Institut Néel - CNRS
Institut Laue Langevin

Computing low energy excitations in strongly correlated systems: RelaxSE

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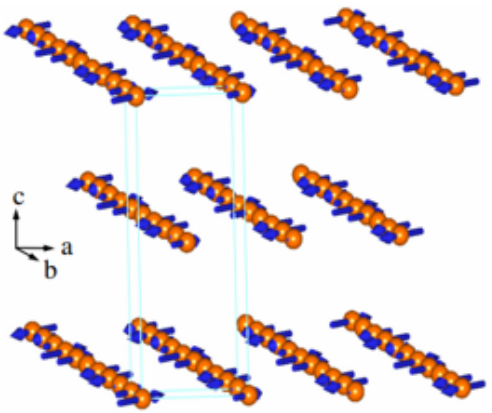
GDR NBODY - Toulouse, Jan. 10th - 13th 2022

Magnetism at ILL



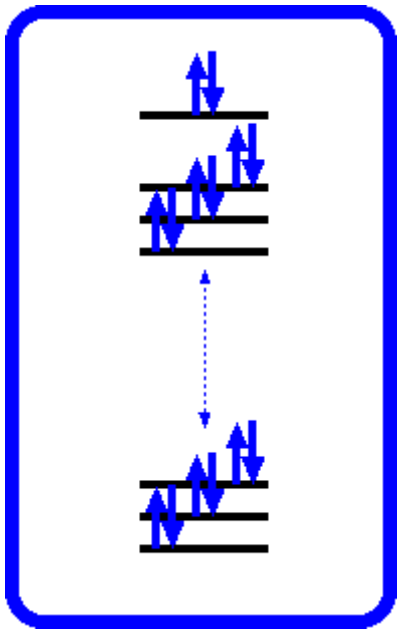
Incommensurate magnetic structure of $CeCuGa_3$ at 1.7 K investigated on D20 at ILL
V. K. Anand *et al*, *Phys Rev B*, **104**, 174438, (2021)

Strongly correlated systems: what?

Weakly correlated systems

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i - \sum_i \sum_N \frac{Z_N}{|\vec{r}_i - \vec{R}_N|}}_{\text{kinetic energy dominant}} + \underbrace{\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\bar{e}\text{-}\bar{e}\text{ repulsion weak}}$$

Minimal description : $|\Phi_0\rangle$



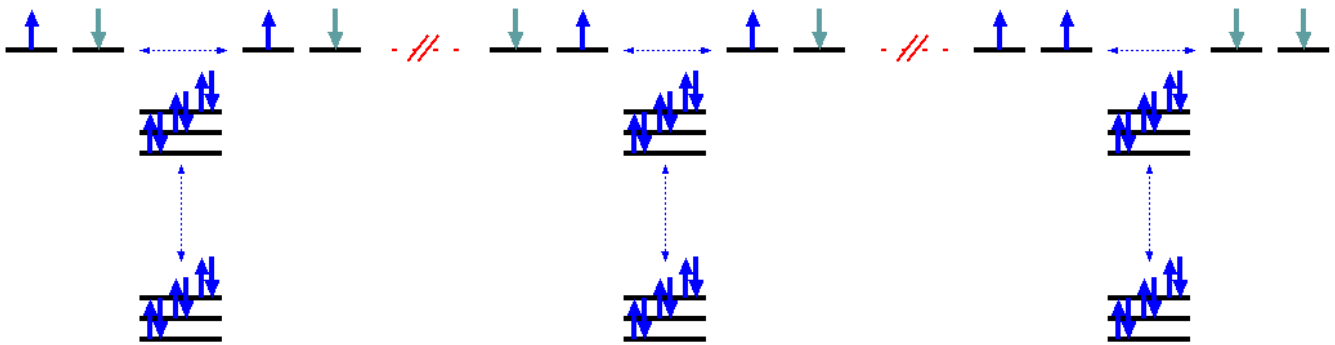
- Band-structure / shell model valid
- Mean-field description qualitatively correct
- well treated in DFT-based methods (DFT, TDDFT, etc. . . .)
- or single ref + perturbation-based methods (GW, Bethe-Salpeter, etc. . . .)

Strongly correlated systems: what?

Strongly correlated systems

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i - \sum_i \sum_N \frac{Z_N}{|\vec{r}_i - \vec{R}_n|}}_{\text{kinetic energy sub-dominant}} + \underbrace{\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\bar{e}\text{-}\bar{e} \text{ repulsion dominant}}$$

Minimal description : $\sum_I c_I |\Phi_I\rangle$



Strongly correlated systems: what?

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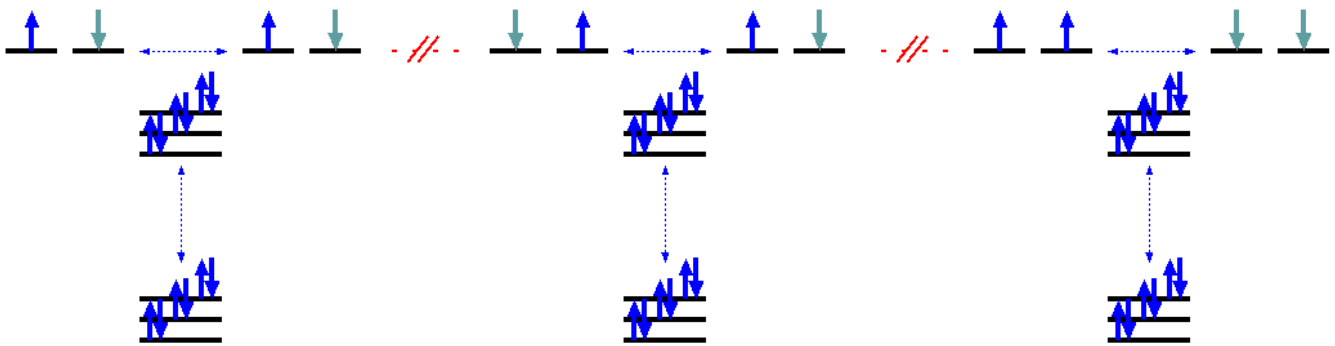

Prop. depending on total density
Small error in mean-field
$\Rightarrow$ well treated in DFT

$\Rightarrow$

- Structural properties
- Phonons
- Polarisation
- Elastic properties
- ...

Strongly correlated systems: what?

Strongly correlated systems

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i - \sum_i \sum_N \frac{Z_N}{|\vec{r}_i - \vec{R}_n|}}_{\text{kinetic energy sub-dominant}} + \underbrace{\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\bar{e}\text{-}\bar{e} \text{ repulsion dominant}}$$

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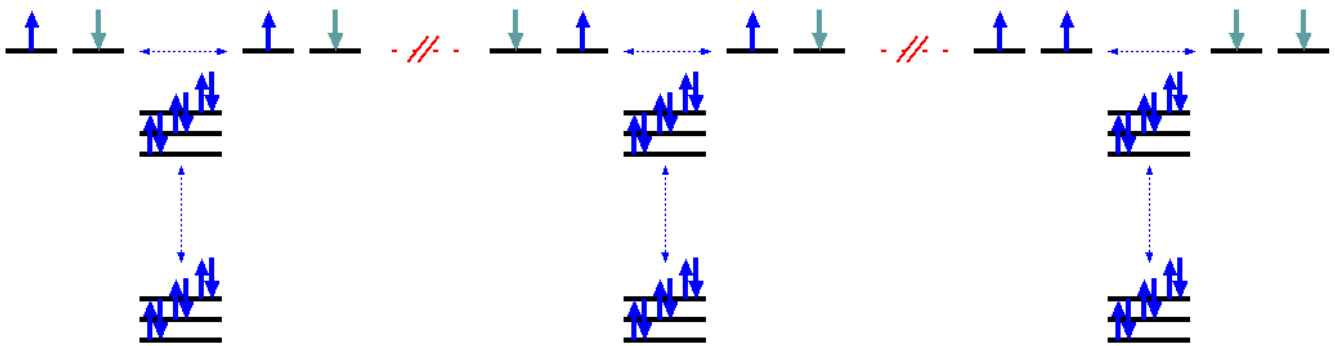


Prop. depending on
Fermi level density

Mean-field unreliable
$\Rightarrow$ need to be treated with
Multi Ref. Wave Funct. Th.

$\Rightarrow$

- Magnetic exchange
- Excitations
- Magnetic excitations
- ...

Strongly correlated systems: why?

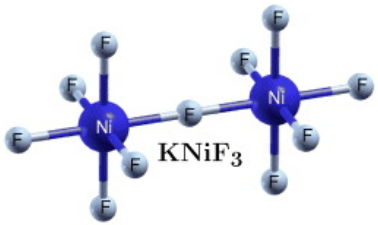
- Expression of many degrees of freedom (spin, orbital, lattice...)
- Multiple quasi-degenerate GS highly sensitive to ext. pert.
- Low energy excited states
- Remarkable properties
  - high T_c superconductivity
  - magnetism
  - multiferroïcity
  - collossal magneto-resistance
  - ...
- Properties originate in low energy excitations

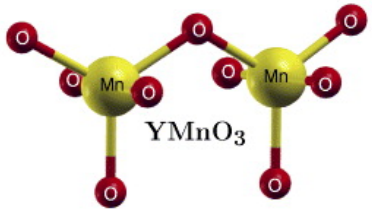
Focus of the talk :

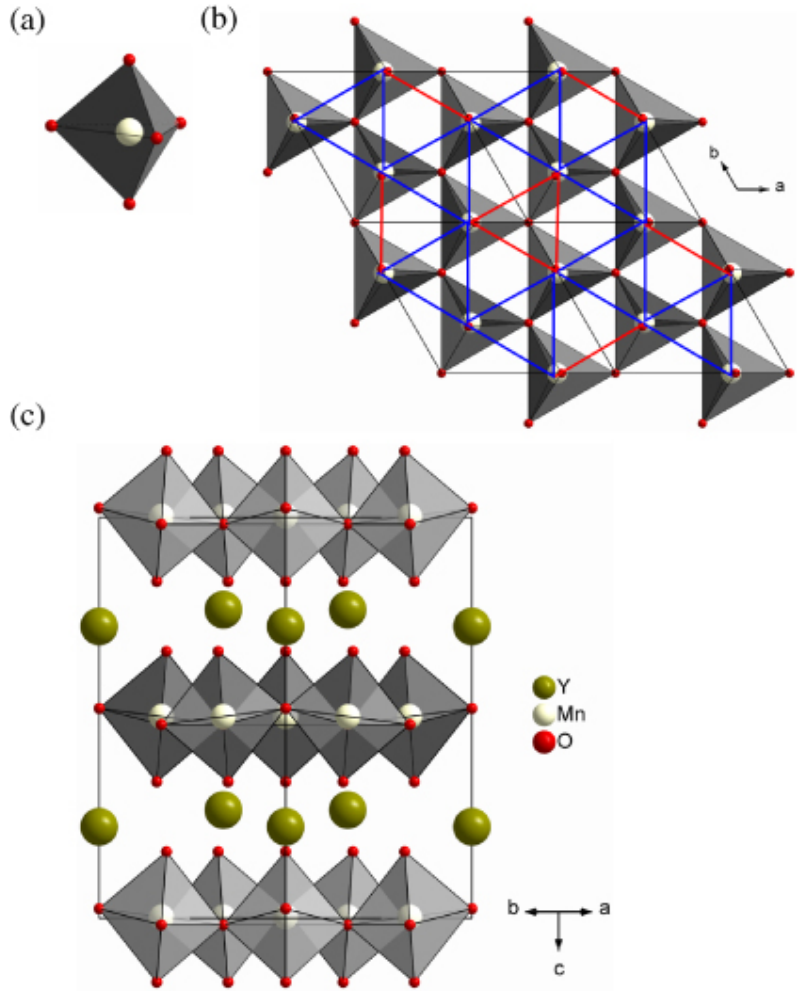
- magnetic systems
- computation of low energy excitations

Ab-initio determination of magnetic interactions

- Transition Metal Oxides ($YMnO_3$, RMn_2O_5..)
- Rare-Earth Oxides



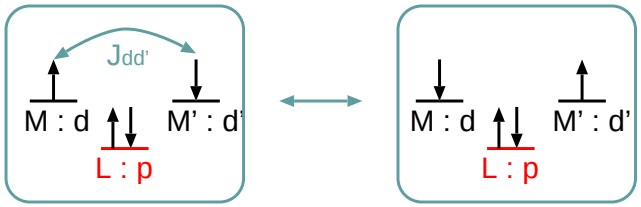




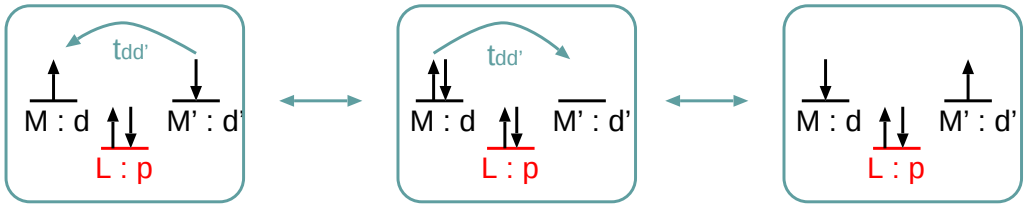
Magnetic excitation : effective magnetic exchange

Ex : singlet-triplet excitation $\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \rightarrow E_S$ $\frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \rightarrow E_T$

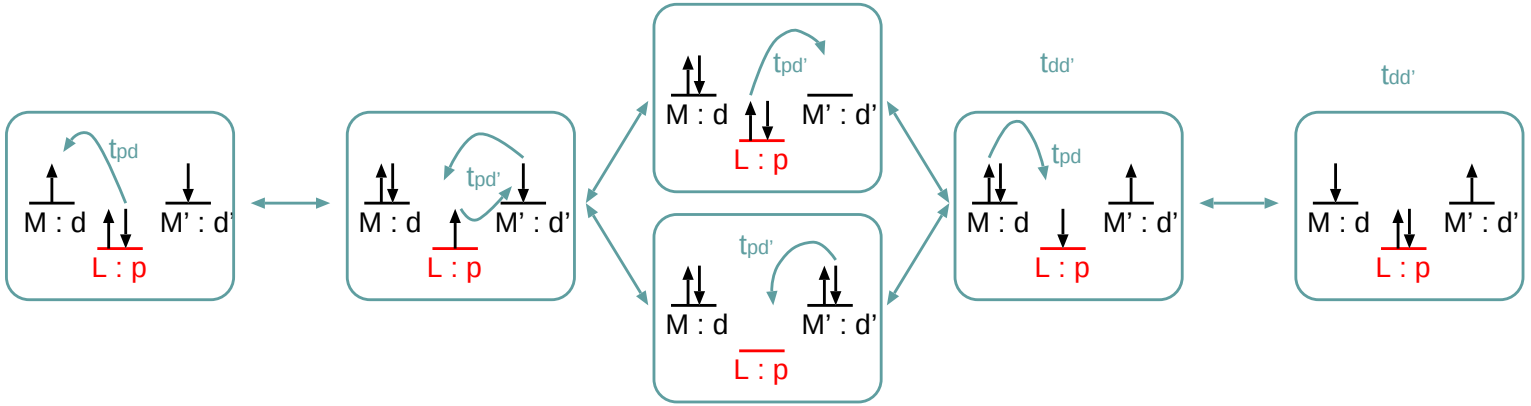
Direct



Through space

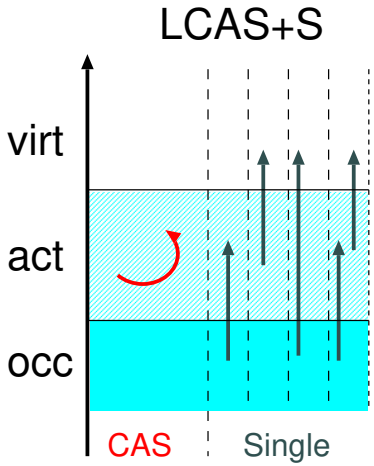


Through bridge



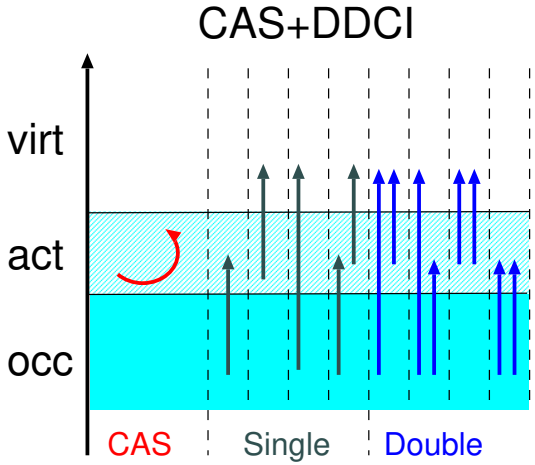
State of the art

Large Complete Active Space + single excitations (LCAS+S)



C J. Calzado and J. F. Sanz and J. P. Malrieu, *J. Chem. Phys.*, **112**, 5158, (2002)

CAS+Difference Dedicated Configuration Interaction (CAS+DDCI)

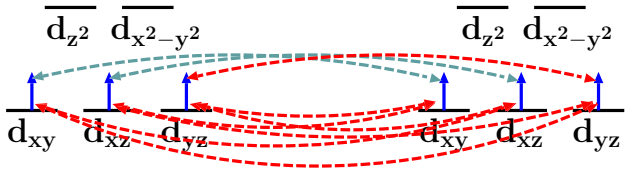


J. Miralles and J. P. Daudey and R. Caballol, *Chem. Phys. Lett.*, **198**, 555, (1992)
V. M. García *et al.*, *Chem. Phys. Lett.*, **238**, 222, (1995)
V. M. García and M. Reguero and R. Caballol, *Theor. Chem. Acc.*, **98**, 50, (1997)

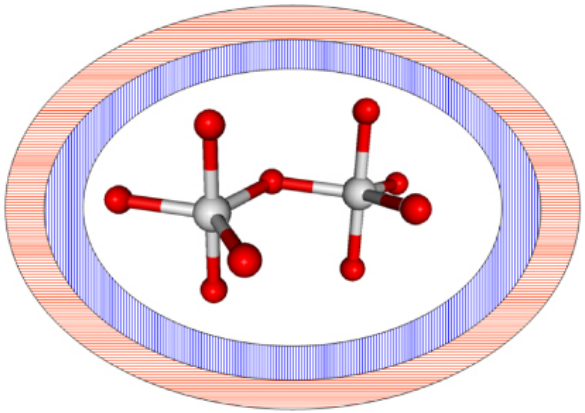
Systems of interest

1																		18
1	1 H Hydrogène	2											13	14	15	16	17	2 He Hélium
2	3 Li Lithium	4 Be Beryllium											5 B Bore	6 C Carbone	7 N Azote	8 O Oxygène	9 F Fluor	10 Ne Néon
3	11 Na Sodium	12 Mg Magnésium	3	4	5	6	7	8	9	10	11	12	13 Al Aluminium	14 Si Silicium	15 P Phosphore	16 S Soufre	17 Cl Chlore	18 Ar Argon
4	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titane	23 V Vanadium	24 Cr Chrome	25 Mn Manganèse	26 Fe Fer	27 Co Cobalt	28 Ni Nickel	29 Cu Cuivre	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Sélénium	35 Br Brome	36 Kr Krypton
5	37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdène	43 Tc Technétium	44 Ru Ruthénium	45 Rh Rhodium	46 Pd Palladium	47 Ag Argent	48 Cd Cadmium	49 In Indium	50 Sn Étain	51 Sb Antimoine	52 Te Tellure	53 I Iode	54 Xe Xénon
6	55 Cs Césium	56 Ba Baryum	71 Lu Lutetium	72 Hf Hafnium	73 Ta Tantale	74 W Tungstène	75 Re Rhénium	76 Os Osmium	77 Ir Iridium	78 Pt Platine	79 Au Or	80 Hg Mercure	81 Tl Thallium	82 Pb Plomb	83 Bi Bismuth	84 Po Polonium	85 At Astate	86 Rn Radon
7	87 Fr Francium	88 Ra Radium	103 Lr Lawrencium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Fl Flérovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium

57 La Lanthane	58 Ce Cérium	59 Pr Praséodyme	60 Nd Néodyme	61 Pm Prométhium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Américium	96 Cm Curium	97 Bk Berkélium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelévium	102 No Nobélium



Methodological approach



How to reach experimental accuracy?

- Embedded cluster (quantum, pseudo-potential and point charges) $\rightsquigarrow$ finite systems
- State-of-the-art ab-initio calculations for strongly correlated systems

Challenges

Size of the problem growing exponentially with the number of open shells $\rightsquigarrow$ computational wall

Magnetic excitation: effective magnetic exchange

WF requirements :

- multi configurational
- equal treatment for GS & exct. states
- $\Rightarrow$ all previous conf. have to be included at 0^{th} order (ref. conf.)
- screening effects have to be included on all ref. conf.
  - dynamical correlation
  - single-excitation on all ref. conf.
  - modify relative weight between ref. conf.
  - $\Rightarrow$ need to be in non-contracted CI

WF non-requirements : (vert. excitations only)

- common part of screening effects between GS & exct. states can be skipped

SAS+S method: for many magn. orb. per atom

SASS : A. Gellé, J. Varignon and M.-B. Lepetit, *EPL*, **88**, 37003 (2009).

All reference configurations need to be treated on equal footing

- Magnetic and bridging orb. $\in$ CAS (Large Complete Active Space)
  $\rightsquigarrow$ Impossible when number of magn. orb. increases

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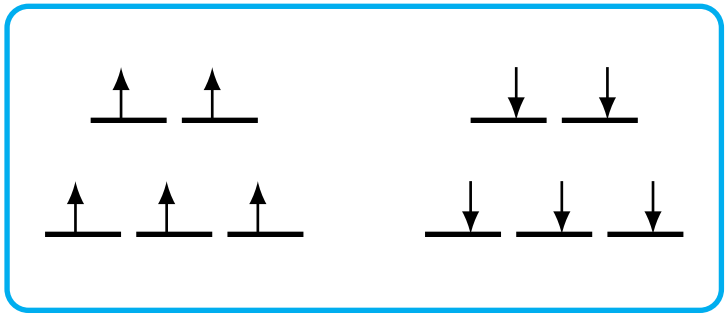
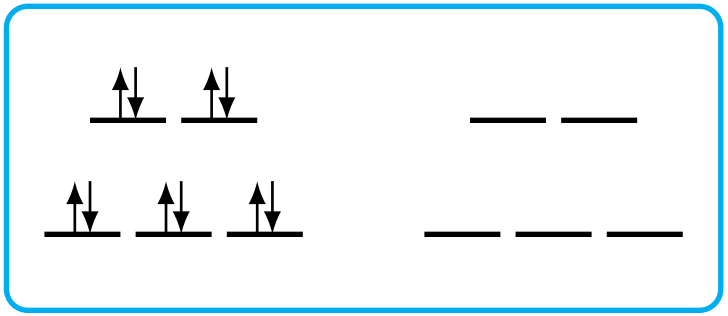
Physically relevant (large weight)



Physically irrelevant (very small weight)



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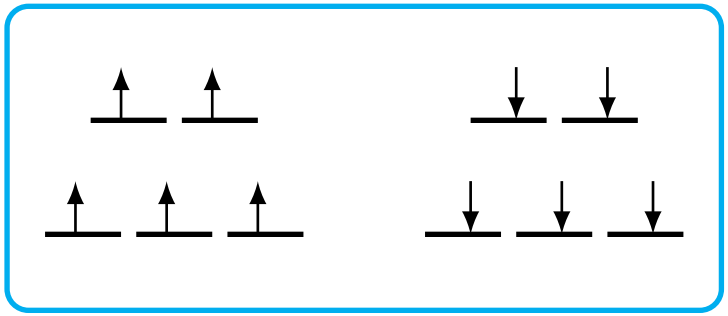

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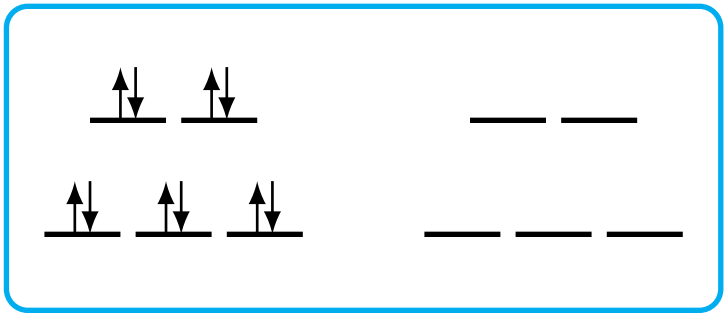

- Ref. conf. : only dominant conf. in LCAS : SAS+S
  Selected Active Space + Single-excitation from bridging orbitals

SAS+S method: for many magn. orb. per atom

SASS : A. Gellé, J. Varignon and M.-B. Lepetit, *EPL*, **88**, 37003 (2009).

$$|\Psi_m^{SASS}\rangle = \overbrace{\underbrace{\sum_I C^0_{I,m}|\Phi^0_I\rangle}_{\text{zeroth-order : ref0 dominant magn. conf.}} + \underbrace{\sum_J C^1_{J,m}|\Phi^1_J\rangle}_{\text{charge transfer + static corr : ref1}}}^{\text{references}} + \overbrace{\underbrace{\sum_{J^*} C_{J^*,m}|\Phi_{J^*}\rangle}_{\text{Single-excitations on ref.}}}^{\text{screening}}$$

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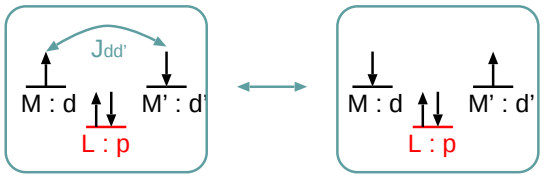
- Select the important configurations on the active (magnetic) orbitals (ref 0)



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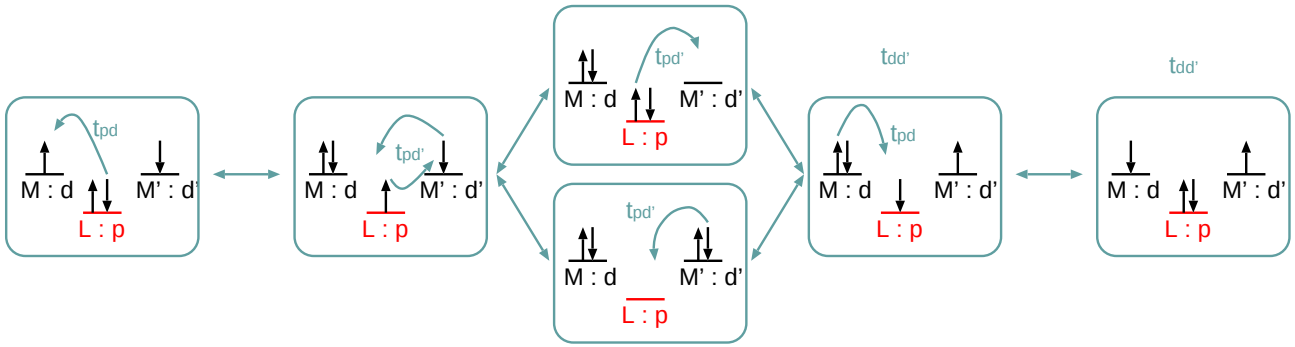
(references) (screening)

- Select the important configurations on the active (magnetic) orbitals (ref 0)
- From them: build the additional important configurations (metal/metal), (ligand-metal) and/or (metal-ligand) for the exchange mechanism (ref 1)
- + all conf. for S^2 eigenfunctions



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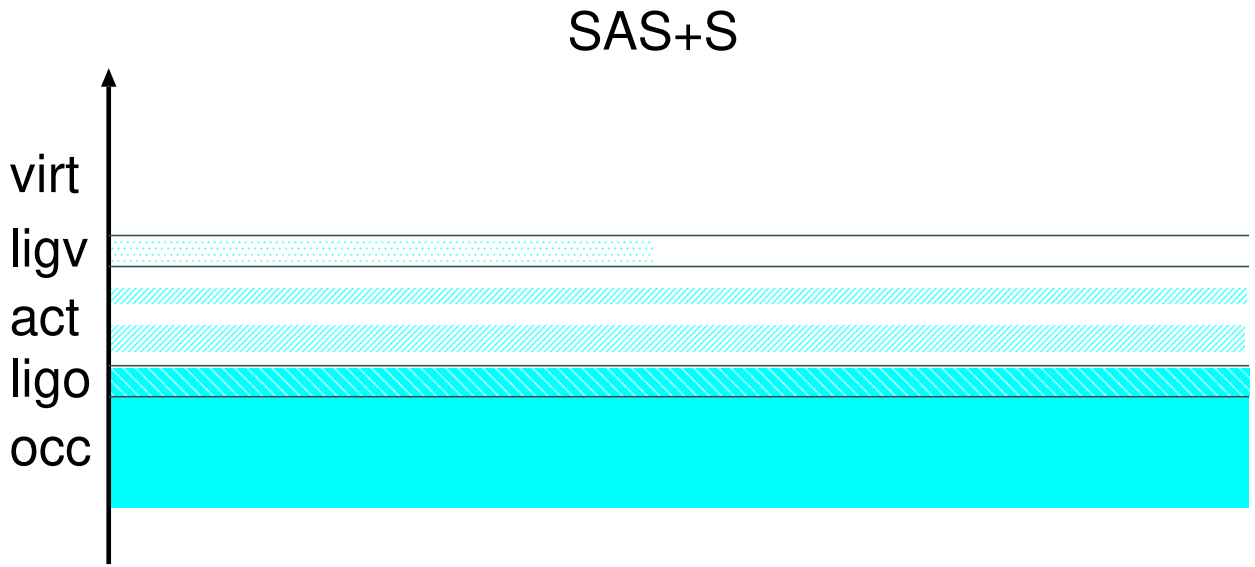
- + all conf. for S^2 eigenfunctions
- Screening from single excitations on the references

SAS+S method: orbital partitioning and determinant generation

5 classes of orbitals:

occupied, active, virtual, ligand occupied and ligand virtual



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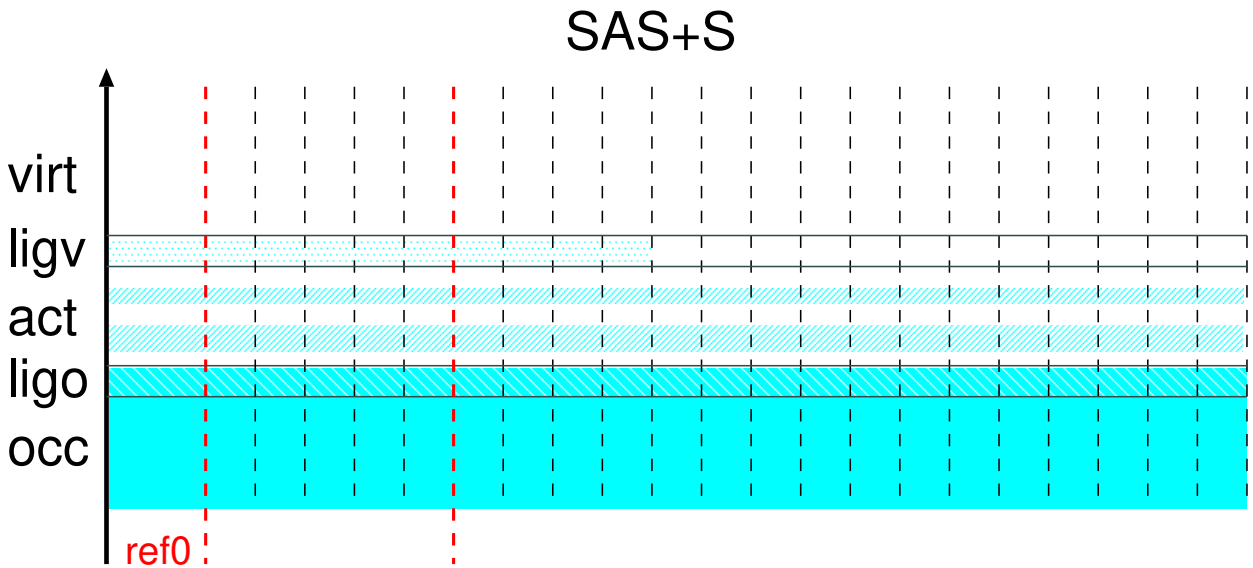

- The dominant magn. conf. : ref0

SAS+S method: orbital partitioning and determinant generation

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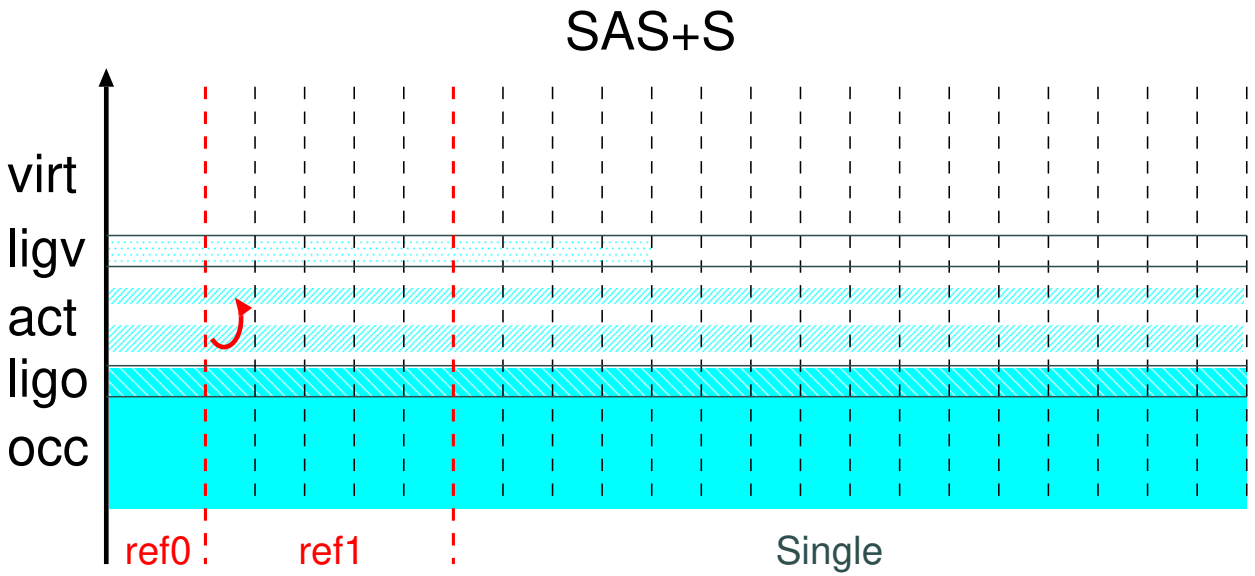

- The dominant magn. conf. : ref0
- The magn. orb $\rightarrow$ magn.orb excitations on ref0: ref1
- The ligand - magn. site charge transferts on ref0: ref1

SAS+S method: orbital partitioning and determinant generation

5 classes of orbitals:

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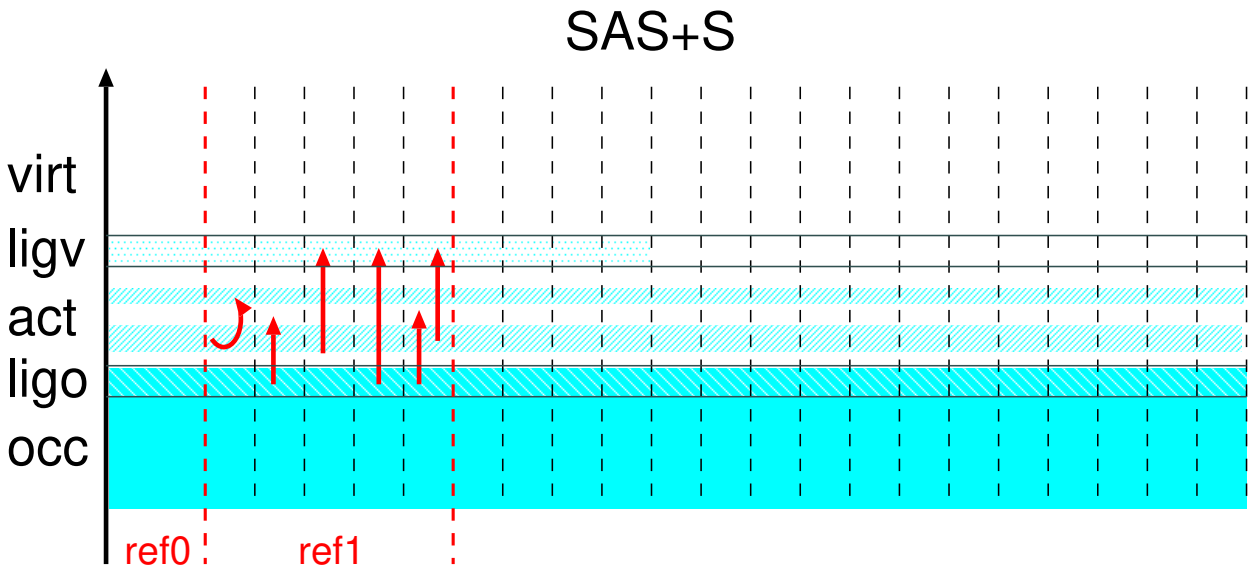

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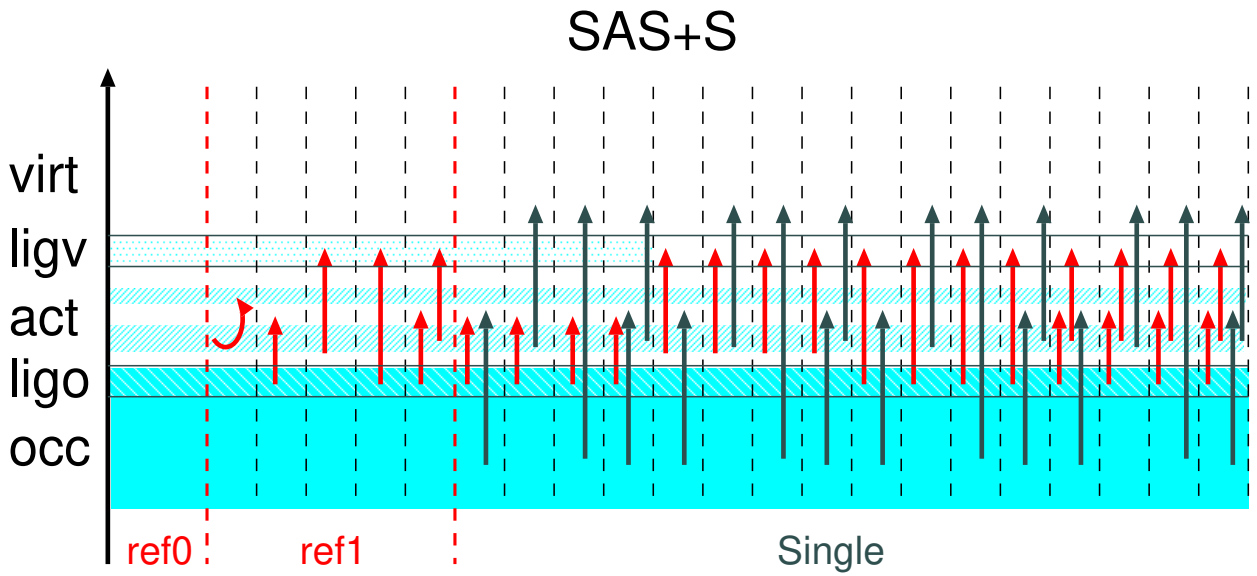


- The dominant magn. conf. : ref0
- The magn. orb $\rightarrow$ magn.orb excitations on ref0: ref1
- The ligand - magn. site charge transferts on ref0: ref1
- The screening effects: all singles on ref0 + ref1

The RelaxSE code: Challenges

Memory

- Number of configurations (up to 10^9)
- Hamiltonian matrix cannot be stored
- Iterative Davidson algorithm to compute the first eigenvalues and eigenvectors

Disk Access

- One- and two-electron integrals read from disk
- Optimize procedure to minimize the number of disk access (integral driven)

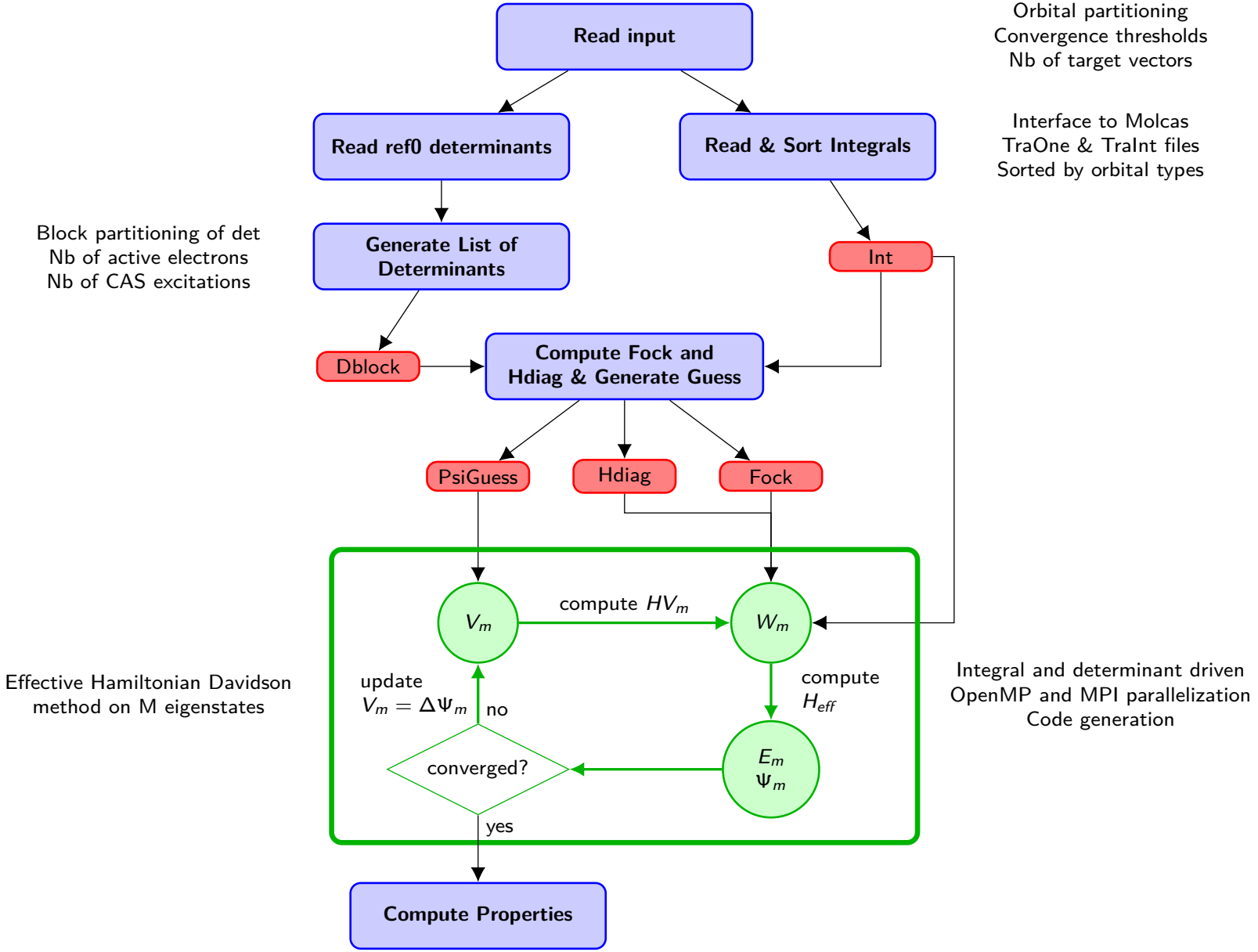
CPU/Total Time

- Iterative procedure: re-computation of (independent) vectors for each iteration
- Time consuming but massively parallelizable (determinant driven)

User Friendliness/Modularity

- Minimal input from the user
- Interface to mainstream CAS-SCF codes

The RelaxSE code: Flowchart



RelaxSE code: Summary

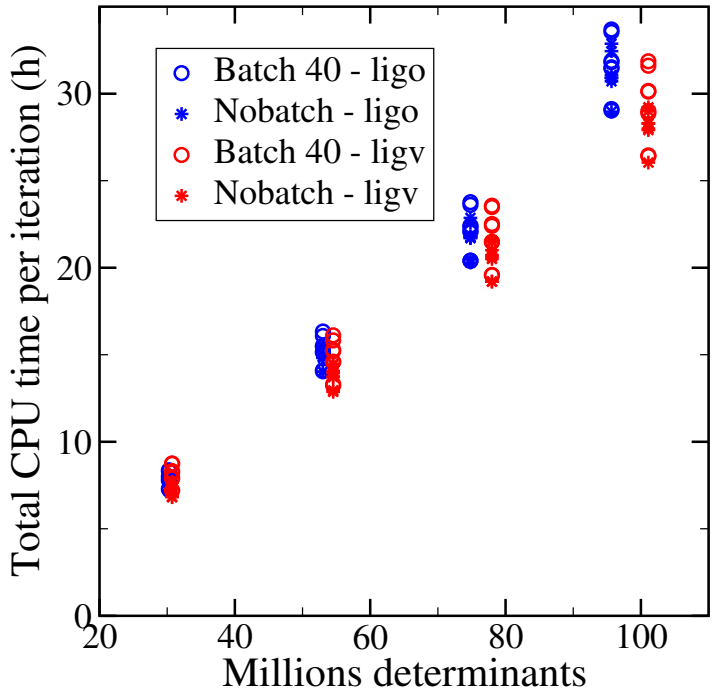
- Preliminary calculations
  - CASSCF on magn orb.
  - localisation of active orbitals
  - identification of bridging ligand orbitals
  - integral transformation
- Configuration interaction
- 5 SAS+S classes of orb. + frozen occupied and deleted virtual orbitals
- SAS+S, CAS+DDCI, CAS+S, CAS+SD
- OpenMP + MPI parallelisation
- Up to 10^9 determinants
- Interfaced with Molcas
- LGPL license

The RelaxSE code: Performance

Table: Orbital partitioning in the $YMnO_3$ calculations.

Set	N_{occ}	N_{ligo}	N_{act}	N_{ligv}	N_{virt}	N_{det}
LIGO	49	2	8	0	140	30 267 828
	47	4	8	0	140	53 017 324
	45	6	8	0	140	74 811 684
	43	8	8	0	140	95 650 908
LIGV	51	0	8	2	138	30 721 372
	51	0	8	4	136	54 531 036
	51	0	8	6	134	77 992 188
	51	0	8	8	132	101 104 828
BIG	47	4	8	6	134	1 097 706 172

Figure: CPU scaling as a function of N_{det}

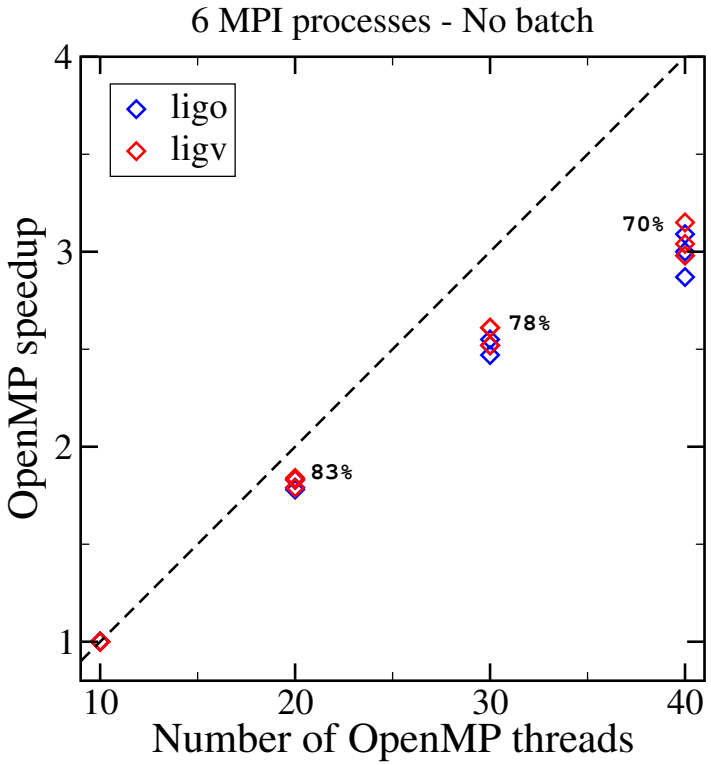


The RelaxSE code: Performance

Table: Orbital partitioning in the $YMnO_3$ calculations.

Set	N_{occ}	N_{ligo}	N_{act}	N_{ligv}	N_{virt}	N_{det}
LIGO	49	2	8	0	140	30 267 828
	47	4	8	0	140	53 017 324
	45	6	8	0	140	74 811 684
	43	8	8	0	140	95 650 908
LIGV	51	0	8	2	138	30 721 372
	51	0	8	4	136	54 531 036
	51	0	8	6	134	77 992 188
	51	0	8	8	132	101 104 828
BIG	47	4	8	6	134	1 097 706 172

Figure: OpenMP speedup compared to calculations with 10 OpenMP treads



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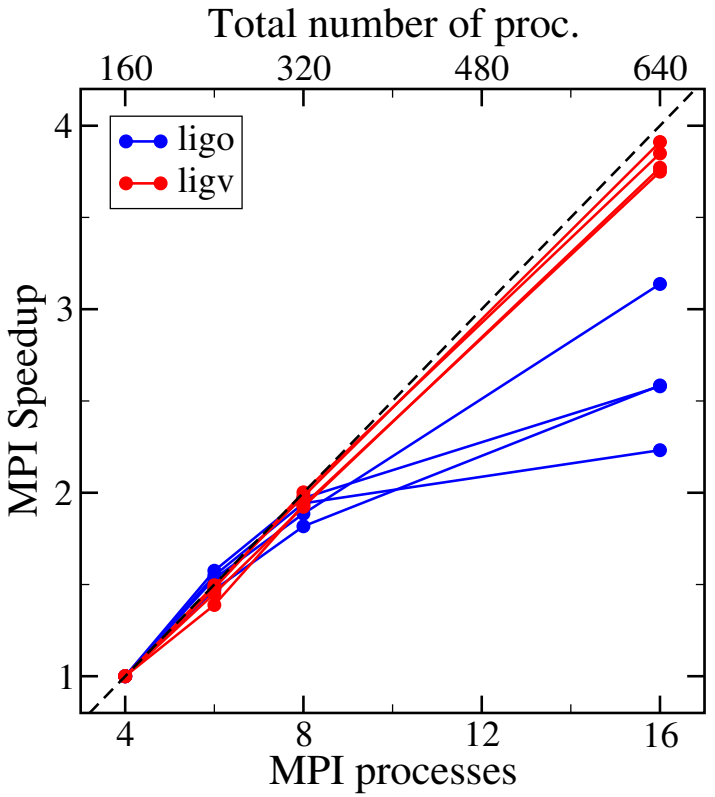
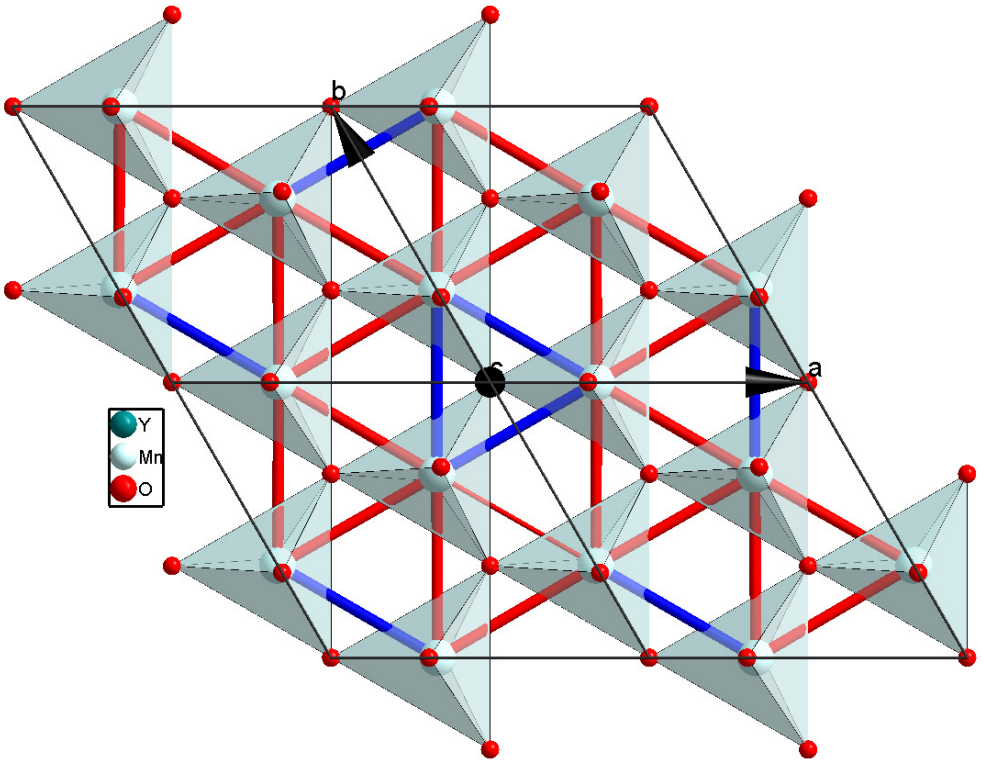
	51	0	8	8	132	101 104 828
BIG	47	4	8	6	134	1 097 706 172

Figure: MPI speedup compared to a calculation with 4 MPI processes



Application: hexagonal $YMnO_3$ compound

Magnetic pattern



Magnetic interactions

$$J_1 = -\mathbf{3.19}\,\text{meV}$$
$$J_2 = -\mathbf{3.41}\,\text{meV}$$
$$J_{av} = -2.3\,\text{meV}\ [1]$$
$$J_{av} = -3.0\,\text{meV}\ [2]$$

1 S. Petit *et al*, Phys. Rev. Letters **99**, 266604 (2007).
2 J. Park *et al*, Phys. Rev. **B 68**, 104426 (2003). (2003).

Conclusions and Perspectives

Conclusions

- SAS+S, CAS+DDCI, CAS+S, CAS+SD
- OpenMP + MPI parallelisation
- Up to 10^9 determinants
- Interfaced with Molcas
- LGPL license

Perspectives

- Determination of the bridging orbitals
- Inclusion of spin-orbit effects
- Decreasing the memory usage

Thank you for your attention

References

- **SAS+S method**
  A. Gellé, J. Varignon and M.-B. Lepetit, *EPL*, **88**, 37003 (2009).
- **RelaxSE code**
  E. Rebolini and M.-B. Lepetit, *J. Chem. Phys.*, **154**, 164116 (2021).
- **RelaxSE git repository** https://code.ill.fr/relaxse/relaxse-code.git

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