.505|3, 0\rangle - 0.161|7, 0\rangle,$$

$$|\Psi_{3,4}, E_{1u}\rangle \approx 0.352|1, \pm 1\rangle + 0.768|3, \pm 1\rangle + 0.522|5, \pm 1\rangle + 0.107|7, \pm 1\rangle,$$

$$|\Psi_{5,6}, E_{1g}\rangle \approx 0.636|2, \pm 1\rangle + 0.712|4, \pm 1\rangle + 0.294|6, \pm 1\rangle.$$  

Here, the irreducible representation of $D_{\infty h}$ is used, and these states, $|\Psi_i, \Gamma\rangle$, belong to the eigenvalues $E_{1,2} = -0.278523$, $E_{3,4,5,6} = -0.243015$, respectively. The low-energy exchange states are not necessarily mainly contributed by the ground state of the antiferromagnetic Heisenberg Hamiltonian (1). $|J, M\rangle = |0, 0\rangle$. The Heisenberg interaction (1) is not adequate to describe the exchange interaction between $J$-multipolets.

\textbf{Dy$^{3+}$ dimer bridged by N$_2^{2-}$}

The difference between the eigenstates of the exact exchange Hamiltonian $\hat{H}_{\text{ex}}$ (3), $|\Psi_i, \Gamma\rangle$, and those of the Heisenberg type Hamiltonian (1), $|J, M\rangle$, are compared as in the case of the linear system. The low-energy states are using the basis of $\{|J, M\rangle\}$ [3].

Here, the exchange states, $|\Psi_i, \Gamma\rangle \ (i = 1, 2, \ldots, 6)$, 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, and the irreducible representation $\Gamma$ of $D_{2h}$ symmetry is used. Again, the low-energy states are not well described by $\hat{H}_{\text{Heis}}$.

With the $1/U$ approximation the low-energy states become

| Table S1. Reduced matrix elements of the creation operator for the ground state of Dy$^{3+}$. |
|-----------------|-----------------|
| $\Gamma$       | Reduced matrix element |
|-----------------|-----------------|
| $^7F$           | $(-1)^{2(l+1/2)}(f_{10}, |\Psi_i\rangle [f_8, \Gamma]/\Pi_{LS}$ |
| $^5D(1)$        | $-\frac{3}{8} \sqrt{7}$ |
| $^5D(2)$        | $-\frac{3}{8} \sqrt{7}$ |
| $^5D(3)$        | $\frac{3}{8} \sqrt{15}$ |
| $^5F(1)$        | $-\frac{3}{8} \sqrt{7}$ |
| $^5F(2)$        | $-\frac{3}{8} \sqrt{7}$ |
| $^5G(1)$        | $-\frac{3}{8} \sqrt{15}$ |
| $^5G(2)$        | $-\frac{3}{8} \sqrt{15}$ |
| $^5G(3)$        | $\frac{3}{8} \sqrt{7}$ |
| $^5H(2)$        | $-1$ |
| $^5I(1)$        | $\frac{3}{8} \sqrt{21}$ |
| $^5I(2)$        | $\frac{3}{8} \sqrt{21}$ |
| $^5K$           | $-\frac{15}{14}$ |
| $^5L$           | $\frac{15}{14}$ |
| $^5D$           | $(-1)^{2(l+1/2)}(f_{10}, \Gamma |\emptyset [f_8, \Gamma]/\Pi_{LS}$ |
| $^5F$           | $-\frac{2}{8} \sqrt{35}$ |
| $^5G$           | $-\frac{2}{8} \sqrt{35}$ |
| $^5I$           | $\frac{2}{8} \sqrt{35}$ |
As discussed in the main text, the order of the exchange states is changed by this approximation.

The interchanges of the exchange levels arise due to the variation of the balance of the contributions from the intermediate states to the kinetic exchange interaction. The kinetic exchange Hamiltonian is a sum of the terms from the intermediate states,

\[ \hat{H}_{\text{ex}} = \sum_{\mu J} \sum_{\nu J'} \hat{h}_{\text{ex}}(\mu J, \nu J'), \quad (S51) \]

where \( \hat{h}_{\text{ex}}(\mu J, \nu J') \) indicates the term which only includes the contribution from one set of the intermediate state \((\mu J, \nu J').\) Thus, the contribution from each intermediate process is measured by the width of the eigenvalues of \( \hat{h}_{\text{ex}}(\mu J, \nu J'), \) \( w.\) The widths \( w \) for \( \text{Dy}^{3+}-\text{N}_2^- \) and \( \text{Dy}^{5+} \) for the exact Hamiltonian \( \hat{H}_{\text{ex}} \) and that with \( 1/U \) approximation, \( \hat{H}_{\text{ex}}^{1/U}, \) are shown in Figure S1(a), (b), respectively. In comparison with the contributions in \( \hat{H}_{\text{ex}} \), those from the high energy states are exaggerated in \( \hat{H}_{\text{ex}}^{1/U}. \)

---

**TABLE S2.** Excitation energies of Dy\(^{2+}\) and Dy\(^{4+}\) (meV).

| LS-term | Dy\(^{2+}\) | | Dy\(^{4+}\) | | Dy\(^{4+}\) |
|---------|------------|------------|------------|------------|------------|
|         | \( J \) | \( \Delta E_{\mu J} \) | \( \mu J \) | \( \Delta E_{\mu J} \) | \( \mu J \) |
| \( ^5I \) | 8 | 0.000 | | 7 | 0.000 | |
|         | 7 | 458.212 | | 5 | 309.504 | |
|         | 6 | 859.148 | | 4 | 508.583 | |
|         | 5 | 1202.808 | | 4 | 13934.562 | |
|         | 4 | 1489.190 | | 4 | 7642.320 | |
| \( ^5D \) | 4 | 5667.150 | | 4 | 3298.723 | |
|         | 5 | 2369.357 | | 5 | 5838.268 | |
|         | 4 | 2655.740 | | 4 | 5936.666 | |
| \( ^5G \) | 6 | 3412.346 | | 5 | 11206.930 | |
|         | 5 | 3756.005 | | 4 | 11118.121 | |
|         | 4 | 4042.388 | | 4 | 6925.862 | |
| \( ^5H(2) \) | 6 | 8925.862 | | 5 | 7272.721 | |
|         | 5 | 7272.721 | | 4 | 7423.960 | |
|         | 4 | 4540.837 | | 3 | 4613.355 | |
| \( ^5G(2) \) | 6 | 13458.95 | | 5 | 13323.410 | |
|         | 5 | 13323.410 | | 4 | 13191.767 | |
|         | 4 | 8096.483 | | 3 | 8392.826 | |
|         | 3 | 8603.858 | | 2 | 8409.212 | |

\[ |\Psi_1^{1/U}, a_{0}\rangle = 0.509|0,0\rangle + 0.696|2,0\rangle + 0.434|4,0\rangle + 0.222|6,0\rangle, \]
\[ |\Psi_2^{1/U}, b_{1a}\rangle = 0.740|1,0\rangle + 0.559|3,0\rangle + 0.330|5,0\rangle + 0.115|7,0\rangle, \]
\[ |\Psi_3^{1/U}, b_{3a}\rangle = 0.554|{-}1,{-}1\rangle + |1,1\rangle + 0.205|{-}3,{-}1\rangle + |3,1\rangle + 0.193|{-}3,{-}3\rangle + |3,3\rangle - 0.234|{-}5,{-}1\rangle + |5,1\rangle \]
\[ + 0.220|{-}5,{-}3\rangle + |5,3\rangle, \]
\[ |\Psi_4^{1/U}, b_{2a}\rangle = 0.608|{-}2,{-}1\rangle + |2,1\rangle - 0.188|{-}4,{-}1\rangle + |4,1\rangle + 0.279|{-}4,{-}3\rangle + |4,3\rangle, \]
\[ |\Psi_5^{1/U}, a_{0}\rangle = 0.489|0,0\rangle - 0.263|2,0\rangle - 0.374|{-}2,{-}2\rangle + |2,2\rangle - 0.430|4,0\rangle - 0.265|{-}4,{-}2\rangle + |4,2\rangle + 0.141|6,0\rangle \]
\[ + 0.127|{-}6,{-}2\rangle + |6,2\rangle - 0.103|{-}6,{-}4\rangle + |6,4\rangle, \]
\[ |\Psi_6^{1/U}, b_{1a}\rangle = 0.351|1,0\rangle - 0.618|3,0\rangle + 0.471|3,{-}2\rangle + |3,2\rangle + 0.109|5,{-}4\rangle + |5,4\rangle. \]
TABLE S3. $\mathcal{K}_{kk}^{(1)}$ and $\mathcal{K}_{kk'}^{(2)}$.

| $\mathcal{K}_{kk}^{(1)}$ | $\mathcal{K}_{kk'}^{(2)}$ |
|-------------------------|-------------------------|
| $\mathcal{K}_{30}^{(1)}$ | $2.4458 \times 10^{-3}$ | $3.2245 \times 10^{-3}$ |
| $\mathcal{K}_{32}^{(1)}$ | $-2.3903 \times 10^{-3}$ | $-3.2216 \times 10^{-4}$ |
| $\mathcal{K}_{34}^{(1)}$ | $1.7181 \times 10^{-4}$ | $1.5888 \times 10^{-5}$ |
| $\mathcal{K}_{36}^{(1)}$ | $-1.7242 \times 10^{-6}$ | $-1.8049 \times 10^{-7}$ |
| $\mathcal{K}_{11}^{(2)}$ | $1.0908 \times 10^{-2}$ | $4.8351 \times 10^{-5}$ |
| $\mathcal{K}_{13}^{(2)}$ | $-1.1514 \times 10^{-3}$ | $-4.6269 \times 10^{-6}$ |
| $\mathcal{K}_{15}^{(2)}$ | $3.5361 \times 10^{-5}$ | $7.4785 \times 10^{-8}$ |
| $\mathcal{K}_{17}^{(2)}$ | $-2.9084 \times 10^{-7}$ | $4.3815 \times 10^{-5}$ |
| $\mathcal{K}_{20}^{(2)}$ | $2.9710 \times 10^{-3}$ | $-2.1423 \times 10^{-6}$ |
| $\mathcal{K}_{24}^{(2)}$ | $-1.3026 \times 10^{-4}$ | $2.3716 \times 10^{-8}$ |
| $\mathcal{K}_{26}^{(2)}$ | $1.2614 \times 10^{-6}$ | $4.502 \times 10^{-7}$ |
| $\mathcal{K}_{33}^{(2)}$ | $1.1745 \times 10^{-4}$ | $-7.2365 \times 10^{-9}$ |
| $\mathcal{K}_{35}^{(2)}$ | $-3.3571 \times 10^{-6}$ | $1.0531 \times 10^{-7}$ |
| $\mathcal{K}_{37}^{(2)}$ | $2.6060 \times 10^{-8}$ | $-1.1732 \times 10^{-9}$ |
| $\mathcal{K}_{44}^{(2)}$ | $5.4544 \times 10^{-6}$ | $1.1839 \times 10^{-9}$ |
| $\mathcal{K}_{66}^{(2)}$ | $-4.9672 \times 10^{-8}$ | $1.3155 \times 10^{-11}$ |
| $\mathcal{K}_{55}^{(2)}$ | $7.4109 \times 10^{-8}$ | |
| $\mathcal{K}_{57}^{(2)}$ | $-3.9138 \times 10^{-10}$ | |
| $\mathcal{K}_{66}^{(2)}$ | $4.1115 \times 10^{-10}$ | |
| $\mathcal{K}_{77}^{(2)}$ | $0.00000$ | |

**Dy$^{3+}$ dimer bridged by N$_2^3$−**

The interchange of the three-fold degenerate ground $t_{1g}$ level and the first excited nondegenerate $a_{2g}$ level is seen due to the $1/U$ approximation in Dy$^{3+}$-radical system. Here, the irreducible representation of $O_h$ group is used because the exchange Hamiltonian is accidentally isomorphic to it. With the increase of $U$, these levels become degenerate around $U \approx 9.8$ eV, and the gap between them is further enhanced due to the limit $U \to \infty$ where the electronic structure is negligible.

As in the previous case, the change in the balance of the contributions of the intermediate states are investigated (Figure S2). Due to the $1/U$ approximation, the contributions from the excited intermediate states are enhanced. The enhanced contributions cause the interchange of the exchange levels.

[S1] P. W. Anderson, Phys. Rev. 115, 2 (1959).
[S2] P. W. Anderson, in Solid state physics, Vol. 14, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1963) pp. 99–214.
[S3] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Claredon Press, Oxford, 1970).
[S4] D. van der Marel and G. A. Sawatzky, Phys. Rev. B 37, 10674 (1988).
[S5] V. S. Mironov, L. F. Chibotaru, and A. Ceulemans, Phys. Rev. B 67, 014424 (2003)
[S6] B. R. Judd, Second Quantization and Atomic Spectroscopy (The Johns Hopkins Press, Baltimore, 1967).
[S7] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, Singapore, 1988).
[S8] C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the $p^0$, $d^n$, and $f^n$ Configurations (MIT Press, Cambridge, 1963).
[S9] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-à. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, et al., J. Comput. Chem. 31, 224 (2010).
FIG. S1. The contributions from the intermediate states \( w (t^2/U) \) with respect to the excitation energy \( \Delta E \) for (a) the exact exchange interaction \( \hat{H}_\text{ex} \) and (b) the exchange within the \( 1/U \) approximation \( \hat{H}_{\text{ex}}^{1/U} \).

FIG. S2. The contributions from the excited states to the net exchange interaction \( (t^2/U) \) for (a) the exact exchange interaction and (b) the exchange within the \( 1/U \) approximation for the Dy-radical system \((n = 3)\).