Resonant inelastic X-ray scattering in the study of transition metal oxides.

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in collaboration with

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Outline

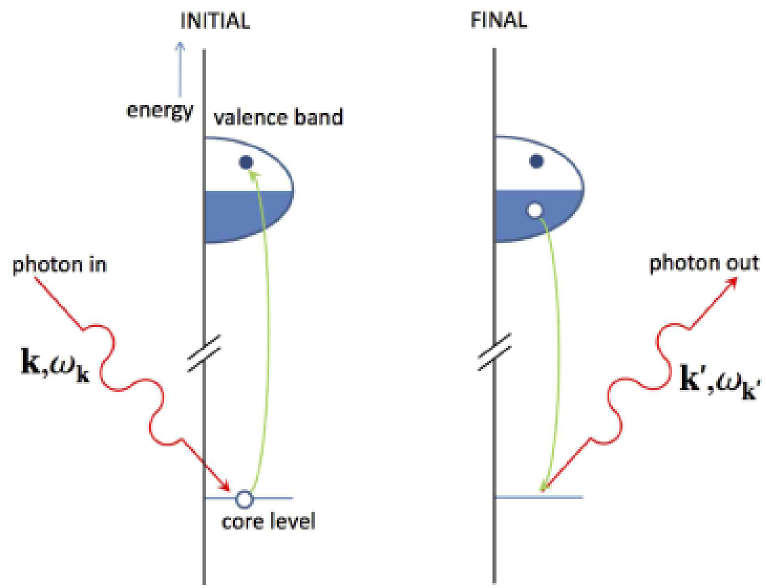
- General view on *RIXS processes and electronic excitations* in strongly correlated 3*d*-, 4*d*, and 5-*d* electron systems (transition metal oxides);

- Theory of RIXS : *basic formulation*;

- Correlated electron systems : layered high-T_c cuprates, RVO_3 with nearly cubic perovskite structure and iridium oxides with pyrochlore structure $A_2Ir_2O_7$;

- Local and collective excitations in these materials detected by RIXS and their model description;

- Application of ab initio quantum-chemical cluster calculations of local electronic properties measured by RIXS;



General view on RIXS process

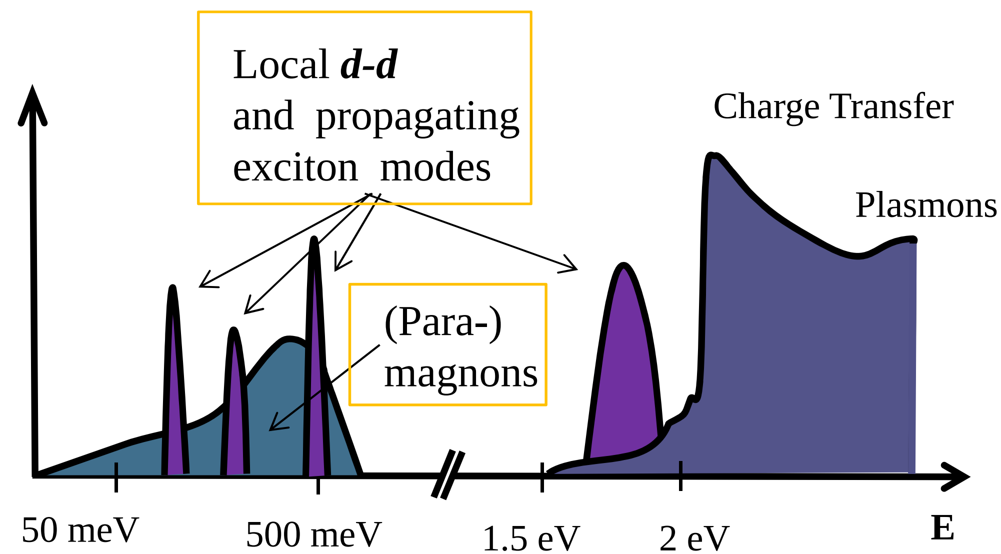
RIXS process creates a valence excitation with momentum $\hbar\mathbf{k}' - \hbar\mathbf{k}$ and energy $\hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$, with resolution

$$\Delta E \approx 100 \text{ meV}$$

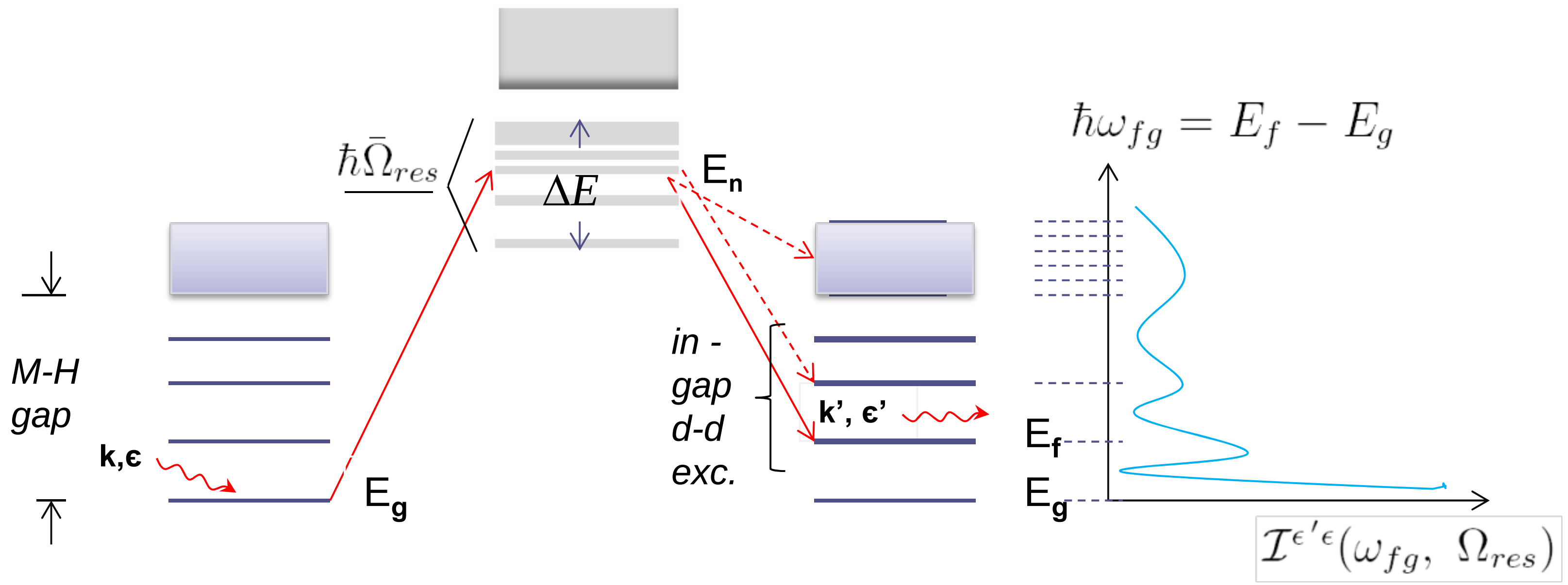
Understanding the excitation spectrum of a system is the understanding the system.

Electronic excitations accessible by RIXS in TM oxides.

Further we focus on local d-d, propagating excitons and magnons



Theory of RIXS in multiorbital correlated electronic systems



$$\mathcal{I}^{\epsilon'\epsilon}(\mathbf{k}', \mathbf{k};\ \omega_{fg}, \Omega_{res}) = \sum_f \mid \mathcal{F}_{fg}^{\epsilon'\epsilon}\ (z_{\mathbf{k}}) \mid^2 \delta(\hbar\omega_{\mathbf{k}} + E_g - \hbar\omega_{\mathbf{k}'} - E_f);$$

In the *dipole* limit, the total scattering amplitude is **(** $\mathrm{D}_{\mathbf{k}} = \sum_j^{N_e} \mathbf{r}_j \exp(i\mathbf{k}\cdot\mathbf{r}_j)$ **):**

$$\mathcal{F}_{fg}^{\epsilon'\epsilon} \sim < \Phi_f^N \mid \left(\boldsymbol{\epsilon}'^* \cdot \mathbf{D}_{\mathbf{k}'}^\dagger\right) \mathcal{G}(z_{\mathbf{k}})\,(\boldsymbol{\epsilon}\cdot\mathbf{D}_{\mathbf{k}}) \mid \Phi_g^N >$$

intermediate-state propagator

$$\mathcal{G}(z_{\mathbf{k}}) = \sum_n \frac{|\Phi_n^{N+1},\ \underline{c}><\Phi_n^{N+1},\ \underline{c}|}{z_{\mathbf{k}} - (E_n - E_g)}$$

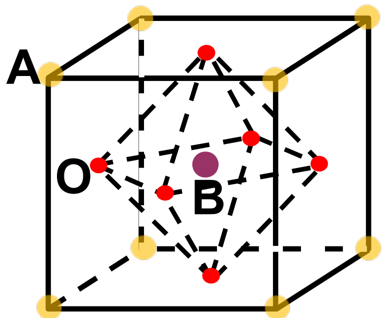
$$z_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} + i\Gamma,$$

Transition Metal elements

(3*d*)	21 **Sc** 44.9559 Scandium	22 **Ti** 47.867 Titanium	23 **V** 50.9415 Vanadium	24 **Cr** 51.9961 Chromium	25 **Mn** 54.938 Manganese	26 **Fe** 55.845 Iron	27 **Co** 58.9332 Cobalt	28 **Ni** 58.6934 Nickel	29 **Cu** 63.546 Copper	30 **Zn** 65.4089 Zinc
(4*d*)	39 **Y** 88.9058 Yitrium	40 **Zr** 91.224 Zirconium	41 **Nb** 92.9064 Niobium	42 **Mo** 85.94 Molybdenum	43 **Tc** 98 Technetium	44 **Ru** 101.07 Ruthenium	45 **Rh** 102.9055 Rhodium	46 **Pd** 106.42 Palladium	47 **Ag** 107.8682 Silver	48 **Cd** 112.411 Cadmium
(5*d*)	71 **Lu** 174.967 Lutetium	72 **Hf** 178.49 Hafnium	73 **Ta** 180.9497 Tantalum	74 **W** 183.84 Tungsten	75 **Re** 186.207 Rhenium	76 **Os** 190.23 Osmium	77 **Ir** 192.217 Iridium	78 **Pt** 195.084 Platinum	79 **Au** 196.9666 Gold	80 **Hg** 200.59 Mercury

correlations

spin-orbit

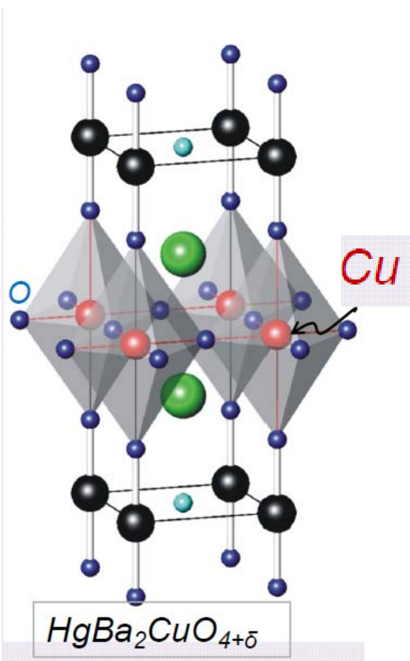


Nearly cubic perovskites ABO_3

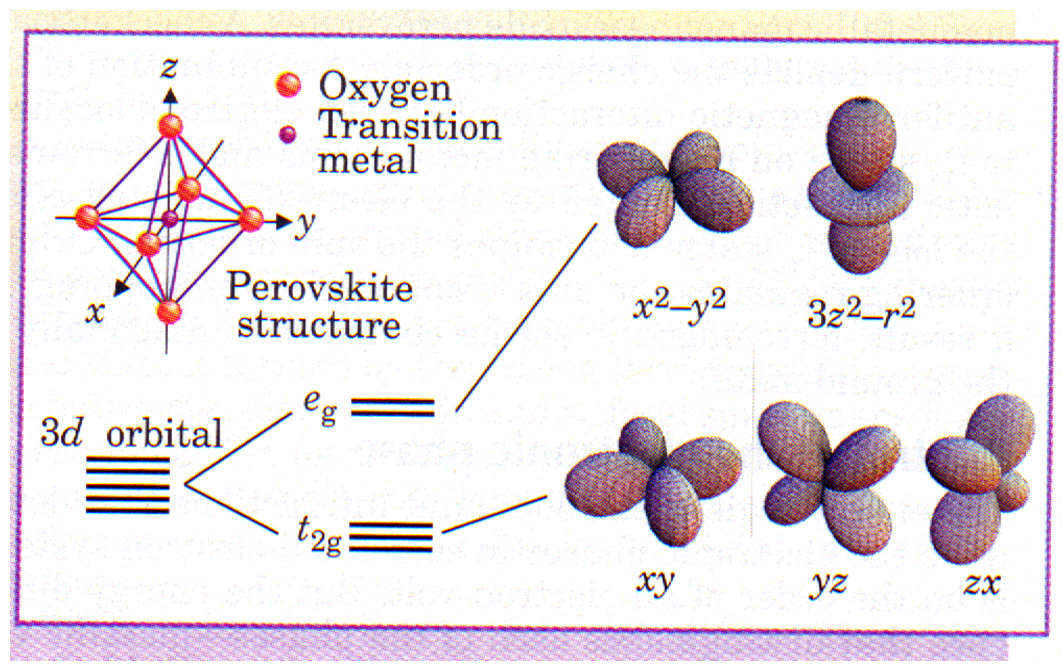
A= Ba, Sr, La, R;

B= Ti, V, Co, Mn, …- transition metal (TM) ions of iron (3*d*) group;

(i) $BaTiO_3$: *FE*   *(ii)* $La_{1-x}Ca_xMnO_3$: *CMR* ; *etc.*



(iii) High-T_c cuprate



3d orbitals of the TM ion in cubic (O_h) crystal field

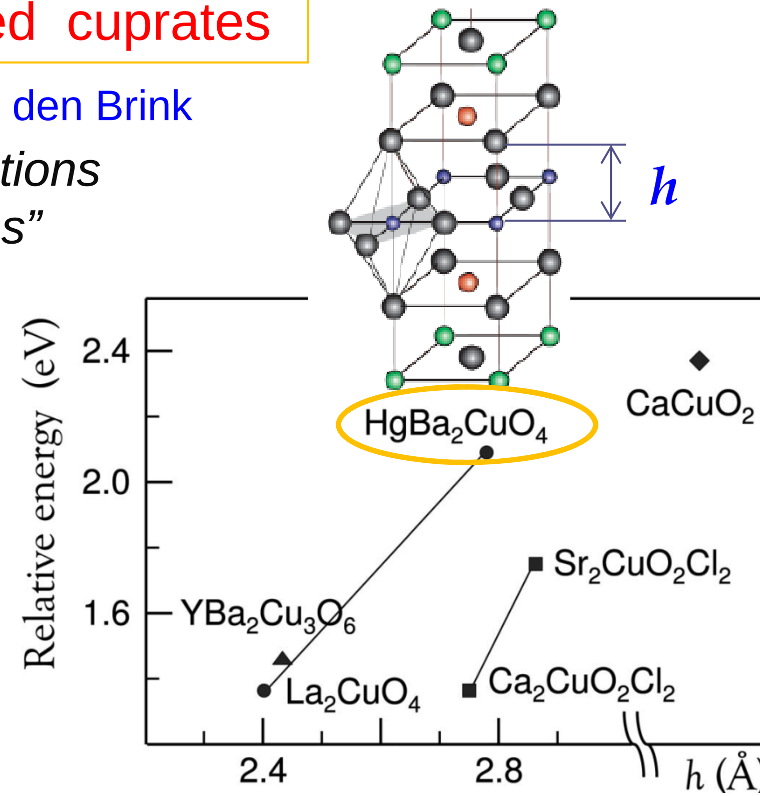
Crystal - field *dd* excitations in undoped cuprates

L. Hozoi, L. Siurakshina, P. Fulde & J. van den Brink

"Ab Initio quantum-chemical cluster calculations of Cu 3d orbital energies in copper oxides"

PHYS. REV. B **84** (2011) 235125

(with the use of MOLPRO 2010)

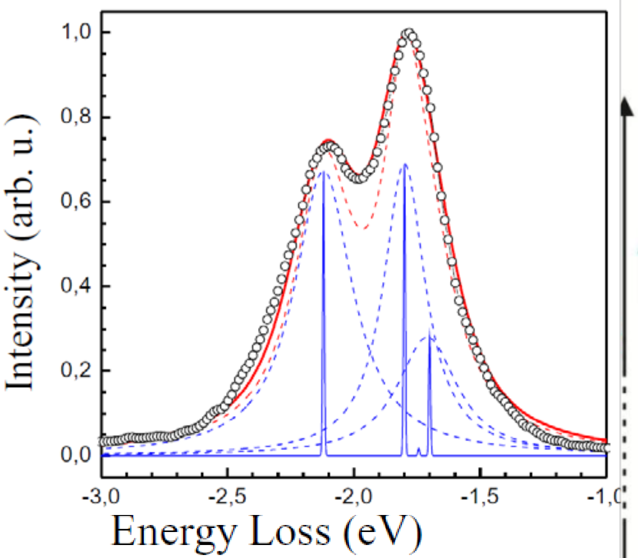


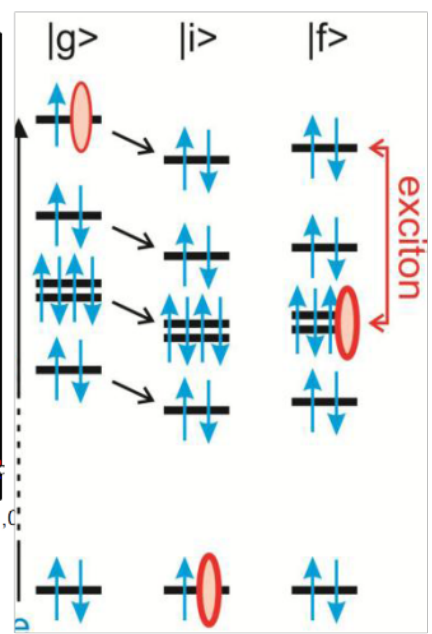
Relative energy $\Delta(e_g)$ as function of the distance h between the Cu and apical ligands in different cuprates

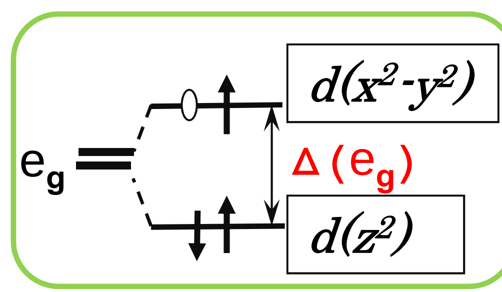
Moretti-Sala et al., New J. of Physics **13** (2011) 043026

Energy and symmetry of dd excitations in undoped layered cuprates measured by Cu L_3 resonant inelastic x-ray scattering

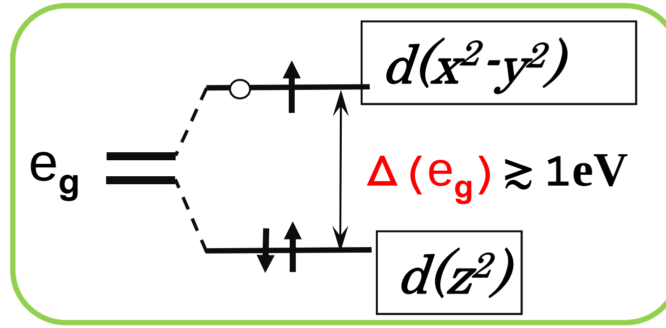
(ADRESS beamline at PSI using SAXES spectrometer)





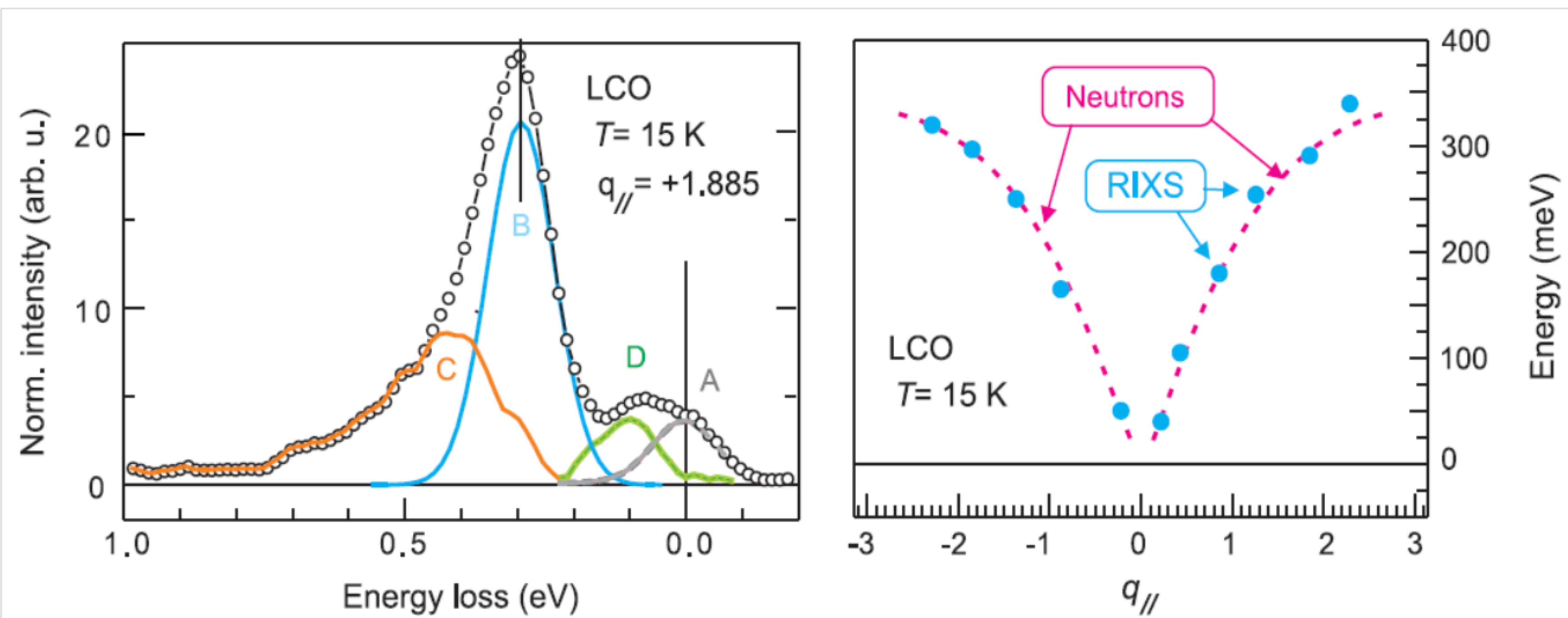


In undoped cuprates with tetragonally split e_g orbitals, the orbital inter-site fluctuations are quenched and the spin exchange dynamic is allowed only.

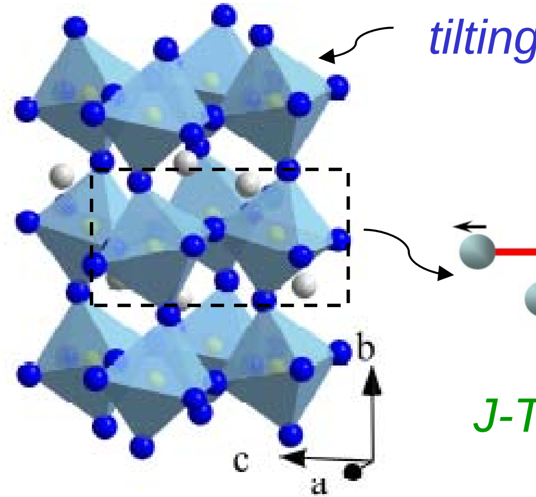


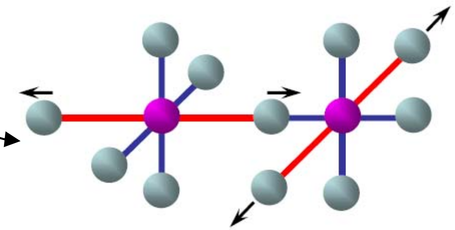
$$\mathcal{H}_{eff} = \mathcal{H}_J = J \sum_{ij} \mathbf{S_i S_j}$$

L. Ament et al., PRL **103** (2009) – *theory;*
L. Braicovich et al., PRL **104** (2010) – *first observation of single-magnon RIXS in* La_2CuO_4



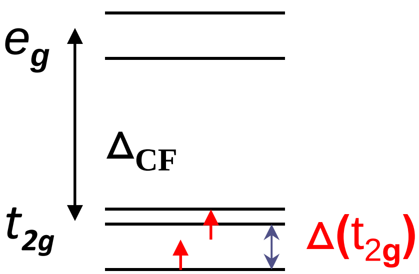
In actual perovskites O_h symmetry and degeneracy of e_g and t_{2g} orbitals are slightly lifted due to cooperative ***J-T distortion*** *and* a ***tilting*** of oxygen octahedra.





J-T distortion for $LaMnO_3$

RVO_3 (t_{2g}^2)

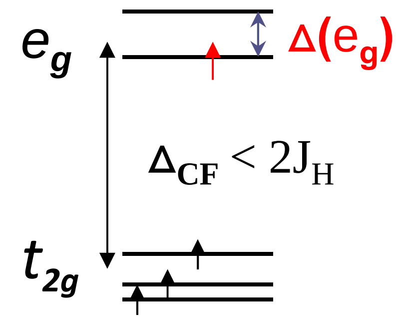


$S_i = 1$
$\tau_i = 1/2$

$$\mathcal{H}_{cf} = \sum_{m,\sigma} \epsilon_m^d \; d_{m\sigma}^\dagger d_{m\sigma}$$

$\Delta(t_{2g})$, $\Delta(e_g)$ ~ 0.1 ev

$LaMnO_3$ (e_g^1)



$S_i = 1/2$
$\tau_i = 1/2$

Both the spin (S_i) and orbital (τ_i) degrees of freedom ***are equally important*** in understanding the low-energy physics,

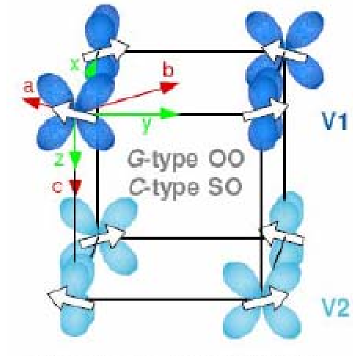
which is captured by a generalized Kugel - Khomskii model = superexchange spin-orbital lattice model.

Low-energy superexchange spin-orbital model for RVO_3

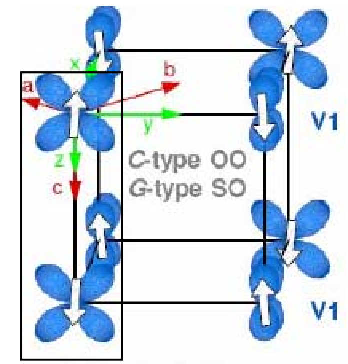
A. Oles et al., PRB **75** (2007) 184434; $J \sim 50\ meV$

$$\mathcal{H}_{eff} = \mathcal{H}_{spin-orb} = J \sum_{<ij>||(\gamma)} \left[(\vec{S}_i \cdot \vec{S}_j + 1)\hat{\mathcal{J}}_{ij}^{(\gamma)} + \hat{\mathcal{K}}_{ij}^{(\gamma)} \right],$$

$$\hat{\mathcal{J}}_{ij}^{(\gamma)}, \hat{\mathcal{K}}_{ij}^{(\gamma)} = \mathcal{C}_{1,2}\left(\vec{\tau}_i \cdot \vec{\tau}_j + \frac{1}{4} n_i n_j\right)^{(\gamma)} \pm \mathcal{C}_3\left(\vec{\tau}_i \otimes \vec{\tau}_j + \frac{1}{4} n_i n_j\right)^{(\gamma)}$$



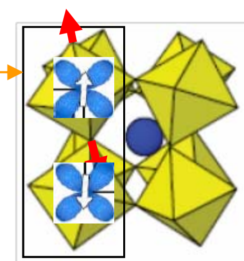
(b) 77K < T < 200K ($P2_1/b$)

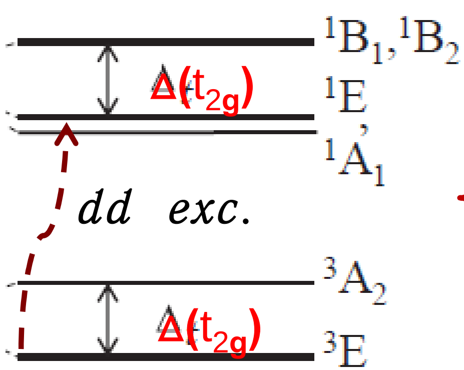


(a) T < 77K ($Pbnm$)

Orbital and spin ordering patterns in YVO_3

Model parameters ⇦ *ab intio* quantum - chemical calculations for a small lattice fragment (cluster) of TM oxides with **experimental** structural lattice parameters.

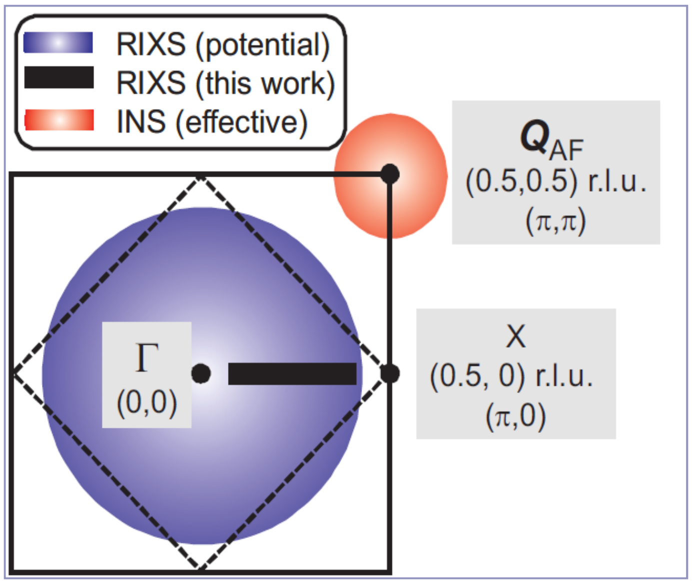




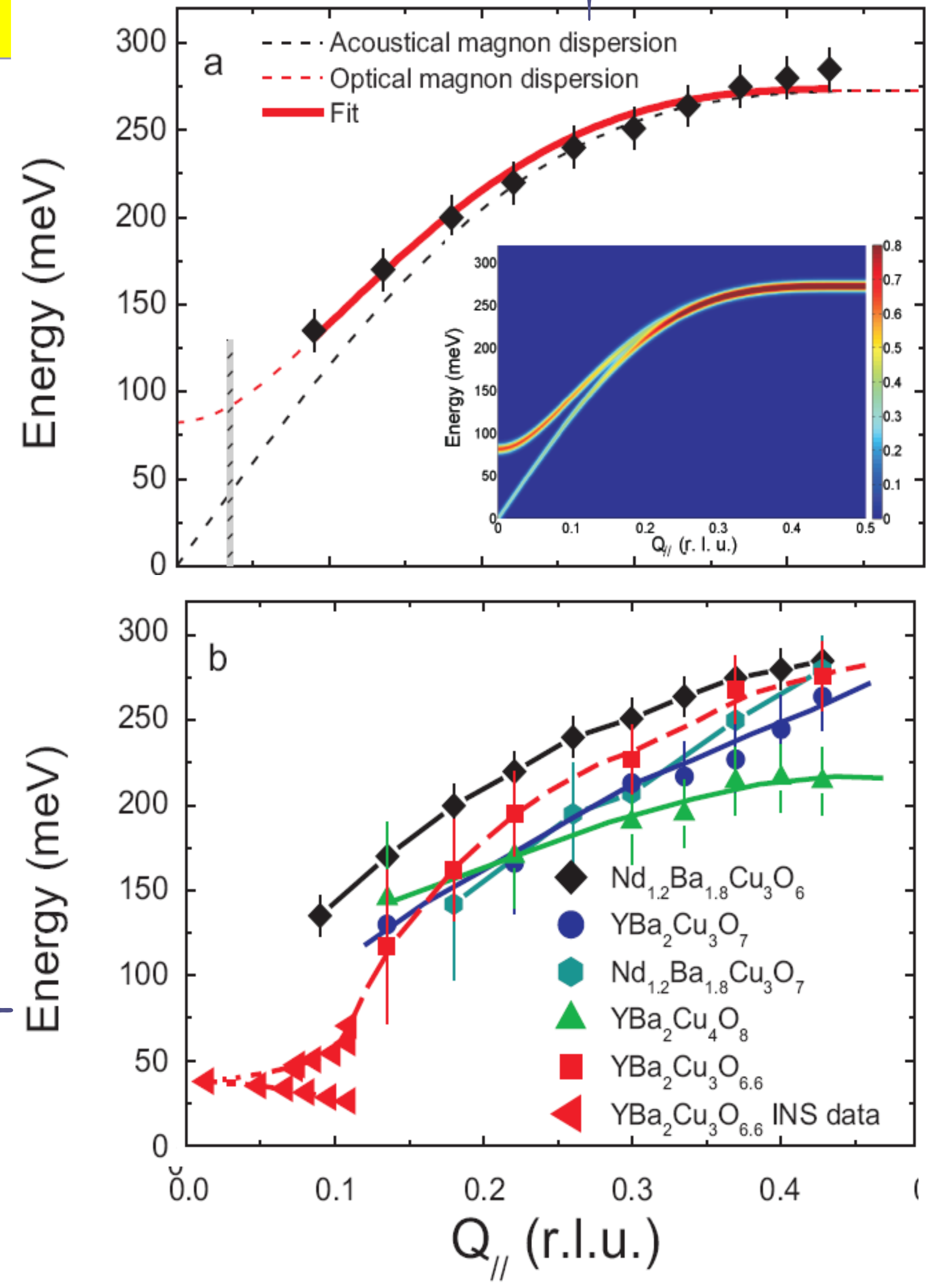
V. Yushankhai & L. Siurakshina
Int. J. Modern Phys., 27 (2013) 1350185

"*Ab initio* analysis of crystal-field multiplets of V^{3+} ion in YVO_3 for **RIXS** "

Magnetic excitations in high-T_c cuprates detected by RIXS



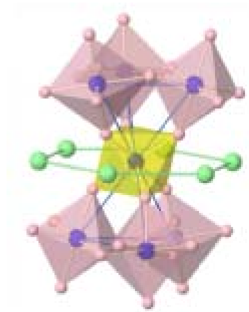
$Nd_{1.2}Ba_{1.8}Cu_3O_6$ (*AFM ordered*)



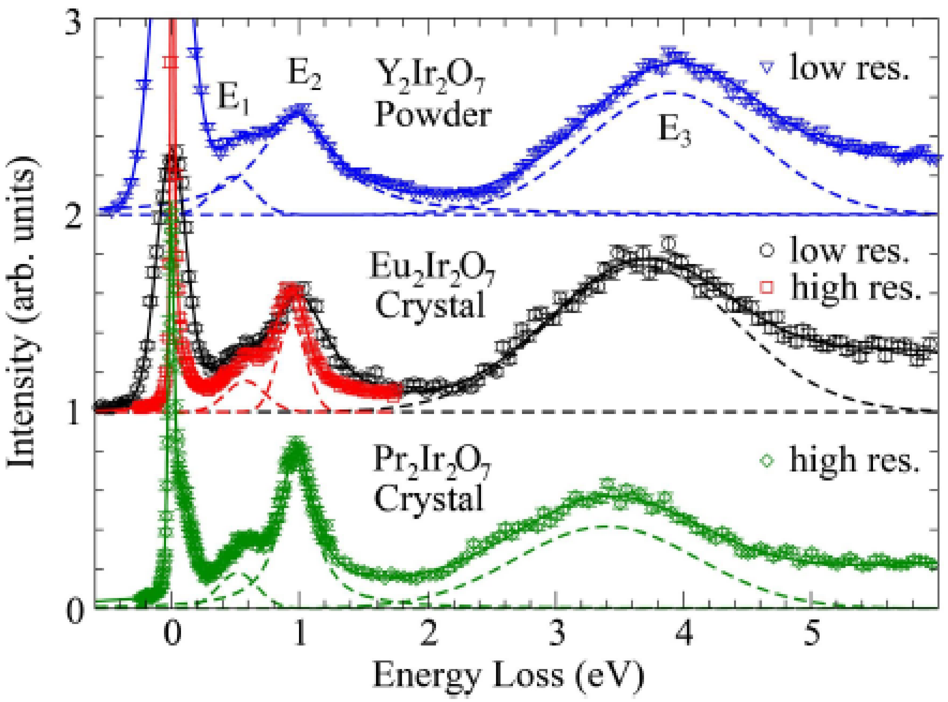
In doped and *AFM disordered* cuprates, intense paramagnons (*damped spin excitations*) survive in a large domain of Q-space

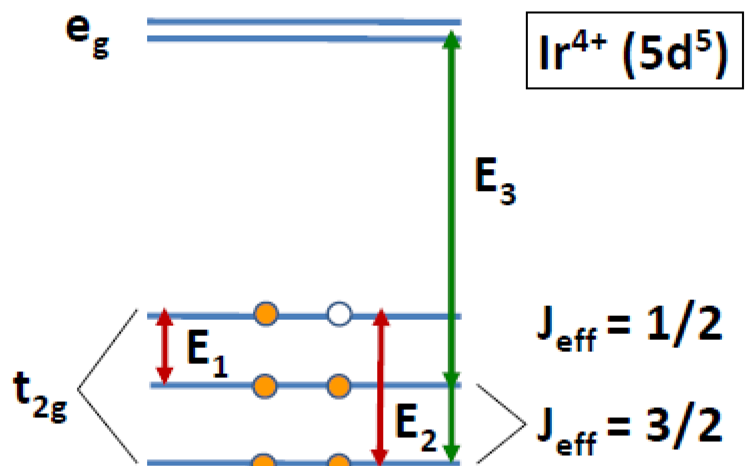
M. Le Tacon, et al., Nature Physics ***7****, 725 (2011); Phys. Rev. B* ***88****, 020501 (2013).*

d-d Excitations in $A_2Ir_2O_7$ (A = Y, Eu, Pr)



L. Hozoi, H. Gretarsson, V. Yushankhai, et al.,
PHYS. REV. B **89,** (2014) 115111

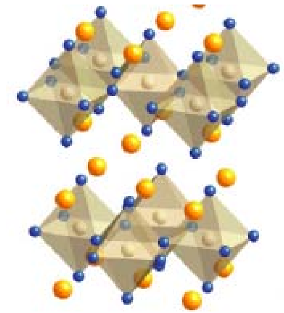




Compound	E_1 (Exp)	E_1 (Calc)	E_2 (Exp)	E_2 (Calc)	E_3 (Exp)	E_3 (Calc)	λ (SOC)	Δ (CEF)
$Y_2Ir_2O_7$	0.53 eV	0.58 eV	0.98 eV	0.94 eV	3.87 eV	3.48-4.84 eV	0.43 eV	0.56 eV
$Eu_2Ir_2O_7$	0.59 eV	0.60 eV	0.95 eV	0.91 eV	3.68 eV	3.39-4.72 eV	0.46 eV	0.46 eV
$Pr_2Ir_2O_7$	0.52 eV	---	0.98 eV	---	3.40 eV	---	0.42 eV	0.57 eV

Magnetic excitation spectra of Sr_2IrO_4 probed by RIXS: Links to cuprate superconductors

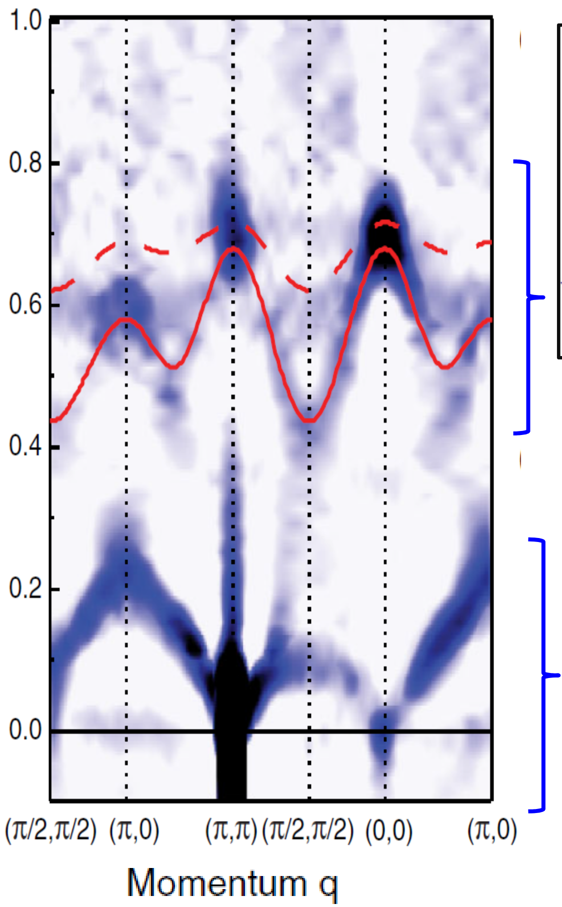
J. Kim, *et al., PRL, **108** (2012)*



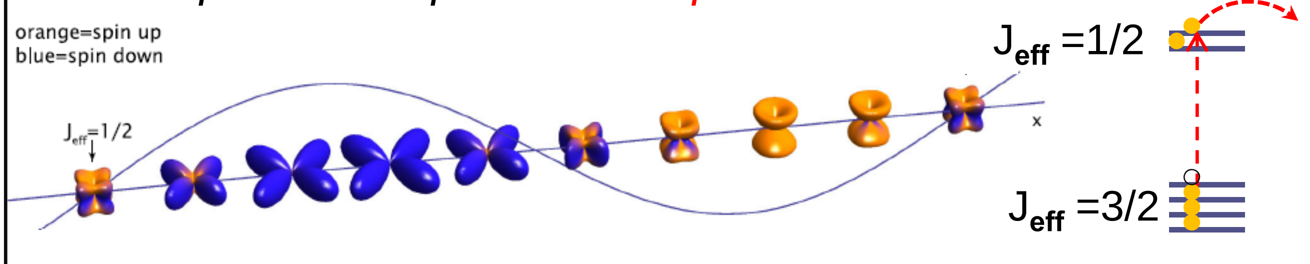
Sr_2IrO_4

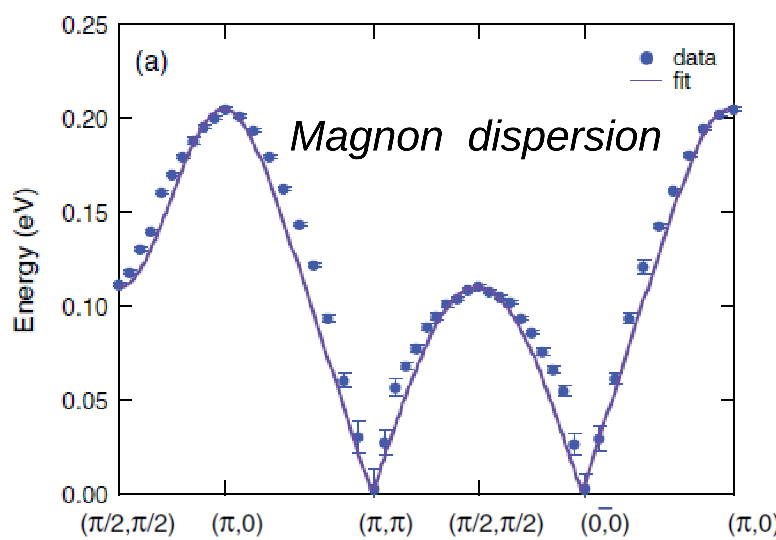
F.Wang & T.Senthil
PRL, **106** (2011)

A doped Sr_2IrO_4 – a novel platform for high-T_c superconductivity ?



A real space description of the spin-orbit exciton



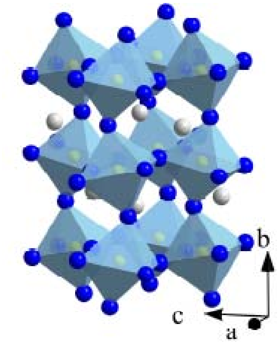


Conclusion

1. Large scattering phase, i.e., the range of energies and momenta transferred in the scattering event, makes RIXS a powerful tool in measuring spin and orbital excitations in solids.

2. The ***ab initio*** ***quantum-chemical cluster calculations*** for the local electronic structure of complex transition-metal oxides combined with complementary ***theoretical analysis*** of the local ***d-d*** excitation spectra accessible by RIXS may ***become a routine procedure;***

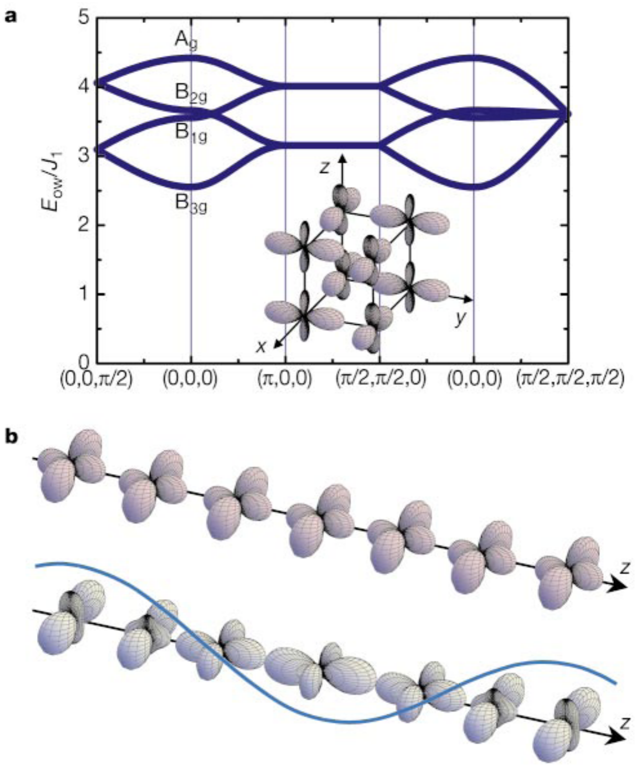
Orbital waves in $LaMnO_3$ (e_g^1)



$$\vec{T}(i) = \frac{1}{2}\sum_{\gamma\gamma' s} c^{\dagger}_{\gamma s}(i)\vec{\sigma}_{\gamma\gamma'} c_{\gamma' s}(i),$$

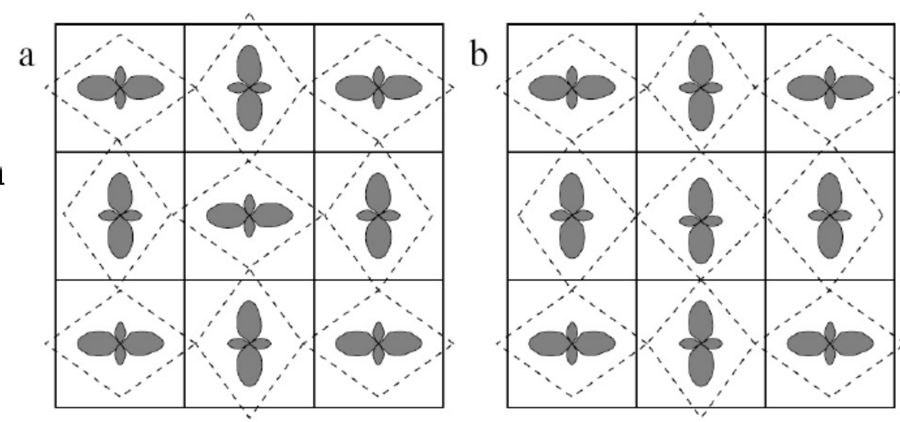
$$\begin{pmatrix} \widetilde{T}_z(i) \\ \widetilde{T}_x(i) \end{pmatrix} = \begin{pmatrix} \cos\theta(i) & \sin\theta(i) \\ -\sin\theta(i) & \cos\theta(i) \end{pmatrix} \begin{pmatrix} T_z(i) \\ T_x(i) \end{pmatrix}$$

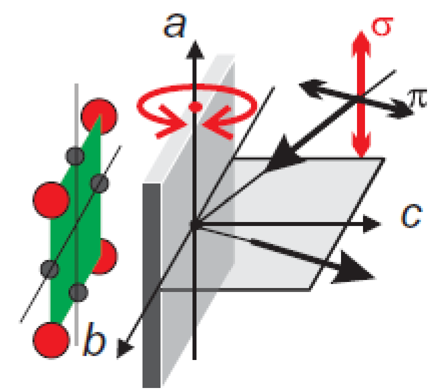
$$\widetilde{T}_z(i) \sim \frac{1}{2} - a^{\dagger}(i)a(i),$$
$$\widetilde{T}_x(i) \sim \frac{1}{2}\{a^{\dagger}(i) + a(i)\}$$



Theoretical results for the dispersion relation of the orbital wave in $LaMnO_3$.

(E. Saitoh *et al*, Nature **410** (2001) 180.)





a
σ
π
c
b