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

- 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 correspondence with experimental Curie temperature

![Graphs and images showing $J_{ij}$ vs. $r_{ij}$ for bcc Fe, hcp Co, and fcc Ni with calculated and experimental Curie temperatures.](image)

<table>
<thead>
<tr>
<th>System</th>
<th>$T_C$ [K]</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Fe</td>
<td>1321</td>
<td>1040</td>
<td></td>
</tr>
<tr>
<td>hcp Co</td>
<td>1640</td>
<td>1131</td>
<td></td>
</tr>
<tr>
<td>fcc Ni</td>
<td>445</td>
<td>627</td>
<td></td>
</tr>
</tbody>
</table>

XC: GGA-PBE
PAO: s2p2d2
$J_{ij}$ for rare earth metals, for various basis sets

• However, $j_x$ 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


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

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 contribution 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:

\[ |i \rangle^{(LO)} = \sum_{j'} |j' \rangle S^{-1/2} |j', i \rangle. \]

Löwdin orthogonalization (LO)

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)

\[
|\langle SO \rangle_i^i \rangle \equiv |i\rangle - \sum_{j' \neq i} \sum_{j'' \neq i} |j'\rangle S_{j',i}^{-1} |j''\rangle \langle j'',j'|i\rangle \\
|\langle SO \rangle_i^j \rangle \equiv |j\rangle, \ j \neq i,
\]

\( S_{j',i}^{-1} \): Submatrix of overlap matrix for \( i \)-site element

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

\[ J_{ij}^{\text{(SOS)}} = \frac{\Delta n_i}{\Delta n_{ij}^{\text{(SO)}}} \frac{\Delta n_j}{\Delta n_{ij}^{\text{(SO)}}} J_{ij}^{\text{(SO)}} \]

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

\[ \rho_{R_g,R'_g} = (\tilde{\chi}_{R_g} \mid \hat{P} \mid \tilde{\chi}_{R'_g}), \]

\[ S_{R_g,R'_g} = (\chi_{R_g} \mid \chi_{R'_g}). \]

\[ \Lambda_g = \sum_{R_g,R'_g} \rho_{0g,R_g} S_{R_g,R'_g,0g} \]

\[ \Lambda^\dagger \Lambda_g = Y_g \Omega^2 G^\dagger, \]

\[ |\bar{y}_{g,\nu}\rangle = \frac{|y_{g,\nu}\rangle}{\sqrt{\langle y_{g,\nu} \mid S_{0g,0g} \mid y_{g,\nu}\rangle}}, \]

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

FIG. 3. CWFs for (a) Si, (b) Cu, (c) TTF in TTF-TCNQ, and (d) TCNQ in TTF-TCNQ. In all the cases, isovales of ±0.04 (orange:0.04, blue:-0.04) are used for drawing the isosurfaces 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.