Calculation of Multipolar Exchange Interactions in Spin-Orbital Coupled Systems

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A new method of computing multipolar exchange interaction in spin-orbit coupled systems is developed using multipolar tensor expansion of the density matrix in local density approximation + U electronic structure calculation. Within the mean field approximation, exchange constants can be mapped into a series of total energy calculations by the pair-flip approximation technique. The application to uranium dioxide shows an antiferromagnetic superexchange coupling in dipoles but a ferromagnetic one in quadrupoles which is very different from past studies. Further calculation of the spin-lattice interaction indicates it is of the same order with the superexchange and characterizes the overall behavior of the quadrupolar part as a competition between them.

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Magnetic systems with strong spin-orbit coupling, such as rare-earth and actinides compounds, have been a challenging problem for decades due to their complex magnetic behavior [1]. They display a rich coupled dynamics of spins and higher ranked moments which are frequently accompanied by the hybridization with phonons as is well known in archetypal nuclear fuel material, uranium dioxide (UO_2) [2]. They exhibit silent phenomena of hidden order phases as observed in URu_2Si_2 [3], NpO_2 [4], and some other systems. They not only have active orbital degrees of freedom, which make their physics rich in magnetic properties, but they also possess a large number of parameters in the form of corresponding intersite multipolar exchange interactions [1,5–15]. Those complex multipolar interactions have been suggested as the primary mechanism that induces those phases.

Unfortunately, efficient computational techniques to access the multipolar exchange interactions and solve the corresponding model Hamiltonians are not presently available. In the 1960s, Schrieffer *et al.* [5–7] proposed a framework regarding the exchange interactions mediated by the Ruderman-Kittel-Kasuya-Yosida mechanism in such systems. Unlike a traditional spin $1/2$ problem where a simple Heisenberg model describes the low-energy physics well [16], the orbital degrees of freedom introduce more complicated couplings, accompanied by large intersite anisotropy, which makes the problem computationally difficult [1]. In the 1980s, Cooper *et al.* [8–15] solved the Coqblin-Schrieffer Hamiltonian for Cerium compounds and, in the 1990s, proposed a scheme to compute the exchange constants via advanced electronic calculations. Although their works are in good agreement with experiments for selected simple materials, an efficient and systematic method to calculate the exchange interaction is still lacking.

In this work, we introduce a new method combined with electronic structure calculations based on density functional theory in its local density approximation (LDA) or including the correction due to the Hubbard U via the so-called LDA + U method [17], to compute the exchange interactions of systems with strong spin-orbit coupling. It is based on the theorem that multipolar tensor harmonics form a complete orthonormal basis set with respect to the trace inner product. Applying this theorem to the density matrix of the correlated magnetic orbital, well-defined scalar, dipole, quadrupole, and higher multipoles can be extracted [1]. By flipping a pair of tensor harmonics with respect to the ground-state density matrix, we can find the exchange interaction by relating (or mapping) it to the total energy cost of the tensor flip (which is obtained by the LDA + U calculation).

To test our new method, we use UO_2 as a test candidate due to the presence of dipolar and quadrupolar order in its ground state. UO_2 has been one of the widely discussed actinide compounds due to its applications in the nuclear energy industry. It is a Mott insulator with a cubic structure and well-localized $5f^2$ electrons (uranium configuration U^{4+} by naive charge counting). Below $T_N = 30.8$ K it undergoes a first-order magnetic and structural phase transition where a noncollinear an tiferromagnetic phase with transverse 3-$\mathbf{k}$ magnetic ordering accompanied by the cooperative Jahn-Teller distortion occurs [19] [Fig. 1(b)]. The two-electron ground state forms a Γ_5 triplet holding pseudospin $S = 1$ rotation symmetry, making it a good choice to test our method, as it is a minimal challenge beyond the $S = 1/2$ Heisenberg model. A description of a $S = 1$ exchange interaction requires the existence of dipolar and quadrupolar moments, and it is commonly believed that there are two major mechanisms to induce exchange coupling: (1) superexchange (SE) and (2) spin-lattice (SL) interaction. The former contributes to both the dipole and quadrupole and the latter contributes to the quadrupole only because of the symmetry of the distortion. The dominance of SE or SL in affecting the quadrupole

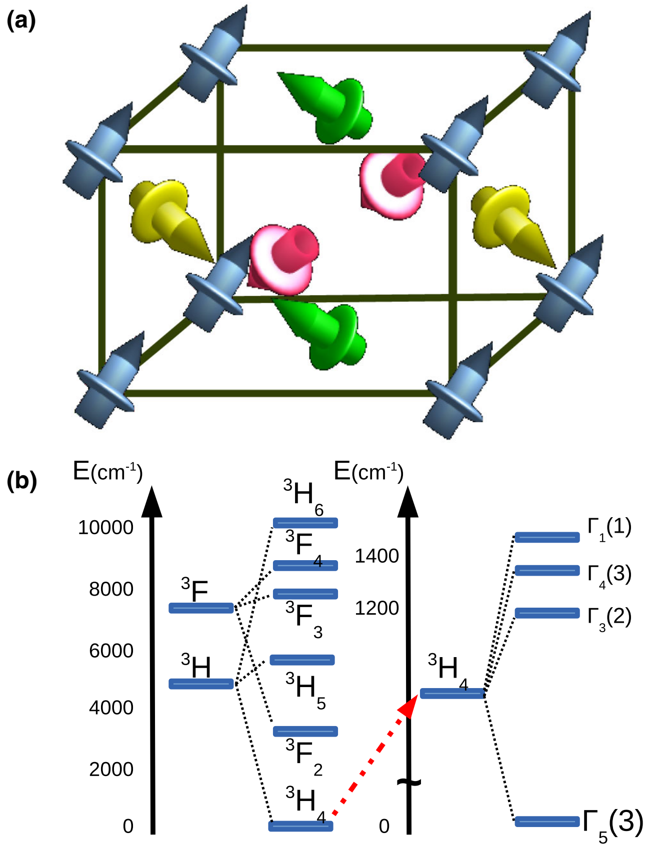

FIG. 1 (color online). (a) Magnetic moments of dipole (arrows) and quadrupoles (disks) in the 3-**k** structure. (b) The energy splitting of low lying states of UO_2 [19]. The ^3H and ^3F states of the free U^{4+} ion is split into $^3H_4$ multiplets and other excited states by spin-orbital coupling and further split into the Γ_5 triplet ground state by crystal fields. Inside the parentheses are their degeneracy.

exchange remains a controversial issue [18–21] [Fig. 1(a)]. Since our method is based on a static electronic calculation, we do not explore dynamical effects in all their details. Therefore, separate calculations using the coupled frozen-phonon and frozen-magnon techniques were performed to extract the SL coupling constants. Although we have chosen UO_2 as our test sample whose static exchange interactions originate from the superexchange mechanism, it should be emphasized that our method should be able to work for any other types of exchange processes.

A non-Hermitian unit spherical tensor operator is defined as

$$Y_K^Q(J) = \sum_{MM'}(-1)^{J-M}(2K+1)^2 \times \begin{pmatrix} J & J & K \\ M' & -M & Q \end{pmatrix} |JM\rangle\langle JM'|.$$

We can further define Hermitian cubic tensor harmonics $T_K^Q(J) = (1/\sqrt{2})[(-1)^Q Y_K^Q(J) + Y_K^{-Q}(J)]$ and $T_K^{-Q}(J) = (i/\sqrt{2})[Y_K^Q(J) - (-1)^Q Y_K^{-Q}(J)]$ [1]. Since we only focus on $J = 1$, the label of J will be omitted in the following. Based on the irreducible representations of $J = 1$, we can classify the cubic tensor harmonics as T^s for rank 0 (scalar), T^x, T^y, T^z for rank 1 (dipole), and T^{xy}, T^{yz}, T^{zx}, $T^{x^2-y^2}$, $T^{3z^2-r^2}$ for rank 2 (quadrupole) [18,20,22]. Since the Γ_5 triplet exhibits $S = 1$ symmetry, it is convenient to denote them using the basis states: $|p\rangle$, $p = +1, 0, -1$. The ground-state density matrix of a U ion can be expanded by cubic tensor harmonics: $\rho_i = \sum_m \alpha_i^m T_i^m$, where i is the site index, m is the projection index for cubic harmonics, and $\alpha_i^m = \mathrm{tr}(\rho_i^\dagger T_i^m)$ is the expansion coefficient. Since the triplet degeneracy of Γ_5 is further split below T_c, we can approximate the ground state as $|GS\rangle = |-1\rangle$, the lowest energy state of an isolated U ion in the 3-**k** magnetic phase. 3-**k** ordering requires the four U sublattice moments all point in inequivalent (1,1,1) directions, which means the $|-1\rangle$ states are defined in different local coordinates for each U sublattice [19]. Thus, we need to make a rotation on each site to ensure everything is in a common global coordinate. In the global system, the nonvanishing quadrupole components of the ground-state 3-**k** quadrupole order are xy, yz, and zx. Thus, the model Hamiltonian of the nearest-neighbor exchange interaction between magnetic U atoms is assumed to be

$$\begin{aligned} h^{EX} &= h^{\mathrm{SE}} + h^{\mathrm{SL}} \\ &= \sum_{m,i,j} C_{ij}^{mm} T_i^m T_j^m + \sum_{n,i,j} K_{ij}^{nn} T_i^n T_j^n \\ m &\in x, y, z, xy, yz, zx;\ n \in xy, yz, zx, \end{aligned} \tag{1}$$

where (i, j) are the nearest-neighbor site indices and $(C_{ij}^{mm}, K_{ij}^{nn})$ are the exchange constants from SE and SL, respectively. Couplings between tensor operators with different symmetry indices are prohibited by cubic symmetry. Since the coupling in h^{SL} is a dynamical effect, we will only focus on the h^{SE} part here and leave the h^{SL} part to a later discussion. The energy of h^{SE} under the mean field approximation is $E_0 = \langle h^{\mathrm{SE}} \rangle \simeq 2\sum_{m,i,j} C_{ij}^{mm} \langle T_i^m \rangle \langle T_j^m \rangle$. Suppose we make a transformation of the tensor components of the density matrices on U sublattices (i, j) in the same unit cell, say in the components of T_i^{xy} and T_j^{xy}: $\alpha_{i(j)}^{xy} \rightarrow \alpha_{i(j)}'^{xy}$. If so, $\langle T_{i(j)}^{xy} \rangle \rightarrow \langle T_{i(j)}^{xy} \rangle' = \langle T_{i(j)}^{xy} \rangle + \delta \langle T_{i(j)}^{xy} \rangle$ with $\delta \langle T_{i(j)}^{xy} \rangle = (\alpha_{i(j)}'^{xy} - \alpha_{i(j)}^{xy})$. When we calculate the energy difference between the transformed and original configurations, $(E' - E^0) = (\langle h^{\mathrm{SE}} \rangle' - \langle h^{\mathrm{SE}} \rangle)$, one can easily obtain a relation which is also true in general for other exchange constants:

$$C_{ij}^{mn} = \frac{1}{8} \frac{\delta^2 E_{ij}^{mn}}{\delta \langle T_i^m \rangle \delta \langle T_j^n \rangle}, \tag{2}$$

where $\delta^2 E_{ij}^{mn} = (\delta E_{ij}^{mn} - \delta E_i^m - \delta E_j^n)$ is the interaction energy of the transformed pair, $\delta E_i^m = (E_i^m - E_0)$ is the energy cost from making a transformation on the T_i^m component, and, similarly, $\delta E_{ij}^{mn} = (E_{ij}^{mn} - E_0)$ is the energy cost from making transformations on both T_i^m and T_j^n components. The prefactor $(1/8) = (1/4) \times (1/2)$ comes from the correction for the number of bonds between the U sublattice (i, j), the mean field factor, as well as any geometric or trigonometric factor due to the noncollinear order.

The basic idea of our method is to make the above transformations on the density matrices of the correlated magnetic ions in the LDA + U calculation. We then perform just one iteration in the self-consistent loop (to avoid any change in the input density matrices) and compute the correlation energy $\delta^2 E_{ij}^{mn}$ from the resulting band energies [16] as prescribed by the Andersen force theorem [23]. Obviously, a single exchange constant will need at least four values: no change (E_0), single-site change (E_i, E_j), and double-site changes (E_{ij}). The choice of the transformation has to preserve the symmetry of the crystal field, the charge density, and the magnitude of the magnetic moment to prevent any unwanted energy cost. A reasonable choice is to “flip” the orientation of magnetic moment by adding a minus sign on the expansion coefficient of the corresponding tensor component. When this is done, $\delta\langle T_i^m\rangle$ is always $-2\langle T_i^m\rangle$, which is equivalent to making a π rotation on the (x, y, z) components of the dipole and a $\pi/2$ rotation on the (xy, yz, zx) components of the quadrupole.

To generate density matrices that are compatible with the single-particle based LDA + U calculation, we introduce the reduced density matrix (RDM) as a useful single-particle approximation to the Γ_5 states [24] It is fulfilled by replacing the self-consistent density matrices by the pure $|\Gamma_5, -1\rangle$ RDMs on all uranium sites and treating them as the true ground state due to their identical symmetry and similar physical properties. We assume that the multipolar exchange Hamiltonian in spin-orbit coupling f-orbital space is built by replacing all tensor operators, density matrices, and mean values in the $S = 1$ space to their corresponding single-particle RDM: $\langle T_i^m\rangle \to \langle \mathcal{T}_i^m\rangle$, $\langle \rho_i\rangle \to \langle \mathcal{D}_i\rangle$. The single-particle exchange Hamiltonian shares the same exchange constants as the $S = 1$ two-particle version. Two things to notice here are (1) the RDM exhibits $J = (5/2)\oplus(7/2)$ symmetry instead of $S = 1$ and this means the rotation from local coordinates to the global coordinates has to be made in $S = 1$ space, or else the pseudospin quasiparticle description will be violated, and (2) the RDM replacement will rescale the length of an operator, i.e., $\mathrm{tr}(\mathcal{T}^\dagger\mathcal{T}) \neq \mathrm{tr}(T^\dagger T)$. Therefore, $\langle \mathcal{T}_i^m\rangle = \mathrm{tr}(\mathcal{D}^\dagger T_i^m)$ is different from $\langle T_i^m\rangle = \mathrm{tr}(\rho^\dagger T_i^m)$. So one has to be cautious when using Eq. (2).

The coupling constants can be simplified by symmetry to the form $C_{i,j}^{m,n} = C^{m,n}(\mathbf{R}) = C_0^{d/q}[1 - 2(1 - \chi_c^{d/q})\tau_m\tau_n]\delta_{m,n}$, where d/q means dipole or quadrupole and $\tau = \mathbf{R}/R$ is the direction vector between (i, j). These constants are shown in Table I, where the isotropic and anisotropic parts are described by $C_0^{d/q}$ and $\chi_c^{d/q}$, respectively [18]. With the comparison to other studies, the dipole part is similar, but the quadrupole part gives the opposite result from past calculations obtained by the best fit with experiments [20,21]. Not only is the anisotropy effect much smaller, but the sign is also different, which means the quadrupoles tend to be ferromagnetic. It also means that the SL effects must be as important as the SE and their combination makes the whole system antiferromagnetic.

TABLE I. Comparison between our calculated exchange interaction parameters using the LDA + U method with $U = 4.0$ eV and $J = 0.7$ eV and the existing experimental fits. C_0^d, C_0^q, K_0^q are in units of meV; others are dimensionless. Because all the works use different models to simulate the SL part, there is no appropriate values for them (labeled by *). Reference [21] obtained SL via a fully dynamic calculation with a long-range and frequency dependence. Note also that Ref. [18] assumes the quadrupole coupling only comes from SL with a real space exchange constant of the 3-$\mathbf{k}$ symmetric form: $K_{ij}^{\Gamma} = K_0 e^{i\mathbf{q}_\Gamma(\mathbf{R}_i - \mathbf{R}_j)}$. Reference [19] only calculates the SE part. Their parameters were obtained via the integrals of Coulomb interaction directly and has no a simple anisotropy form.

Reference	C_0^d	χ_c^d	C_0^q	χ_c^q	K_0^q	χ_K^q
Our Letter	1.70	0.3	−3.10	0.90	2.6	1.18
[21]	3.1	0.25	1.9	0.25	*	*
[18]	1.25	0.8	0	0	0.33	*
[19]	∼1	*	∼0.1	*	×	×

To explain the behavior of the quadrupolar part, we need to include the effect of the dynamic contribution from the SL. The coupling between spins and optical phonons can be written as

$$H_{\mathrm{SL}} = \sum_{\mathbf{q},n,j} V^n(\mathbf{q}, j) T^n(\mathbf{q}) u(\mathbf{q}, j),$$

where $T^n(\mathbf{q}) = \sum_{\mathbf{R}} T^n(\mathbf{R}) e^{i\mathbf{q}\cdot\mathbf{R}}$, $u(\mathbf{q}, j) = [a^\dagger(-\mathbf{q}, j) + a(\mathbf{q}, j)]$, and $a^\dagger(\mathbf{q}, j)$ is the creation operator of a phonon with wave vector $\mathbf{q}$ in mode j. Using the virtual phonon description, the SL exchange constant of h^{SL} can be approximated as

$$K^{n,n}(\mathbf{q}) \simeq \sum_j \frac{|V^n(\mathbf{q}, j)|^2}{h\omega(\mathbf{q}, j)} - \epsilon_0,$$

where $\omega(\mathbf{q}, j)$ is the phonon frequency and ϵ_0 is the on site exchange energy which should be subtracted [18]. The variables $u(\mathbf{q}, j)$ and $\omega(\mathbf{q}, j)$ have been calculated in one of our earlier works [25] and can be fitted to the entire Brillouin zone using a simple rigid-ion model [26,27]. If we further assume the quadrupoles only couple to t_{2g}^a and t_{2g}^b quadrupolar distortions of the O cage around each U ion, the coupling constants are assumed to have the form $V^n(\mathbf{q}, j) = \gamma_a \psi_a^n(\mathbf{q}, j) + \gamma_b \psi_b^n(\mathbf{q}, j)$, where $\gamma_{a/b}$ are the parameters to be determined, $\psi^n_{a/b}(\mathbf{q},j)$ are the inner products (projection) between the phonon distortion $u(\mathbf{q},j)$ and $t^{a/b}_{2g}$ distortion, and $u(\mathbf{q},j)$ can be regarded as the distortion due to a phonon mode [28]. We estimate the parameters $\gamma_{a/b}$ by using the following coupled frozen-phonon and frozen-magnon techniques. (1) Make a $t^{a/b}_{2g}$ distortion of the O cage around a U ion. (2) Flip a particular tensor component of the single-ion RDM on a particular site. (3) Calculate the correlation energies, $\delta^2 E^{mn}_{a/b} = [\delta E^{mn}_{a/b} - \delta E^{0n}_{a/b} - \delta E^{m0}]$, where the first superscript is the symmetry index of the quadrupole and the latter index is of $t^{a/b}_{2g}$, so $\delta^2 E^{mn}_{a/b}$ is the extra energy of making the "flip + frozen phonon distortion" simultaneously compared to the energies of the individual flip plus the individual "frozen-phonon distortion." (4) Then, the parameters are roughly $\gamma_a \sim \delta^2 E^{mn}_a/\sqrt{2}\langle T^m\rangle\psi^n_a$ and $\gamma_b \sim \delta^2 E^{mn}_b/\langle T^m\rangle\psi^n_b$. There is a factor $\sqrt{2}$ in γ_a because when we make the same displacement of each coordinate component, the length of the total displacement is $\sqrt{2}$ larger than t^b_{2g}. By assuming the unit of phonon vibration about 0.014 Å (as is the static Jahn-Teller distortion [19]) and making a t_{2g} distortion 3% of the lattice constant, we have $\gamma_a = 34$ meV and $\gamma_b = 48$ meV. We can access nearest-neighbor constants by calculating $K^{n,n}(\mathbf{q},j)$ at $\mathbf{q} = [0,0,0]$ and $\mathbf{q} = (2\pi/a)[1,0,0]$, and by a subsequent fit to a cosine function with the on site exchange energy assumed to be the average of the curve [18]. We then have $K^{m,n}_{i,j} = K^{m,n}(\mathbf{R}) = K^q_0[1 - 2(1-\chi^q_k)\tau_m\tau_n]\delta_{m,n}$ with $K^q_0 = 2.6$ meV and $\chi^q_k = 1.18$.

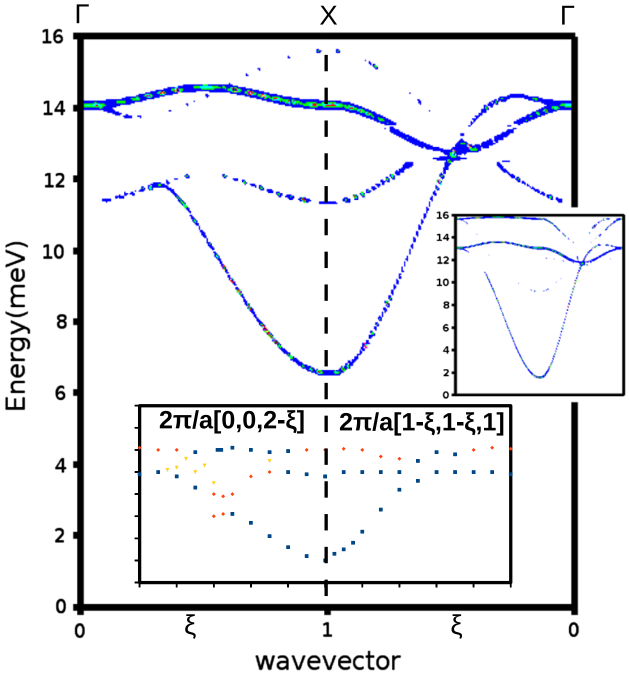

FIG. 2 (color online). Magnetic excitation of UO_2 along two symmetry directions calculated by scanning the color map of the real part two-ion susceptibility of our model Hamiltonian [18] with parameters shown in Table I. Right inset: The same calculation made by requiring the overall quadrupole coupling to have 3-$\mathbf{k}$ symmetry: $K^{\Gamma}_{ij} = K_0 e^{i\mathbf{q}_\Gamma(\mathbf{R}_i - \mathbf{R}_j)}$ with $K_0 = 0.5$ meV [18]. Anisotropy gap is greatly reduced. Bottom inset: Data from inelastic neutron scattering experiments plotted in the same x-y scale [29]. Triangles (yellow) are measured in a direction differing by a reciprocal lattice vector [30]. Rhombuses (orange) are the weaker cross section.

Combined with the superexchange contribution and using the Green's function method with a random phase approximation [18], we calculate the magnetic excitation spectrum that is shown in Fig. 2. We find that the values and the characteristics of our results are basically in agreement with experiments. The major difference is the disappearance of anticrossing at a few $\mathbf{q}$ points and much larger anisotropy (gap) at the X point. The disappearance of the anticrossing is reasonable because it comes from the coupling between the magnon and phonon branches. As for the overestimated anisotropy at the X point, it is believed to come from the oversimplified SL model in our calculation. We have plotted the spin or quadrupolar wave spectrum by enforcing the overall quadrupole coupling to have 3-$\mathbf{k}$ symmetry as in Ref. [21] with the parameter $K_0 = 0.5$ meV (which is almost the same value as our isotropic part) and it gives a much smaller gap which fits the experiments well (see Fig. 2). It demonstrates that a SL model which makes the whole quadrupole coupling to have 3-$\mathbf{k}$ symmetry will be helpful in fitting the experiment but, in this case, the simple form of our model is also lost.

In conclusion, we have developed a new and efficient method for computing the exchange interactions in systems with strong spin-orbit coupling. With its application to UO_2, the superexchange mechanism is found to have a very interesting ferromagnetic quadrupolar coupling which has not been previously reported. We also performed estimates of the spin-lattice coupling via a similar technique and the overall behavior is accounted for by combining both effects. An accurate description of the spin-lattice interaction is still an issue and will be a subject for future work.

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