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Effect of covalency and interactions on the trigonal splitting in Na_xCoO_2

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We calculate the effective trigonal crystal field Δ that splits the t_{2g} levels of effective models for Na_xCoO_2 as the local symmetry around a Co ion is reduced from O_h to D_{3d}. To this end, we solve numerically a CoO_6 cluster containing a Co ion with all $3d$ states and their interactions included, and its six nearest-neighbor O atoms, with the geometry of the system, in which the CoO_6 octahedron is compressed along a C_3 axis. We obtain $\Delta \approx 130$ meV, with the sign that agrees with previous quantum chemistry calculations but disagrees with first-principles results in the local density approximation (LDA). We find that Δ is very sensitive to a Coulomb parameter that controls the Hund coupling and charge distribution among the d orbitals. The origin of the discrepancy with LDA results is discussed.

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I. INTRODUCTION

The doped layered hexagonal cobaltates Na_xCoO_2 have attracted great interest in the last years due to the high thermopower and at the same time low thermal conductivity and resistivity for $0.5 < x < 0.9$,[1,2] and the discovery of superconductivity in hydrated Na_xCoO_2.[3] Further attention was motivated by the fact that first-principles calculations in the local density approximation (LDA)[4–6] predicted a Fermi surface with six prominent hole pockets along the Γ-K direction, which are absent in measured angle-resolved photoemission (ARPES) spectra.[7,8] To explain the discrepancy, several calculations including correlation effects were made.[9–15] These studies used an effective model H_{eff} for the t_{2g} $3d$ states of Co, split by the trigonal crystal field Δ into an a'_{1g} singlet and an e'_g doublet.[16] Except for some simplifications used in the different works, H_{eff} has the form

$$\begin{aligned} H_{\text{eff}} = {} & \sum_{i,\sigma} \Delta \left(\sum_{\beta \in e'_g} \tilde{d}^{\dagger}_{i\beta\sigma} \tilde{d}_{i\beta\sigma} - \tilde{d}^{\dagger}_{ia'_{1g}\sigma} \tilde{d}_{ia'_{1g}\sigma} \right) \\ & + \sum_{i\delta\beta\gamma\sigma} \tilde{t}^{\beta\gamma}_{\delta} (\tilde{d}^{\dagger}_{i+\delta,\beta\sigma} \tilde{d}_{i\gamma\sigma} + \text{H.c.}) + U_{\text{eff}} \sum_{i\beta} \tilde{n}_{i\beta\uparrow} \tilde{n}_{i\beta\downarrow} \\ & + \frac{1}{2} \sum_{i,\gamma\neq\beta,\sigma\sigma'} (U'_{\text{eff}} \tilde{n}_{i\gamma\sigma} \tilde{n}_{i\beta\sigma'} + J_{\text{eff}} \tilde{d}^{\dagger}_{i\gamma\sigma} \tilde{d}^{\dagger}_{i\beta\sigma'} \tilde{d}_{i\gamma\sigma'} \tilde{d}_{i\beta\sigma}) \\ & + J'_{\text{eff}} \sum_{\gamma\neq\beta} \tilde{d}^{\dagger}_{i\gamma\uparrow} \tilde{d}^{\dagger}_{i\gamma\downarrow} \tilde{d}_{i\beta\downarrow} \tilde{d}_{i\beta\uparrow}, \end{aligned} \tag{1}$$

where $\tilde{d}^{\dagger}_{i\beta\sigma}$ creates a hole on an *effective* t_{2g} orbital at site i with spin σ. The first term is the effective trigonal splitting mentioned above, the second term describes the hopping between orbitals at a distance δ and the remaining terms are effective interactions discussed for example in Ref. 17.

In most works, Δ and $\tilde{t}^{\beta\gamma}_{\delta}$ were derived from fits to the LDA bands and the interaction parameters were estimated. These fits give either $\Delta = -10$ meV (Ref. 9) or $\Delta = -130$ meV (Ref. 10). With these parameters and realistic values of the Coulomb repulsion U_{eff}, correlations are not able to reconcile theory with experiment, as shown by different dynamical-mean-field-theory (DMFT) studies.[12,13,15] The pockets still remain in the calculations.

Using instead an H_{eff} derived from a multiband Co-O model H_{mb} through a low-energy reduction procedure,[17] and the value $\Delta = 315$ meV obtained from quantum-chemistry configuration-interaction calculations,[18] these pockets are absent and the electronic dispersion near the Fermi energy agrees with experiment.[15] In this procedure, no LDA results were used. The parameters of H_{mb} were taken from previous fits of of polarized x-ray absorption spectra,[19] and the parameters of H_{eff} other than Δ were obtained fitting the energy levels of an undistorted CoO_6 cluster (O_h symmetry) and calculating the effective hopping between different CoO_6 clusters,[17] following similar ideas that were successful in the superconducting cuprates.[20–22] In these systems, low-energy reduction procedures that eliminate the O degrees of freedom, simplifying the problem to an effective one-band one,[20,23–29] have been very successful, in spite of the fact that doped holes enter mainly at O atoms.[30–32] Optical properties related with O atoms were calculated using these one-band models, which do not contain O states.[20,21]

Summarizing previous results, if Δ is taken as a parameter, a positive Δ has the effect of shrinking the pockets, and for large enough Δ, the pockets disappear from the Fermi surface, reconciling theory with ARPES experiments.[12,13,15] A positive value has been obtained by quantum-chemistry methods[18] and a negative one is obtained fitting the LDA dispersion with H_{eff}.[9,10] Thus the origin of the discrepancy between different methods and the actual value of Δ remains a subject of interest.

It is known that in general, the LDA underestimates gaps and has difficulties in predicting one-particle excitations energies. Thus one might suspect that the parameters of H_{eff}, including Δ calculated with LDA are not accurate enough when covalency and interactions are important. This is the case of NiO, for which agreement with experiment in LDA+DMFT calculations is only achieved once the O bands are explicitly included in the model,[33] or when the O atoms have been integrated out using low-energy reduction procedures, which take into account correlations from the beginning.[33,34]

In covalent materials, the crystal-field splitting of transition-metal ions is dominated by the hopping of electrons between these ions and their nearest ligands.[35] In particular for Na_xCoO_2, an estimate based on point charges gives $\Delta = -25$ meV.[36] This shows that the effect of interatomic repulsions is small and of the opposite sign as that required to explain the ARPES spectra. The effects of covalency of Co and its nearest-neighbor O atoms and all Co-Co interactions are included in a CoO_6 cluster in the realistic (D_{3d}) symmetry. In this work, we solve numerically this cluster and calculate the effective splitting Δ, neglecting interatomic repulsions. We also analyze the effects of different parameters on Δ. The main result is that $\Delta \simeq 130$ meV and is very sensitive to a parameter that controls the Hund rules. It is also sensitive to the cubic crystal-field splitting $10Dq$. A possible reason of the discrepancy with the LDA results is discussed.

In Sec. II, we describe the model, parameters, and briefly the formalism. Section III contains the results. Section IV is a summary and discussion.

II. THE MODEL AND ITS PARAMETERS

The multiband model from which $H_{\rm eff}$ is derived, describes the $3d$ electrons of Co and the $2p$ electrons of the O atoms, located in the positions determined by the structure of $Na_{0.61}CoO_2$ at 12 K.[37] In this work, we restrict the calculation to a cluster of one Co atom and its six nearest-neighbor O atoms. The relevant filling for the calculation of Δ corresponds to formal valences Co^{4+} and O^{2-}, or 41 electrons to occupy the $3d$ shell of Co and the $2p$ shells of the six O atoms. This corresponds to five holes in the CoO_6 cluster. Thus, it turns out to be simpler to work with hole operators (which annihilate electrons) acting on the vacuum state in which the Co ion is in the $3d^{10}$ configuration and the O ions are in the p^6 one. The most important physical ingredients are the interactions inside the $3d$ shell H_I and the Co-O hopping ($t_j^{\eta\xi}$ below), parameterized as usual, in terms of the Slater-Koster parameters.[38] We include a cubic crystal field splitting $\epsilon_{t_{2g}} - \epsilon_{e_g} = 10Dq$

The Hamiltonian for the CoO_6 cluster takes the form

$$H_{\rm mb} = \sum_{\alpha\in e_g,\sigma} \epsilon_{e_g} d^\dagger_{\alpha\sigma} d_{\alpha\sigma} + \sum_{\beta\in t_{2g},\sigma} \epsilon_{t_{2g}} d^\dagger_{\beta\sigma} d_{\beta\sigma} + H_I + \sum_{j\eta\sigma} \epsilon_{\rm O} p^\dagger_{j\eta\sigma} p_{j\eta\sigma} + \sum_{j\eta\xi\sigma} t_j^{\eta\xi} (p^\dagger_{j\eta\sigma} d_{\xi\sigma} + {\rm H.c.}). \quad (2)$$

The operator $d^\dagger_{\xi\sigma}$ creates a hole on the orbital ξ of Co with spin σ. Similarly, $p^\dagger_{j\eta\sigma}$ creates a hole on O $2p$ orbital η at site j with spin σ. The first two terms corresponds to the energy of the e_g orbitals ($x^2 - y^2$, $3z^2 - r^2$) and t_{2g} orbitals (xy, yz, zx) written on a basis in which x, y, and z, point to the vertices of a regular CoO_6 octahedron (symmetry O_h). The compression along the axis $x + y + z$ reduces the symmetry to D_{3d} and splits the states of symmetry $xy + yz + zx$ (a'_{1g} in D_{3d}[16]) from the other two t_{2g} ones (e'_g in D_{3d}).

H_I contains all interactions between d holes assuming spherical symmetry [the symmetry is reduced to O_h by the cubic crystal field $10Dq$ and to D_{3d} by the last (hopping) term of Eq. (2)]. The expression of H_I is lengthy. It is included in Appendix [Eq. (A4)] together with a brief description of its derivation for the interested reader. A more detailed discussion is in Ref. 17. The form of H_I is rather simple and well known when either only e_g orbitals[39] or only t_{2g} orbitals [as in Eq. (1)][40,41] are important, although the correct expressions were not always used.[40,42] In the general case, H_I contains new terms which are often disregarded. For example, in a recent study of Fe pnictides,[43] a simplified expression derived previously[44] was used. More recently, to estimate the effective Coulomb interaction for transition-metal atoms on metallic surfaces, only density-density interactions were included.[45] Some of the effects of these simplifications were discussed in Ref. 17.

All interactions are given in terms of three free parameters $F_0 \gg F_2 \gg F_4$. For example, the Coulomb repulsion between two holes or electrons at the same $3d$ orbital is $U = F_0 + 4F_2 + 36F_4$, and the Hund rules exchange interaction between two e_g (t_{2g}) electrons is $J_e = 4F_2 + 15F_4$ ($J_t = 3F_2 + 20F_4$). Thus F_2 is the main parameter responsible for the spin and orbital polarizations related with the first and second Hund rules, respectively.

Note that in Eq. (2) there is no trigonal splitting. This means that we take the *bare* value of the splitting $\Delta_0 = 0$ (neglecting the effect of interatomic repulsions). The *dressed* value Δ that enters the effective Hamiltonian Eq. (2) is calculated as

$$\Delta = E(e'_g) - E(a'_{1g}), \quad (3)$$

where $E(\Gamma)$ is the energy of the lowest lying state that transforms under symmetry operations according to the irreducible representation Γ of the point group D_{3d}.[16]

As in previous calculations for the regular CoO_6 octahedron (with symmetry O_h),[17] the diagonalization is simplified by the fact that several linear combinations of O $2p$ orbitals do not hybridize with the Co $3d$ ones, forming nonbonding orbitals. However, in the present case, the reduced D_{3d} symmetry increases the bonding $2p$ combinations to seven, and a different basis should be used, but still the size of the relevant Hilbert space is small enough to permit the diagonalization numerically by the Lanczos method.[46]

As a basis for the present study, we take parameters determined previously[19] from a fit of polarized x-ray absorption spectra of Na_xCoO_2 to the results of a CoO_6 cluster with four and five holes including the core hole. In the present case, we have neglected the O-O hopping for simplicity (this allows a reduction of the relevant Hilbert space). Thus the parameters of $H_{\rm mb}$ in eV are[19]

$$\begin{gathered} F_0 = 3.5,\ F_2 = 0.2,\ F_4 = 0.006, \\ \epsilon_{\rm O} = 13,\ \epsilon_{t_{2g}} = 1.2, \epsilon_{e_g} = 0, \\ (pd\pi) = \frac{-\sqrt{3}}{4}(pd\sigma) = 1. \end{gathered} \quad (4)$$

The choice of the origin of on-site energies $\epsilon_{e_g} = 0$ is arbitrary. The resulting values of $U = 4.516$ eV and charge transfer energies are similar to those derived from other x-ray absorption experiments.[47] We note that while above $\epsilon_{t_{2g}} - \epsilon_{e_g} = 10Dq = 1.2$ eV, the effect of hybridization increases the splitting between t_{2g} and e_g orbitals to more than 3 eV.

III. RESULTS

The splitting Δ is determined from Eq. (3). We have also calculated the occupation of the a'_{1g} $3d$ orbital in each state to verify that the expected physics is obtained.

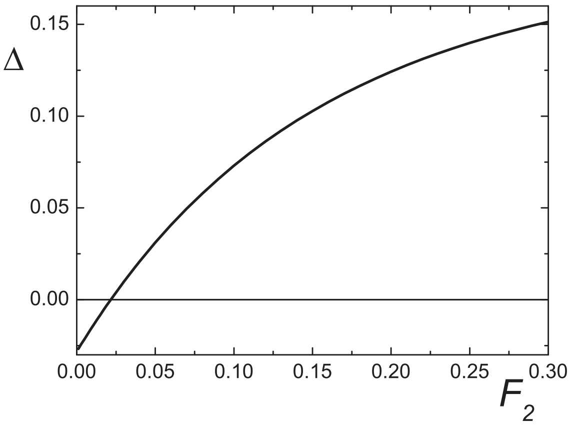

FIG. 1. Trigonal splitting as a function of F_2 keeping the remaining parameters as given by Eq. (4).

For the parameters determined previously [Eq. (4)], we obtain $\Delta = 124$ meV. The sign agrees with quantum-chemistry configuration-interaction calculations[18] which obtained $\Delta \approx 300$ meV, although our magnitude is smaller. The difference might be at least partially due to some uncertainty in our parameters determined from a fitting procedure. Motivated by this possibility, we have studied the effect of different parameters on the results. Of course, since we have neglected interatomic interactions, Δ vanishes if the hopping parameters $pd\sigma$ and $pd\pi$ are zero, and one would expect than an increase in these parameters, has the largest impact on Δ. However, we find that an increase of 50% in the hopping increases Δ by only 25%. In addition, changes of the oxygen energy ϵ_O (the charge transfer energy) or F_0 (which determines the intraorbital Coulomb repulsion U) by 1 eV have an effect of only a few percent on Δ.

Instead, and rather surprisingly, as shown in Fig. 1, Δ is very sensitive to F_2, the most important parameter in the expressions for the exchange between d electrons [J_ν with $\nu = e, t, a$ or b in Eq. (A4)] and the interorbital repulsions ($U - 2J_\nu$) among other interactions. Thus it is the main responsible for the spin and orbital polarizations resulting in the first and second Hund rules. In particular, the repulsion between different e_g (t_{2g}) orbitals is reduced with respect to the intraorbital repulsion U by $2J_e$ ($2J_t$) (see Appendix).

Δ becomes negative for $F_2 < 21$ meV. Curiously, increasing F_4 has a small effect, but in the *opposite* sense as increasing F_2. This points to nontrivial effects of the correlations, particularly those involving both e_g and t_{2g} electrons. When both F_2 and F_4 vanish, we obtain a small positive value $\Delta = 12$ meV. If one adds to this result the contribution -25 meV from the interatomic Coulomb repulsion estimated using point charges,[36] one obtains a value close to -10 meV, obtained in one of the LDA calculations.[9] This suggest that the LDA negative results for Δ might be due to the difficulties of LDA in treating correlations related with the Hund rules. In particular, it is known that orbital-related Coulomb interactions are underestimated in the spin LDA,[48] and empirical orbital polarization corrections[49] are frequently used to cure this problem. This fact has been also analyzed in the framework of a self-consistent tight-binding theory.[50]

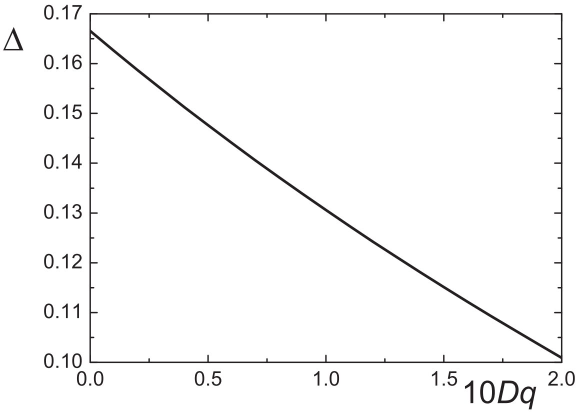

FIG. 2. Trigonal splitting as a function of the cubic crystal field keeping the remaining parameters as given by Eq. (4).

The fact that correlations between both e_g and t_{2g} holes play a role is supported by the dependence of Δ on the cubic crystal field parameter $10Dq$, displayed in Fig. 2. Note that this parameter in the present case represents only the contribution of interatomic repulsion to $10Dq$. The covalency part is included in our calculation and the splitting between hybridized e_g and t_{2g} is larger than 3 eV. Also in the fitting procedure, the best value of $10Dq$ depends on composition x, being 1.2 eV for $x = 0.4$ and 0.9 eV for $x = 0.6$.[19] For the latter, value Δ increases to 134 meV. As it is apparent in Fig. 2, Δ increases with decreasing $10Dq$. This shows that the e_g states play an important role. In fact, the results for the regular octahedron show that although these states are absent in the effective Hamiltonian for the cobaltates, they have a larger degree of covalency than the t_{2g} states.[17] Most of the O holes reside in bonding combinations of e_g symmetry.

IV. SUMMARY AND DISCUSSION

Using exact numerical diagonalization of a CoO_6 cluster, with the realistic geometry of Na_xCoO_2, we have calculated the effects of covalency and interactions on the trigonal crystal-field parameter Δ, which splits the t_{2g} states in O_h symmetry into a'_{1g} and e'_g in the reduced D_{3d} symmetry. This parameter enters effective models [of the form of Eq. (1)] for the description of the electronic structure of Na_xCoO_2 and only positive values (in contrast to the negative ones obtained from LDA) seem consistent with ARPES data.[12,13,15] We obtain $\Delta \approx 130$ meV.

While changes of the order of 1 eV in charge-transfer energy or F_0 (which controls the part of the Coulomb repulsion that does not depend of the symmetry of the orbitals) do not affect Δ very much, we find that Δ is very sensitive to the parameter F_2, which controls (among others) interaction constants related with the Hund rules (exchange interactions and decrease of interorbital repulsions with respect to intraorbital ones). To a smaller extent, it is also sensitive to the cubic crystal field $10Dq$ reflecting the importance of interactions between t_{2g} and e_g states, and the effect on the latter on the effective parameters.

Since the LDA underestimates correlations that affect the orbital polarization of the d states,[48–50] this is likely to be the reason of the failure of LDA approaches and effective models based on LDA parameters, to reproduce the observed ARPES data. In fact, since the exchange and correlations in LDA are based on a homogeneous electron gas, it is expected that this approximation treats F_0 (the part of the repulsion which does not distinguish between different orbitals) in mean field, but does not contain the effects of F_2 and F_4, which depend on the particular orbitals. The exchange of the electron gas taken into account in the LDA helps to follow the first Hund rule (maximum spin), but the second one, related with orbital polarization, is not well described and seems crucial to establish effective energy differences between different orbitals inside an incomplete d shell.

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APPENDIX: INTERACTIONS INSIDE A *d* SHELL

The part of the Hamiltonian that contains the interaction among ten d spin-orbitals is[51]

$$H_I = \frac{1}{2} \sum_{\lambda\mu\nu\rho} V_{\lambda\mu\nu\rho} d^+_\lambda d^+_\mu d_\rho d_\nu, \tag{A1}$$

where d^+_λ creates an electron or a hole at the spin-orbital λ (H_I is invariant under an electron-hole transformation) and (neglecting screening by other electrons),

$$V_{\lambda\mu\nu\rho} = \int d\mathbf{r}_1 d\mathbf{r}_2 \bar{\varphi}_\lambda(\mathbf{r}_1)\bar{\varphi}_\mu(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_\nu(\mathbf{r}_1)\varphi_\rho(\mathbf{r}_2), \tag{A2}$$

where $\varphi_\lambda(\mathbf{r}_1)$ is the wave function of the spin-orbital λ. Assuming spherical symmetry, these integrals can be calculated using standard methods of atomic physics[52] in terms of three independent parameters F_j, $j = 0,2,4$, which are related to decomposition of the Coulomb interaction $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ in spherical harmonics of degree j. To remove uncomfortable denominators, the three free parameters are defined as $F_0 = R^0$, $F_2 = R^2/49$, and $F_4 = R^4/441$, where

$$R^k = e^2 \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R^2(r_1) R^2(r_2) r_1^2 r_2^2 dr_1 dr_2, \tag{A3}$$

$R(r)$ is the radial part of the wave function of the d orbitals and $r_<$ ($r_>$) is the smaller (larger) between r_1 and r_2. The angular integrals are given in terms of tabulated coefficients.[17,52] Screening reduces F_0 significantly, but not F_2 and F_4.

The final result can be written in the form below.[17] To express it in a more compact form, we introduce different sums which run over a limited set of orbitals as follows. The sums over α run over the five d orbitals, those over β,γ run only over the t_{2g} orbitals xy, yz, zx, and those over χ (ζ) run over the pair of orbitals $x^2 - y^2$, xy (zx,zy).

The values of the different interactions energies below are given in terms of the F_j as follows: $U = F_0 + 4F_2 + 36F_4$, $J_e = 4F_2 + 15F_4$, $J_t = 3F_2 + 20F_4$, $J_a = 35F_4$, $J_b = F_2 + 30F_4$, and $\lambda = \sqrt{3}(F_2 - 5F_4)$.

The interaction is

$$\begin{aligned} H_I = {} & U \sum_\alpha n_{\alpha,\uparrow} n_{\alpha,\downarrow} + (U - 2J_e) \sum_\chi \sum_{\sigma_1,\sigma_2} n_{\chi,\sigma_1} n_{3z^2-r^2,\sigma_2} + \frac{U - 2J_t}{2} \sum_{\beta\neq\gamma} \sum_{\sigma_1,\sigma_2} n_{\beta,\sigma_1} n_{\gamma,\sigma_2} + (U - 2J_t) \sum_\zeta \sum_{\sigma_1,\sigma_2} n_{x^2-y^2,\sigma_1} n_{\zeta,\sigma_2} \\ & +(U - 2J_a) \sum_{\sigma_1,\sigma_2} n_{x^2-y^2,\sigma_1} n_{xy,\sigma_2} + (U - 2J_b) \sum_\zeta \sum_{\sigma_1,\sigma_2} n_{3z^2-r^2,\sigma_1} n_{\zeta,\sigma_2} + J_e \sum_\chi \sum_{\sigma_1,\sigma_2} d^\dagger_{\chi,\sigma_1} d^\dagger_{3z^2-r^2,\sigma_2} d_{\chi,\sigma_2} d_{3z^2-r^2,\sigma_1} \\ & + \frac{J_t}{2} \sum_{\beta\neq\gamma} \sum_{\sigma_1,\sigma_2} d^\dagger_{\beta,\sigma_1} d^\dagger_{\gamma,\sigma_2} d_{\beta,\sigma_2} d_{\gamma,\sigma_1} + J_t \sum_\zeta \sum_{\sigma_1,\sigma_2} d^\dagger_{x^2-y^2,\sigma_1} d^\dagger_{\zeta,\sigma_2} d_{x^2-y^2,\sigma_2} d_{\zeta,\sigma_1} + J_a \sum_{\sigma_1,\sigma_2} d^\dagger_{x^2-y^2,\sigma_1} d^\dagger_{xy,\sigma_2} d_{x^2-y^2,\sigma_2} d_{xy,\sigma_1} \\ & + J_b \sum_\zeta \sum_{\sigma_1,\sigma_2} d^\dagger_{3z^2-r^2,\sigma_1} d^\dagger_{\zeta,\sigma_2} d_{3z^2-r^2,\sigma_2} d_{\zeta,\sigma_1} + J_e \sum_\chi (d^\dagger_{\chi,\uparrow} d^\dagger_{\chi,\downarrow} d_{3z^2-r^2,\downarrow} d_{3z^2-r^2,\uparrow} + \text{H.c.}) + J_t \sum_{\beta\neq\gamma} d^\dagger_{\beta,\uparrow} d^\dagger_{\beta,\downarrow} d_{\gamma,\downarrow} d_{\gamma,\uparrow} \\ & + J_t \sum_\zeta (d^\dagger_{x^2-y^2,\uparrow} d^\dagger_{x^2-y^2,\downarrow} d_{\zeta,\downarrow} d_{\zeta,\uparrow} + \text{H.c.}) + J_a (d^\dagger_{x^2-y^2,\uparrow} d^\dagger_{x^2-y^2,\downarrow} d_{xy,\downarrow} d_{xy,\uparrow} + \text{H.c.}) \\ & + J_b \sum_\zeta (d^\dagger_{3z^2-r^2,\uparrow} d^\dagger_{3z^2-r^2,\downarrow} d_{\zeta,\downarrow} d_{\zeta,\uparrow} + \text{H.c.}) + \lambda \sum_{\sigma_1,\sigma_2} [2(n_{yz,\sigma_1} - n_{zx,\sigma_1})(d^\dagger_{3z^2-r^2,\sigma_2} d_{x^2-y^2,\sigma_2} + \text{H.c.}) \\ & - 2(d^\dagger_{3z^2-r^2,\sigma_1} d_{xy,\sigma_1} + \text{H.c.})(d^\dagger_{zx,\sigma_2} d_{yz,\sigma_2} + \text{H.c.}) + \sqrt{3}(d^\dagger_{x^2-y^2,\sigma_1} d_{zx,\sigma_1} + \text{H.c.})(d^\dagger_{xy,\sigma_2} d_{yz,\sigma_2} + \text{H.c.}) \\ & - \sqrt{3}(d^\dagger_{x^2-y^2,\sigma_1} d_{yz,\sigma_1} + \text{H.c.})(d^\dagger_{xy,\sigma_2} d_{zz,\sigma_2} + \text{H.c.}) + (d^\dagger_{3z^2-r^2,\sigma_1} d_{zx,\sigma_1} + \text{H.c.})(d^\dagger_{xy,\sigma_2} d_{yz,\sigma_2} + \text{H.c.}) \\ & + (d^\dagger_{3z^2-r^2,\sigma_1} d_{yz,\sigma_1} + \text{H.c.})(d^\dagger_{xy,\sigma_2} d_{zx,\sigma_2} + \text{H.c.}) + (d^\dagger_{3z^2-r^2,\sigma_1} d^\dagger_{zx,\sigma_2} d_{x^2-y^2,\sigma_2} d_{zx,\sigma_1} - d^\dagger_{3z^2-r^2,\sigma_1} d^\dagger_{yz,\sigma_2} d_{x^2-y^2,\sigma_2} d_{yz,\sigma_1} + \text{H.c.})] \\ & + \lambda[(d_{x^2-y^2,\downarrow} d_{3z^2-r^2,\uparrow} - d_{x^2-y^2,\uparrow} d_{3z^2-r^2,\downarrow})(d^\dagger_{zx,\uparrow} d^\dagger_{zx,\downarrow} - d^\dagger_{yz,\uparrow} d^\dagger_{yz,\downarrow}) + \text{H.c.}]. \end{aligned} \tag{A4}$$

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