

Orbital order in classical models of transition-metal compounds

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Abstract

We consider the classical 120-degree and related orbital models. These are the classical limits of quantum models which describe the interactions among orbitals of transition-metal compounds both with and without Jahn-Teller effects. We demonstrate that at low temperatures these models exhibit a long-range order which arises via an "order by disorder" mechanism. This strongly indicates that there is orbital ordering in the quantum version of these models, notwithstanding recent results on the absence of spin order in these systems.

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The properties of transition-metal (TM) compounds are a topic of long-standing interest. Here, the energy scales governing the transfer of charge and spin are well separated so all charges remain localized and electronic properties are determined by effective interactions. The fractional filling of the $3d$ -shells in the TM ion provides an additional novel facet: The splitting of the t_{2g} and e_g orbitals by crystal field can produce situations with a single dynamical electron (or a hole) on each site along with multiple orbital degrees of freedom [1–3]. Pertinent examples are found among the vanadates (e.g., V_2O_3 [4], $LiVO_2$ [5], $LaVO_3$ [6]), cuprates (e.g., $KCuF_3$ [2]) and derivatives of the colossal magnetoresistive manganite $LaMnO_3$ [7, 8]. The presence of the extra degrees of freedom raises the theoretical possibility of global, cooperative effects; i.e., orbital ordering. Such ordering has been observed via associated orbital-related magnetism and electric quadrupolar moments (via standard neutron and X-ray scattering), and by resonant X-ray scattering techniques wherein the $3d$ orbital order is detected by its effect on excited $4p$ states [9–13]. The case for orbital ordering has been further bolstered by detailed calculations [4, 5, 13, 14] and other considerations [15–17]. However, alternate perspectives [18] and various conceptual doubts [19, 20] have been raised concerning the entire picture. In particular, at the theoretical level, the case for orbital ordering has not yet been founded. In this paper, we present arguments which irrefutably demonstrate that orbital ordering indeed occurs. We discuss primarily the 120° -model which, e.g., corresponds to occupation of e_g orbitals by a single valance electron.

In TM-compounds, the 120° -model can be arrived at by either of two routes depending on whether or not we account for the Jahn-Teller effects. Starting with an appropriate itinerant electron model and *neglecting* the strain-field induced interactions among orbitals, a standard super-exchange calculation leads to the KK model [2] with the Hamiltonian given by

$$H = \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} H_{\text{orb}}^{\mathbf{r}, \mathbf{r}'} (\mathbf{s}_{\mathbf{r}} \cdot \mathbf{s}_{\mathbf{r}'} + \frac{1}{4}). \quad (1)$$

Here $\mathbf{s}_{\mathbf{r}}$ denotes the spin of the electron at site \mathbf{r} and $H_{\text{orb}}^{\mathbf{r}, \mathbf{r}'}$ are operators acting on the orbital degrees of freedom. For the TM-atoms arranged in a cubic lattice, these take the form

$$H_{\text{orb}}^{\mathbf{r}, \mathbf{r}'} = J(4\hat{\pi}_{\mathbf{r}}^\alpha \hat{\pi}_{\mathbf{r}'}^\alpha - 2\hat{\pi}_{\mathbf{r}}^\alpha - 2\hat{\pi}_{\mathbf{r}'}^\alpha + 1), \quad (2)$$

where the $\hat{\pi}_{\mathbf{r}}^\alpha$ denote orbital pseudospin operators acting on the appropriate orbital multiplet and $\alpha = x, y, z$ is the direction of the bond $\langle \mathbf{r}, \mathbf{r}' \rangle$. For the case at hand, $\hat{\pi}_{\mathbf{r}}^\alpha = \frac{1}{4}(-\sigma_{\mathbf{r}}^z \pm \sqrt{3}\sigma_{\mathbf{r}}^x)$ for $\alpha = x$ and y and $\hat{\pi}_{\mathbf{r}}^z = \frac{1}{2}\sigma_{\mathbf{r}}^z$.

We have not yet studied the full version of this model; here we just discuss the *orbital-only* approximation in which the spin degrees of freedom are suppressed. This approximation may be presumed to capture the essential orbital physics of the systems at hand, as discussed in Refs. [8, 14, 21]. Notwithstanding, the model itself is of direct relevance. Indeed, when the effects of the strain field cannot be neglected, there are Jahn-Teller orbital-orbital interactions mediated by this field which resolve the orbital degeneracy. For the case of e_g -type compounds it is well known (see [22]) that the effective interactions between the orbitals are exactly of the 120° -type.

The situation in the t_{2g} -compounds (e.g., LaTiO_3) is somewhat more complicated. Neglecting Jahn-Teller effects, an interaction as in Eqs. (1-2) emerges, but now the operators are given by $\hat{\pi}_{\mathbf{r}}^\alpha = \frac{1}{2}\sigma_{\mathbf{r}}^\alpha$ for $\alpha = x, y, z$, see [21]. This is called the *orbital compass* model; the associated orbital-only approximation is derived analogously. When the strain fields are introduced, the upshot is another orbital-only term akin to those discussed so far. In the t_{2g} cases our analysis is not yet complete. Hence, in this paper, we will confine the bulk of our attention to the 120° -model.

We remark that in all of these models, ordering among the spins is not necessarily a question of pertinence. Indeed, in the itinerant-electron version of the orbital compass model, the elegant Mermin-Wagner argument of Ref. [20] apparently precludes this possibility. However, the results in Ref. [20] do *not* preclude the physically relevant possibility of orbital ordering which, as we show in this paper, is realized at least in the classical versions of these systems.

Henceforth, we will deal only with the orbital pseudo-spins which we denote by $\mathbf{S}_{\mathbf{r}}$ instead of $\hat{\pi}_{\mathbf{r}}$. In the context of the orbital-only models, we consider the standard $S \rightarrow \infty$ finite temperature limit. As is well known [23, 24], this results in the classical analogues of the respective Hamiltonians, where the quantum variables are replaced by classical two or three-component spins. We proceed with a concise definition.

Classical orbital-only models. We start with the 120° -model which is the most prominent of all of the above. The model is defined on the usual cubic lattice where at each site \mathbf{r} there is a unit-length two-component spin (associated with the two dimensional e_g subspace) denoted by $\mathbf{S}_{\mathbf{r}}$. Let $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$ denote three evenly-spaced vectors on the unit circle separated by 120° . To be specific let us have $\hat{\mathbf{a}}$ point at 0° with $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$ pointing at $\pm 120^\circ$, respectively. We define the projection $S_{\mathbf{r}}^{(\hat{\mathbf{a}})} = \mathbf{S}_{\mathbf{r}} \cdot \hat{\mathbf{a}}$, and similarly for $S_{\mathbf{r}}^{(\hat{\mathbf{b}})}$ and $S_{\mathbf{r}}^{(\hat{\mathbf{c}})}$. Then the 120° orbital model Hamiltonian is given by

$$\mathcal{H} = -J \sum_{\mathbf{r}} (S_{\mathbf{r}}^{(\hat{\mathbf{a}})} S_{\mathbf{r}+\hat{\mathbf{e}}_x}^{(\hat{\mathbf{a}})} + S_{\mathbf{r}}^{(\hat{\mathbf{b}})} S_{\mathbf{r}+\hat{\mathbf{e}}_y}^{(\hat{\mathbf{b}})} + S_{\mathbf{r}}^{(\hat{\mathbf{c}})} S_{\mathbf{r}+\hat{\mathbf{e}}_z}^{(\hat{\mathbf{c}})}), \quad (3)$$

where the classical nature of the interaction always allows us to set $J > 0$.

The Hamiltonian of the orbital compass model has an identical form, i.e., we can still write

$$\mathcal{H} = -J \sum_{\mathbf{r}, \alpha} S_{\mathbf{r}}^{(\alpha)} S_{\mathbf{r}+\hat{e}_\alpha}^{(\alpha)}, \quad (4)$$

only now $\mathbf{S}_{\mathbf{r}}$ are three-component spins and the superscripts represent the corresponding Cartesian components. The seminal feature of both models is an infinite degeneracy of the ground state. In particular, any constant spin-field, $\mathbf{S}_{\mathbf{r}} = \mathbf{S}$, is a ground state in both cases. This is established by noting that $\sum_{\alpha} [S_{\mathbf{r}}^{(\alpha)}]^2$ is constant in both problems. Thus, up to an irrelevant constant, the general Hamiltonian of Eq. (4) is

$$\mathcal{H} = \frac{J}{2} \sum_{\mathbf{r}, \alpha} (S_{\mathbf{r}}^{(\alpha)} - S_{\mathbf{r}+\hat{e}_\alpha}^{(\alpha)})^2, \quad (5)$$

which is obviously minimized when $\mathbf{S}_{\mathbf{r}}$ is constant. We emphasize that the continuous symmetries which underscore these ground states are just symmetries of the states and *not* of the Hamiltonian itself. Therefore, at least in the classical orbital-only models, we are not in a setting where a Mermin-Wagner argument can be applied.

Matters are further complicated because, as it turns out, the constant spin fields are *not* the only ground states. Indeed, in the 120° -model, starting from some constant-field ground state, another ground state may be obtained, e.g., by reflecting all spins in the xy -plane through the vector \hat{c} . This new state can be further mutated by introducing more flips of this type in other planes parallel to the xy -plane. Obviously, similar alterations of the “pristine” states can take place in the other two coordinate directions. What is not so obvious, but nevertheless true, is that the abovementioned exhaust all the possible ground states for the 120° -model: There is one direction of stratification (layering); the corresponding projection of $\mathbf{S}_{\mathbf{r}}$ is constant throughout the system, leaving two possibilities for the other projections. In the various planes orthogonal to the stratification directions either of these choices can be independently implemented. This classification is proved by considering all possibilities of an elementary cube with a single spin fixed, and ensuring consistency in the tiling of the lattice, see Fig. 1. The ground state situation for the orbital compass model is far more complicated and it will not be discussed till the end of this paper.

Let us now investigate the effects of finite temperature. Here, in general, we will see there is a fluctuation driven stabilization—sometimes known as “order by disorder” [25]—that selects only a few of the ground states. The arguments differ from the established standards, in part due to the

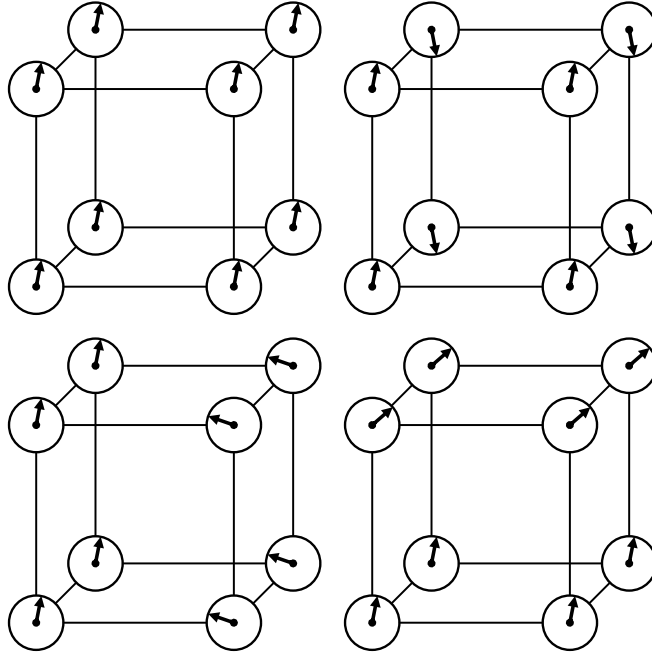


FIG. 1: The four possible ground states for the 120° model on a cube with one spin fixed. The stratification structure of any (global) ground state is demonstrated by checking for consistency between all neighboring cubes.

complications caused by the stratified ground states. We will focus on the 120° -model. Here we can parameterize each spin $\mathbf{S}_{\mathbf{r}}$ by the angle $\theta_{\mathbf{r}}$ with the x -axis. In this language, let us consider the finite-temperature fluctuations about the “pristine” ground states where each $\theta_{\mathbf{r}} = \theta^*$. At low temperatures, nearby spins will tend to be aligned, so we can work with the variables $\vartheta_{\mathbf{r}} = \theta_{\mathbf{r}} - \theta^*$. Neglecting terms of order higher than quadratic in $\vartheta_{\mathbf{r}}$, the Hamiltonian (5) becomes

$$\mathcal{H}_{\text{sw}} = \frac{J}{2} \sum_{\mathbf{r}, \alpha} q_{\alpha}(\theta^*) (\vartheta_{\mathbf{r}} - \vartheta_{\mathbf{r} + \hat{\mathbf{e}}_{\alpha}})^2, \quad (6)$$

where $\alpha = x, y, z$ while $q_x(\theta^*) = \sin^2(\theta^*)$, $q_y(\theta^*) = \sin^2(\theta^* + 120^\circ)$ and $q_z(\theta^*) = \sin^2(\theta^* - 120^\circ)$.

Our preliminary goal is to compute the free energy as a function of θ^* . Let us assume that we are on a finite torus of linear dimension L . Interpreting θ^* as the *average* of $\theta_{\mathbf{r}}$ on the torus, we let $Z_L(\theta^*)$ to denote the partition function

$$Z_L(\theta^*) = \int \delta\left(\sum_{\mathbf{r}} \vartheta_{\mathbf{r}} = 0\right) e^{-\beta \mathcal{H}_{\text{sw}}} \prod_{\mathbf{r}} \frac{d\vartheta_{\mathbf{r}}}{\sqrt{2\pi}}. \quad (7)$$

A standard Gaussian calculation then yields

$$-\log Z_L(\theta^*) = \frac{1}{2} \sum_{\mathbf{k} \neq \mathbf{0}} \log \left\{ \sum_{\alpha} \beta J q_{\alpha}(\theta^*) E_{\alpha}(\mathbf{k}) \right\}, \quad (8)$$

where $\mathbf{k} = (k_x, k_y, k_z)$ is a vector in the reciprocal lattice and $E_{\alpha}(\mathbf{k}) = 2 - 2 \cos k_{\alpha}$. The right-hand side divided by L^3 produces in the limit $L \rightarrow \infty$ the (dimensionless) spin-wave free energy $F(\theta^*)$ for deviations around direction θ^* .

A tedious and rather unenlightening bit of analysis now shows that the spin-wave free energy $F(\theta^*)$ has *strict* minima at $\theta^* = 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ$ and 300° . As for the stratified states, we have shown that the only states which need explicitly be considered are the period-2 states. To illustrate, consider the state which alternates between $\theta \equiv \theta^*$ and $\theta \equiv -\theta^*$ in the planes perpendicular to the x direction. Here the limiting free energy is given by

$$\tilde{F}(\theta^*) = \frac{1}{4} \int_{[-\pi, \pi]^3} \frac{d\mathbf{k}}{(2\pi)^3} \log \det(\beta J \Pi_{\mathbf{k}}(\theta^*)), \quad (9)$$

where $\Pi_{\mathbf{k}}(\theta^*)$ is the matrix

$$\Pi_{\mathbf{k}}(\theta^*) = \begin{pmatrix} q_1 E_1 + q_+ E_+ & q_- E_- \\ q_- E_- & q_1 E_1^* + q_+ E_+ \end{pmatrix}. \quad (10)$$

Here we have let $q_{\alpha} = q_{\alpha}(\theta^*)$ and $E_{\alpha} = E_{\alpha}(\mathbf{k})$ be as above, and abbreviated $E_{\alpha}^*(\mathbf{k}) = E_{\alpha}(\mathbf{k} + \pi \hat{e}_{\alpha})$, $q_{\pm} = (q_2 \pm q_3)/2$ and $E_{\pm} = E_2 \pm E_3$. Some convexity analysis shows that $\tilde{F}(\theta^*) > F(0^\circ)$ for $\theta^* \neq 0^\circ, 180^\circ$ (while, as is readily checked, $\tilde{F}(0^\circ)$ equals $F(0^\circ)$). Further arguments can be enacted which demonstrate that, in general, the stratified ground states are suppressed, exponentially, according to the total area of the ‘‘stratificational’’ defects. Thus, at the level of spin-wave approximation, it is clear that finite-temperature effects will select six ground states above all others. Of course, this is only the beginning of a complete mathematical analysis: One must account for all other possible thermal disturbances and their interactions, the interactions of said additional disturbances with the spin waves and, not to mention, the interaction of spin waves with one another. Any such approach is, of course, hopeless even at the level of perturbation theory. (The latter, as can be readily verified, is beset with infrared divergences even at the lowest non-vanishing order.)

Our approach, which automatically circumvents these (and as yet other unnamed) issues, is to *block* the lattice. We then tabulate—with controllable tolerance—whether or not each block mimics the harmonic behavior of a favored ground state embellished with spin-wave excitations.

The key is to show that with large probability such regions are indeed heavily favored and, of equal importance, distinct regions of this type corresponding to *different* favored ground states are separated by domain walls which exhibit a positive stiffness. We note, in accord with this approach, that in the spin-wave approximations the ratios of the per site partition functions depend only on θ^* and not on temperature. Hence the domain-wall stiffness will not diverge as $T \rightarrow 0$ implying the existence of ostensibly large scale events at low temperatures. For our purposes this means that the desired suppression of the domain walls between the above ground states can be extracted only after an appropriately large coarse graining of the system.

The argument begins by the consideration of two scales: a spin-deviation scale Δ and the block scale B . The principal idea is that if every pair of spins satisfies $|S_{\mathbf{r}}^{(\alpha)} - S_{\mathbf{r}+\hat{\mathbf{e}}_\alpha}^{(\alpha)}| < \Delta$, the Gaussian approximation is “good” while if a neighboring pair violates this condition, the energetic cost is ruinous. It is not hard to check that these requirements are met if $\beta J \Delta^2 \gg 1$ while $\beta J \Delta^3 \ll 1$; thus, for large β , an acceptable choice would be $\Delta = \beta^{-\frac{5}{12}}$. We partition the circle into six ample regions centered around the spin-wave free energy minima, i.e., at $\theta = 0^\circ, \pm 60^\circ$, etc. These six regions are separated by six intervals of size proportional to $B \Delta$ (with $B \Delta \ll 1$) centered around $\pm 30^\circ, \pm 90^\circ$ and $\pm 150^\circ$, which altogether partition the unit circle.

Next we consider our blocks of spins with block-scale B . These will all be translates of a single block Λ_B of $(B + 1)^3$ sites by vectors $B\mathbf{t}$ where \mathbf{t} is a vector with integer components. The size of B will be determined momentarily; we reemphasize that although B has to be taken somewhat large, its value will be independent of temperature. In order to determine a working definition of a *domain wall*, we define a block to be *good* if all spins within the block satisfy the aforementioned $|S_{\mathbf{r}}^{(\alpha)} - S_{\mathbf{r}+\hat{\mathbf{e}}_\alpha}^{(\alpha)}| < \Delta$ *and* all have values in one and only one of the six regions about the free energy minima. Those blocks which do not satisfy these criteria, the *bad blocks*, constitute the elements of our domain walls. This nomenclature is justified by the observation that since neighboring blocks share a face of sites in common, no neighboring pair of good blocks can exhibit distinct types of goodness. The latter implies that connected components of good blocks must be homogeneous in regards of their type and that regions of distinct type of goodness are separated by closed “surfaces” (domain walls, contours, etc.) composed of bad blocks.

Keeping in mind that we must establish “good behavior” with high-probability, let us dissect the complementary event, i.e., classify all types of “bad behavior” on a single block. We will distinguish three types of bad blocks: First, a block might have an “excited” bond, where the energy condition is violated. Next, recalling that $B \Delta \ll 1$, it is clear that if the spins themselves have

only small deviations but not all spins are in the same ground-state region, then all of the spins must be concentrated in the dividing regions on the circle, i.e., far away from the free energy minima. Finally, we might have no energetic deviations but still not all spins in a single ground-state region. This implies that the block is a miniature portrait of a stratified state. We anticipate that these probabilities will go as $B^3(c_1\beta J)^{B^3/2}e^{-\beta Jc_1\Delta^2}$, $e^{-c_2B^3}$ and $e^{-c_3B^2}$, respectively, where c_i are numbers of order unity.

Assuming the above is (provably) correct, we must still tend to the question of the domain-wall stiffness. As it turns out, a particular sort of estimate demonstrating a small probability of bad events can also be translated into an estimate which establishes a substantial domain wall stiffness. Indeed, we will bring into play various techniques based on *reflection positivity* which come under the heading of *chessboard estimates* [26, 27]. These go roughly as follows: To each (reflection-symmetric) event \mathcal{A} which can take place in Λ_B we may define the quantity $\mathfrak{z}_\beta(\mathcal{A})$ which is the partition function per site computed under the constraint that \mathcal{A} occurs in every translate of Λ_B (by integer multiples of B). Then the thermal probability of observing \mathcal{A} is bounded by

$$\mathbb{P}_\beta(\mathcal{A}) \leq \left(\frac{\mathfrak{z}_\beta(\mathcal{A})}{\mathfrak{z}_\beta} \right)^{B^3} \quad (11)$$

where \mathfrak{z}_β is the unconstrained partition function per site. Moreover, the probability of the simultaneous occurrence of $n \geq 1$ translates of the event \mathcal{A} is bounded by the right-hand side of Eq. (11) raised to the n -th power.

Evidently, all that is needed to establish that the right-hand side of Eq. (11) is small enough when \mathcal{A} is one of the bad events. For the homogeneous badness this is exactly the spin-wave calculation discussed earlier. For a block with ℓ layers of stratification it turns out, perhaps not surprisingly, that the right-hand side of Eq. (11) decays like $e^{-\kappa\ell B^2}$, for some $\kappa > 0$. Finally, the energetic “disasters” can also be estimated along the lines of what was anticipated above for this case. Thus, increasing β and B (and adjusting Δ so that the spin-wave approximation is meaningful), we can estimate the total cost of a bad block by a number as small as we like. Hence, the good blocks are prevalent and different types of good blocks, even if well separated, cannot easily coexist within the same sample due to the suppression of domain walls. These are exactly the ingredients needed for a Peierls argument and we may conclude that, at low temperatures, there are (at least) six distinct infinite-volume states. At high temperatures the Gibbs state is unique so at some point a phase transition has to occur.

The situation in the orbital-compass model is considerably more complicated due to the pro-

fusion of additional ground states. Here, starting from a homogeneous ground state, the spins in an entire plane can be continuously rotated about the axis perpendicular to that plane without any disruption of the energetics. Thus, unlike in the 120° -model, an elementary cube with one spin fixed has a *continuum* of distinct ground states. Notwithstanding, it has been established [28] that even in this case orbital ordering occurs. However, the nature of the thermal states differs, in certain details, from that of the 120° -model. E.g., $\langle \mathbf{S}_r \rangle$ vanishes at each site with the ordering being something along the lines of a nematic type.

In conclusion, we have demonstrated that the classical 120° -model exhibits long-range ordering at sufficiently low temperatures. The key feature is that the degeneracy of the ground states is broken at positive temperature via a kind of “order-by-disorder” mechanism. A complete argument, on a level of mathematical theorems, has already been constructed for the 120° -model [29] and similar (albeit less explicit) results hold for the orbital compass model [28]. All of this strongly indicates that there is orbital ordering in the full-blown quantum/itinerant-electron versions of these orbital models.

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