Theoretical investigation of excitonic magnetism in $LaSrCoO_4$

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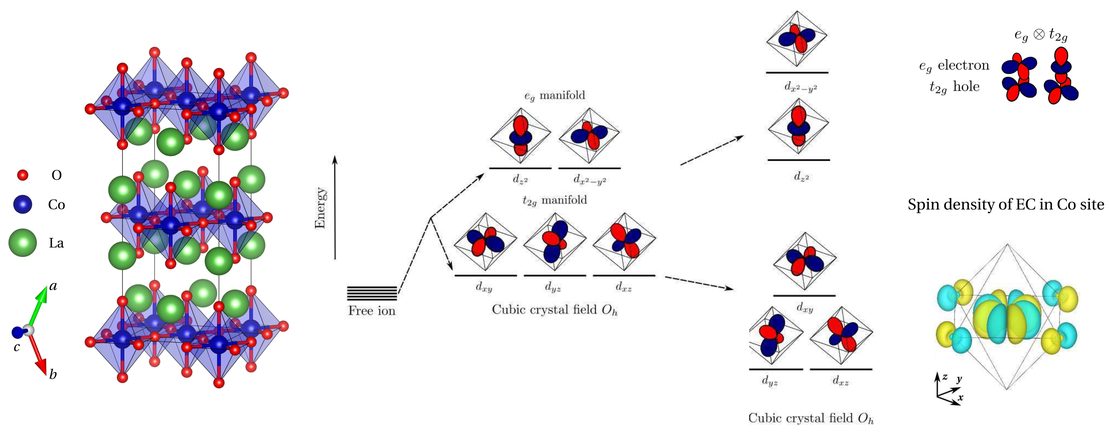
In this work we use the LDA+U approach to search for excitonic ordered ground states of $LaSrCoO_4$. We find an ordered state characterized by the staggered arrangement of magnetic multipoles to be stable over a broad range of Co $3d$ interaction parameters. The ordered state can be described as a $d_{xy} \otimes d_{x^2-y^2}$ excitonic condensate carrying spin $S = 1$. We have also constructed an effective strong-coupling model in to investigate the excitonic gap. We also provide a comparison with previous studies on $LaCoO_3$ and we find that for the same interaction parameters the excitonic gap is smaller (possibly vanishing) in the layered cobaltite.

1 DFT computational details

The $La_{2-x}Sr_xCoO_4$ structure consists of single layers of CoO_6 corner-sharing octahedra separated by a random distribution of La and Sr ions. In order to investigate the possibility of excitonic condensation we simulate the $LaSrCoO_4$ compound employing the virtual crystal approximation on the La atom ($Z_{La} = 56.5$). With this approach the Co will have $+3$ valence with a $3d^6$ electronic configuration. The unit cell vectors used in the calculation are highlighted in on the picture below left panel and correspond to the parameters $a = 6.8019$ Å, $b = 6.8019$ Å, $c = 5.3796$ Å, $\alpha = \pi/2$, $\beta = \pi/2$, and $\gamma = 2.3284$.

The calculations were performed within the density functional theory framework. We used the LDA as exchange-correlation potential and the Coulomb interaction 'U' added as a spin-polarized mean field term for the $3d$ shell of Co. The double-counting was corrected with the so called fully localized limit. The Brillouin zone was sampled with a $4 \times 4 \times 4$ k-mesh, the muffin-tin radii was set to: 2.5 for La, 1.91 for Co and 1.65 for O in bohr units, and the plane wave cut-off $R_{mt}K_{max} = 6$. The calculations were carried out with the WIEN2k software package.



2 Excitonic order parameter

In compounds with a cubic crystal field and d^6 electronic filling, a low-energy exciton is a bound state of an e_g electron and a t_{2g} hole. These excitons correspond to excitations from low spin LS to intermediate spin states IS. Due to the layered structure of La_2CoO_4 only the excitons with $d_{x^2-y^2} \otimes d_{xy}$ orbital configuration will condense. The excitonic order will contribute with an extra anomalous term to the density matrix

$$\Gamma' = 4i \begin{pmatrix} 0&0&0&0&-1\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 1&0&0&0&0 \end{pmatrix} \quad \Gamma'' = 4i \begin{pmatrix} -1&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&0\\ 0&0&0&0&1 \end{pmatrix} \quad D = D_0 + \sum_{\beta=x,y,z} (\phi'_\beta \Gamma' + \phi''_\beta \Gamma'') \otimes \tau_\beta,$$

where Γ' and Γ'' are expressed in the spherical harmonic basis and D_0 is the occupation matrix in the normal phase. We can describe this excitonic state with a three-dimensional complex order parameter $\boldsymbol{\phi}$.

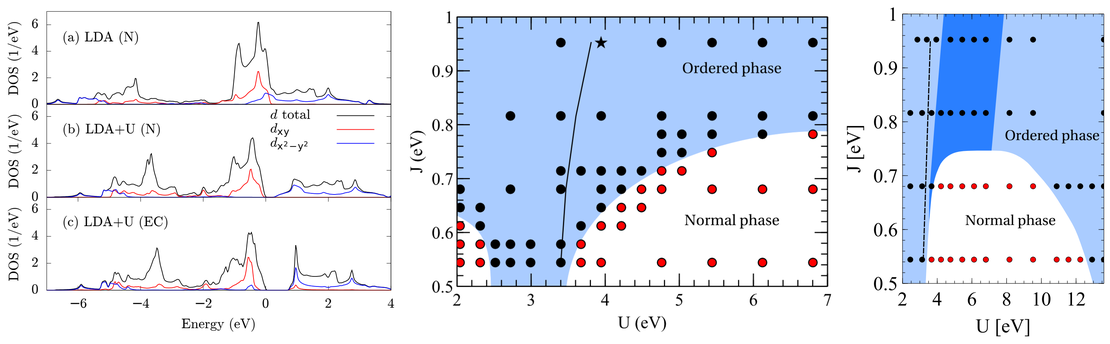
$$\hat{O}'_\beta = \frac{i}{4} \sum_{\sigma,\sigma'=\uparrow,\downarrow} (\tau_\beta)_{\sigma\sigma'} (\hat{c}^\dagger_{2\sigma}\hat{c}_{-2\sigma'} - \hat{c}^\dagger_{-2\sigma}\hat{c}_{2\sigma'})$$
$$\hat{O}''_\beta = \frac{1}{4} \sum_{\sigma,\sigma'=\uparrow,\downarrow} (\tau_\beta)_{\sigma\sigma'} (\hat{c}^\dagger_{-2\sigma}\hat{c}_{-2\sigma'} - \hat{c}^\dagger_{2\sigma}\hat{c}_{2\sigma'}) \qquad \phi_\beta = \langle \hat{O}'_\beta \rangle + i\langle \hat{O}''_\beta \rangle = \phi'_\beta + i\phi''_\beta,$$

where $\hat{c}^\dagger_{m\sigma}$ ($\hat{c}_{m\sigma}$) are the creation (annihilation) operators for $3d$ electrons on the same Co atom (the site indices are not shown for sake of simplicity). The orbital index m refers to the spherical harmonic $Y_{2,m}$ basis with the z quantization axis. The Pauli matrices τ_β ($\beta = x, y, z$) capture the spin-triplet character of the exciton. When the oder parameter is zero, there is no excitonic order and the excitonic spin density on the Co site vanishes.

2.1 LDA+U calculations

LDA+U calculations without SOC lead to a non-zero excitonic order parameter $\boldsymbol{\phi} = (-1)^k(0, 0, \lambda')$ with staggered arrangement in the Co-O plane. This electron-hole coupling lowers the energy and increases the band gap. We studied the stability of the EC as function of the Coulomb interaction U and the Hund's coupling J. The phase diagram resembles previous results obtained for $LaCoO_3$.

Layered $LaSrCoO_4$ [5] — $LaCoO_3$ perovskite [4]



The spin-orbit interaction introduces a non-zero value of the hybridization between e_g and t_{2g} orbitals. $\langle xy, \sigma|\hat{l}_z\hat{s}_z|x^2 - y^2, \sigma\rangle$ coupling generates a non-zero contribution to ϕ''_z. For U= 3.94 and J= 0.95 eV (star-shaped point in the La_2CoO_4 phase diagram) we found two distinct excitonic phases with different symmetries. As shown in the table, the excitonic in-plane excitonic order was found to be the ground state.

Staggered — Uniform

$$\boldsymbol{\phi}^{\parallel}_j = (-1)^j(\ 0\quad 0\ \lambda'_\parallel) + i(0\ 0\ \lambda''_\parallel)$$
$$\boldsymbol{\phi}^{\perp}_j = (-1)^j(\lambda'_\perp\ \lambda'_\perp\ 0) + i(0\ 0\ \lambda''_\perp)$$

Solution	Approach	$\lvert\boldsymbol{\phi}'\rvert$	$\lvert\boldsymbol{\phi}''\rvert$	ΔE (meV/f.u.)
EC	LDA+U	0.289	0.000	-14.25
$EC^\perp$	LDA+U+SOC	0.274	0.098	-14.83
$EC^\parallel$	LDA+U+SOC	0.299	0.096	-17.58

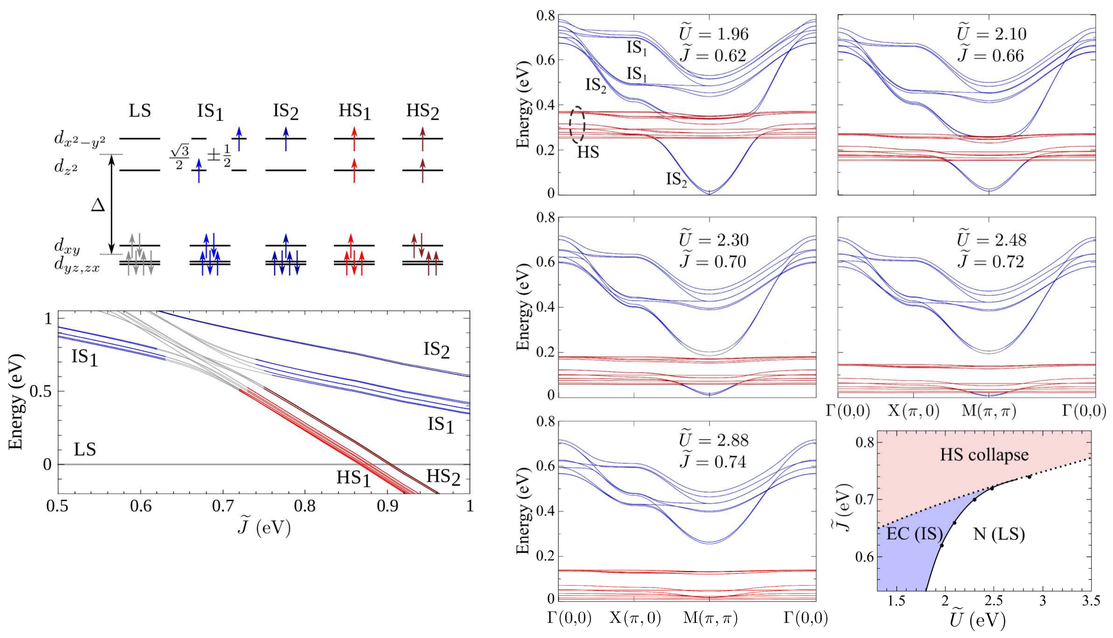
2.2 Strong coupling model

We have build an effective bosonic model to study the excitonic dispersion for different interaction parameters where the starting point was the Cod-shell Hubbard hamiltonian. To this end, we used the set of the 25 lowest energy many-body LS, IS and HS sates of d^6 electronic configuration to treat the non local terms of $\hat{\mathcal{H}}_t^{(\mathbf{r})}$.

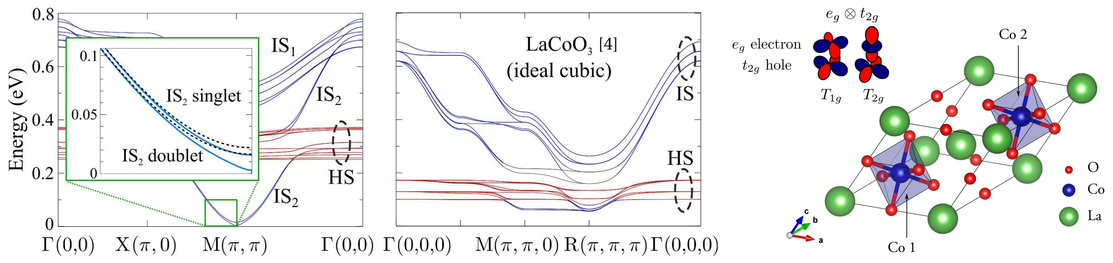
Co d-shell Hubbard model — d^6 LS, IS, HS effective model

$$\hat{\mathcal{H}} = \sum_i \hat{\mathcal{H}}^{(i)}_{\text{at}} + \sum_{\mathbf{r}} \hat{\mathcal{H}}^{(\mathbf{r})}_t$$
$$\hat{\mathcal{H}}^{(i)}_{\text{at}} = \sum_{\alpha\beta} h^{ii}_{\alpha\beta}\hat{c}^\dagger_{i\alpha}\hat{c}_{i\beta} + \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta}\hat{c}^\dagger_{i\alpha}\hat{c}^\dagger_{i\beta}\hat{c}_{i\gamma}\hat{c}_{i\delta} \qquad \hat{\mathcal{H}}_{\text{eff}} = \sum_{ij,\,\alpha\beta} (\varepsilon^{ij}_{1\alpha\beta}\hat{d}^\dagger_{i\alpha}\hat{d}_{j\beta}\hat{s}_i\hat{s}^\dagger_j + \varepsilon^{ij}_{2\alpha\beta}\hat{d}^\dagger_{i\alpha}\hat{d}^\dagger_{j\beta}\hat{s}_i\hat{s}_j) + \text{H.c.} + \hat{\mathcal{H}}_{\text{int}}$$
$$\hat{\mathcal{H}}^{(\mathbf{r})}_t \equiv \hat{\mathcal{H}}^{(ij)}_t = \sum_{\alpha\beta} h^{ij}_{\alpha\beta}\hat{c}^\dagger_{i\alpha}\hat{c}_{j\beta},\ i \neq j$$

In this model we consider the LS state as the bosonic vacuum, $|\emptyset\rangle_i = \hat{s}^\dagger_i|0\rangle$, and other states bosonic flavors α are characterized by the creation (annihilation) operators $\hat{d}^\dagger_{i\alpha}$ ($\hat{d}_{i\alpha}$) on the lattice site i. From the on-site terms of the Hubbard model we obtained the atomic picture of the Tanabe-Sugano diagram where we set up the LS state to be the zero energy point for each $\widetilde{J}$ value. From the diagonalization of the effective bosonic hopping we obtained the energy dispersions of the considered LS, IS and HS manifolds. We found three distinct regions in the phase diagram: normal, IS and HS phases.



We also performed calculations on the ideal $LaCoO_3$ perovskite to compare the excitonic gap obtained for $LaSrCoO_4$ for $\widetilde{U} = 1.96$ and $\widetilde{J} = 0.92$ eV. We observed that the gap almost vanishes in layered $LaSrCoO_4$ cobaltite while it is sizable (around 55 meV) for $LaCoO_3$ compound. Also notice that the HS excitations lay higher for the layered structure than for the cubic one.



3 Conclusions

- LDA+U calculations showed that the excitonic condensate is an stable solution for a large range of U and J interaction parameters studied.
- This excitonic phase was found to lower the energy of the non-ordered state.
- The effective strong-coupling model suggest that the $LaSrCoO_4$ is close to the excitonic instability.

Funding

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References

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