An effective spin-orbital Hamiltonian for the double perovskite \( \text{Sr}_2\text{FeWO}_6 \): Derivation of the phase diagram.

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We formulate a superexchange theory of insulating double-perovskite compounds such as \( \text{Sr}_2\text{FeWO}_6 \). An effective spin-orbital Hamiltonian is derived in the strong coupling limit of Hubbard model for \( d \)-electrons on Fe and W ions. The relevant degrees of freedom are the spins \( S = 2 \) and the three-fold orbital degeneracy of \( \text{Fe}^{2+} \)-ions. W-sites are integrated out by means of a fourth-order perturbative expansion. The magnetically and orbitally ordered ground states of the effective Hamiltonian are discussed as a function of the model parameters. We show that for realistic values of such parameters the ground state is antiferromagnetic, as experimentally observed. The order found is of type-II, consisting of \{111\} ferromagnetic planes stacked antiferromagnetically. The orbital order energy scale found is one order of magnitude less than the spin one.

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I. INTRODUCTION.

Transition metal oxides have been the subject of numerous experimental and theoretical studies after the discovery of a variety of novel physical phenomena and a diversity of ordered phases.\(^1\) Their ground state can be insulating, metallic or superconducting, depending on temperature and stoichiometry and their magnetic structure varies from ferromagnetic (FM) to different antiferromagnetic (AFM) types. The insulating behavior is generally attributed to a large Coulomb interaction that localizes the \( d \)-electrons in Mott-Hubbard or charge-transfer regimes.\(^2\) In this case low energy excitations can be described by the spin degrees of freedom through an effective superexchange model. Often, the ground state of the transition metal ion possesses an orbital degeneracy in addition to its that originating from the spin. In such cases, orbital degrees of freedom are also incorporated in the superexchange theory and the system is described by means of an effective spin-orbital model.\(^3\)

The purpose of the present work is to formulate such a superexchange theory and derive a spin-orbital Hamiltonian for the antiferromagnetic insulator \( \text{Sr}_2\text{FeWO}_6 \). The experimental value of its Ne\(\acute{e}\)el temperature \( T_N \) is quite low and reported in the literature as \( 15 \) K. \( \text{Sr}_2\text{FeWO}_6 \) belongs to a family of double perovskite compounds with general formula \( \text{A}_2\text{BB’O}_6 \). It has, however, electronic and magnetic properties which differ significantly from those of the other members of the family. For example, \( \text{Sr}_2\text{FeMoO}_6 \) and \( \text{Sr}_2\text{FeReO}_6 \), that have been the subject of the intense studies since the discovery of room temperature magnetoresistance in these compounds are half-metallic ferromagnets with fairly high magnetic transition temperatures.\(^7\) One of the reason why \( \text{Sr}_2\text{FeWO}_6 \) is so different from the other members of the group has been suggested by band structure analysis.\(^7\) In this picture, the antibonding \( W(5d) \) states are pushed higher in energy by the stronger hybridization with oxygen \( p \)-orbitals.\(^7\) (In the case of \( \text{Re}(5d) \) states this effect is compensated by the deeper \( 5d \)-level of \( \text{Re} \) ion.) Because of this, \( 5d \)-electron prefer to move away from \( \text{W} \) site, leaving it in a \( \text{W}^{6+} \) configuration, and stay on the Fe \( 3d \)-level even at the cost of paying an extra Coulomb energy. As a result, in \( \text{Sr}_2\text{FeWO}_6 \) iron is in a \( \text{Fe}^{2+} \) (\( 3d^6 \)) valence state and the moderately large Fe-W charge transfer gap, in the presence of strong Coulomb interaction on Fe sites, causes the insulating behavior.

In the perovskite structure, the octahedral ligand field of oxygens splits \( d \)-levels into a low-lying triplet \( (t_{2g}) \) and a higher doublet \( (e_g) \). There are several experimental evidences\(^5\) suggesting that \( \text{Fe}^{2+} \) ion is in the high spin configuration \( t_{2g}^3 \) with \( S = 2 \). As four electrons occupy the threefold degenerate \( t_{2g} \)-levels, the ground state of \( \text{Fe}^{2+} \) has a threefold orbital degeneracy. This degeneracy, similarly to the spin one, can be described by pseudospin quantum numbers. The spin \( S = 2 \) and pseudospin \( \tau = 1 \) are thus the building blocks of an effective theory for insulating \( \text{Sr}_2\text{FeWO}_6 \). In the double perovskite structure of \( \text{Sr}_2\text{FeWO}_6 \) Fe and W ions form a rock-salt structure. Each type of ions resides on a face-centered-cubic (fcc) sublattice. The fcc lattice is weakly frustrated and allows ordered anisotropic AFM structures. But weak frustration of the lattice alone can not be responsible for the very low magnetic transition temperature. The reason why \( T_N \) is low, we believe, is as follows. The superexchange interaction, that couples magnetic moments of Fe ions, is mediated by two types of diamagnetic ions, along the path Fe-O-W-Fe, with 90° and 180° angles between Fe and W ions. Because of this, the resulting Fe-Fe exchange is rather weak and the corresponding transition temperature is low. The nearest-neighbor (nn) and next-nearest-neighbor (nnn) Fe moments are coupled, respectively, by 90° and 180° Fe-W-Fe bonds. Depending on values and signs of the nn and nnn exchange energies,
different types of AFM structures can be stabilized on the fcc lattice. To our knowledge no experimental determination of the kind of AFM order taking place in Sr$_2$FeWO$_6$ has ever been undertaken.

In this paper we derive an effective spin-orbital model from the Hubbard Hamiltonian of correlated Fe-3d electrons hybridized with uncorrelated 5d electrons of W and determine the magnetic ground-state structure as a function of the model parameters. We assume that oxygen degrees of freedom are integrated out and consider an effective hybridization between Fe and W d-states. Performing a fourth order perturbation expansion in the hopping parameters around the atomic limit we get an effective $S = 2$ Hamiltonian for a system with six electrons in five d orbitals. It may be worthwhile to note that our derivation is based only on the geometrical structure and electronic configuration of the system. As such it can be applied to a variety of systems presenting the same characteristics: any rock-salt with a high-spin $t_{2g}^3 e_g^2$ configuration, like, e.g., FeO.

The paper is organized as follows: In the next section we introduce the multi-band Hubbard Hamiltonian, perform the fourth order perturbation expansion and write the effective spin-orbital Hamiltonian in which the orbital degrees of freedom are described in terms of the pseudospin representation. The derivation of the effective Hamiltonian demands a lot of algebra with rather cumbersome expressions. To facilitate the reader, we have tried to use, whenever possible, a pictorial representation of states and processes, relegating both the fourth order perturbation scheme and all the final expressions in the Appendices A and B, correspondingly. In section III the classical ground state phase diagram of the effective spin-orbital model is discussed, as a function of model parameters, within a variational procedure. In the same section we also discuss the range of the external parameters appropriate to the case of Sr$_2$FeWO$_6$ and sketch some results. In section IV we draw our conclusions.

II. EFFECTIVE HAMILTONIAN.

Here we introduce the five-band Hubbard Hamiltonian, and perform a perturbative expansion in the hopping parameters up to the fourth order to describe all the low-lying excited states of the Fe-W system in terms of spin and orbital degrees of freedom of iron sites, only.

A. Ground state.

We start from the multi-band Hubbard Hamiltonian:

$$H = H_0 + H_{el} + H_{0W} + H'_1,$$  

where $H_0$ is the on-site term of the form:

$$H_0 = U_1 \sum_{i,\alpha} n_{i\alpha \uparrow} n_{i\alpha \downarrow} + \frac{1}{2} (U_2 - J) \sum_{i,\sigma,\alpha \neq \alpha'} n_{i\sigma \alpha} n_{i\sigma' \alpha'}$$

$$+ U_2 \sum_{i,\alpha \neq \alpha'} n_{i\alpha \uparrow} n_{i\alpha' \downarrow} + J \sum_{i,\alpha \neq \alpha'} d_{i\alpha \downarrow}^\dagger d_{i\alpha' \uparrow} + d_{i\alpha' \downarrow}^\dagger d_{i\alpha \uparrow}$$

$$- J \sum_{i,\alpha \neq \alpha'} d_{i\alpha \downarrow} d_{i\alpha' \uparrow} + d_{i\alpha' \downarrow} d_{i\alpha \uparrow},$$  

(2)

$U_1$ and $U_2$ are the Coulomb repulsion among electrons in the same and in different orbitals, respectively, and $J$ is the Hund’s coupling constant. Due to the cubic symmetry, the relation $U_1 = U_2 + 2J$ holds. The annihilation and creation operators, $d_{i\sigma \alpha}$ and $d_{i\sigma' \alpha}$, refer to Fe-3d orbitals at site $i$, of type $\alpha$ (one of $x^2 - y^2$, $3z^2 - r^2$, $xy$, $xz$ or $yz$) and with spin $\sigma = \uparrow, \downarrow$. $n_{i\sigma \alpha} = d_{i\sigma \alpha}^\dagger d_{i\sigma \alpha}$.

The octahedral crystal field splitting of d-orbitals into a $e_g$-doublet ($x^2 - y^2$ and $3z^2 - r^2$) and a lower-lying $t_{2g}$ triplet ($xy$, $xz$ and $yz$) is taken into account for both Fe and W ions by the term:

$$H_{ef} = \Delta_{eg} \sum_{ii',\alpha = x^2 - y^2,3z^2 - r^2} (n_{i\sigma \alpha} + \tilde{n}_{i'\sigma \alpha})$$

(3)

where $\tilde{n}_{i'\sigma \alpha}$ counts the electrons on W sites $i'$. The summation is for all $i$ and $i'$ running over Fe and W sublattices, respectively. Finally, the last term of the local part of the Hamiltonian, $H_{0W}$, represents the single particle energy level of the W ion with respect to Fe$^{6+}$:

$$H_{0W} = \Delta_{CT} \sum_{i'\sigma' \alpha} \tilde{n}_{i'\sigma' \alpha},$$

(4)

where $\Delta_{CT} = E(\text{Fe}^{6+}W^{1+}) - E(\text{Fe}^{6+}W^{0})$ is the charge transfer energy, i.e., the minimum energy needed to remove one electron from Fe$^{6+}$ ion and put it to an empty W$^{0}$ site. Here and below an upper index denotes the number of d-electrons on a given ion. The kinetic term $H'_1$ is considered as a perturbation:

$$H'_1 = - \sum_{ii'\sigma' \alpha} t_{\alpha\beta} (d_{i\sigma \alpha}^\dagger d_{i'\sigma' \beta} + \text{h.c.})$$

(5)

The summation is over nearest-neighbor Fe-W sites, and all possible spin and orbital indices. Here $d_{i\sigma \alpha}^\dagger (d_{i\sigma \alpha})$ creates (annihilates) a 5d-electron on W ions, with spin $\sigma$ in the orbital $\alpha$. In a cubic lattice there is no hopping between $e_g$ and $t_{2g}$. The transfer matrix $t_{\alpha\beta}$ is diagonal in the $t_{2g}$ manifold for all the orbitals $xy$, $xz$, $yz$, with non-zero matrix elements $t$ only for the bonds laying in the corresponding plane (i.e., along $x$ direction, the hopping integral is zero for $yz$ orbitals and equal to $t$ for the other two). Due to the shape of the $e_g$ orbitals, their hybridization is different in the three cubic directions thus leading to direction dependent hopping with the anisotropic transfer matrix elements $t_{\alpha\beta} (\alpha = 3z^2 - r^2$ and $\beta = x^2 - y^2$) given by:

$$t_{\alpha\beta}^{x,y} = t_e \left( \begin{array}{cc} 1/4 & \mp \sqrt{3}/4 \\ \mp \sqrt{3}/4 & 3/4 \end{array} \right), \quad t_{\alpha\beta}^{z} = t_e \left( \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right)$$

(6)

In constructing the effective Hamiltonian we also assume that the Hund’s coupling $J$ is strong enough.
to win the competition with the crystal field splitting $\Delta_{eg}$. This implies that Fe$^{2+}$-ion in the ground state is in the high-spin configuration $t_{2g}^4e_{g}^2$ with total spin $S = 2$, and justifies the exclusion from our zeroth order of the low-spin state, $t_{2g}^6e_{g}^0$ ($S = 0$) and of the intermediate-spin state, $t_{2g}^5e_{g}^1$ ($S = 1$), both higher in energy. We can write the ground state as a collection of atomic states $|\alpha_j\rangle$, each characterized by two quantum numbers: the spin $\vec{S}$ and pseudospin $\vec{\tau}$. This latter describes the orbital occupation, namely the position of double occupied orbital in the $t_{2g}$-manifold. Since there are three possibilities to put the double occupied orbital in the manifold, we can describe it by $\vec{\tau} = 1$, with the same algebra of the usual spin operator. The orbital quantization axis can be selected arbitrarily, and we choose the following convention which pictorially can be presented as:

\[
\begin{align*}
\uparrow \uparrow & \quad |\alpha_1\rangle = |S_z = 2, \tau_z = 1\rangle \\
\uparrow \uparrow & \quad |\alpha_2\rangle = |S_z = 2, \tau_z = 0\rangle \\
\uparrow \uparrow & \quad |\alpha_3\rangle = |S_z = 2, \tau_z = -1\rangle
\end{align*}
\]

where $|\alpha\rangle$ and $|\alpha'\rangle$ are two possible ground-states for $H_0$ (all the Fe$^{2+}$-ions in the $t_{2g}^4e_{g}^2$ configuration, all 5d W-orbitals empty), while $|\beta_{m(\alpha)}\rangle$ denotes all possible intermediate excited states, as imposed by $H'_t$. The first and third step states, $|\beta_{m(\alpha)}\rangle$, must have five electrons on one Fe-ion and one electron in an adjacent W-ion (Fe$^{5+}$W$^{1+}$), while the second-step state, $|\beta_l\rangle$, must be of the kind Fe$^{6+}$W$^{0+}$Fe$^{7+}$ or Fe$^{5+}$W$^{2+}$Fe$^{5+}$ on the three sites involved in the hopping process (see Fig. 1). Our aim is to find out a representation of the effective Hamiltonian, leading to this same eigenvalue equation, in terms of the spin and orbital degrees of freedom of iron only. We consider the full multiplet structure of the intermediate states with five and seven electrons which can be grouped according to their energies and the total value of the spin. Moreover, depending on the orbital occupation of Fe$^{6+}$ ion in the ground state and the orbital symmetry ($e_g$ or $t_{2g}$) of the hopping electron, different intermediate configurations can be reached. As already stated, in the cubic symmetry the hopping is allowed only within $t_{2g}$-manifold and $e_g$-manifold, separately.

In this notation, the upper boxes represent the $e_g$ orbital doublet, $e_{g}^{(1)} = 3z^2 - r^2$ (left upper box) and $e_{g}^{(2)} = x^2 - y^2$ (right upper box). The lower boxes refer to the three-fold degenerate $t_{2g}$ orbitals, with $t_{2g}^{(1)} = xy$ (left box), $t_{2g}^{(2)} = yz$ (central box) and $t_{2g}^{(3)} = xz$ (right box). The atomic ground state energy is $E_{g}^{(6)} = 15\Delta_{z} - 8J + 2\Delta_{eg}$. Because of the three-fold orbital and the five-fold spin degeneracies, the ground state is 15-fold degenerate. Such a degeneracy is then lifted by the hopping term, $H'_t$, as detailed below.

### B. Excited states and perturbation theory.

In this subsection we briefly describe the perturbation scheme and classify the excited states according to their total spin $S$, their $S_z$ projection and orbital configurations. Since we are interested in describing the superexchange interactions between iron sites, we need to go beyond second order perturbation theory in the hopping Hamiltonian $H'_t$ and deal with fourth-order perturbative expansion. In fact, we neglect the direct Fe-Fe hopping and consider only the hopping through the W sites. The explicit form of $H'_t$ is such that the fourth order eigenvalue equation simplifies to (see Appendix A):

\[
\sum_{\alpha\alpha'} \frac{\langle \alpha|H'_t|\beta_m\rangle\langle \beta_m|H'_t|\beta_l\rangle\langle \beta_l|H'_t|\beta_n\rangle\langle \beta_n|H'_t|\alpha'\rangle}{(E_\alpha - E_{\beta_m})(E_\alpha - E_{\beta_l})(E_\alpha - E_{\beta_n})} - E = 0 \tag{7}
\]

Consider the excited states which involve $t_{2g}$ hopping, first. The intermediate atomic states with seven electrons Fe$^{7+}$ have total spin $S = 3/2$. The manifold is 12-fold degenerate (4×(spin)×3(orbital)) and one of the possible states can be depicted as:

\[
\text{Fe}^{7+}_t = \begin{array}{c}
\uparrow \uparrow \uparrow \\
W \uparrow \uparrow \uparrow
\end{array}
\]

The three-fold orbital degeneracy arises from the $t_{2g}$ unpaired electron. The energy of this state is $E_{t}^{(7)} = 21U_2 - 7J + 2\Delta$. The intermediate states with five electrons split over a manifold with different values of total spin and energies.

The excited states with maximum spin configuration have $S = 5/2$ and no orbital degeneracy. The 6-fold degeneracy is entirely due to the spin. The state with maximum $S_z$ is:
\[ \text{Fe}_b^{(5)} = \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array} \]

The energy is \( E_{b}^{(5)} = 10U_2 - 10J + 2\Delta \), the minimum excitation energy of \( \text{Fe}_b^{(5)} \) states.

All the other \( \text{Fe}_b^{(5)} \) states with all orbitals singly occupied have total spin \( S = 3/2 \) and can be pictured as:

\[ \text{Fe}_b^{(5)} = \frac{1}{\sqrt{2}} \left( \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} - \begin{array}{c}
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\end{array} \right) \]

\[ \text{Fe}_b^{(5)} = \frac{1}{\sqrt{2}} \left( \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} - \begin{array}{c}
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\end{array} \right) \]

\[ \text{Fe}_b^{(5)} = \frac{1}{\sqrt{2}} \left( \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} - \begin{array}{c}
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\end{array} \right) \]

\[ \text{Fe}_b^{(5)} = \frac{2}{3} \sqrt{\frac{3}{10}} \left( \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} - \begin{array}{c}
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\end{array} + \begin{array}{c}
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array} \right) \]

Each of these states is 4-fold degenerate because of the spin (only the states with maximum \( S_z \) are shown). They give the same contribution to the effective Hamiltonian and below, for convenience, we denote them with the common notation \( \text{Fe}_b^{(5)} \). Their energy is \( E_b^{(5)} = 10U_2 - 5J + 2\Delta \).

Finally, there are the states with one unoccupied orbital. They have total spin \( S = 3/2 \) and the global degeneracy is 24 \((4\text{(spin)}\times6\text{(orbital)})\).

\[ \text{Fe}_{c_\pm}^{(5)} = \frac{1}{\sqrt{2}} \left( \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} \pm \begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array} \right) \]

The energies of these states are \( E_{c_\pm}^{(5)} = 10U_2 - 5J + 2\Delta \) and \( E_{c_\pm}^{(5)} = 10U_2 - 3J + 2\Delta \).

Now we consider the intermediate states which can be reached by \( e_g \) hopping. Those with seven electrons have spin \( S = 3/2 \) and can be presented as the following:

\[ \text{Fe}_c^{(7)} = \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\end{array} \]

Their degeneracy is \( 4\text{(spin)}\times3\text{(orbital)}\times2\text{(orbital)}=24 \). Their energy is: \( E_c^{(7)} = 21U_2 - 7J + 3\Delta \).

The states with five electrons arising from the \( e_g \) hopping have also total spin \( S = 3/2 \) and can be drawn as

\[ \text{Fe}_{d_z}^{(5)} = \frac{1}{\sqrt{N_z}} \left( \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\end{array} \pm \begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\end{array} \right) \]

where the normalization factors are defined as \( N_z = \frac{J_z^2 + \Delta_\pm^2}{\Delta_\pm} \), \( \alpha = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{\Delta}{\sqrt{J_z^2 + \Delta_\pm^2}}} \), and \( \Delta_\pm = \Delta \pm \sqrt{J_z^2 + \Delta_\pm^2} \).

These states have energy \( E_{d_z}^{(5)} = 10U_2 - 4J + 2\Delta \mp \sqrt{J_z^2 + \Delta_\pm^2} \) and their degeneracy is \( 4\text{(spin)}\times3\text{(position of doubly occupied orbital)}\times2\text{(position of hole)}=24 \).

### C. Classification of virtual processes and derivation of the spin-orbital Hamiltonian.

In order to derive the effective spin-orbital Hamiltonian in the simplest way it is useful to classify all the allowed hopping processes depending on the specific geometry of the fcc lattice. It becomes then possible to select the orbital dependence for each process and for a given projection of the spin coupling (whether FM or AFM) along the direction \( ij \) of the bond. The general form for the Hamiltonian turns out to be:

\[ H_{\text{eff}} = \sum_{ij} \left[-\left[\vec{S}_i \cdot \vec{S}_j + 6\right]O_{ij}^{(F)} + \left[\vec{S}_i \cdot \vec{S}_j - 4\right]O_{ij}^{(A)}\right] \]  

where \( ij \) denote the summation over both nn and nnn Fe-ions of the fcc lattice. The terms \( O_{ij}^{(F/A)} \) are the orbital, energy-dependent, contributions to the effective Hamiltonian for FM or AFM bonds \( ij \), respectively, which are explicitly given in Appendix B. The two spin-dependent terms are projectors over \( \vec{S}_i + \vec{S}_j = 4 \) (FM coupling) and \( \vec{S}_i + \vec{S}_j = 0 \) (AFM coupling), respectively. Below we clarify the procedure adopted to derive the spin-orbital Hamiltonian \([\text{5}]\). We try to avoid as much as possible formulas and present the derivation in a pictorial way. Following Fig. 1 we consider four types of processes (from \( A \) to \( D \), according to the way the intermediate states can be reached.

Depending on the kind and number of ions involved in the intermediate steps, it is possible to distinguish the following processes:

- **A - processes**:
  \[ \text{Fe}^{(6)} \text{W}^{(0)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(5)} \text{W}^{(0)} \text{Fe}^{(7)} \]
  \[ \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(6)} \text{W}^{(0)} \text{Fe}^{(6)} \]

- **B/C - processes**:
  \[ \text{Fe}^{(6)} \text{W}^{(0)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(5)} \text{W}^{(2)} \text{Fe}^{(5)} \]
  \[ \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(6)} \text{W}^{(0)} \text{Fe}^{(6)} \]

- **D - processes**:
  \[ \text{Fe}^{(6)} \text{W}^{(0)} \text{W}^{(0)} \text{Fe}^{(6)} \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{W}^{(0)} \text{Fe}^{(6)} \]
  \[ \rightarrow \text{Fe}^{(5)} \text{W}^{(1)} \text{W}^{(1)} \text{Fe}^{(5)} \rightarrow \text{Fe}^{(6)} \text{W}^{(0)} \text{W}^{(1)} \text{Fe}^{(5)} \]
  \[ \rightarrow \text{Fe}^{(6)} \text{W}^{(0)} \text{W}^{(0)} \text{Fe}^{(6)} \]
where the upper index denotes the number of electrons on each ion. A first basic distinction is easily drawn between the \( A \)-process and all the others. The former involve the formation of a \( \text{Fe}^{(7)} \) state at the second step, while none of the latter type processes does.

On the contrary, all \( B \)-, \( C \)- and \( D \)-processes are characterized by a \( \text{Fe}^{(5)} \) state for both iron ions involved in a virtual process. The difference among them lies in the way these states are reached. For \( B \)- and \( C \)-processes there is only one intermediate \( W \) ion with two electrons on it, differently from the \( D \)-process, where two distinct \( W \) ions are involved. Finally, the difference between \( B \)- and \( C \)-processes lies in the behavior of the two virtual electrons. In the first case they go back to the original \( \text{Fe} \)-ion where they came from. On the contrary for \( C \)-processes there is an exchange of the two electrons, as shown in Fig. 1, and each of them moves toward the other \( \text{Fe} \)-ion. For the sake of clarity it should be reminded that we are considering the specific case of the fcc sublattice of \( \text{Fe} \) ions in \( \text{Sr}_2\text{FeWO}_6 \): this allows some simplifications in the derivation of the effective spin-orbital Hamiltonian, \( H_{\text{eff}} \). In particular, it is possible to build the following table, where we list the contributions to \( H_{\text{eff}} \) depending on the characteristics of each single term.

| \( A \) | \( B \) | \( C \) | \( D \) |
|---|---|---|---|
| \( aa \) | FM | AFM (T1) | FM (T2,nnn) | FM (T1,nn) |
| \( bb \) | AFM | AFM (T1) | FM (T2,nnn) | FM (T1,nn) |
| \( cc \) | AFM | AFM (T1) | FM (T2,nnn) | FM (T1,nn) |
| \( dd \) | AFM | AFM (T1) | FM (T2,nnn) | FM (T1,nn) |
| \( ac \) | – | FM (T1) | AFM (T2,nnn) | AFM (T1,nn) |
| \( bc \) | – | AFM (T1) | FM (T2,nnn) | FM (T1,nn) |
| \( ab \) | – | FM (T1) | AFM (T2,nnn) | AFM (T1,nn) |

Each column in the table represents one of the four possible processes drawn in Fig. 1. Each row represents the states of the \( \text{Fe}^{(5)} \)-ion reached at the second step of the virtual process. For example, for \( B \)-, \( C \)- and \( D \)-processes, \( aa \) means that the virtual intermediate state is made of both \( \text{Fe}^{(5)}_a \), while \( ac \) indicates one \( \text{Fe}^{(5)} \)-state and one \( \text{Fe}^{(5)}_{\pm} \)-state. In the case of the \( A \) process, only one \( \text{Fe}^{(5)} \)-state is present and “\( aa \)” refers to this single \( \text{Fe}^{(5)}_a \)-state, while \( ac \) has no meaning. The table gives us the magnetic character of the bond \( ij \) involved in the process (whether FM or AFM), if it requires a nn or a nnn contribution, and its orbital signature. In this respect T1 means that only one type of orbital is allowed in the process (ie, a contribution proportional to \( t_{xy}^4 \)), while T2 means that there must be two different orbitals (for example a contribution proportional to \( t_{xy}^2 t_{xz}^2 \)). If there are no orbital or neighbors specifications, it means that both kinds are allowed. With this in mind, the derivation of the orbital part reported in Appendix B follows quite straightforward.

As an example, we show how to derive the term (6) (see Appendix B), corresponding to the A-process towards states \( c_{\pm} \). In order to have a state \( c_{\pm} \) on a \( \text{Fe}^{(5)} \)-ion, the electron that jumps to the \( W \) site and then forms the \( \text{Fe}^{(7)} \) state, must belong to one of the singly occupied \( t_{2g} \)-states of the original \( \text{Fe}^{(6)} \)-ion. Only in this case, in fact, the \( \text{Fe}^{(5)} \)-ion is left with one doubly occupied, one singly occupied and one vacant \( t_{2g} \)-state. The electron is free to jump on \( W \) site, that is empty, and it has some restriction to hop to the next \( \text{Fe}^{(6)} \) ion, because of the Pauli principle. Only some jumps are allowed and they depend on the relative orbital occupations of the two \( \text{Fe}^{(6)} \)-ions involved in the process. It is worthwhile to note that, if the spins of the two \( \text{Fe}^{(6)} \)-ions involved were ferromagnetically coupled, no hopping processes could have taken place because of the Pauli principle: the hopping electron would find all the singly occupied orbitals of the final \( \text{Fe}^{(6)} \)-ion filled with the same spin projection. Thus, superexchange between \( c_{\pm} \) states can take place only when the two \( \text{Fe}^{(6)} \) ions are coupled antiferromagnetically, as shown in the previous table.

Let us now analyze the orbital dependence. For simplicity we consider two specific configurations, of those that we called T1 and T2 in the table, e.g., the term depending on \( t_{xy}^4 \) and that depending on \( t_{xy}^2 t_{xz}^2 \). The first hopping process is allowed only when \( \tau_{iz} \neq 1 \) and \( \tau_{jz} \neq 1 \), i.e. \( xy \)-orbital states are singly occupied at both \( i \) and \( j \) Fe-sites involved. The second is active only when both \( \tau_{iz} \) and \( \tau_{jz} \) are either 1 or -1, i.e. either \( xy \)- or \( xz \)-orbital states are doubly occupied at both sites. During this process both orbital quantum numbers are either reduced or increased by two, respectively. In the case of a doubly occupied \( xy \)-orbital, the \( xz \)-electron hops leaving a hole in this orbital state. The resulting state is not an eigenstate of the Hamiltonian \( \mathcal{H} \) and is then projected over an eigenstate \( c_{\pm} \) given by the superposition of states with \( xy \)- and \( xz \)-holes. Therefore, an electron from the doubly occupied \( xy \)-orbital of \( \text{Fe}^{(7)} \) can hop back to \( \text{Fe}^{(5)} \) ion. This changes the initial orbital configuration \( \tau_{iz} = \tau_{jz} = 1 \) to the final \( \tau_{iz} = \tau_{jz} = -1 \) form. In terms

![Fig. 1: Different hopping processes: dashed and full lines correspond to different electrons.](image)
of the pseudospin quantum numbers, the two contributions are:

\[ t^{4}_{s} \left[ (1 - \tau_{iz}^{2}) + \frac{1}{2} \tau_{iz}(\tau_{sz} - 1) \right] \left[ (1 - \tau_{jz}^{2}) + \frac{1}{2} \tau_{jz}(\tau_{sz} - 1) \right] \]

\[ \pm \frac{1}{4} t^{2}_{s} t^{2}_{z} \pm \tau_{iz}^{2} \tau_{jz}^{2} + \tau_{iz} \tau_{jz} \]

where ± depends on which of the \( c_{\pm} \) states are considered. These terms enter into Eq. 7 with a weight taking into account both spin (through Clebsch-Gordan coefficients) and orbital projection of the single Slater determinant into the correlated state \( c_{\pm} \). The weight, or normalization coefficient (see the Table in Appendix B), of a given process is obtained by equating the matrix elements of the Hamiltonian (8) to the corresponding ones of the present process this weight is approximately as \( \frac{1}{8} \). The factorization is justified because of the two different energy scales governing these degrees of freedom: spins are coupled by virtual processes that involve spin flips, while only the latter electrons generate the coupling between the orbital degrees of freedom, as \( e_{s} \) orbitals are half-filled. The ratio of spin and orbital exchange energies thus scales approximately as \( t_{s}^{2} / t_{4}^{2} \) and is much larger than unity in the situation of interest. Therefore, it is reasonable to average out spin degrees of freedom, first, by considering all possible ordered magnetic structures on a fcc centered cubic lattice and then for each type of magnetic ordering find an orbital configuration, that minimizes the total energy by means of a variational procedure.

We consider the following magnetic structures that are possible ordered states for a nn and a nnn Heisenberg Hamiltonian on a fcc lattice:

1) Ferromagnetic state (FM);
2) Type-I antiferromagnetic (AFM-I) ordering, which consists of ferromagnetic \{110\} planes stacked antiferromagnetically in the third direction;
3) Type-II antiferromagnetic (AFM-II) structure, consisting of ferromagnetic \{111\} planes, each being antiferromagnetically coupled to adjacent layers. This magnetic structure is presented in Fig. 2 where only the Fe atoms are shown.

A. Minimization procedure.

The trial wave function can be written in general as follows:

\[ |\Psi\rangle = \Pi_{i} |\psi_{i}^{o}\rangle|\phi_{i}^{s}\rangle \]

where \( |\psi_{i}^{o}\rangle \) and \( |\phi_{i}^{s}\rangle \) refer to orbital and spin states at site \( i \), respectively. Since \( H_{eff} \) factors into an orbital \( H_{eff}^{o} \) and a spin \( H_{eff}^{s} \) part and its action involves two sites at a time, its average value over the above state takes the form:

\[ \langle \Psi_{i}|(\psi_{j}^{o}|H_{eff}^{o}|\psi_{j}^{o})|\psi_{i}^{o}\rangle = \langle \phi_{i}^{s}|(\phi_{j}^{s}|H_{eff}^{s}|\phi_{j}^{s})|\phi_{i}^{s}\rangle \]

The orbital part of the variational wave function can be written as

\[ \| \psi_{i}^{o} \| = \cos \theta_{i} |0_{i} + \sin \theta_{i}(\cos \phi_{i}|1_{i} + \sin \phi_{i}|1_{i}) \]

allowing all three orbital states \( |\tau_{z} = 0_{i} \), \( |\tau_{z} = 1_{i} \) and \( |\tau_{z} = -1_{i} \), with a relative weight determined by the minimization procedure with respect to the variational parameters \( \theta_{i} \) and \( \phi_{i} \). The expectation values of \( H_{eff}^{o} \) over the trial orbital wave function for both ferromagnetic and antiferromagnetic bonds are then expressed in terms of variational parameters \( \theta_{i} \) and \( \phi_{i} \) and are quite lengthy. On the contrary, the average of spin variables is straightforward in a mean field treatment. For a ferromagnetic
bond \(\langle \vec{S}_i \cdot \vec{S}_j \rangle + 6 = 10\) and for an antiferromagnetic bond \(\langle \vec{S}_i \cdot \vec{S}_j \rangle - 4 = -8\) in the classical ground state.

The energy per Fe atom, \(E_{\text{Fe}}\), is given by the sum of the energy contributions from all the bonds contained in the cell, divided by the number of atoms (each Fe-ion has 12 nn and 6 nnn). AFM-II phase has the biggest cell, with eight Fe atoms (see Fig. 3), and for generality we consider it as the unit cell for both FM and AFM-I phases, too. Hence, we have sixteen variational parameters (\(\theta_{1-8}\) and \(\psi_{1-8}\) for the eight sites of the unit cell).

We have then performed a numerical minimization of the energy contributions from all the bonds contained in the cell, divided by the number of atoms (each Fe-ion has 12 nn and 6 nnn). AFM-II phase has the biggest cell, with eight Fe atoms (see Fig. 3), and for generality we consider it as the unit cell for both FM and AFM-I phases, too. Hence, we have sixteen variational parameters (\(\theta_{1-8}\) and \(\psi_{1-8}\) for the eight sites of the unit cell).

We have then performed a numerical minimization of the ground state energy with respect to all the sixteen independent angular variational angles \(\theta_1\) and \(\psi_1\). By taking the absolute minimum we determine the orbital configuration that minimizes the total energy of the system for a given magnetic order. The ground state magnetic and orbital structure are determined by selecting the state with the lowest energy. The results are presented below.

### B. Model parameters

In order to proceed further with the ground state phase diagram of \(H_{\text{eff}}\), we fix below the values of the parameters that have already been estimated in the literature and we try to give a reasonable guess for the remainings.

- **Crystal field splitting \(\Delta_{e_g}\):** The value of the \(e_g - t_{2g}\) splitting \(\Delta_{e_g} \approx 1.24\) eV has been estimated for Fe\(^{2+}\) ion in Ref. [12] and we take this value in our analysis.

- **Exchange parameter \(J\):** The exchange part of Coulomb energy is known to be little screened in solids. It can thus be estimated through the atomic values of Racah parameters \(B\) and \(C\) (\(J = 5/2B + C\)). Given the values of \(B\) and \(C\) from Ref. [12] one obtains \(J \approx 0.78\) eV.

- **Coulomb energy \(U_2\):** Intra-atomic Coulomb repulsion is generally considerably screened in solids and can not be simply related to its atomic value. The estimates reported in the literature suggest that \(U_2 = 5 - 7\) eV (Refs. [12, 13, 14]), however we also consider variation of \(U_2\) in a wider range.

- **Transfer integrals \(t\) and \(t_{e_g}\):** We fix, in most of the cases, the ratio of \(e_g\) and \(t_{2g}\) transfer integrals to be \(t_{e_g}/t = 3\) as suggested by the Muffin-Tin Orbital theory.¹⁵ We are not aware of any estimates of absolute values of the transfer integrals between Fe and W ions. However \(t_{2g}\) hopping amplitude has been estimated to be \(t \approx 0.25\) eV for Fe-Re bond.¹⁵ We may consider the same value of \(t_{2g}\) transfer for Fe-W bond too, since for both Re and W ions this transfer involves 5d-shell.

- **Charge-transfer gap \(\Delta_{\text{CT}}\):** We can estimate a lower boundary for the charge transfer gap between the high spin state of Fe\(^{6}\) and W ions in two possible ways as follows. First, the difference in \(\Delta_{\text{CT}}\) for Re and W based systems can be approximately taken equal to the energy mismatch of 5d-levels of these ions: \(\Delta_{\text{CT}}(\text{W}) - \Delta_{\text{CT}}(\text{Re}) = E^{(5d)}(\text{W}) - E^{(5d)}(\text{Re})\). The latter mismatch is of the order of \(\sim 1.4\) eV.³⁰

A lower estimate of \(\Delta_{\text{CT}}(\text{W})\) is then obtained by putting \(\Delta_{\text{CT}}(\text{Re}) = 0\) for the metallic Re based compound. We get \(\Delta_{\text{CT}} > 1.4\) eV for the W based compound. Second, the insulating behavior of the system implies that the charge-transfer gap is larger than the bandwidth of those electrons that are involved in the lowest energy charge-transfer.¹⁵,¹⁶,¹⁷ Taking the above reported value for \(t_{2g}\) transfer one obtains the even more strict constraint \(\Delta_{\text{CT}} > 2\) eV.

### C. Results and discussion

In Fig. 3 we show the ground state phase diagram of the spin-orbital model in \(\Delta_{\text{CT}} - U_2\) plane. Here AFM-II denotes type-II antiferromagnetic ordering, OO-I and OO-II correspond to two types of orbital ordering described in the text.
directly linked to the nnn exchange energy. Therefore the contributions from explicitly given in Table I. The structure of these orbital states is explicitly and all equally populated. Switching on the inter-sublattice couplings (i.e. nn spin-orbital couplings) also contribute to the ground state energy. The orbitals are ordered ferromagnetically, and the moments are coupled only by antiferromagnetic superexchange for a given sublattice is maximized when \( t_1 = \frac{1}{3} \). At some critical value of the Coulomb parameter plane. Here \( U_2 = 5 \) eV, and consider the phase diagram in \( t_e \) and \( \Delta_{\text{CT}} \) parameter plane. The result is presented in Fig. 4. For small values of \( e_g \) hopping, a ferromagnetic phase is stabilized. Its orbital ordering (OO-III) is shown in Table I. In this configuration the system maximizes the nn ferromagnetic exchange, \( J_1 > 0 \). The exchange between nn neighbors is always antiferromagnetic, \( J_2 < 0 \), and increases with \( t_e \). At some critical value of the \( e_g \) transfer, at which \( J_1 + J_2 = 0 \), the FM ordering becomes unstable and a transition to the AFM-II state takes place (see filled circles in Fig. 4). For smaller values of the Coulomb energy, \( U_2 \), the phase space for ferromagnetic ordering is enlarged and the transition to the AFM-II state occurs for larger values of \( t_e \). The FM–AFM-II phase boundary for \( U_2 = 2.5 \) eV is shown as open circles in Fig. 4.

TABLE I: Types of orbital ordering with corresponding structures

|   | OO-I       | OO-II       | OO-III      |
|---|------------|-------------|-------------|
| 1 | \(|yz\)|    | \(|yz| + |xz|\)/\(\sqrt{2}\) | \(|xz\)|    |
| 2 | \(|xy\)|    | \(|xy\)|    | \(|xy\)|    |
| 3 | \(|xz\)|    | \(|xz\)|    | \(|xz\)|    |
| 4 | \(|yz| + |xz|\)/\(\sqrt{2}\) | \(|yz| + |xy|\)/\(\sqrt{2}\) | \(|xy\)|    |
| 5 | \(|yz\)|    | \(|yz| + |xz|\)/\(\sqrt{2}\) | \(|yz\)|    |
| 6 | \(|xy\)|    | \(|xy\)|    | \(|yz\)|    |
| 7 | \(|xz\)|    | \(|xz\)|    | \(|xz\)|    |
| 8 | \(|yz| + |xz|\)/\(\sqrt{2}\) | \(|yz| + |xz|\)/\(\sqrt{2}\) | \(|xy\)|    |

To summarize, we have developed a superexchange theory for insulating double-perovskite compounds such

D-processes). In Table I we list the types of orbital orderings together with the corresponding structure. The numbers from 1 to 8 label the eight atoms of the unit cell shown in Fig. 2. The ket-vectors denote the type of doubly occupied \( t_{2g} \) orbital at each atom for each orbital ordering.

To understand the orbital structure of the AFM-II state it is convenient to divide the fcc lattice of Fe ions, in four simple cubic sublattices. These four sublattices are generated by the pairs of nonequivalent atoms of the unit cell: (1,5), (2,6), (3,7), and (4,8) (see Fig. 2). Each sublattice is AFM and the moments are coupled stronger than nearest-neighbor ones.

FIG. 4: Same as in Fig. 3 in \( \Delta_{\text{CT}} \) vs \( t_e \) parameter plane. Here FM denotes ferromagnetic phase and OO-III corresponds to the orbital ordering described in the text. Filled and open circles stand for the FM–AFM-II phase boundaries for \( U_2 = 5 \) and \( 2.5 \) eV, respectively.\[ \text{meV for } t = 0.25 \text{ eV. The exchange energy scales as the forth power of the transfer integrals and is thus very sensitive to the variation of } t, \text{ nonetheless we can conclude that the superexchange theory gives the correct order of magnitude of the experimental transition temperature.} \]

IV. SUMMARY

To summarize, we have developed a superexchange theory for insulating double-perovskite compounds such
as Sr$_2$FeWO$_6$. The superexchange interaction, that couples the magnetic moments of Fe$^{2+}$ ions through the diamagnetic W$^{6+}$ ions, takes place on Fe-W-Fe bonds with 90° and 180° angles. The theory has been implemented in an effective spin-orbital Hamiltonian formulated in terms of spin ($S = 2$) and orbital pseudo-spin ($\tau = 1$) degrees of freedom of the iron ion only, arising from the threefold degeneracy of $t_{2g}$-levels. We have studied magnetically and orbitally ordered states and constructed the classical ground state phase diagram of the effective Hamiltonian. We have shown that for realistic values of the model parameters the ground state is antiferromagnetic, as experimentally observed. Our results suggest, that the antiferromagnetic order is of type-II, i.e., \{111\} ferromagnetic planes stacked antiferromagnetically. This prediction can be tested by means of polarized neutron experiments. We have evaluated the exchange energies for these magnetic structure and showed that the theory gives an estimate of the transition temperature which is compatible with the experimental value. The magnetic structure is accompanied by an orbital ordering in which each cubic-sublattice of iron ions shows a ferro-type orbital ordering. The type of occupied orbital states changes from one sublattice to the other. The energy scale of orbital degrees of freedom is one order of magnitude smaller than the spin one. This is due to the fact that orbitals are coupled by $t_{2g}$ electrons, only, while both $\epsilon_g$ (with larger transfer amplitude) and $t_{2g}$ virtual processes lift the spin degeneracy. Finally, we note that in the present paper we have just dealt with the electronic mechanisms to lift the ground state orbital degeneracy. However, there are two other possible mechanisms, not discussed here, that can lift the orbital degeneracy, such as the lattice distortion, or Jahn-Teller (JT) effect, and the spin-orbit coupling. The latter breaks the rotational spin invariance and opens a spin gap: Therefore a correct order of magnitude for this effect could be obtained by the experimental measurement of the spin-wave gap. As for the lattice mechanism, it should support the orbital ordering that minimizes the electronic energy of the system and thus enlarge the stability range of the orbital order, because the JT effect in this compound is mainly governed by the physics of isolated clusters rather than by cooperative effects. In fact, the oxygen octahedra surrounding Fe ions are independent one another, as they do not share any common oxygen-ion. Therefore JT distortions are not correlated as far as change in the electronic energy is concerned: Distortions of the octahedra around W ions with empty 5$d$-level do not cause any considerable change in the electronic energy.

In conclusion, if the electronic mechanism dominates the other two, then the orbital order can be stabilized only at very low temperatures, much lower than the magnetic transition temperature and in between the system is magnetically ordered but orbitally disordered. In order to clarify which of the above mechanisms is dominant further experimental studies of the magnetic and structural properties of the system are necessary.

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APPENDIX A: DERIVATION OF THE FOURTH ORDER ENERGY CORRECTION.

Consider the Hamiltonian:

$$ H = H_0 + \lambda H' $$  \hspace{1cm} (A1)

where $H_0$ is exactly solvable ($H_0\psi_0 = E_0\psi_0$) and $\lambda$ is some “small” non-dimensional parameter. Following, for example Ref[12], it is straightforward to write the coupled equations to get eigenvalue and eigenvector corrections to $E_0$ and $\psi_0$ up to the fourth order in $\lambda$:

$$ (H_0 - E_0)\psi_0 = 0 \Rightarrow (H' - E_1)\psi_0 + (H_0 - E_0)\psi_1 = 0 \Rightarrow (H' - E_1)\psi_1 + (H_0 - E_0)\psi_2 - 2E_2\psi_0 = 0 , $$$$

$$ (H' - E_1)\psi_2 + (H_0 - E_0)\psi_3 - E_2\psi_1 - 4E_4\psi_0 = 0 , $$$$ (H' - E_1)\psi_3 + (H_0 - E_0)\psi_4 - 2E_2\psi_2 - 2E_3\psi_1 - 4E_4\psi_0 = 0 . $$

Multiplying scalarly all equations by $(\psi_0)^*$ and solving with respect to the fourth order energy correction, $E_4$, we get:

$$ E_4 = \sum_{l\neq k} \sum_{m\neq k} \left( \sum_{n\neq k} \frac{H'_{kl}H'_{lm}H'_mH'_nH'_{nk}}{(E_k - E_l)(E_k - E_m)(E_k - E_n)} - \sum_{n\neq k} \frac{H'_{kl}H'_{lm}H'_mH'_nH'_{nk}}{(E_k - E_l)(E_k - E_m)(E_k - E_n)} \right) $$

$$ - \frac{H'_{kl}H'_{km}H'_m + H'_{kl}H'_{lm}H'_m H'_{nk} - H'_{kl}H'_mH'_{nk} H'_{mk}}{(E_k - E_m)(E_k - E_l)^2} $$

where we use notation: $H'_{km} = \langle \psi_k | H' | \psi_m \rangle$. Given the form of $H'$, Eq. [4], it follows that $H'_{kk} = 0$, i.e. the second, fourth and fifth terms do not contribute. Also the third term can be neglected, because it does not give rise to an effective exchange between Fe-sites, being the product of two second-order processes. This justifies our formula [7] in Sec.II.A.
APPENDIX B: ORBITAL TERMS AND ENERGY DENOMINATORS.

Here we write explicitly the orbital contributions to the effective Hamiltonian [3].

First we consider virtual processes with $t_{2g}$-electrons involved. All orbital contributions $O_{ij}^{(F(A))}$ for a bond $ij$ can be written in the following general form:

$$O_{ij}^{(F(A))} = \sum_{p,l'} O_{ij,p}^{ll'} , \text{ where } O_{ij,p}^{ll'} = \frac{\gamma_{ll'}^{ij}}{D_p^{ll'}} \tilde{O}_{ij,p}^{ll'}$$

and $D_p^{ll'}$ denotes an energy denominator, $\tilde{O}_{ij,p}^{ll'}$ is an orbital contribution expressed by means of the pseudospin operators, $\gamma_{ll'}^{ij}$ are normalization factors, which are given in the Table at the end of the Appendix B, $P$ denotes one of the four virtual hopping processes $A, B, C, \text{ and } D$, depicted in Fig. II and $l$ and $l'$ are the kind of excited states involved in the hopping process (i.e. $a, b, \text{ and } c$ introduced in Sec. II.B).

In the following, we list all the terms, classified for the kind of process.

$A$-process: For processes involving excited states of $a$- and $b$- type the orbital contributions differ only because of the energy denominators:

$$D_A^{aa(bb)} = \Delta_{CT,a(b)}^2 \left[ E^{(7)}_t + E^{(5)}_{a(b)} - 2E^{(6)}_g \right] ,$$

here and below $\Delta_{CT,l}$ denotes energy needed for an electron transfer from Fe$^{(6)}$ to W$^{(0)}$ when iron ion is left in a Fe$^{(5)}$ state. This energy is given by $\Delta_{CT,l} = \Delta_{CT} + E^{(5)}_l - E^{(6)}_a$. The state $a$ is the lowest energy configuration of Fe$^{(5)}$ and $\Delta_{CT} = \Delta_{CT,a}$ is the lowest energy necessary for the Fe$^{(6)} \rightarrow W^{(0)}$ charge transfer.

The corresponding pseudospin part is:

$$\tilde{O}_{ij,A}^{aa(bb)} = \frac{t^2_y}{2} \tau_{iz}(\tau_{iz} + 1) \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} - 1) + (1 - \tau^2_{jz}) \right] + \frac{t^4_y}{2} \tau_{iz}(\tau_{iz} - 1) \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} + 1) + (1 - \tau^2_{jz}) \right] + t^4_{yz}(1 - \tau^2_{jz}) \tau_{jz}^2$$

$$+ \frac{t^2_x t^2_y}{4} \left[ \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \frac{t^2_x t^2_y}{2} \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \frac{t^2_x t^2_y}{2} \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} \right]$$

If the excited state is Fe$^{(5)}_{c \pm}$ then the purely orbital contribution can be written as:

$$\tilde{O}_{ij,A}^{cc} = \frac{t^4_x}{4} \left[ 1 - \tau_{iz} \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} - 1) \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} + 1) \right] + \frac{t^4_x}{4} \tau_{iz}(\tau_{iz} - 1) \tau_{jz}(\tau_{jz} + 1)$$

$$+ \frac{t^2_x t^2_y}{4} \left[ \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \frac{t^2_x t^2_y}{2} \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} + \frac{t^2_x t^2_y}{2} \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz} \right]$$

where $c$ can be either $c_+$ or $c_-$, and respectively, either upper or lower sign should be taken in Eq. (B4). Corresponding energy denominator is given by:

$$D_A^{cc} = \Delta_{CT,c}^2 \left[ E^{(7)}_t + E^{(5)}_c - 2E^{(6)}_g \right] .$$

$B$-process: It has only diagonal orbital contributions, as shown in the Table of section II. If $aa-, bb-, ab-$ excited states are involved then the pure orbital part is the same, and can be written as:

$$\tilde{O}_{ij,B}^{ll'} = \frac{t^4_y}{4} \tau_{iz}(\tau_{iz} + 1) \tau_{jz}(\tau_{jz} + 1) + \frac{t^4_y}{4} \tau_{iz}(\tau_{iz} - 1) \tau_{jz}(\tau_{jz} + 1) + t^4_{yz}(1 - \tau^2_{jz})(1 - \tau^2_{jz})$$

For cc-hopping processes the orbital contribution $\tilde{O}_{ij,B}^{cc}$ is equal to diagonal part of $\tilde{O}_{ij,A}^{cc}$ and reads as

$$\tilde{O}_{ij,B}^{cc} = \frac{t^4_x}{4} \left[ 1 - \tau_{iz} \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} - 1) \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} + 1) \right] + \frac{t^4_x}{4} \tau_{iz}(\tau_{iz} - 1) \tau_{jz}(\tau_{jz} + 1)$$

$$+ t^4_{xz} \left[ 1 - \tau_{iz} \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} + 1) \right] \left[ \frac{1}{2} \tau_{jz}(\tau_{jz} + 1) \right] + t^4_{yz} \tau_{iz} \tau_{jz} \tau_{iz} \tau_{jz}$$
As for ac- and bc- processes, their orbital part are equal to the diagonal part of $\tilde{O}_{ij,bb}^{ac(bb)}$ given by

$$\tilde{O}_{ij,bt}^{ac(bb)} = \frac{t_{xy}^2}{2}\tau_{iz}(\tau_{iz} + 1)\left[\frac{1}{2}\tau_{jz}(\tau_{jz} - 1) + (1 - \tau_{jz}^2)\right] + \frac{t_{xz}^4}{2}\tau_{iz}(\tau_{iz} - 1)\left[\frac{1}{2}\tau_{jz}(\tau_{jz} + 1) + (1 - \tau_{jz}^2)\right] + t_{yz}^4(1 - \tau_{iz}^2)\tau_{jz}^2$$

(B8)

The general form for B-processes energy denominators is

$$D_B^{ll'} = \Delta_{CT,l}\Delta_{CT,l'}\left[\Delta_{CT,l} + \Delta_{CT,l'}\right]$$

(B9)

C-process: In this process two electrons with the same spin directions are exchanged between iron sites. The intermediate step involves the formation of a doubly occupied W site. This implies that two different orbitals must participate to the hopping process because of Pauli principle. The orbital contributions are thus only non-diagonal. They are the same for all processes of the kind aa, bb, cc, and ab:

$$\tilde{O}_{ij,C}^{ll'} = \pm \frac{t_{xy}^2 t_{xz}^2}{4}\left[\tau_{iz} - \tau_{iz}\tau_{jz} + \tau_{iz}\tau_{jz}\tau_{jz} - \tau_{iz}\tau_{jz}\tau_{jz}\tau_{jz}\right]$$

$$\pm \frac{t_{xz}^2 t_{yz}^2}{2}\left[\tau_{iz} - \tau_{iz}\tau_{jz} + \tau_{iz}\tau_{jz}\tau_{jz} - \tau_{iz}\tau_{jz}\tau_{jz}\tau_{jz}\right]$$

where the lower sign should be taken only when $l = c_-$ and $l' = c_+$. These processes differ one another only by the energy denominators.

For ac- and bc- processes we have

$$\tilde{O}_{ij,C}^{ac(bc)} = \pm \frac{t_{xy}^2 t_{xz}^2}{4}\left(\tau_{iz} + \tau_{iz}\tau_{jz}\tau_{jz} - \tau_{iz}\tau_{jz}\tau_{jz}\tau_{jz}\right)$$

$$\pm \frac{t_{xz}^2 t_{yz}^2}{2}\left(\tau_{iz} + \tau_{iz}\tau_{jz}\tau_{jz} - \tau_{iz}\tau_{jz}\tau_{jz}\tau_{jz}\right)$$

(B11)

where upper sign (+) and lower sign (−) correspond to $c = c_+$ and $c = c_-$, respectively.

We note that along 90° Fe-W-Fe bond (nn Fe ions) hopping is allowed only for one kind of orbital. Therefore, being orbitally nondiagonal, C-processes are effective only for 180° bond (nnn Fe ions), as shown in the Table of Sec. II.C. Energy denominators for all orbital contributions have the following common form:

$$D_C^{ll'} = \Delta_{CT,l}\Delta_{CT,l'}\left[\Delta_{CT,l} + \Delta_{CT,l'}\right].$$

(B12)

D-process: This type of processes is effective only for 90° Fe-W-Fe bonds by definition [see Fig. 1] and thus can only be orbitally diagonal. All orbital contributions and energy denominators are equal to the corresponding ones of B-processes [see Eqs. (86-89)]

Now we consider $e_g$ hopping processes. The contributions to the Hamiltonian from such processes does not depend on the orbital degree of freedom:

$$O_{ij,P}^{dd} = \gamma_P^{dd}\delta_{P}^{E_{eg}^{(4)}}$$

(B13)

Here the extra factors, which depend on the type of process, and appear due to the anisotropic form of $e_g$ transfer [9], are included in normalization factors $\gamma_P^{dd}$ given in the Table below.

The energy denominators for different processes can be written in the following forms. For A-process

$$D_{A}^{dd} = \Delta_{CT,d}^2\left[E_{c}^{(7)} + E_{d}^{(5)} - 2E_{g}^{(6)}\right].$$

(B14)

and for B-, C- and D-processes

$$D_{C}^{ll'} = \Delta_{CT,l}\Delta_{CT,l'}\left[\Delta_{CT,l} + \Delta_{CT,l'}\right].$$

(B15)

where $d$ and $d'$ can be either $d_+$ or $d_-$ excited states.
In the following Table we list all normalization coefficients $\gamma^{ll'}_P$:

|   | $aa$ | $bb$ | $cc$ | $dd$ | $ac$ | $bc$ | $ab$ |
|---|------|------|------|------|------|------|------|
| $A$ | $1/10$ | $1/10$ | $1/16$ | $1/8N_\pm$ | $-$ | $-$ | $-$ |
| $B$ | $1/8$ | $2/25$ | $1/32$ | $1/(8N_\pm^2)$ | $1/20$ | $1/20$ | $2/25$ |
| $C$ | $1/10$ | $8/125$ | $1/40$ | $1/(10N_\pm^2)$ | $1/16$ | $1/25$ | $1/10$ |
| $D$ | $1/10$ | $8/25$ | $1/40$ | $1/(10N_\pm^2)$ | $1/16$ | $1/25$ | $1/10$ |

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