Improvement of J_{ij} calculation for extended basis sets having large non-orthogonality:
# current situation and problem

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Experimental background: complexity of multi-phase structure of permanent magnet

- To create strong permanent magnets…
  - Main phase: strong ferromagnetism and strong magnetic anisotropy
 - Grain boundary phase: magnetic insulation of main phase grains
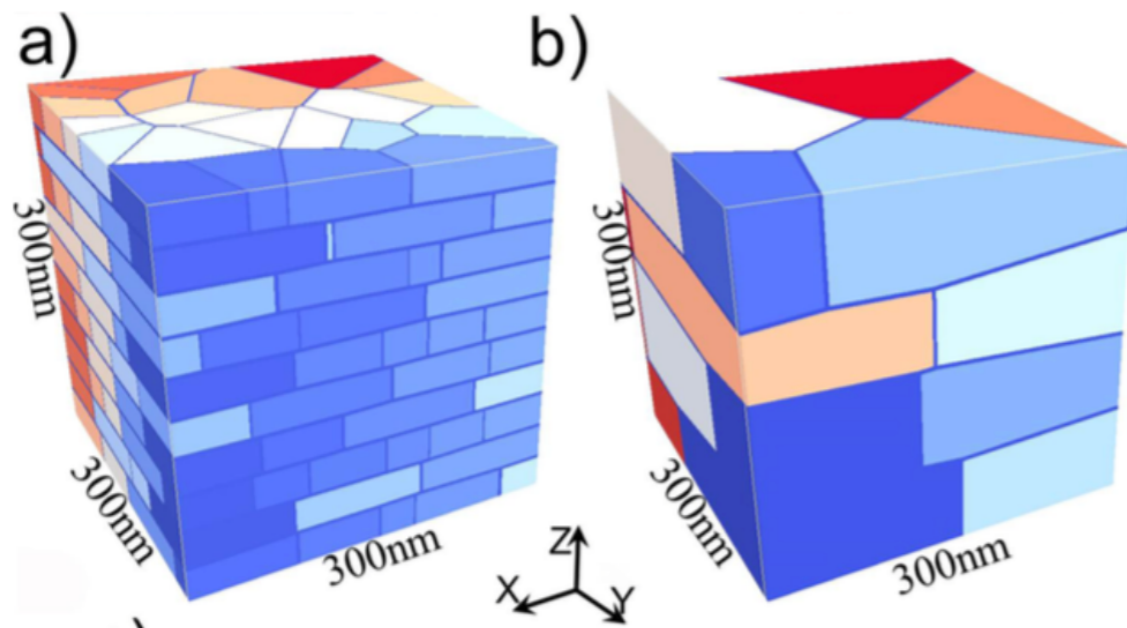
If not, magnetic reversal easily spread in the presence of demagnetization field

Magnetic insulation mechanism
Mat. Trans. **57** (2016), 1221-1229

Computational study of permanent magnets

- Calculation of exchange coupling constant J_{ij}
  - for systems including rare earth elements, e.g. Nd, Sm, Dy
  - for sufficiently large systems that can represent different phases and multi-phase structures of permanent magnets
    - Minimum ~ 50 atoms
    - Maximum ~ a few hundreds or a few thousands of atoms
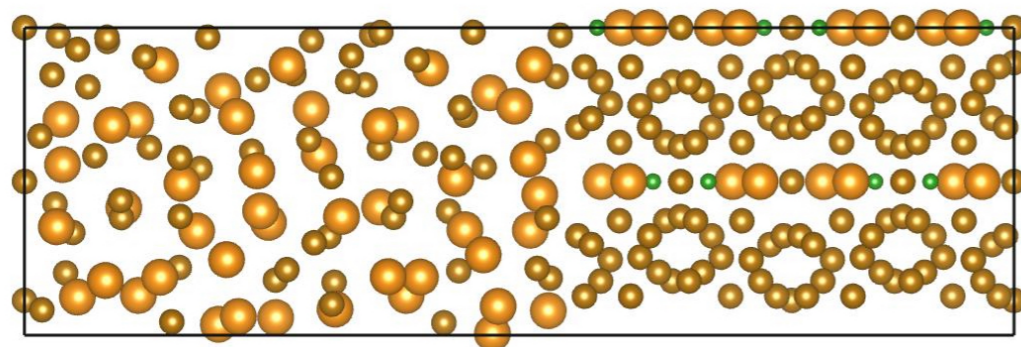
A bit too large,
but anyway this cannot be
attained without development of code

# jx: J_{ij} calculation code for OpenMX post-processing

- Post-process calculation of exchange coupling constant J_{ij} using ground state density and second perturbation theory [J. Magn. Magn. Mat **67**, 65–74 (1987)]

- Applicable for isolated systems and periodic systems

- MPI parallelization for periodic systems

- Efficient algorithm for energy integration

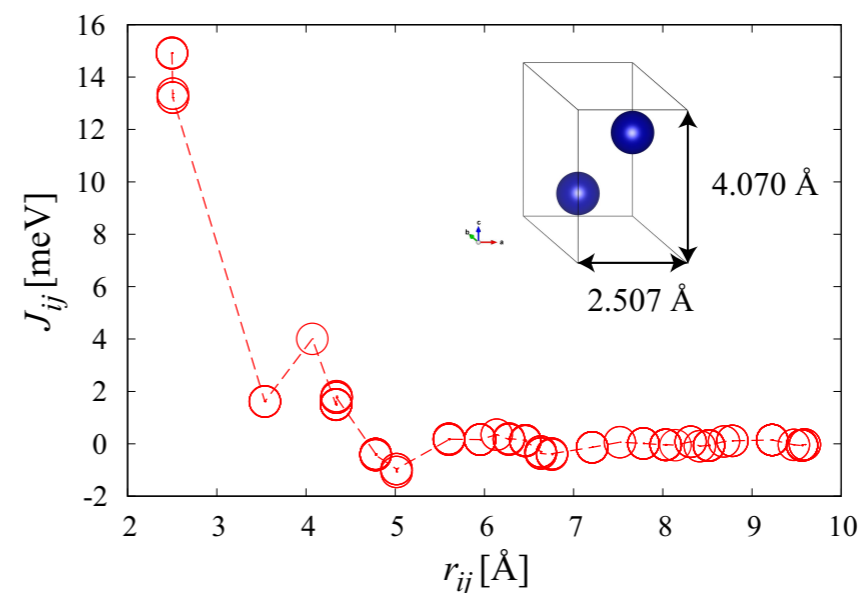- To use jx, you need to choose relatively small basis set.
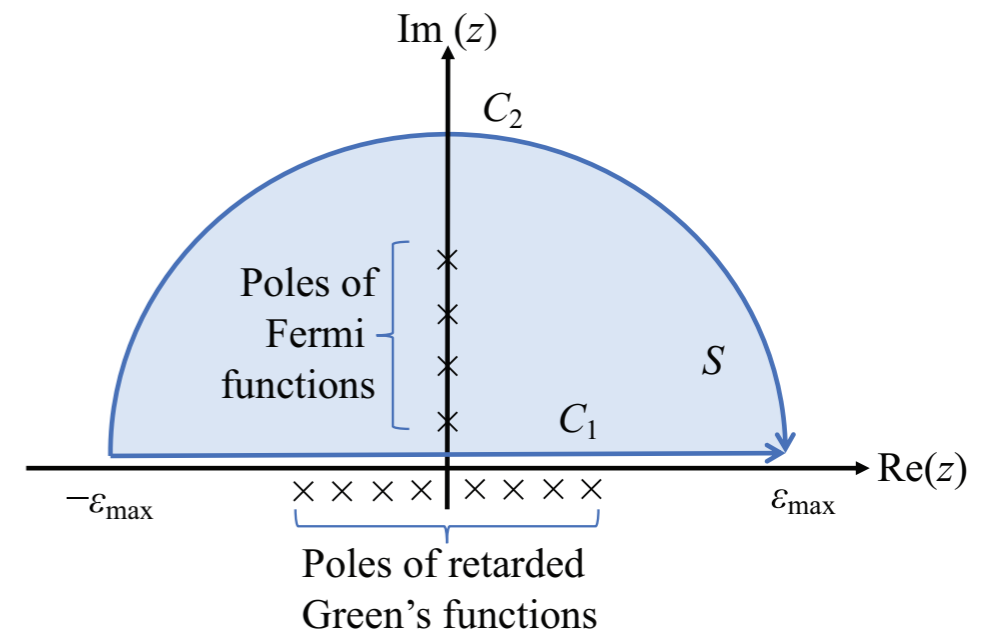
[T. Ozaki, PRB,75, 035123 (2007)]
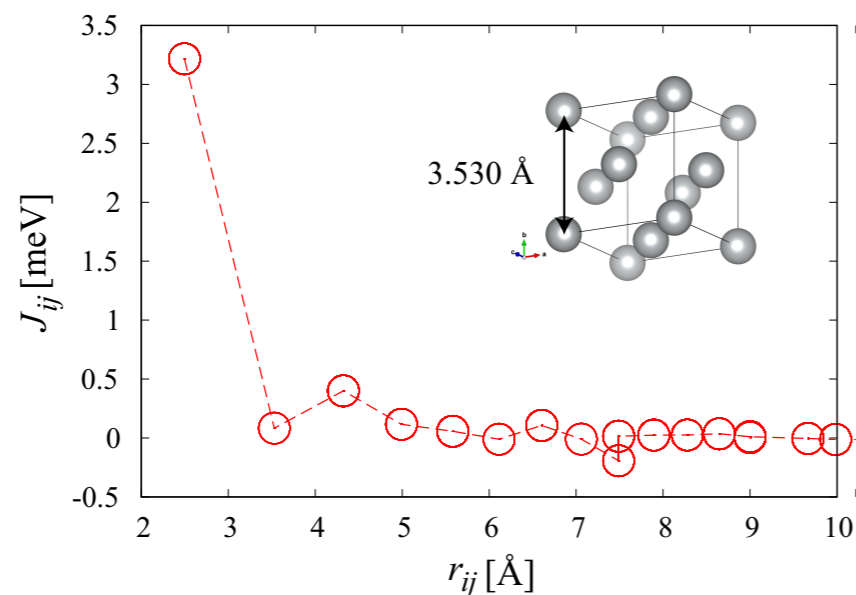[AT *et al.*, JPSJ 88, 114706 (2019)]

J_{ij} for transition metals

- Fair correpondence with experimental Curie temperature
-
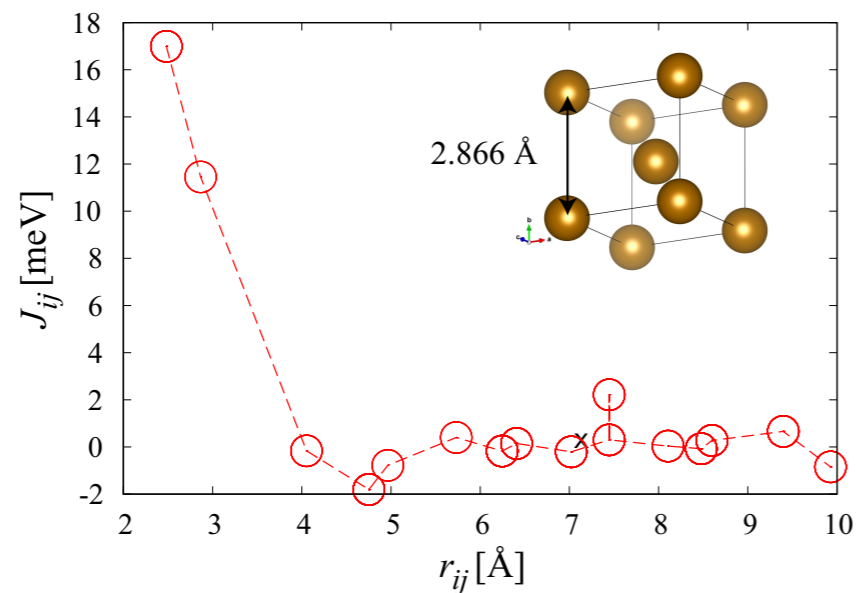
(a) bcc Fe, k-grid = 27×27×27

(b) hcp Co, k-grid = 32×32×20

(c) fcc Ni, k-grid = 24×24×24

System	T_C [K]	
	calculated	experimental
bcc Fe	1321	1040
hcp Co	1640	1131
fcc Ni	445	627

XC: GGA-PBE
PAO: s2p2d2

J_{ij} for rare earth metals, for various basis sets
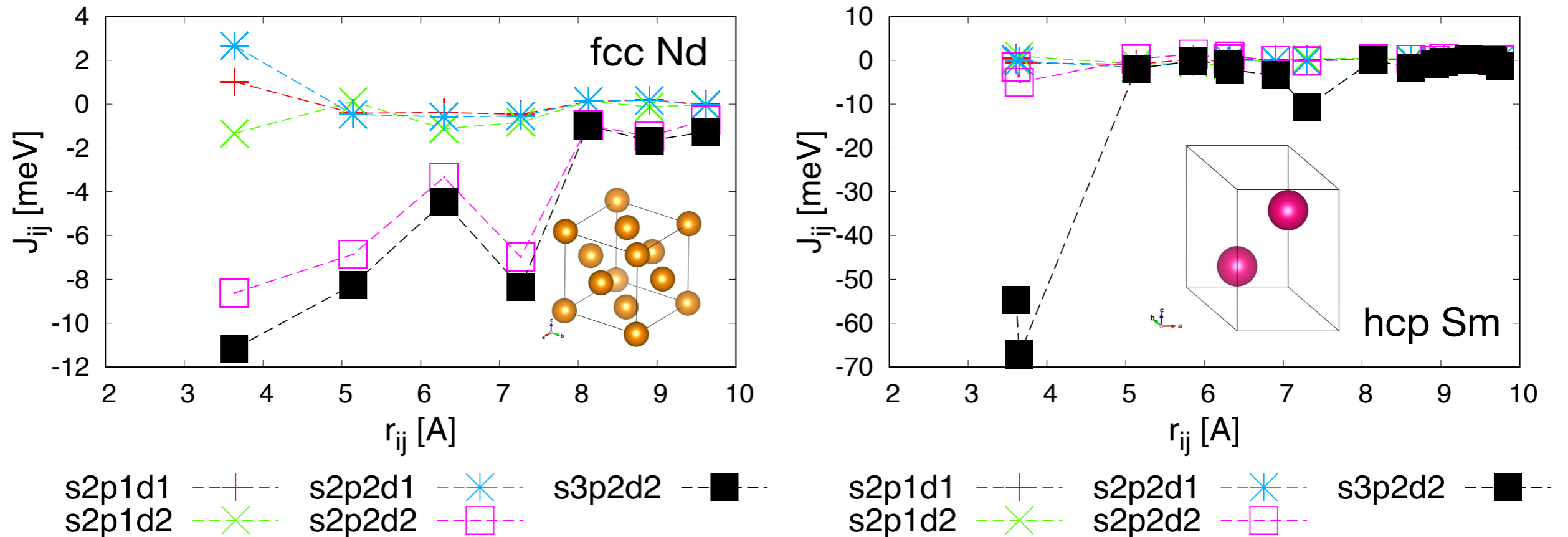
- However, jx seems to work bad in calculations of rare earth metals…

  - Strong dependence on basis sets in density functional calculation

  - Diverges when choosing large number of basis!

Problem

- What is the origin of divergence in rare earth metal calculation?

- How can we eliminate it?

- How can we calculate very accurate and converged J_{ij} for large number of basis?

What is clear is that …

- Electronic state itself will be converged when choosing very large number of basis

- This problem comes from the calculation method of J_{ij}

Non-Orthogonality problem

- Implemented ecuation to calculate J_{ij} using Liechtenstein method [J. Magn. Magn. Mat **67**, 65–74 (1987)][AT *et al.*, JPSJ 88, 114706 (2019)]

$$J_{ij} = \frac{1}{2}\sum_{p=1}^{N_{\mathrm{P}}}\tilde{R}_p\sum_{\mu,\nu\in i}\sum_{\mu',\nu'\in j}\left\{[\hat{P}_i]_{\nu\mu}G_{i\mu,j\nu'}^{+}(\downarrow,\tilde{z}_p)[\hat{P}_j]_{\nu'\mu}G_{j\mu',i\nu}^{+}(\uparrow,\tilde{z}_p)\right\}.$$

Contribution from atomic sites i and j

- Currently, in P_i and P_j, we just put the difference of diagonal element of Hamiltonian for spin up and down.

- For large basis sets, Atomic sites will be ill-depicted by this definition, because of large overlap of wide basis functions
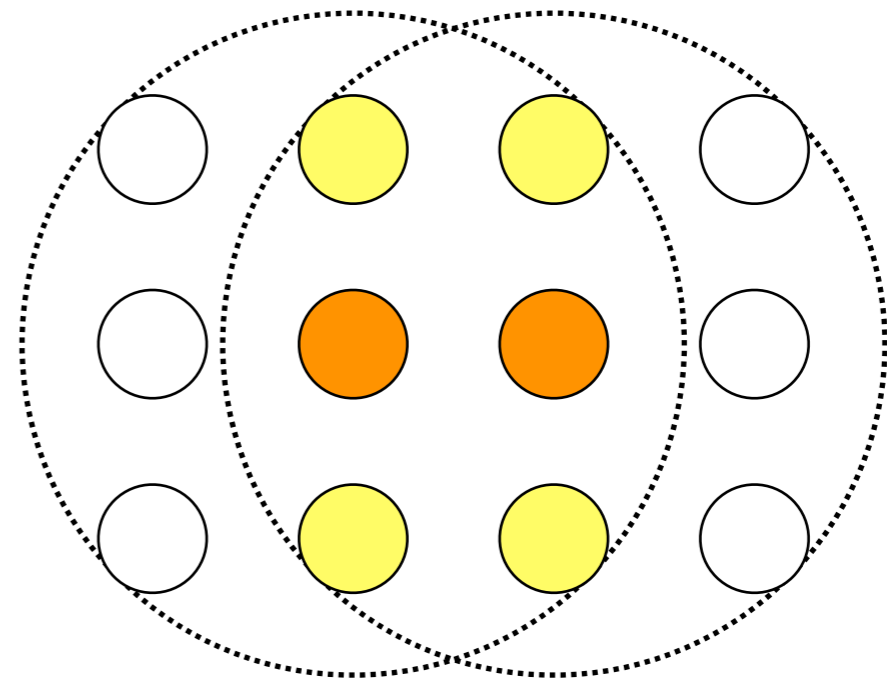
Atomic sites by valence state

- First, we tried definition of atomic sites by valence state only.

- In this method, we sum up the constribution of valence state for Liechtenstein calculation, while using extended basis set for electronic state calculation.
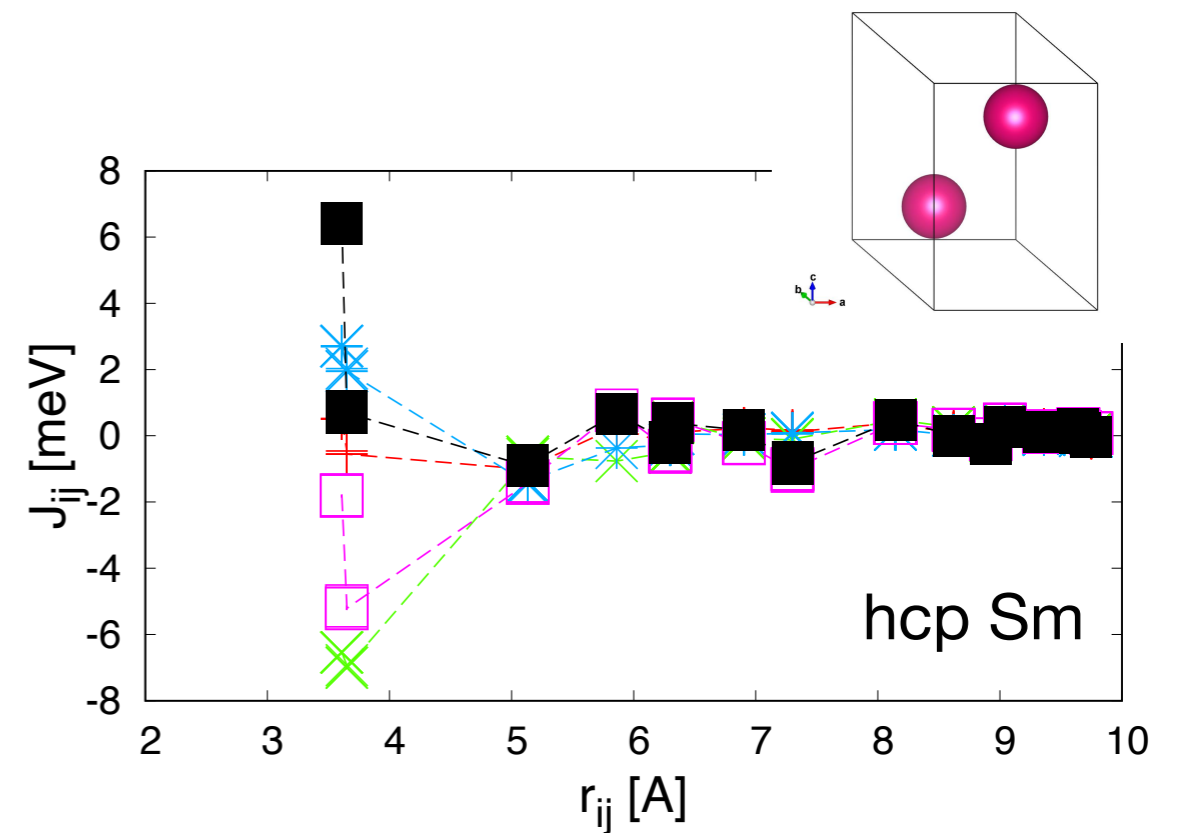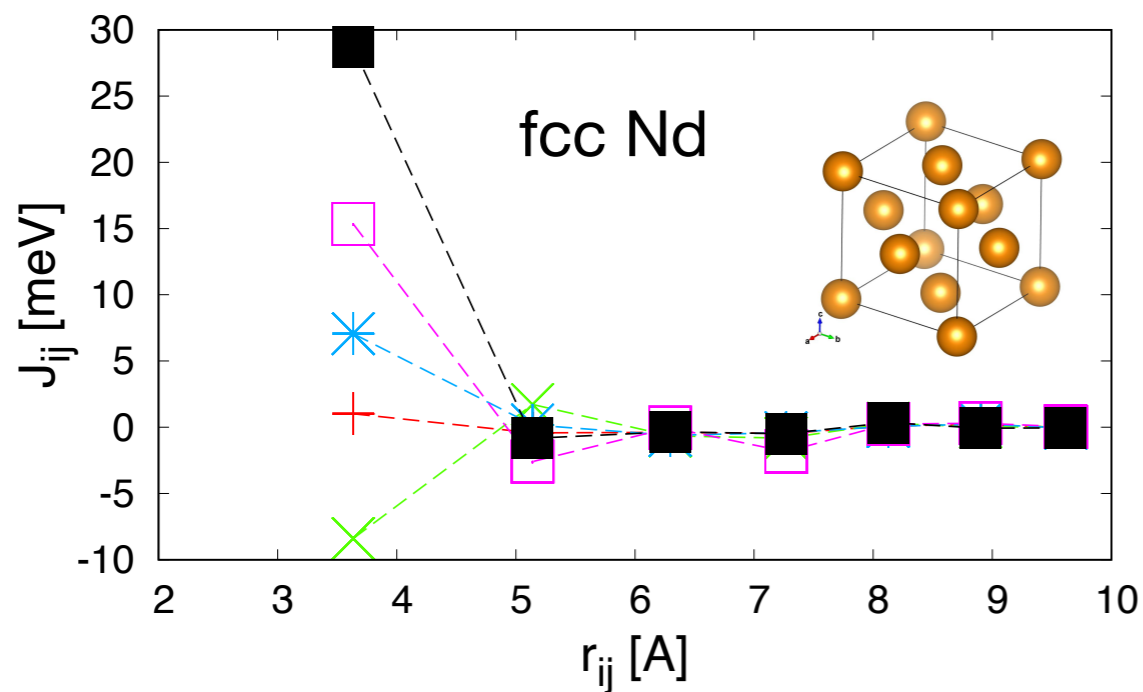
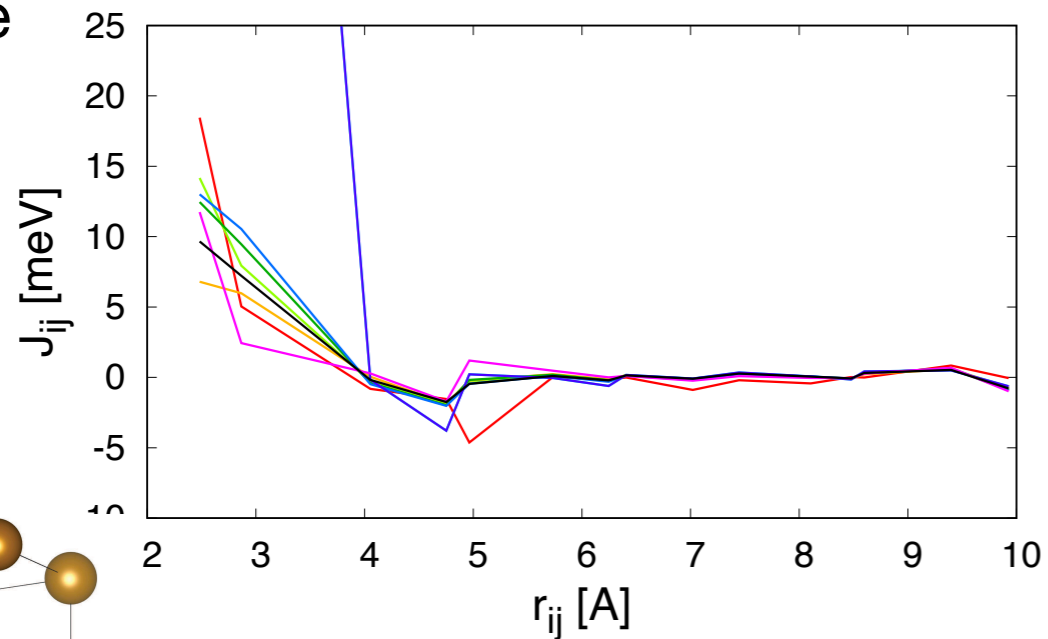- This didn't solve the problem!

- Strong dependence on basis set for 1st NN

Orthogonalization of atomic orbitals
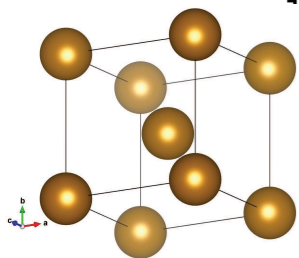
- Then, we tried orthogonalized atomic orbitals:

Löwdin orthogonalization (LO)

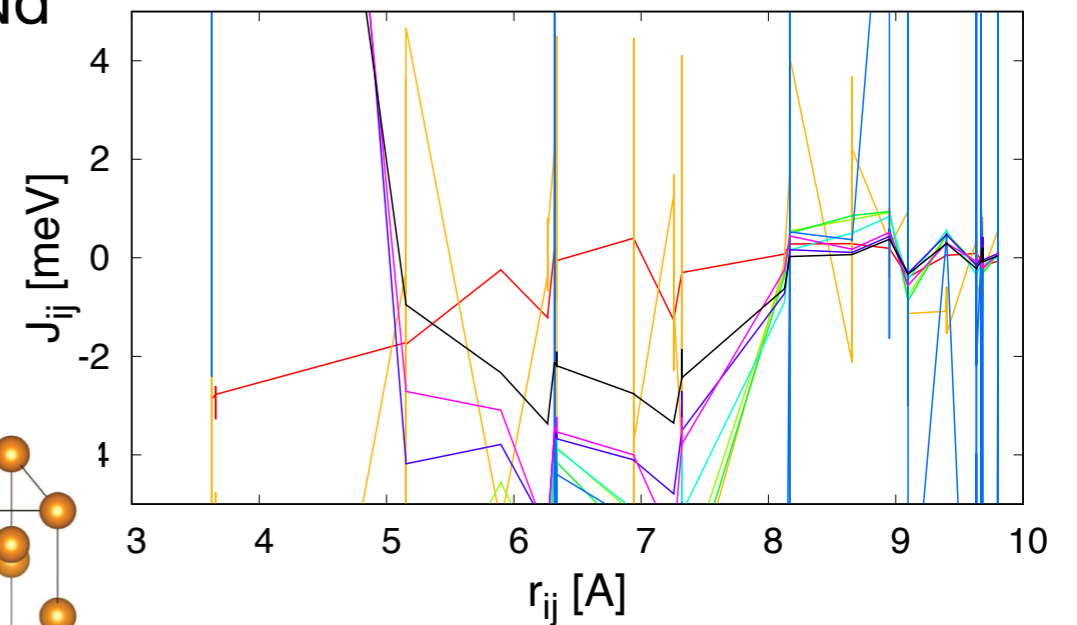$$|i\rangle^{(\mathrm{LO})} \equiv \sum_{j'} |j'\rangle \mathbf{S}^{-1/2}\big|_{j'i}.$$
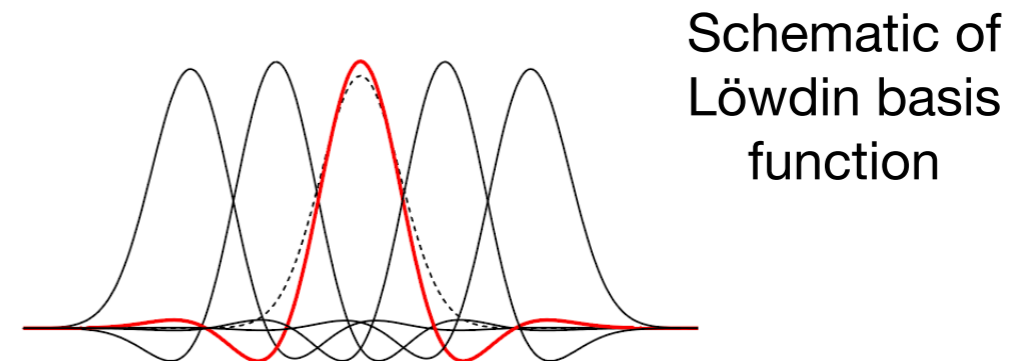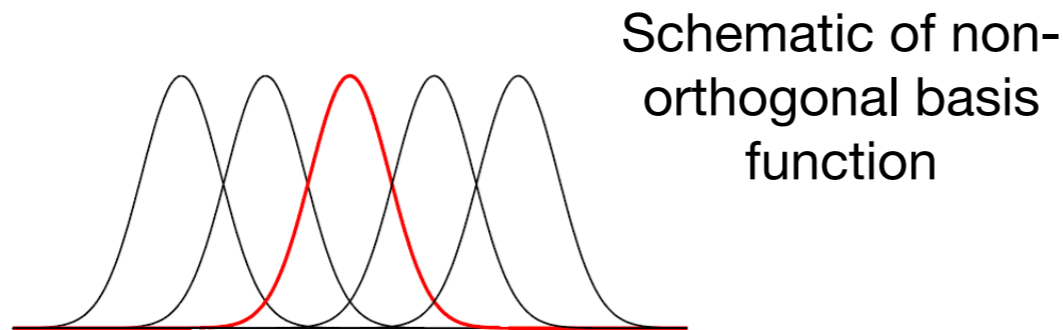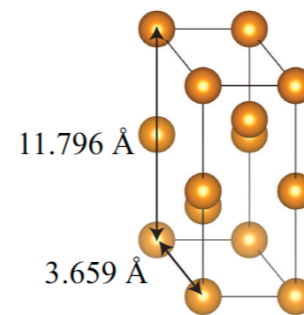
Schematic of non-orthogonal basis function

Schematic of Löwdin basis function

bcc Fe

dhcp Nd

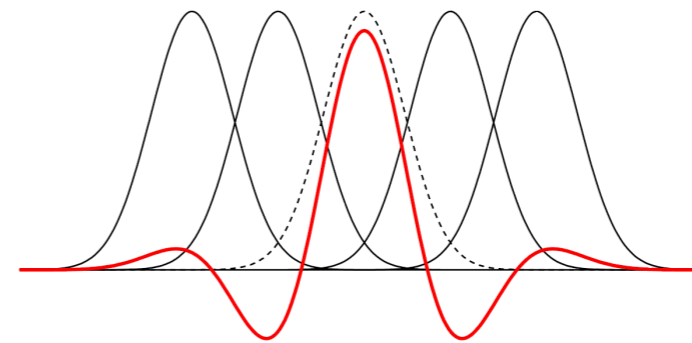**Do not converge at all!**

Orthogonalization of atomic orbitals

- We also tried another orthogonalization method:
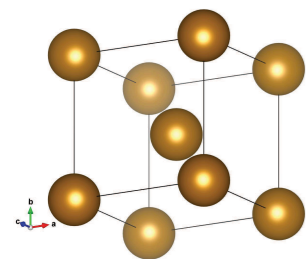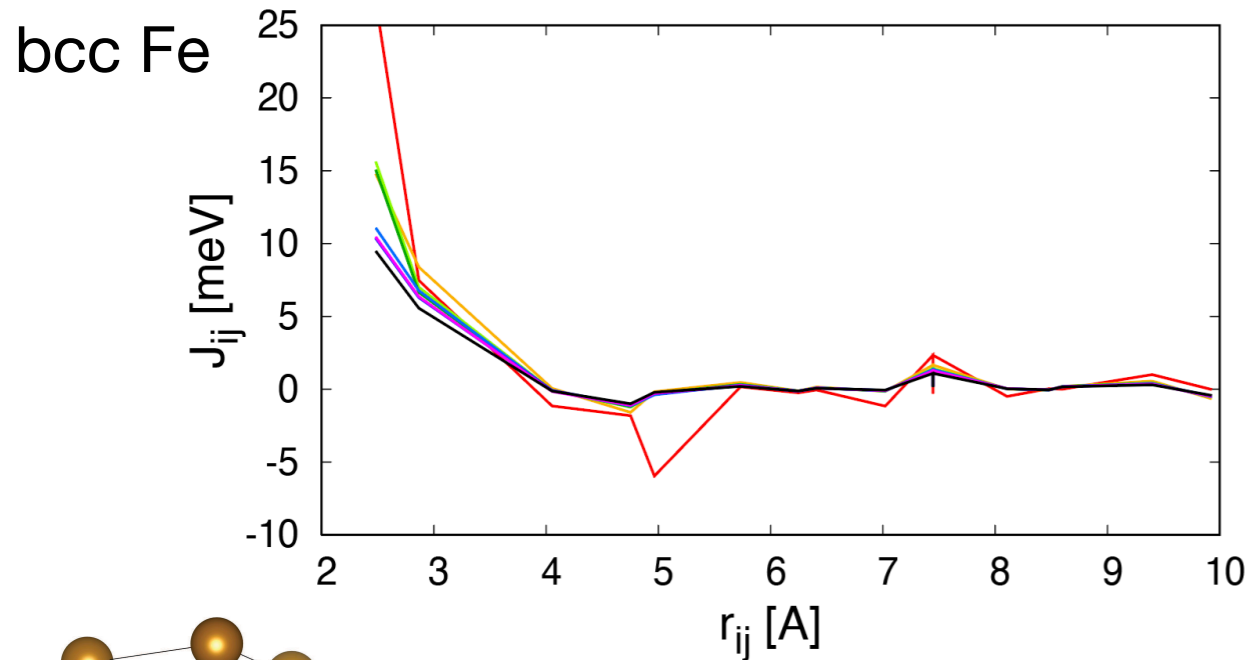
Single-site orthogonalization (SO)

$$|i\rangle_i^{(SO)} \equiv |i\rangle - \sum_{j'\neq i}\sum_{j''\neq i} |j'\rangle \mathbf{S}_{\bar{i},\bar{i}}^{-1}|_{j'j''}\langle j''|i\rangle$$
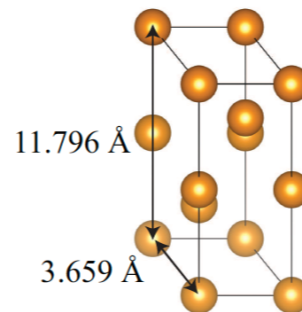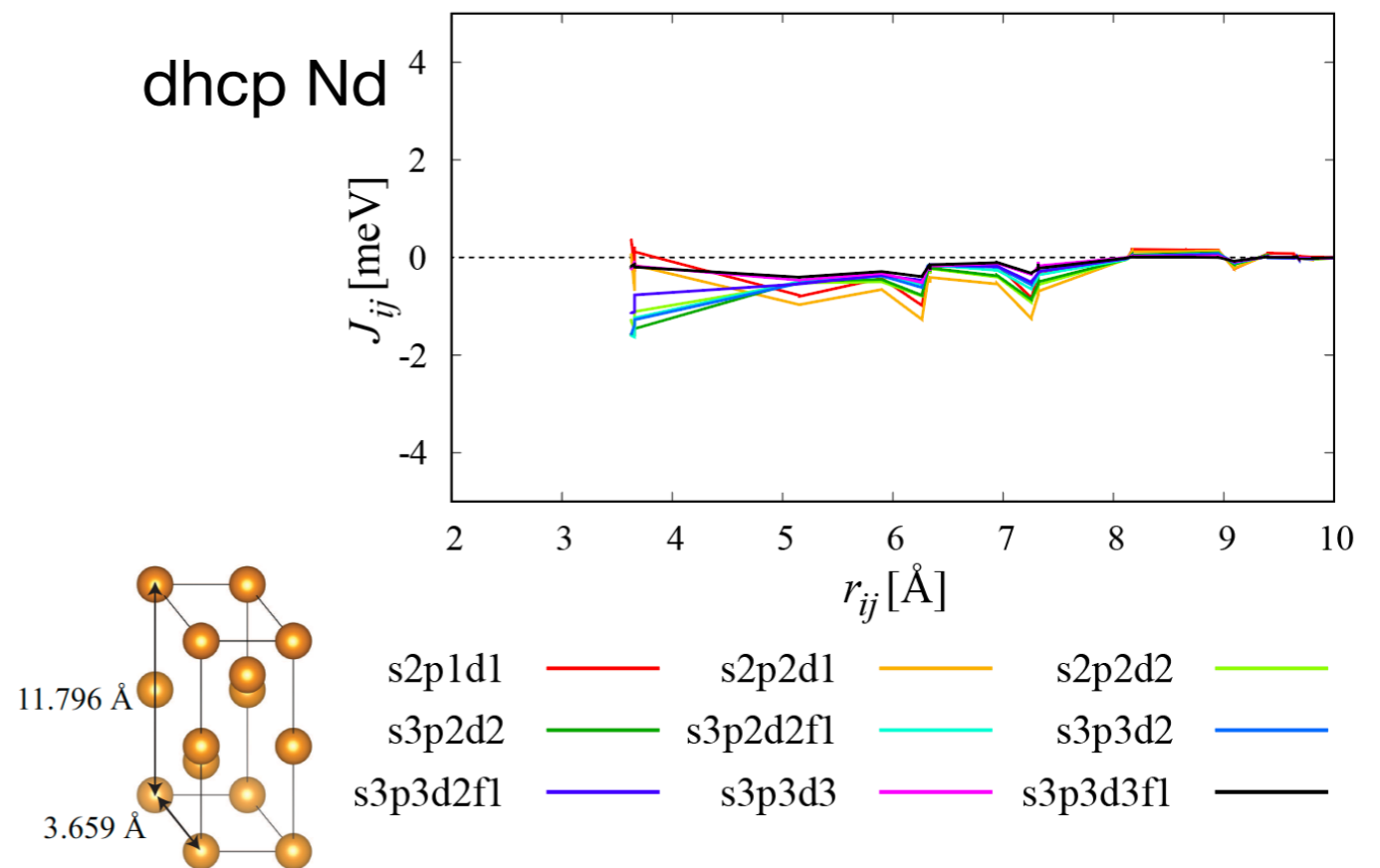
$$|j\rangle_i^{(SO)} \equiv |j\rangle, \ j\neq i,$$

$\mathbf{S}_{\bar{i},\bar{i}}^{-1}$: Submatrix of overlap matrix for i-site element

Schematic of single-site orthogonalized basis function

bcc Fe

J_{ij} [meV] vs r_{ij} [A]

s2p1d1
s2p2d1
s2p2d2
s3p2d2
s3p2d2f1
s3p3d2
s3p3d2f1
s3p3d3
s3p3d3f1

dhcp Nd

J_{ij} [meV] vs r_{ij} [Å]

s2p1d1
s2p2d1
s2p2d2
s3p2d2
s3p2d2f1
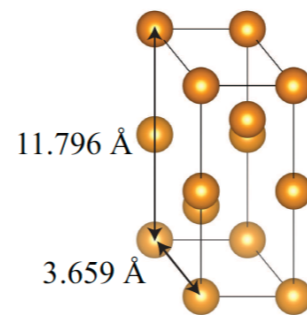s3p3d2
s3p3d2f1
s3p3d3
s3p3d3f1

11.796 Å

3.659 Å

Become slightly smaller as increasing the number of basis functions

Spin population scaling

- Because it turns out that the SO basis underestimate the spin population slightly, we tried spin-population scaling for SO results

Spin-population scaling
$$J_{ij}^{(\text{SOS})} = \frac{\Delta n_i}{\Delta n_j^{(\text{SO})}} \frac{\Delta n_j}{\Delta n_j^{(\text{SO})}} J_{ij}^{(\text{SO})}$$

bcc Fe

dhcp Nd
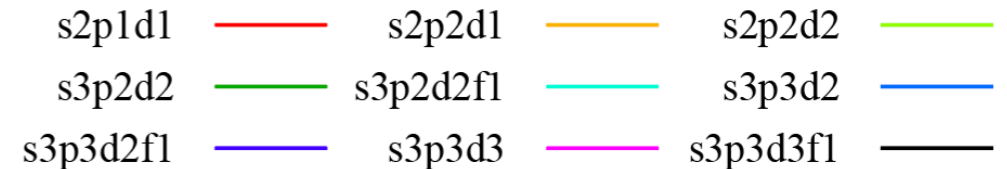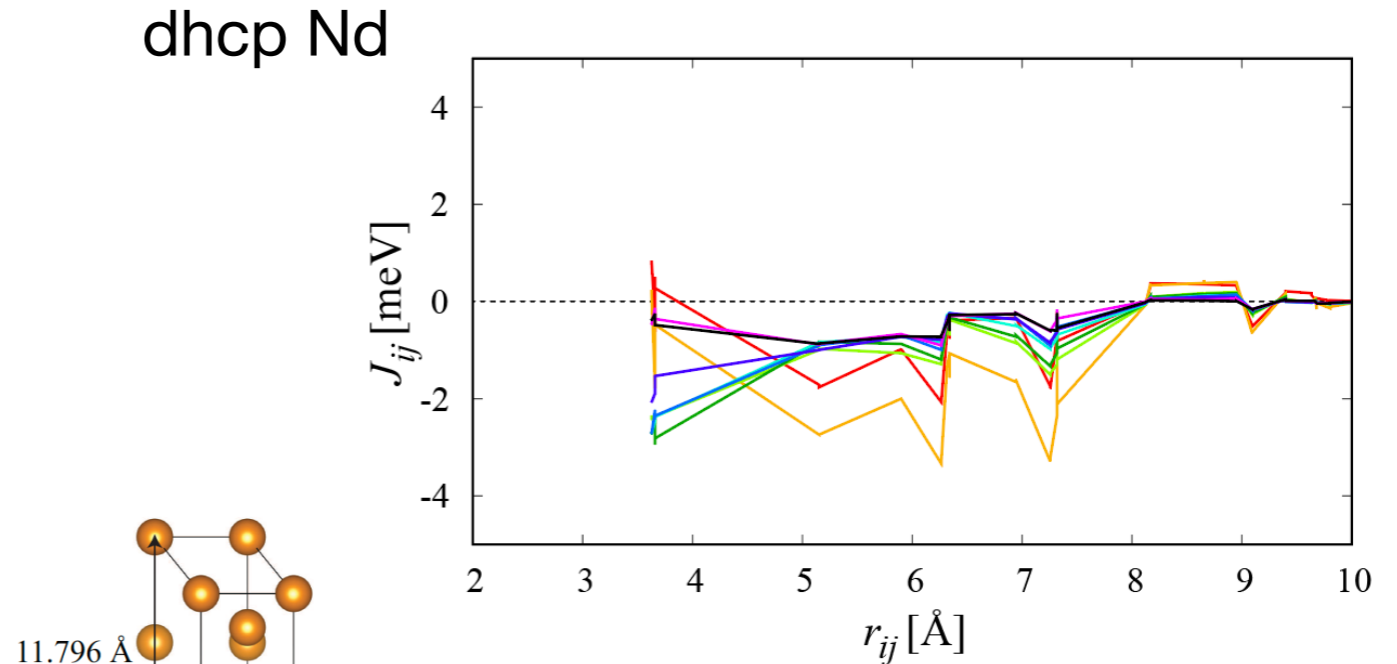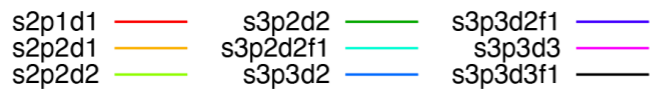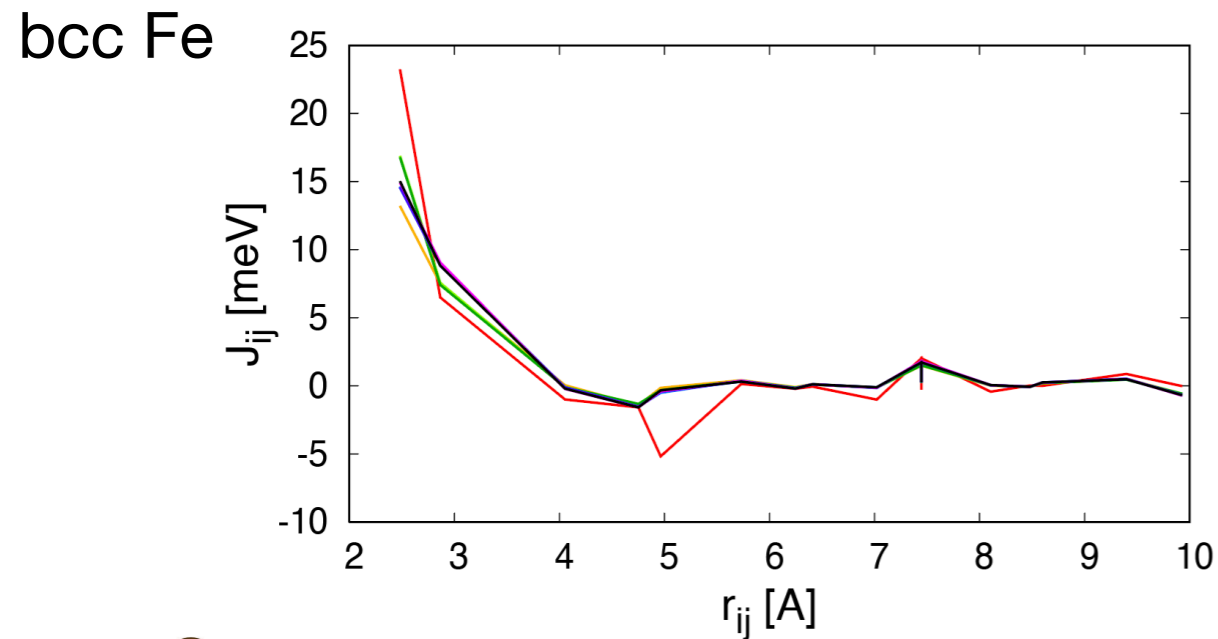
Good convergence, but physical meaning?

Discussion

- jx: fails when taking large number of basis functions
- Redefinition of atomic sites by valence state only
  - Works bad for rare earth metals, particularly when the number of basis function is very large.
- Redefinition of atomic sites by orthogonalized orbitals
  - Löwdin orthogonalization scheme does not converge J_{ij} at all.
  - Single-site orthogonalization scheme underestimates the spin population slightly, and it affects the calculated value of J_{ij}.
  - Although the convergence can be improved by spin population scaling, it makes the physical meaning of calculated values unclear.

Discussion

- Physically-meaningful definition of atomic sites?
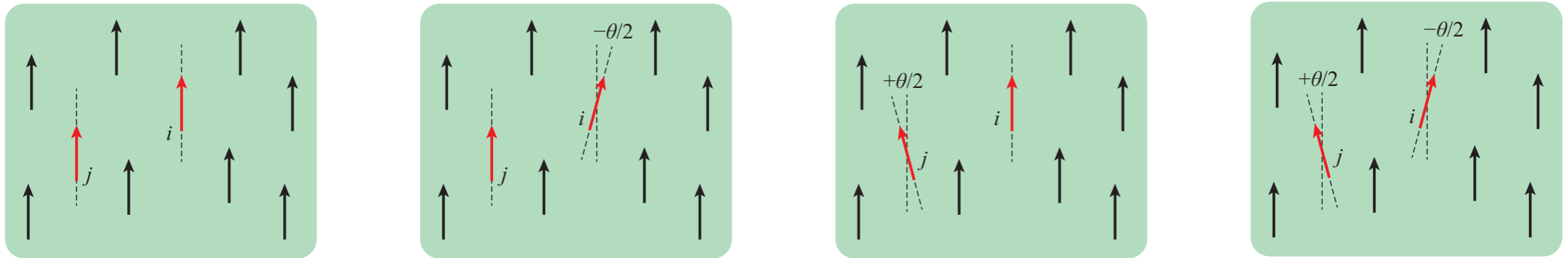
- Because Liechtenstein method is based on Heisenberg model of localized spins, we need to define atomic sites by the spin rotation on the atoms.

- How does it rotate? ...

- Definition of atomic sites by its electronic occupation
  - We should try (or, have tried) Wannier functions...

Future works

- Implementation of closest Wannier functions to a given set of localized orbitals

  - https://arxiv.org/abs/2306.15296

$$\rho_{\mathbf{R}g,\mathbf{R}'g'} = (\widetilde{\chi}_{\mathbf{R}g}|\hat{P}|\widetilde{\chi}_{\mathbf{R}'g'}),$$
$$S_{\mathbf{R}g,\mathbf{R}'g'} = (\chi_{\mathbf{R}g}|\chi_{\mathbf{R}'g'}).$$

$$\Lambda_g = \sum_{\mathbf{R}g'} \rho_{\mathbf{0}g,\mathbf{R}g'} S_{\mathbf{R}g',\mathbf{0}g}$$

$$\Lambda_g^\dagger \Lambda_g = Y_g \Omega_g^2 Y_g^\dagger,$$

$$|\bar{y}_{g,\nu}\rangle = \frac{|y_{g,\nu}\rangle}{\sqrt{\langle y_{g,\nu}|S_{\mathbf{0}g,\mathbf{0}g}|y_{g,\nu}\rangle}},$$
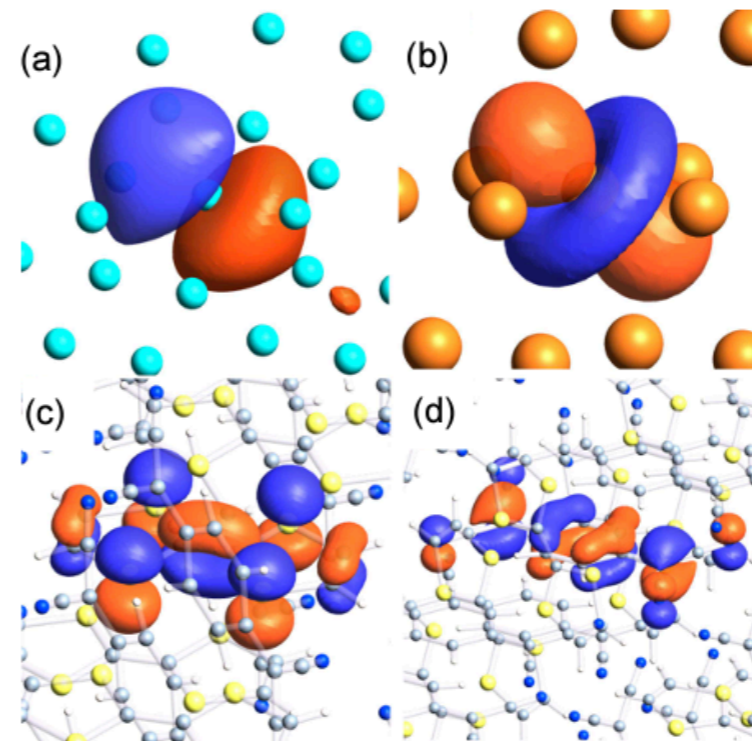

FIG. 3. CWFs for (a) Si, (b) Cu, (c) TTF in TTF-TCNQ, and (d) TCNQ in TTF-TCNQ. In all the cases, isovalues of ±0.04 (orange:0.04, blue:-0.04) are used for drawing the iso-surfaces using OpenMX Viewer [33]. The computational conditions for (a), (b), (c), and (d) are the same as those in Fig. 2 (b), Fig. 4 (a), Fig. 5 (b), and Fig. 5 (b), respectively.

We then should make our way by just, simply coding.