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# Orbital-dependent singlet dimers and orbital-selective Peierls transitions in transition-metal compounds

Sergey V. Streltsov[1,2,*] and Daniel I. Khomskii[3]
[1]*Institute of Metal Physics, S. Kovalevskoy Street 18, 620990 Ekaterinburg, Russia*
[2]*Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia*
[3]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln, Germany*

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We show that in transition-metal compounds containing structural metal dimers there may exist in the presence of different orbitals a special state with partial formation of singlets by electrons on one orbital, while others are effectively decoupled and may give, e.g., long-range magnetic order or stay paramagnetic. A similar situation can be realized in dimers spontaneously formed at structural phase transitions, which can be called the orbital-selective Peierls transition. This can occur in the case of strongly nonuniform hopping integrals for different orbitals and small intra-atomic Hund's rule coupling $J_H$. Yet another consequence of this picture is that for an odd number of electrons per dimer there exists competition between the double-exchange mechanism of ferromagnetism and the formation of a singlet dimer by the electron on one orbital, with the remaining electrons giving a net spin of a dimer. The first case is realized for strong Hund's rule coupling, typical for 3$d$ compounds, whereas the second is more plausible for 4$d$-5$d$ compounds. We discuss some implications of these phenomena, and consider examples of real systems, in which the orbital-selective phase seems to be realized.

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*Introduction*. Molecular-like clusters exist in many inorganic transition-metal (TM) compounds. Sometimes these are determined just by the crystal structure, such as dimers in $CuTe_2O_5$ [1,2] or trimers in $Ba_4Ru_3O_{10}$ [3]. However such molecular clusters may also appear spontaneously from a homogeneous solid, e.g., due to the Peierls or spin-Peierls transition, which results in the formation of dimers in $VO_2$ [4], $MgTi_2O_4$ [5], or $CuGeO_3$ [6], trimers in $LiVO_2$ [7], tetramers in $CaV_4O_9$ [8], or even heptamers like in $AlV_2O_4$ [9]. In many such cases the TM ions have several electrons in different orbital states, and often just one particular orbital is responsible for the formation of a molecular cluster. The question arises, what is in such a case the role and the "fate" of other electrons which can exist on a TM ion.

Usually the intra-atomic Hund's rule exchange $J_H$ binds all electrons of an ion into a state with maximum spin, and, e.g., when one particular electron on a certain orbital forms a valence bond with the neighboring site, other electrons just follow, so that all electrons are in a spin singlet state with the neighboring site. However it is not the only possibility. One can argue that if the intersite electron hopping is large compared with the Hund's exchange (which can happen especially in 4$d$ and 5$d$ systems, in which the covalency is strong, but $J_H$ is reduced), only one "active" electron at a site would participate in the formation of a molecular orbital (MO), the other electrons being, in a sense, decoupled and able to live their own life. For example if the remaining electrons would interact with other sites, they could form some magnetically ordered state, which would coexist with the molecular orbitals formed by "active" electrons. That is, in this case we can speak about the *orbital-dependent dimer formation*, or *orbital-dependent Peierls transition.* The same mechanism leads to the competition between double-exchange ferromagnetism and the formation of singlet dimers for a fractional number of electrons per center.

In this Rapid Communication we substantiate this picture by different means, using analytical and numerical calculations, and discuss some experimental examples, in which this phenomenon seems to take place.

*Model treatment*. Suppose we have a dimer, or a chain of dimers with different orbitals at each site, only one of which has a strong overlap with neighboring sites [white orbitals in Fig. 1(a)]. Those orbitals provide strong intersite hopping $t_c$. If there will be two electrons per site in a dimer, then one electron is localized on the bonding combination of $c$ orbitals, while another electron can occupy the orbital which has no, or much smaller, overlap and hopping $t_d$ with the neighbors [shaded orbitals in Fig. 1(a)]. These localized electrons ($d$ electrons) interact with the "mobile" $c$ electrons by the Hund's rule interaction $H_{\rm Hund} = -J_H(\frac{1}{2} + 2\vec{S}_{id}\vec{S}_{ic})$, where $S_{id}$ and $S_{ic}$ are spins of localized and mobile electrons at site $i$. And of course all electrons in principle would experience a local (Hubbard) repulsion $U$. Thus the total model for the case of two different orbitals per site can be written in the following form:

$$H = \sum_{\langle ij\rangle\sigma}(-t_c c^{\dagger}_{i\sigma}c_{j\sigma} - t_d d^{\dagger}_{i\sigma}d_{j\sigma}) + U\sum_{i\sigma\sigma'} n_{i\sigma}n_{i\sigma'} - J_H\sum_i\left(\frac{1}{2} + 2\vec{S}_{id}\vec{S}_{ic}\right) + H_{\rm inter}. \quad (1)$$

Here the first three terms describe electrons in a dimer, and $H_{\rm inter}$ takes into account electron hopping and other coupling terms (e.g., the exchange interaction) between dimers. The ground state of a dimer would be different depending on the ratios of different parameters in Eq. (1).

(1) If we first ignore the Hubbard interaction and assume the strong hopping, $t_c \gg J_H$ (and $t_d$ is small), the $c$ electrons would form a singlet state, a bonding state described by the

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[*] streltsov@imp.uran.ru

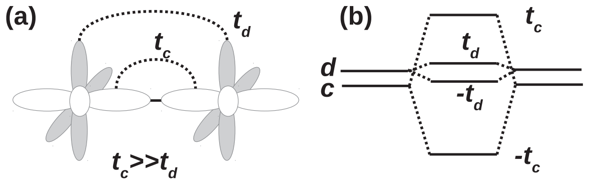

FIG. 1. (a) The sketch illustrating how different hopping integrals may appear in the system. The $t_{dd\sigma}$ hopping between white orbitals is larger than between gray $t_{dd\delta}$. (b) Corresponding level splitting.

usual MO [see Fig. 1(b)]: $|\mathrm{MO}\rangle = \frac{1}{2}|(c^\dagger_{1\uparrow} + c^\dagger_{2\uparrow})(c^\dagger_{1\downarrow} + c^\dagger_{2\downarrow})\rangle$. The other electrons, not participating in formation of this singlet, would be then effectively decoupled; i.e., the total wave function would be

$$|\widetilde{\mathrm{MO}}\rangle = \tfrac{1}{2}|(c^\dagger_{1\uparrow} + c^\dagger_{2\uparrow})(c^\dagger_{1\downarrow} + c^\dagger_{2\downarrow})\Psi_d\rangle. \tag{2}$$

The $d$ electrons can be also described by the singlet state [but in Heitler-London (HL) form more appropriate for localized electrons]: $\Psi^{\mathrm{HL}}_d = |d^\dagger_{1\uparrow}d^\dagger_{2\downarrow} - d^\dagger_{1\downarrow}d^\dagger_{2\uparrow}\rangle/\sqrt{2}$, or by other combinations of localized spins, e.g., $\Psi^{\mathrm{AFM}}_d = |d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}\rangle$ or $\Psi^{\mathrm{FM}}_d = |d^\dagger_{1\uparrow}d^\dagger_{2\uparrow}\rangle$, to model partially ordered states. A particular choice of $\Psi_d$ depends on properties of the system, but the orbital-selective behavior can be observed in any of them. If we chose the HL form of $\Psi^{\mathrm{HL}}_d$, then one gains in $\widetilde{\mathrm{MO}}$ the full bonding energy given by $t_c$, but does not lower the total energy due to the Hund's term, $\langle\widetilde{\mathrm{MO}}|H_{\mathrm{Hund}}|\widetilde{\mathrm{MO}}\rangle = 0$.

(2) If, instead, $J_H > t_c (\gg t_d)$, then first of all the strong Hund's exchange would couple two spins at a site into one common state with $S = 1$, and then we should form a singlet out of these two states $S = 1$ at neighboring sites. The corresponding wave function would have the form [10]

$$\begin{aligned} |\widetilde{\mathrm{HL}}\rangle = |S_{\mathrm{tot}} = 0\rangle &= \frac{1}{\sqrt{3}}\big(\big|S^z_1 = 1, S^z_2 = -1\big\rangle \\ &\quad + \big|S^z_1 = -1, S^z_2 = 1\big\rangle - \big|S^z_1 = 0, S^z_2 = 0\big\rangle\big) \\ &= \frac{1}{\sqrt{3}}\Big(|c^\dagger_{1\uparrow}d^\dagger_{1\uparrow}c^\dagger_{2\downarrow}d^\dagger_{2\downarrow}\rangle + |c^\dagger_{1\downarrow}d^\dagger_{1\downarrow}c^\dagger_{2\uparrow}d^\dagger_{2\uparrow}\rangle \\ &\quad - \frac{1}{2}|(c^\dagger_{1\uparrow}d^\dagger_{1\downarrow} + c^\dagger_{1\downarrow}d^\dagger_{1\uparrow})(c^\dagger_{2\uparrow}d^\dagger_{2\downarrow} + c^\dagger_{2\downarrow}d^\dagger_{2\uparrow})\rangle\Big). \end{aligned} \tag{3}$$

We see that for strong Hund's coupling the dimer wave function has actually not MO, but HL form, the two-electron analog of the usual HL wave function $|\mathrm{HL}\rangle = \frac{1}{\sqrt{2}}|c^\dagger_{1\uparrow}c^\dagger_{2\downarrow} - c^\dagger_{1\downarrow}c^\dagger_{2\uparrow}\rangle$: it does not contain ionic configurations of the type $c^\dagger_{1\uparrow}c^\dagger_{1\downarrow}$, etc. For this state we gain the full Hund's energy, but lose large part of the bonding energy, which for $J_H > (t_c, t_d)$ is more favorable.

The same state, (3), one would get also when we have strong Hubbard interaction $[(U, J_H) > (t_c, t_d)]$. It is interesting to notice that both strong Hund's exchange and Hubbard repulsion lead to localization of electrons at respective sites, and to the HL wave function. This is reminiscent of the notion of Hund's metal (or here rather Hund's insulators) [11,12].

These limiting cases (1) and (2) may be not very realistic, and one has to consider intermediate values of parameters and include both the Hund's rule exchange $J_H$ and the Hubbard $U$. But we will see that the effect illustrated on the limiting case $J_H = U = 0$—the formation of a singlet state by electrons on one orbital, other electrons remaining decoupled and "magnetic"—survives also in a more realistic case. For spontaneous dimerization, such as at a Peierls transition, this would mean that we have a (strong coupling) orbital-selective Peierls transition.

In the general case we can consider this situation using the variational procedure, taking the wave function as the superposition of the $\widetilde{\mathrm{MO}}$ and $\widetilde{\mathrm{HL}}$ states:

$$|\Psi\rangle = c(|\widetilde{\mathrm{MO}}\rangle + \alpha|\widetilde{\mathrm{HL}}\rangle), \tag{4}$$

where $c$ is the normalization factor, and minimizing total energy $\langle\Psi|H|\Psi\rangle$. For simplicity the Hund's rule interaction will be treated in the mean-field way, i.e., substituting $\vec{S}$ by $S^z$ in Eq. (1). Straightforward calculations show that indeed the solution approaches to pure $\widetilde{\mathrm{MO}}$ state for $t_c \gg (U, J_H)$, and tends to the $\widetilde{\mathrm{HL}}$ state in the opposite limit. For $J_H \ll t_c$ the coefficient $\alpha \sim J_H/t_c$. In the opposite limit $J_H \gg t_c$ the solution tends to the pure HL state, $1/\alpha \sim t_c/J_H$. For intermediate values the system gradually switches from one regime, in which the first electron forms a singlet dimer with the neighbor and the second is largely decoupled (orbital-selective dimer formation), to a state in which both electrons are in a singlet state.

Using the wave function (4) with the coefficient $\alpha$ determined variationally, we can also find the value of the average spin at a site, e.g., for the case of antiparallel orientation of spins at two sites, i.e., taking $\Psi^{\mathrm{AFM}}_d = |d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}\rangle$ in (2), and the corresponding part of the HL wave function [the first term in (3), with proper normalization]. The coefficient $\alpha$ in this case is $\alpha = J_H/2t_c$ for $J_H/t_c \ll 1$, and $\alpha = 2J_H/t_c$ in the opposite limit. The average spin $\langle S^z_i\rangle$ on the $i$th site in this case interpolates between the values $\langle S^z_i\rangle = 1/2$ for $J_H = 0$ and the "full" value $\langle S^z_i\rangle = 1$ for very large $J_H$. The asymptotic behavior is $\langle S^z_i\rangle = 1/2 + J_H/4t_c$ for $J_H/t_c \ll 1$ and $\langle S^z_i\rangle = 1 - (t_c/J_H)^2/8$ for $J_H/t_c \gg 1$.

It is important to note that at intermediate values of $J_H/t_c$ the average spin at a site has the value intermediate between 1/2 and 1; i.e., the magnetic moment is $1\mu_B < \mu < 2\mu_B$. It is this moment, strongly reduced as compared with $2\mu_B$ usually expected for the $d^2$ configuration, which would be seen in susceptibility and which could eventually participate in magnetic ordering. Such strong quenching of a moment in such systems may be a signature of partial orbital-selective dimerization.

We can also take into account Hubbard repulsion between electrons in the variational procedure. The results are very similar to the case of Hund's coupling only, with the substitution $J_H \to J_H + U/4$ (for the spin-ordered state considered above). Thus we see that if both $(J_H, U) \ll t_c$, the system is in an orbital-selective regime ($c$ electrons form singlet dimers, $d$ electrons are effectively decoupled from those), and for $(J_H, U) \gg t$ (either both, or at least one of them), we have a HL state (3) with the total spin $S$ per site and suppressed ionic configurations. We see that the strong Hubbard and Hund's couplings act in the same direction: they both suppress the MO state, localize electrons at particular sites, and couple spins at the same ion into a total spin $S$. For strong Hubbard

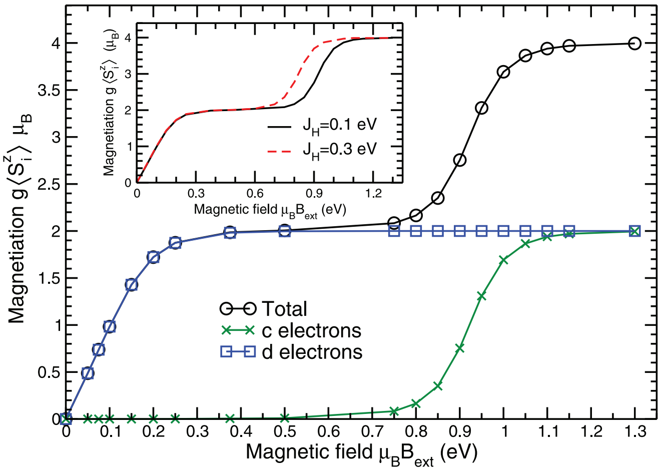

FIG. 2. (Color online) The total and partial magnetization per dimer, calculated in C-DMFT. $t' = 0.1$ eV, $t_d = 0.2$ eV, $t_c = 6t_d$, $J_H = t_d/2$, $U = 5t_d$, $T = 0.1$ eV. Inset shows dependence of total magnetization on Hund's rule exchange.

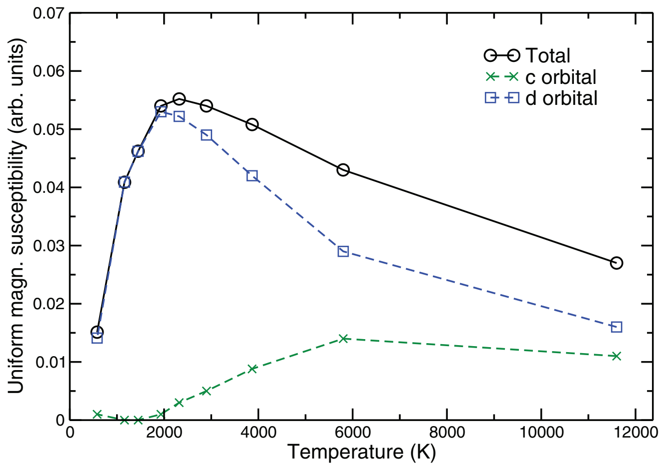

FIG. 3. (Color online) Uniform magnetic susceptibility, calculated in C-DMFT as $\chi = M/B_{\text{ext}}$, where $M$ is magnetization per dimer, and $B_{\text{ext}}$ external magnetic field. $t' = 0.1$ eV, $t_d = 0.4$ eV, $B_{\text{ext}} = 0.1$ eV, $U = 5.25t'$, $t_c = 3t_d$, $J_H = 1.25t_d$.

interactions $U \gg t$ already a relatively weak Hund's coupling $J_H > t^2/U$ is sufficient for that. But in principle we can get the HL state only due to the strong Hund's coupling, even without Hubbard repulsion.

*DMFT calculations*. To check the treatment presented above we consider a model system—a one-dimensional chain of dimers—using the cluster extension of the dynamical mean-field theory (C-DMFT) [13] with the Hirsh-Fye (HF-QMC) solver [14]. There are two orbitals and two electrons per site in the dimer. Intradimer hoppings are $t_d$ and $t_c$, interdimer $-t'$ is the same for both orbitals and allowed only for the neighboring sites. We neglected the intersite Coulomb interaction, so that the sites are coupled by the kinetic energy term only. The on-site Coulomb repulsion term was taken to be $U_{mm}^{\sigma\sigma'} = U$, $U_{mm'}^{\sigma\sigma'} = U - 2J_H$, $U_{mm'}^{\sigma\sigma} = U - 3J_H$. The Hund's rule exchange was considered in the Ising form.

The field dependence of the magnetization presented in Fig. 2 shows that there is no magnetic response in a zero external field (as here both $t_c$ and $t_d$ are nonzero, the ground state of a dimer is a singlet for both electrons). An increase of $B_{\text{ext}}$ drives the systems to the orbital-selective regime, when $c$ electrons initially are predominantly in the MO singlet state, while $d$ electrons are detached, and start to be polarized only at higher fields, and also the $c$-electron singlet is broken and $c$ electrons become polarized. As was argued above an internal exchange field (e.g., Heisenberg exchange) may result in a similar situation. Moreover the range of the orbital-selective phase depends on the $J_H/t_c$ ratio (see inset of Fig. 2).

A different character of the orbitals is also reflected in the temperature dependence of the uniform magnetic susceptibility $\chi(T)$. It is seen in Fig. 3 that the overall temperature behavior of $\chi$ is consistent with what one may expected for dimers: a drastic decrease at low temperatures (LT) due to the spin singlet state formation and Curie-like tail at high temperatures. However partial contributions to the susceptibility is again quite different. The orbital with the smallest hopping provides the largest contribution at low $T$. Corresponding electrons behave as free spins at intermediate temperatures, whereas $c$ electrons are still in a singlet dimer state. Only with further increase of the temperature the second orbital starts to contribute. This may result in the shift of the magnetic susceptibility maximum and has to be taken into account in the fitting procedures (to evaluate exchange integrals) for systems with the orbital-selective behavior.

Thus these results indeed confirm our model treatment presented above: for the chosen parameters one may observe formation of the orbital-selective singlet state, which, if we start from a regular system and make spontaneous dimerization, would correspond to the orbital-selective Peierls transition.

*Real materials*. As we saw above, the orbital-selective singlet state can occur for specific conditions: when hopping for one orbital in a dimer is comparable or larger than the intra-atomic Hund's exchange (and Hubbard repulsion). This is less likely in $3d$ systems, for which $U$ or $J_H$ are usually larger than hopping ($U \sim 3$–6 eV, $J_H \sim 0.7$–1.0 eV), and this is why this situation is not realized in $V_2O_3$ [15], as was proposed by Castellani *et al.* [16].

But such state could easily appear in $4d$ and $5d$ systems, where both $J_H$ and $U$ are strongly reduced, while $t$ is getting larger. Thus for $5d$ metals typically $U \sim 1$–2 eV, $J_H \sim 0.5$ eV, but the radius of $5d$ orbitals is larger than of $3d$, and we can get to the situation with $dd$ hopping at least of order or larger than $(U, J_H)$.

Such a situation may be met in some systems with dimerization, e.g., $Li_2RuO_3$, where Ru-Ru dimers are formed in the common edge (of $RuO_6$ octahedra) geometry. The hopping between two $xy$ orbitals directed to each other in the dimer is ~1.2 eV, which is much larger than between any other of $t_{2g}$ orbitals (~0.3 eV) [17]. This may explain why in the high-temperature phase magnetic susceptibility behaves as for paramagnetic $S = 1/2$, not $S = 1$, centers (as it should be for $Ru^{4+}$) [17].

Also some $3d$ compounds can show the behavior described above, although it is less likely than for $4d$ and $5d$ systems. Most probably this is the situation in $V_4O_7$ [18–20]. The NMR

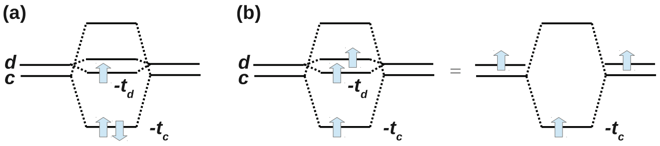

FIG. 4. (Color online) Possible orbital states in the case of the dimer with 2 orbitals per site and 3 electrons per dimer.

data suggest that there is a partial formation of singlets in $V^{3+}$ chains, with the remaining magnetic moment of $V^{3+}$ ($d^2$) strongly reduced [19]. Thus, though this system is hardly an example of complete decoupling of two electrons on each V, it is apparently "half way" to this regime.

Yet another realization of orbital-selective dimerization can exist when electrons on one orbital form dimers, but the others fill three-dimensional bands, so that the resulting state could be a metal, but with dimers. Such state seems to exist in $MoO_2$ [21]. $MoO_2$ has a rutile structure, and Mo ions form dimers similar to those existing below the famous metal-insulator transition in $VO_2$. But, whereas in $VO_2$ there is one electron per site, which forms singlet dimers, so that the LT state of $VO_2$ is a diamagnetic insulator, in Mo there are two electrons per Mo, one of which gives in $MoO_2$ the same dimers as in $VO_2$, and the other electrons provide metallic conductivity.

A special situation can exist if there is fractional occupation of $d$ levels, giving an odd number, e.g., three, of electrons per dimer [22]. When $J_H > t$, one expects the usual double exchange (DE), which gives the state with all spins parallel [Fig. 4(b)] with the energy $E_{2b} = -t_c - J_H$, if the Hund's rule term in Eq. (1) is treated in a mean-field way. In the opposite case [Fig. 4(a)] two electrons form a singlet bonding state, with the remaining unpaired spin-1/2 per dimer and with the energy $E_{2a} = -2t_c - t_d - J_H/2$. Thus the DE ferromagnetism is realized if $J_H > 2(t_c + t_d)$; in the opposite limit a partial singlet formed on strongly overlapping orbitals suppresses DE and reduces total spin. The first situation is typically realized in $3d$ systems with large $J_H$, e.g., in Zener polarons in doped manganites (note that Zener suggested this concept just for Mn dimers) [23,24]. The alternative state, with partial singlets, is more plausible for $4d$-$5d$ systems; e.g., it was found in $Y_5Re_2O_{12}$ [25].

*Conclusions.* Using analytical and numerical calculations we demonstrate that in systems with orbital degrees of freedom there may exist structural dimers in the orbital-selective singlet state, or there may appear a (strong coupling) orbital-selective Peierls transition: electrons on one orbital, having strong overlap and large hopping within the dimers, form a singlet state (bonding MO), whereas other electrons remain essentially decoupled and can, for example, give long-range magnetic ordering (with strongly reduced moment) or stay paramagnetic. This situation resembles somewhat that of the orbital-selective Mott transition [26]. For partial filling of $d$ levels, e.g., three electrons per dimer, this can lead to the suppression of the usual double-exchange mechanism of ferromagnetism: mobile electrons can form singlets, the remaining electrons being decoupled from those. Typically such phenomena may occur when hopping between particular orbitals becomes larger than (or at least comparable to) the Hubbard repulsion $U$ and Hund's exchange $J_H$. It is not very plausible for $3d$ systems (although there are such examples); but it is likely for $4d$-$5d$ compounds, for which both $U$ and $J_H$ are strongly reduced, but the covalency and hopping are increased. We discuss different possible states which may appear in this situation, consider its possible experimental manifestation, and present some real examples of systems in which this physics seems to play a role.

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