DFT and Magnetism theory

Computational Materials Physics Bootcamp

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By Ali Kefayati

UNIVERSITY OF DELAWARE

Density Functional Theory: Basic facts

- Is DFT a mean field theory?!

No, DFT is a map from the many-body system to the Kohn–Sham Auxiliary System.

- Is DFT an approximation?!

No, DFT is an exact theorem. The approximations comes only through the Exchange-Correlation (XC) functionals.

- Does one-particle Schrodinger equation (SE) mean that there is only one particle in the system?!

No, it means that the electron-electron interaction is ignored or mean-field integrated or is included into XC functionals. So, the many-body SE can be written as independent one-particle SE's.

- Is DFT an intuitive theorem?!

Yes, just look at the Poisson equation:

$$\nabla^2 \Phi = -\rho/\epsilon_0$$

One-particle Schrodinger Equation

General form:

$$\mathcal{H}(\boldsymbol{r})\psi_i(\boldsymbol{r}) \equiv \left[-\frac{\hbar^2}{2m_\mathrm{e}}\boldsymbol{\nabla}^2 + U(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_j c_{nj}(\boldsymbol{k})\phi_j(\boldsymbol{k},\boldsymbol{r}) \qquad \phi_j(\boldsymbol{k},\boldsymbol{r}+\boldsymbol{R}_m) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_m}\phi_j(\boldsymbol{k},\boldsymbol{r})$$

$$\sum_j \left[H_{ij}(\boldsymbol{k}) - \varepsilon_{n\boldsymbol{k}}S_{ij}(\boldsymbol{k})\right]c_{nj}(\boldsymbol{k}) = 0$$

$$H_{ij}(\boldsymbol{k}) = \int \phi_i^*(\boldsymbol{k},\boldsymbol{r})\mathcal{H}(\boldsymbol{r})\phi_j(\boldsymbol{k},\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \qquad S_{ij}(\boldsymbol{k}) = \int \phi_i^*(\boldsymbol{k},\boldsymbol{r})\phi_j(\boldsymbol{k},\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

One-particle Schrodinger Equation

Matrix form:

$$\boxed{\det\left[H_{ij}(\boldsymbol{k}) - \varepsilon_{\boldsymbol{k}} S_{ij}(\boldsymbol{k})\right] = 0\,.}$$

Variational form:

$$\left\langle \psi_{n\boldsymbol{k}} \middle| \mathcal{H} \middle| \psi_{n\boldsymbol{k}} \right\rangle = \int \psi^*_{n\boldsymbol{k}}(\boldsymbol{r}) \mathcal{H}(\boldsymbol{r}) \psi_{n\boldsymbol{k}}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \sum_{ij} c^*_{ni}(\boldsymbol{k}) c_{nj}(\boldsymbol{k}) H_{ij}(\boldsymbol{k})$$

$$\left\langle \psi_{n\boldsymbol{k}} \middle| \psi_{n\boldsymbol{k}} \right\rangle = \int \psi^*_{n\boldsymbol{k}}(\boldsymbol{r}) \psi_{n\boldsymbol{k}}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \sum_{ij} c^*_{ni}(\boldsymbol{k}) c_{nj}(\boldsymbol{k}) S_{ij}(\boldsymbol{k}) = 1$$

$$\sum_{ij} c^*_{ni}(\boldsymbol{k}) c_{nj}(\boldsymbol{k}) H_{ij}(\boldsymbol{k}) - \lambda \left[\sum_{ij} c^*_{ni}(\boldsymbol{k}) c_{nj}(\boldsymbol{k}) S_{ij}(\boldsymbol{k}) - 1 \right]$$

One-particle Schrodinger Equation

Method	Basis set
LCAO Method (Linear Combination of Atomic Orbitals)	$\phi_j(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_m \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_m} w_j(\boldsymbol{r}-\boldsymbol{R}_m)$
Plane-Wave Method	$\phi_j(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{\sqrt{V}}\mathrm{e}^{\mathrm{i}(\boldsymbol{k}+\boldsymbol{G}_j)\cdot\boldsymbol{r}}$
Orthogonalized-Plane-Wave Method	$\phi_j(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{\sqrt{V}}\mathrm{e}^{\mathrm{i}(\boldsymbol{k}+\boldsymbol{G}_j)\cdot\boldsymbol{r}} - \sum_\alpha \mu_\alpha(\boldsymbol{k}+\boldsymbol{G}_j)\phi_\alpha(\boldsymbol{k},\boldsymbol{r})$
Pseudopotential Method	$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_j c_{nj}(\boldsymbol{k})\left[\widetilde{\phi}_j(\boldsymbol{k},\boldsymbol{r}) - \sum_\alpha \mu_{j\alpha}(\boldsymbol{k})\phi_\alpha(\boldsymbol{k},\boldsymbol{r})\right]$
Augmented-Plane-Wave Method	$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\mathrm{i}^l j_l(kr)Y_l^{m*}(\theta_k,\varphi_k)Y_l^m(\theta,\varphi)$
Green Function or KKR Method	$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \int_v G(\boldsymbol{k},\boldsymbol{r}-\boldsymbol{r}')v_{\mathrm{a}}(\boldsymbol{r}')\psi_{\boldsymbol{k}}(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'$
LMTO Method (Linear Muffin-Tin Orbital)	$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{lm} B_{lm}(\boldsymbol{k})\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j}\phi_{lm}(\boldsymbol{r}-\boldsymbol{R}_j)$

Density Functional Theory: The Hohenberg–Kohn Theorems

- Theorem I: The ground-state wavefunction and therefore the ground-state energy is a unique functional of the ground-state electron density. This is true for the ground-state expectation value of any observable physical quantity.
- Theorem II: The energy as a functional of the density takes its minimum at the true ground-state density.

$$\begin{array}{ccc} V_{\text{ext}}(\mathbf{r}) & \overset{\text{HK}}{\Longleftarrow} & n_0(\mathbf{r}) \\ \Downarrow & & \Uparrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) \end{array}$$

- Thus, the many-body SE can be mapped to a one-particle fictitious system: The one-particle Kohn–Sham Auxiliary System!

$$\begin{array}{ccccccc} V_{\text{ext}}(\mathbf{r}) & \overset{\text{HK}}{\Longleftarrow} & n_0(\mathbf{r}) & \overset{\text{KS}}{\Longleftrightarrow} & n_0(\mathbf{r}) & \overset{\text{HK}_0}{\Longrightarrow} & V_{\text{KS}}(\mathbf{r}) \\ \Downarrow & & \Uparrow & & \Uparrow & & \Downarrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) & & \psi_{i=1,N_e}(\mathbf{r}) & \Leftarrow & \psi_i(\mathbf{r}) \end{array}$$

Density Functional Theory: The Kohn–Sham System

The many-body system : $\Psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\mathrm{e}})$

$$\mathcal{H}|\Psi_0\rangle \equiv (T + U + V)\,|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$T = \sum_{i=1}^{N_\mathrm{e}} \left(-\frac{\hbar^2}{2m_\mathrm{e}}\boldsymbol{\nabla}_i^2\right) \qquad U = \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N_\mathrm{e}} U(\boldsymbol{r}_i - \boldsymbol{r}_j) \qquad V = \sum_{i=1}^{N_\mathrm{e}} V_\mathrm{ext}(\boldsymbol{r}_i)$$

The KS system:

$$\left[-\frac{\hbar^2}{2m_\mathrm{e}}\boldsymbol{\nabla}^2 + V_\mathrm{s}(\boldsymbol{r})\right]\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r})$$

$$n_\mathrm{e}(\boldsymbol{r}) = \sum_{i=1}^{N_\mathrm{e}} |\phi_i(\boldsymbol{r})|^2$$

Density Functional Theory: The Kohn–Sham Theorem

The Kohn–Sham System:

$$T_\mathrm{s}[n_\mathrm{e}(\boldsymbol{r})] = \langle \Psi_\mathrm{s}|T|\Psi_\mathrm{s}\rangle = \sum_{i=1}^{N_\mathrm{e}} \int \phi_i^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_\mathrm{e}}\boldsymbol{\nabla}^2\right) \phi_i(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

$$T_\mathrm{s}[n_\mathrm{e}(\boldsymbol{r})] \neq T[n_\mathrm{e}(\boldsymbol{r})]$$

$$U_\mathrm{H}[n_\mathrm{e}(\boldsymbol{r})] = \frac{\tilde{e}^2}{2} \iint \frac{n_\mathrm{e}(\boldsymbol{r})n_\mathrm{e}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{r}$$

$$U_\mathrm{H}[n_\mathrm{e}(\boldsymbol{r})] \neq U$$

$$E_\mathrm{ext}[n_\mathrm{e}(\boldsymbol{r})] = \int V_\mathrm{ext}(\boldsymbol{r})n_\mathrm{e}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

$$E[n_\mathrm{e}(\boldsymbol{r})] = \sum_{i=1}^{N_\mathrm{e}} \int \phi_i^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_\mathrm{e}}\boldsymbol{\nabla}^2\right) \phi_i(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + \int V_\mathrm{ext}(\boldsymbol{r})n_\mathrm{e}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + \frac{\tilde{e}^2}{2} \iint \frac{n_\mathrm{e}(\boldsymbol{r})n_\mathrm{e}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{r} + E_\mathrm{xc}[n_\mathrm{e}(\boldsymbol{r})]$$

$$E_\mathrm{xc}[n_\mathrm{e}(\boldsymbol{r})] = T[n_\mathrm{e}(\boldsymbol{r})] - T_\mathrm{s}[n_\mathrm{e}(\boldsymbol{r})] + U[n_\mathrm{e}(\boldsymbol{r})] - U_\mathrm{H}[n_\mathrm{e}(\boldsymbol{r})]$$

Density Functional Theory: The Kohn–Sham Theorem

The Kohn–Sham System:

$$V_{\mathrm{s}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\mathrm{e}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + V_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r})]$$

$$V_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r})] = \frac{\delta E_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r})]}{\delta n_{\mathrm{e}}(\boldsymbol{r})}$$

$$\left[-\frac{\hbar^2}{2m_{\mathrm{e}}} \boldsymbol{\nabla}^2 + V_{\mathrm{ext}}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\mathrm{e}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + V_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r})] \right] \phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r})$$

Density Functional Theory: XC Functional

The XC functional:

$$E_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r})] = \frac{\tilde{e}^2}{2} \iint \frac{n_{\mathrm{e}}(\boldsymbol{r}) n_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' \, \mathrm{d}\boldsymbol{r}$$

$$n_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}') = n_{\mathrm{e}}(\boldsymbol{r}) \left[\tilde{g}(\boldsymbol{r}, \boldsymbol{r}') - 1 \right]$$

$\tilde{g}(r, r')$ is a mean of the pair distribution function over the coupling strength.

There are two main approximation for XC functional:

1. LDA: Local density approximation

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n_{\mathrm{e}}(\boldsymbol{r})] = \int n_{\mathrm{e}}(\boldsymbol{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{hom}}[n_{\mathrm{e}}(\boldsymbol{r})] \, \mathrm{d}\boldsymbol{r}$$

2. GGA: Generalized gradient approximation

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int \mathrm{d}\boldsymbol{r} f(n_{\uparrow}, n_{\downarrow}, \boldsymbol{\nabla} n_{\uparrow}, \boldsymbol{\nabla} n_{\downarrow})$$

Spin Density Functional Theory

The potential includes the exchange field as well:

$$V = \int \left[V_{\mathrm{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) - \boldsymbol{B}(\boldsymbol{r}) \cdot \boldsymbol{m}(\boldsymbol{r}) \right] \mathrm{d}\boldsymbol{r}$$

Now, observables are functional of both charge density and magnetization:

$$\boldsymbol{M}(\boldsymbol{r}) = \langle \Psi | \boldsymbol{m}(\boldsymbol{r}) | \Psi \rangle$$

$$\boldsymbol{m}(\boldsymbol{r}) = g_{\mathrm{e}} \mu_{\mathrm{B}} \sum_i \boldsymbol{s} \delta(\boldsymbol{r} - \boldsymbol{r}_i) = \tfrac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \sum_i \boldsymbol{\sigma} \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

And the KS equation:

$$\sum_{\sigma'} \left\{ \left[-\frac{\hbar^2}{2m_{\mathrm{e}}} \boldsymbol{\nabla}^2 + V_{\mathrm{s}}(\boldsymbol{r}) \right] \delta_{\sigma\sigma'} - \tfrac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \boldsymbol{\sigma}_{\sigma\sigma'} \cdot \boldsymbol{B}_{\mathrm{s}}(\boldsymbol{r}) \right\} \phi_{i\sigma'}(\boldsymbol{r}) = \varepsilon_{i\sigma} \phi_{i\sigma}(\boldsymbol{r})$$

$$V_{\mathrm{s}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\mathrm{e}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + \frac{\delta E_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta n_{\mathrm{e}}(\boldsymbol{r})}$$

$$\boldsymbol{B}_{\mathrm{s}}(\boldsymbol{r}) = \boldsymbol{B}(\boldsymbol{r}) - \frac{\delta E_{\mathrm{xc}}[n_{\mathrm{e}}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta \boldsymbol{M}(\boldsymbol{r})}$$

Spin Density Functional Theory

Spin-polarized system:

$$\rho(\mathbf{r}) = \begin{pmatrix} n_{\uparrow\uparrow}(\mathbf{r}) & n_{\uparrow\downarrow}(\mathbf{r}) \\ n_{\downarrow\uparrow}(\mathbf{r}) & n_{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix} = \frac{1}{2}\left[n(\mathbf{r})\sigma_0 + \mathbf{m}(\mathbf{r})\cdot\boldsymbol{\sigma}\right]$$

$$n(\mathbf{r}) = \mathrm{Tr}\{\rho(\mathbf{r})\}$$

$$\mathbf{m}(\mathbf{r}) = \mathrm{Tr}\{\rho(\mathbf{r})\boldsymbol{\sigma}\} = m(\mathbf{r})\mathbf{u}(\mathbf{r})$$

$$\boldsymbol{\sigma} = \mathbf{e}_x\sigma_x + \mathbf{e}_y\sigma_y + \mathbf{e}_z\sigma_z$$

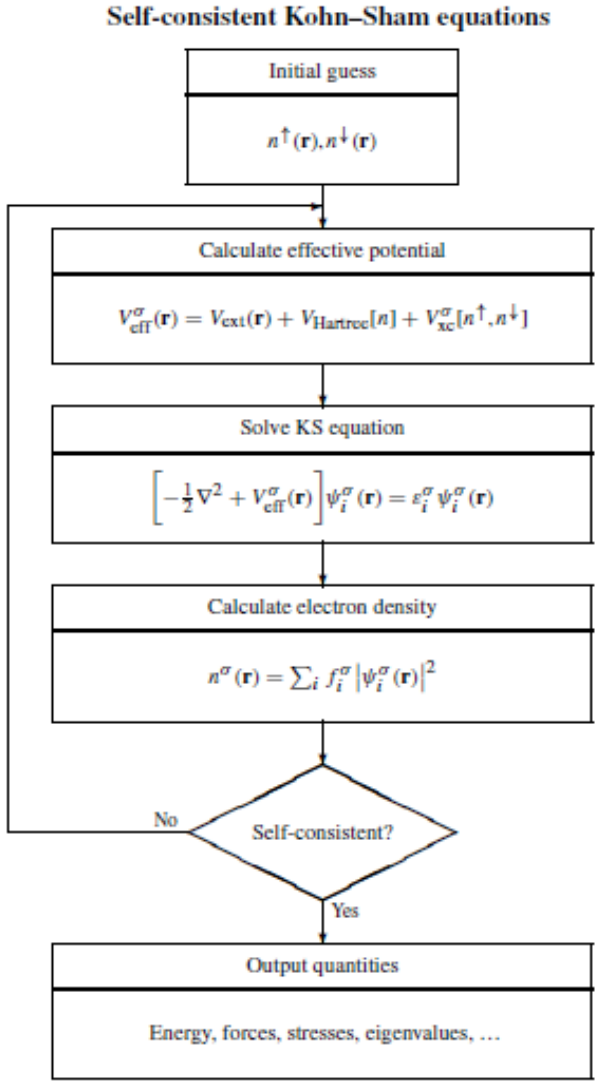
The XC Functional:

$$E_{\mathrm{xc}}[n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r})] = \int \varepsilon_{\mathrm{xc}}[n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r})] n_{\mathrm{e}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

Spin-orbit coupling:

$$\mathcal{H}_{\mathrm{s-o}} = \frac{\hbar^2}{2m_{\mathrm{e}}^2 c^2}\frac{1}{r}\frac{\mathrm{d}U(r)}{\mathrm{d}r}\boldsymbol{l}\cdot\boldsymbol{s}$$

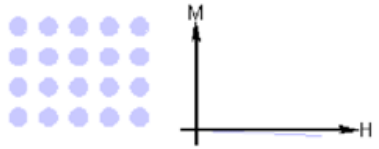
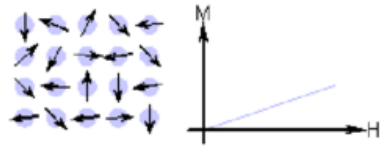
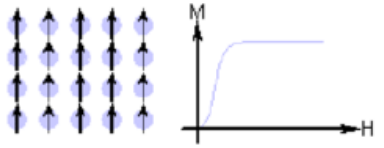
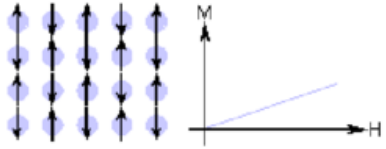
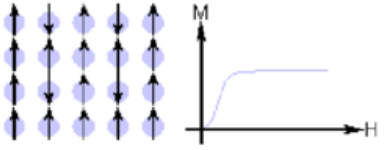
Density Functional Theory: Self-consistent solution



Magnetism: Fundamentals

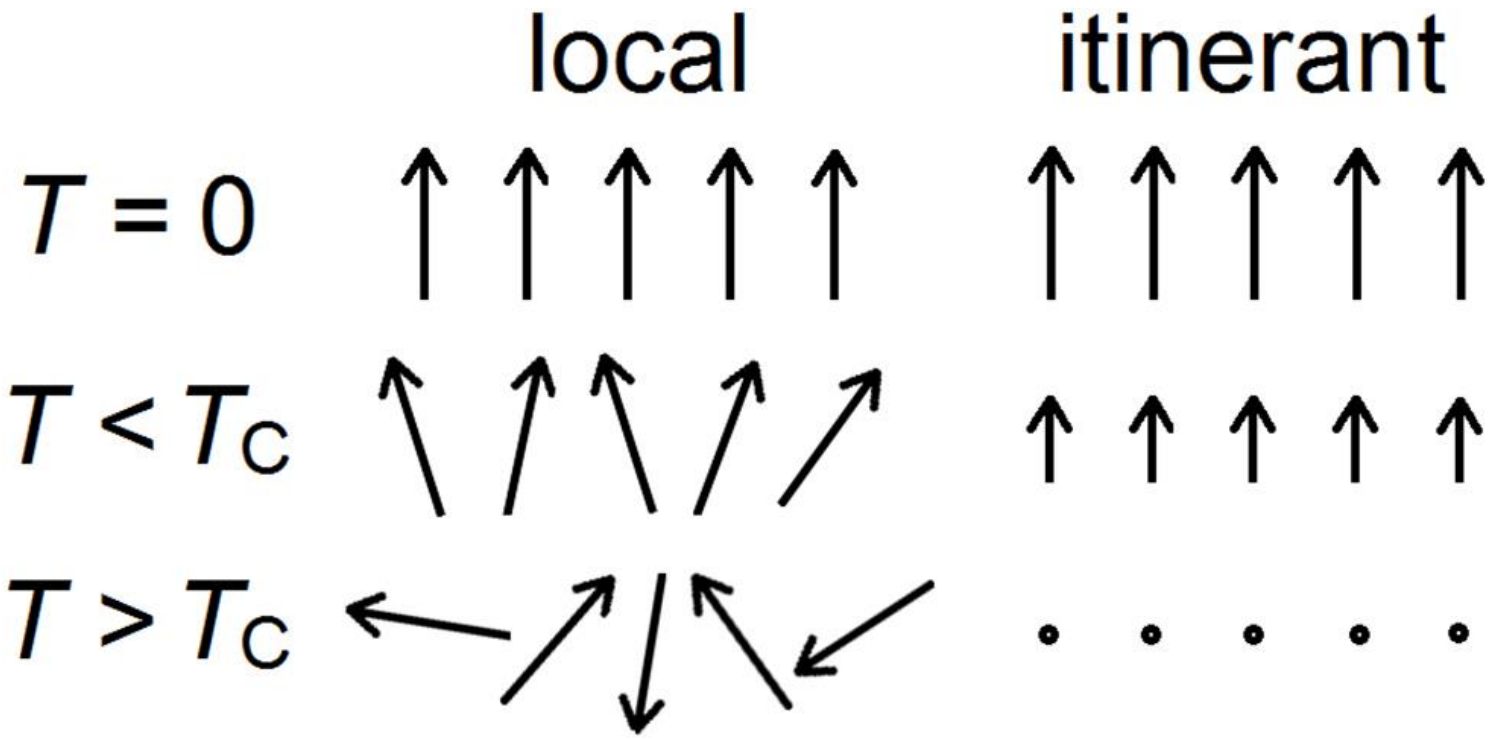
- Exchange interaction: Direct Exchange, Indirect Exchange, Superexchange, Double Exchange
- Magnetic order: random(PM), collinear(FM, AFM), noncollinear(AFM)
- Characterization parameters: Magnetization, Susceptibility, Critical temperature
- Characterization tools: Temperature, Light, External Field
- Spins: classical vectors, (bosonic) quasiparticle
- Phase transitions: FM @ Curie Temperature, AFM @ Neel Temperature

Magnetism: Magnetic materials

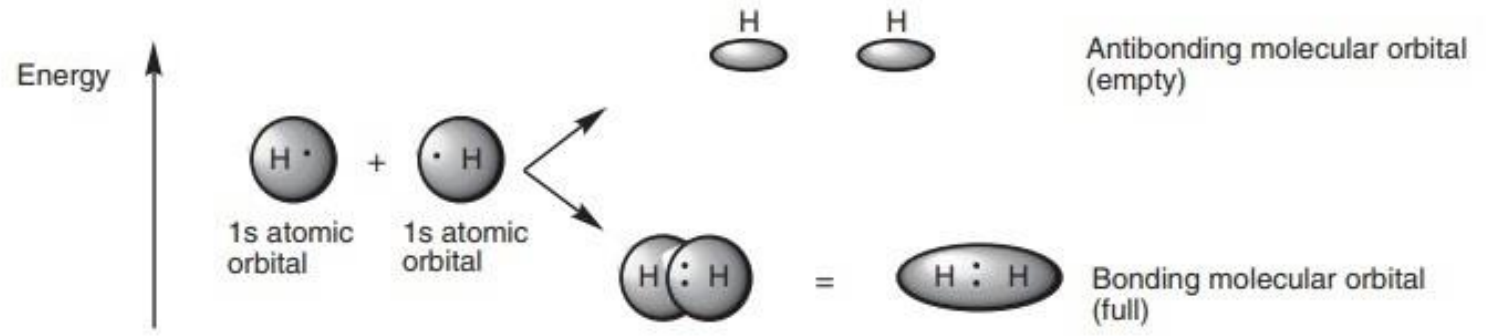
Type of magnetism	Magnetic susceptibility, χ	Atomic / Magnetic Behavior	Temperature dependence	Examples and comments
Diamagnetic	Negative and small, Au: -2.74×10^{-6} Cu: -0.77×10^{-6}		Temperature independent	The shells of the atoms are closed as in the case of covalent solids such as Ge, Si, and metals such as Au, Cu, Ag, etc.
Paramagnetic	Positive and small, β-Sn: 0.19×10^{-6} Pt: 21.04×10^{-6} Mn: 66.10×10^{-6} 10^{-5}-10^{-4}		Temperature independent	Atoms have randomly oriented magnetic moments as in alkali and transition metals
	Positive and small		Follows Curie or Curie-Weiss law: $\chi = \frac{C}{T-\theta}$	Atoms constituting the material have a permanent magnetic moment as in ferromagnets (Fe), antiferromagnets (Cr), ferrimagnets (Fe_2O_3) at high temperatures
Ferromagnetic	Positive and large, function of applied field, microstructure dependent Fe: ~100,000		Ferromagnetic below Curie temperature and paramagnetic above it	Atoms have parallel aligned magnetic moments, possesses large permanent magnetization even without external magnetic field as in some transition metals and rare earths such as Fe, Co, Ni, Gd, Dy
Antiferromagnetic	Positive and small, Cr: 3.6×10^{-6}		Antiferromagnetic below the Néel temperature and paramagnetic above it	Atoms have mixed parallel and anti-parallel aligned magnetic moments Primarily oxides and salts of transition metals such as MnO, NiO, MnF_2.
Ferrimagnetic	Positive and large, function of applied field, microstructure dependent, Ba ferrite: ~3		Ferrimagnetic below the Curie temperature and paramagnetic above it	Atoms have anti-parallel aligned magnetic moments, possesses large magnetization even without external magnetic field

Magnetism: Quantum Theory

- Local Moment Magnetism: localized electrons
- Itinerant Magnetism: delocalized electron



Magnetism: Exchange interaction



$$\mathcal{H}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \mathcal{H}_{\mathrm{A}}(\boldsymbol{r}_1) + \mathcal{H}_{\mathrm{B}}(\boldsymbol{r}_2) + \mathcal{H}_{\mathrm{int}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,,$$

$$\mathcal{H}_{\mathrm{A}}(\boldsymbol{r}_1) = -\frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_1^2 - \frac{\tilde{e}^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_{\mathrm{A}}|} \qquad \mathcal{H}_{\mathrm{B}}(\boldsymbol{r}_2) = -\frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_2^2 - \frac{\tilde{e}^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_{\mathrm{B}}|}$$

$$\mathcal{H}_{\mathrm{int}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\frac{\tilde{e}^2}{|\boldsymbol{r}_1 - \boldsymbol{R}_{\mathrm{B}}|} - \frac{\tilde{e}^2}{|\boldsymbol{r}_2 - \boldsymbol{R}_{\mathrm{A}}|} + \frac{\tilde{e}^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{\tilde{e}^2}{|\boldsymbol{R}_{\mathrm{A}} - \boldsymbol{R}_{\mathrm{B}}|}$$

Magnetism: Exchange interaction

$$\Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(s_1, s_2)$$

$$\psi_\mathrm{s}(\boldsymbol{r}_1, \boldsymbol{r}_2) = N_+\left[\psi_\mathrm{A}(\boldsymbol{r}_1)\psi_\mathrm{B}(\boldsymbol{r}_2) + \psi_\mathrm{A}(\boldsymbol{r}_2)\psi_\mathrm{B}(\boldsymbol{r}_1)\right]$$

$$\chi_\mathrm{s}(s_1, s_2) = \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right]$$

$$\psi_\mathrm{t}(\boldsymbol{r}_1, \boldsymbol{r}_2) = N_-\left[\psi_\mathrm{A}(\boldsymbol{r}_1)\psi_\mathrm{B}(\boldsymbol{r}_2) - \psi_\mathrm{A}(\boldsymbol{r}_2)\psi_\mathrm{B}(\boldsymbol{r}_1)\right]$$

$$\chi_\mathrm{t}(s_1, s_2) = \begin{cases} |\uparrow\rangle_1 |\uparrow\rangle_2 \\ \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2\right] \\ |\downarrow\rangle_1 |\downarrow\rangle_2 \,. \end{cases}$$

$$N_\pm = \frac{1}{\sqrt{2(1 \pm |S_\mathrm{AB}|^2)}}$$

$$S_\mathrm{AB} = \int \psi_\mathrm{A}^*(\boldsymbol{r})\psi_\mathrm{B}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

$$\varepsilon_\mathrm{s} = \langle\psi_\mathrm{s}|\mathcal{H}|\psi_\mathrm{s}\rangle = \varepsilon_\mathrm{A} + \varepsilon_\mathrm{B} + 2N_+^2(C + I)$$

$$\varepsilon_\mathrm{t} = \langle\psi_\mathrm{t}|\mathcal{H}|\psi_\mathrm{t}\rangle = \varepsilon_\mathrm{A} + \varepsilon_\mathrm{B} + 2N_-^2(C - I)$$

$$C = \int \psi_\mathrm{A}^*(\boldsymbol{r}_1)\psi_\mathrm{B}^*(\boldsymbol{r}_2)\mathcal{H}_\mathrm{int}\psi_\mathrm{A}(\boldsymbol{r}_1)\psi_\mathrm{B}(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

$$I = \int \psi_\mathrm{A}^*(\boldsymbol{r}_1)\psi_\mathrm{B}^*(\boldsymbol{r}_2)\mathcal{H}_\mathrm{int}\psi_\mathrm{B}(\boldsymbol{r}_1)\psi_\mathrm{A}(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

Magnetism: Exchange interaction

- Energy difference:

$$\varepsilon_{\mathrm{t}} - \varepsilon_{\mathrm{s}} = 2C\left(N_{-}^{2} - N_{+}^{2}\right) - 2I\left(N_{-}^{2} + N_{+}^{2}\right) = 2\frac{C|S|^{2} - I}{1 - |S|^{4}}$$

- Exchange energy (Heisenberg exchange parameter):

$$\varepsilon_{\mathrm{t}} - \varepsilon_{\mathrm{s}} = -2J$$

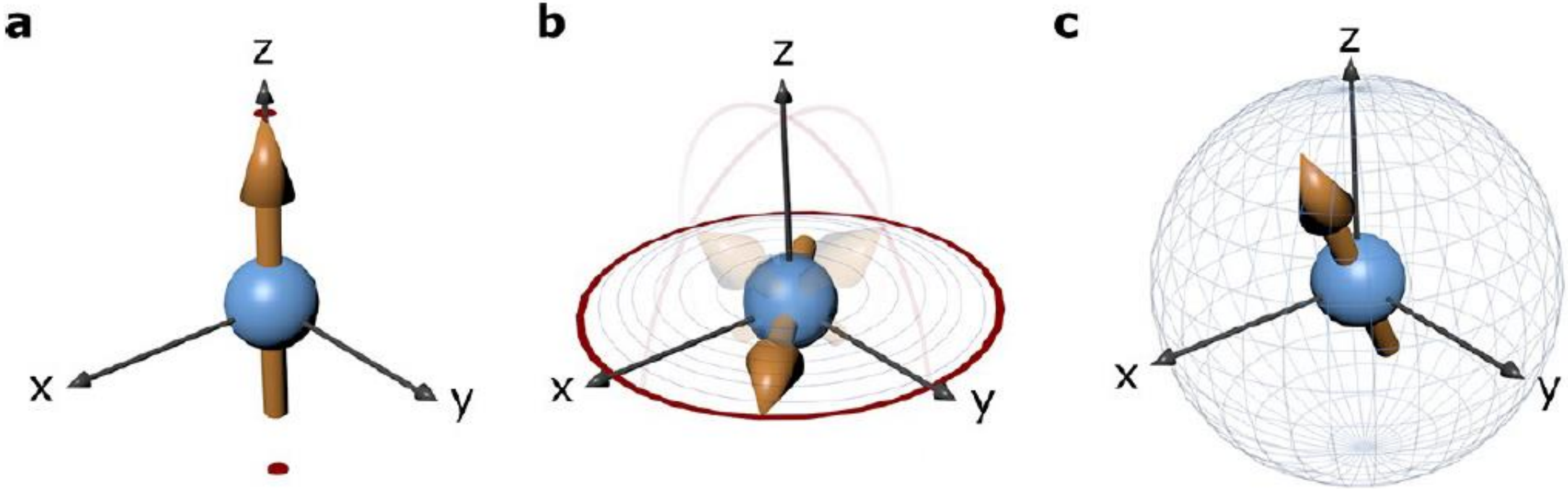
- The eigenvalue of the square of the total spin S = s1 + s2 is zero in the singlet state (S = 0) and two in the triplet state (S = 1), therefore, we can define an effective Hamiltonian,

$$\mathcal{H}_{\mathrm{eff}} = \varepsilon_{\mathrm{s}} + \tfrac{1}{2}(\varepsilon_{\mathrm{t}} - \varepsilon_{\mathrm{s}})\boldsymbol{S}^{2} = \varepsilon_{\mathrm{s}} - J\boldsymbol{S}^{2}$$

- Heisenberg exchange Hamiltonian

$$\mathcal{H}_{\mathrm{eff}} = -2J\left(\boldsymbol{s}_1 \cdot \boldsymbol{s}_2 + \tfrac{3}{4}\right) + \varepsilon_{\mathrm{s}}$$

Magnetism: Hamiltonian Models

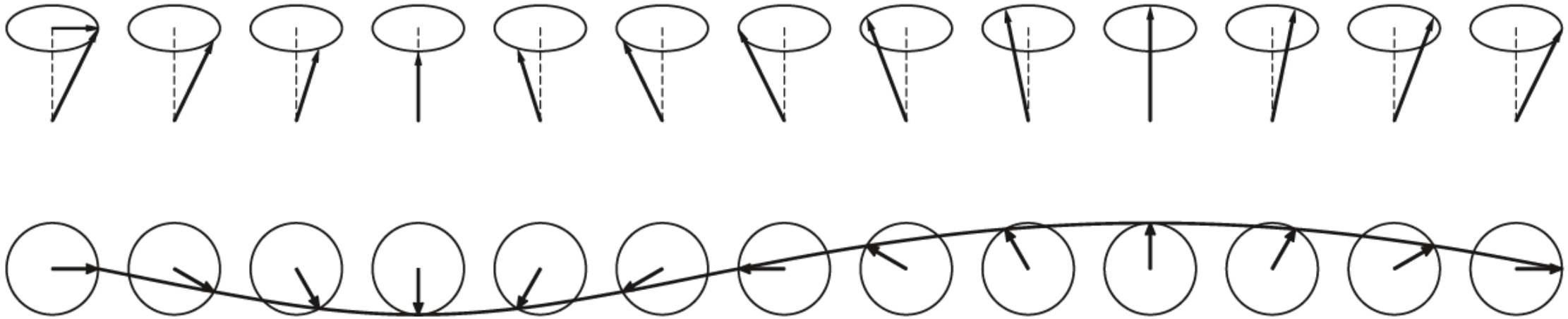


n=1	n=2	n=3
(1D-Ising)	(2D-XY)	(3D-Heisenberg)

Magnetism: Elementary Excitations

- Magnetic moments are not static.

- Thermal or quantum fluctuations result in spin wave excitations (magnon).



Magnons from Density Functional Theory

There are two ways to obtain magnon dispersion from DFT:

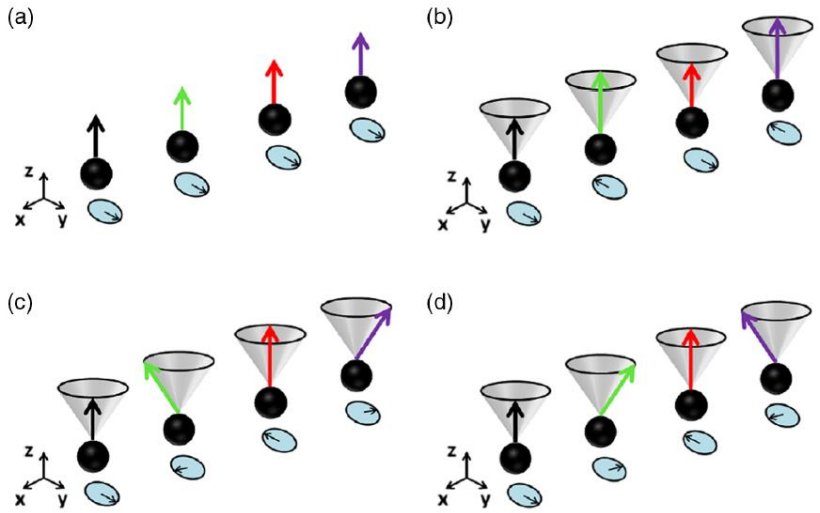
1. The first method is to extract magnon dispersion directly from DFT calculations:
   a) TDDFT (real-time time-dependent DFT)
   b) Dynamic transverse magnetic susceptibility (Linear response)
   c) …

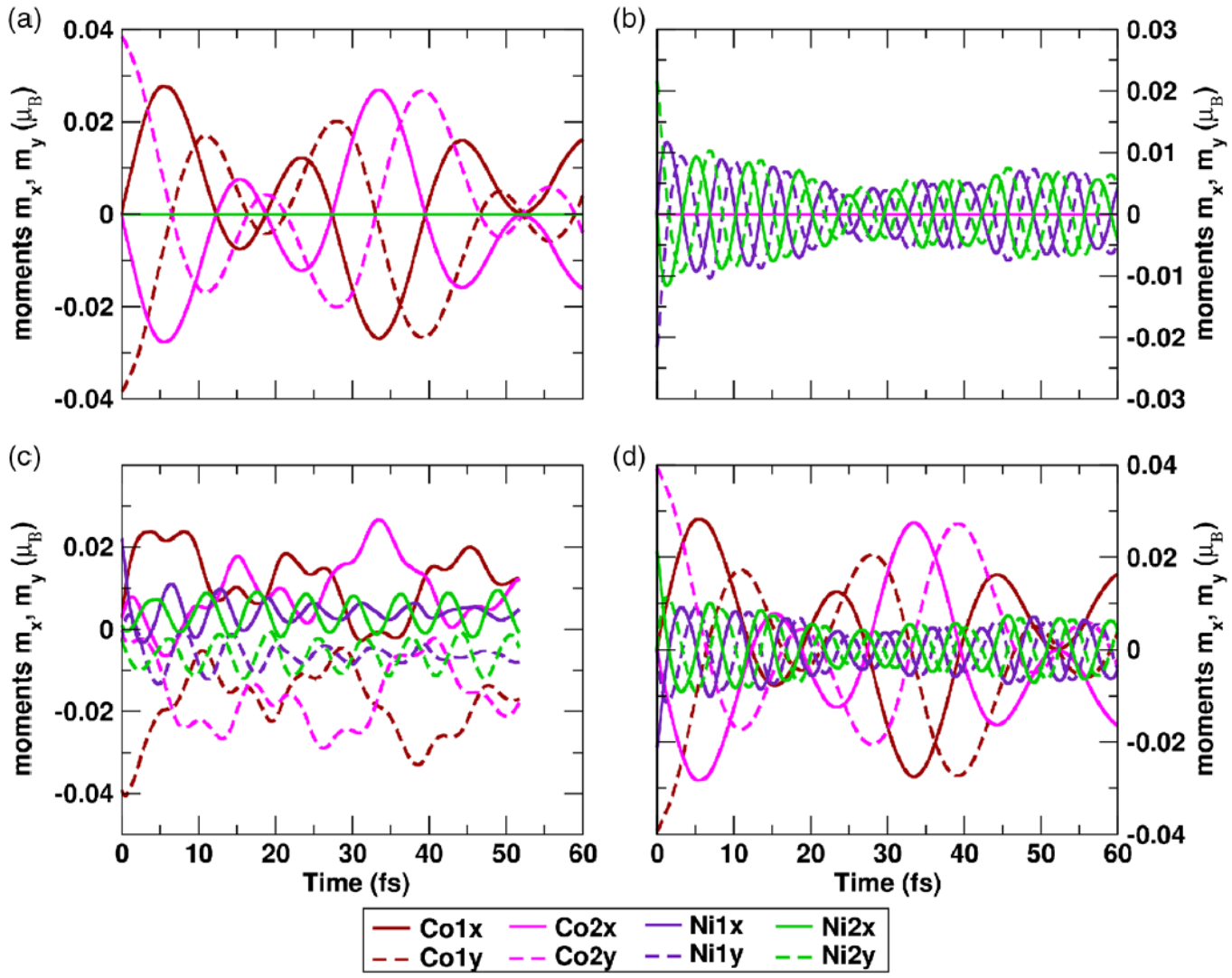
2. The second method is to obtain the Heisenberg exchange constants from DFT:
   a) Spin spiral (Frozen magnon)
   b) Magnetic force theorem
   c) Multiple Scattering Theory (Green's Functions)
   d) …

Magnon Dispersion from real-time TDDFT

TDKS equation:

$$i\frac{\partial \phi_j(\mathbf{r},t)}{\partial t} = \left[\frac{1}{2}\left(-i\boldsymbol{\nabla} + \frac{1}{c}\mathbf{A}_{\text{ext}}(t)\right)^2 + v_S(\mathbf{r},t) + \frac{1}{2c}\boldsymbol{\sigma}\cdot\mathbf{B}_S(\mathbf{r},t) + \frac{1}{4c^2}\boldsymbol{\sigma}\times(\boldsymbol{\nabla}v_S(\mathbf{r},t)\times -i\boldsymbol{\nabla})\right]\phi_j(\mathbf{r},t)$$





https://doi.org/10.1002/pssb.201900654

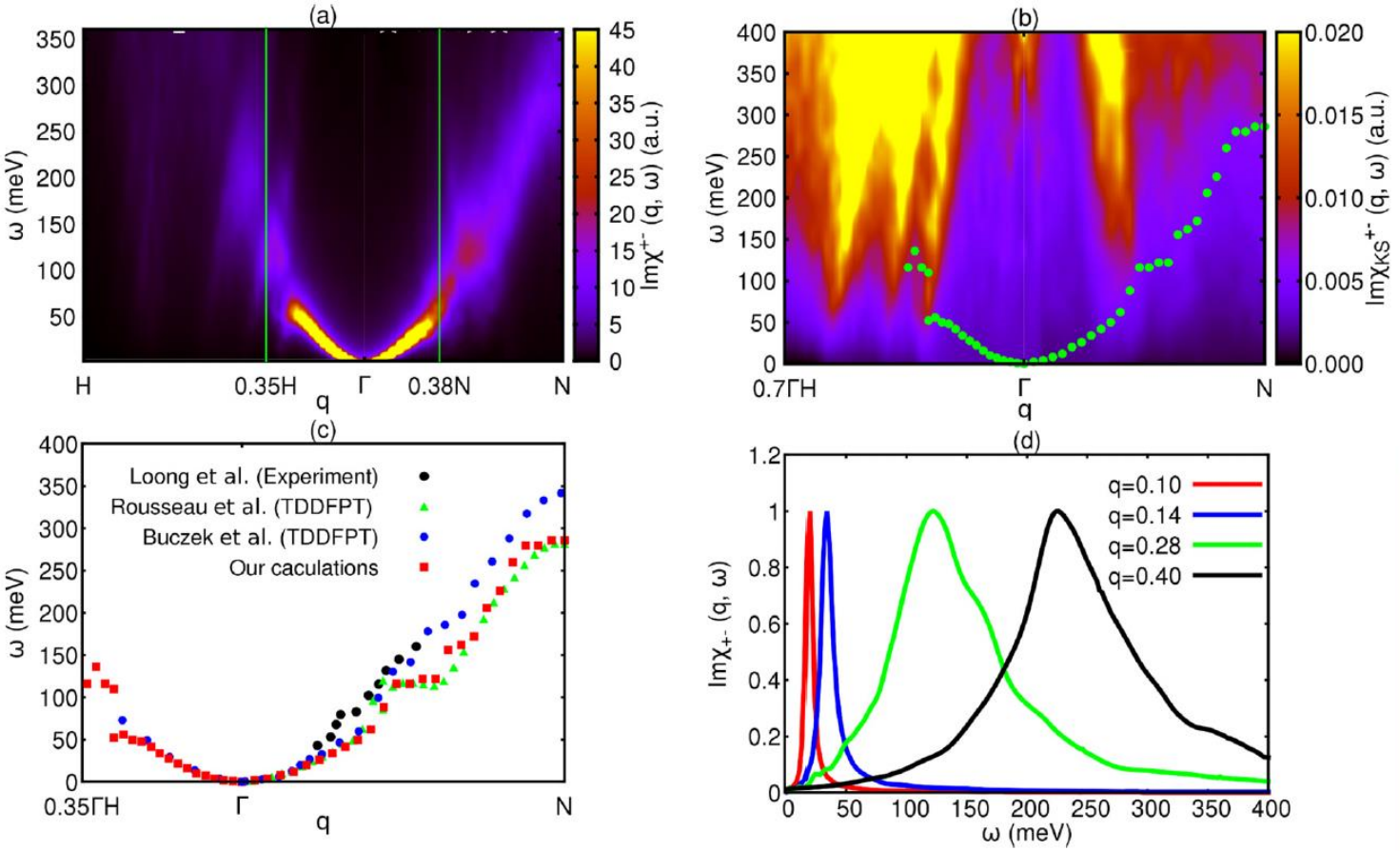
Magnon Dispersion from Transverse Magnetic Susceptibility

Dynamic transverse magnetic susceptibility within linear response theory:

$$\mathrm{Im}\,\chi^{+-}_{\mathrm{KS}}(\mathbf{q},\omega) = \frac{\pi}{2}\frac{1}{N_{\mathbf{k}}}\sum_{nm,\mathbf{k}}(f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}})$$

$$\times\,|\langle \vec{u}_{m\mathbf{k}+\mathbf{q}}|\sigma^{-}|\vec{u}_{n\mathbf{k}}\rangle|^2\delta(\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}} + \omega)$$

$$\frac{\partial^2\Sigma}{\partial\Omega\partial\omega} \propto \mathrm{Im}\,\chi^{+-}(\mathbf{q},\omega)$$



https://doi.org/10.1103/PhysRevB.97.024420

Exchange parameters from DFT: spin spiral

$$H_{\mathrm{ex}} = -\frac{1}{2N}\sum_{mn\alpha\beta} J_{mn}^{\alpha\beta}\mathbf{e}_{m\alpha}\cdot\mathbf{e}_{n\beta}$$

$$\mathbf{e}_{m\alpha} = \sin(\theta)\cos(\gamma_{m\alpha})\mathbf{x} + \sin(\theta)\sin(\gamma_{m\alpha})\mathbf{y} + \cos(\theta)\mathbf{z}$$

$$\gamma_{m\alpha} = \mathbf{q}\cdot\mathbf{R}_{m\alpha} + \phi_{\alpha}.$$

$$E(\mathbf{q}) = -\frac{1}{2N}\sum_{mn\alpha\beta} J_{mn}^{\alpha\beta}\mathbf{e}_{m\alpha}(\mathbf{q}_{hs})\cdot\mathbf{e}_{n\beta}(\mathbf{q}_{hs})$$

$$\begin{aligned} &E[\mathbf{q},(\theta_1,\ldots,\theta_l),(\phi_1,\ldots,\phi_l)] \\ &\quad = E_0 - \frac{1}{2}\sum_{n\alpha\beta} J_{0n}^{\alpha\beta}(\sin(\theta_{\alpha})\sin(\theta_{\beta}) \\ &\qquad \times \cos\left(\mathbf{q}\cdot(\mathbf{R}_{0\alpha} - \mathbf{R}_{n\beta}) + \phi_{\alpha} - \phi_{\beta}\right) - \cos(\theta_{\alpha})\cos(\theta_{\beta})) \end{aligned}$$

$$E_{\alpha\beta}^{\phi}[\mathbf{q},\{\theta\}] = E[\mathbf{q},(\theta_1,\ldots,\theta_l),(\phi_1,\ldots,\phi_l)]$$

$$\begin{aligned} &\frac{2}{\sin^2(\theta)}\left(E_{\alpha\alpha}^{0}[\mathbf{0},\{\theta\}] - E_{\alpha\alpha}^{0}[\mathbf{q},\{\theta\}]\right) \\ &\quad = \sum_{n} J_{0n}^{\alpha\alpha}(1-\cos(\mathbf{q}\cdot\mathbf{R}_{n\alpha})), \end{aligned}$$

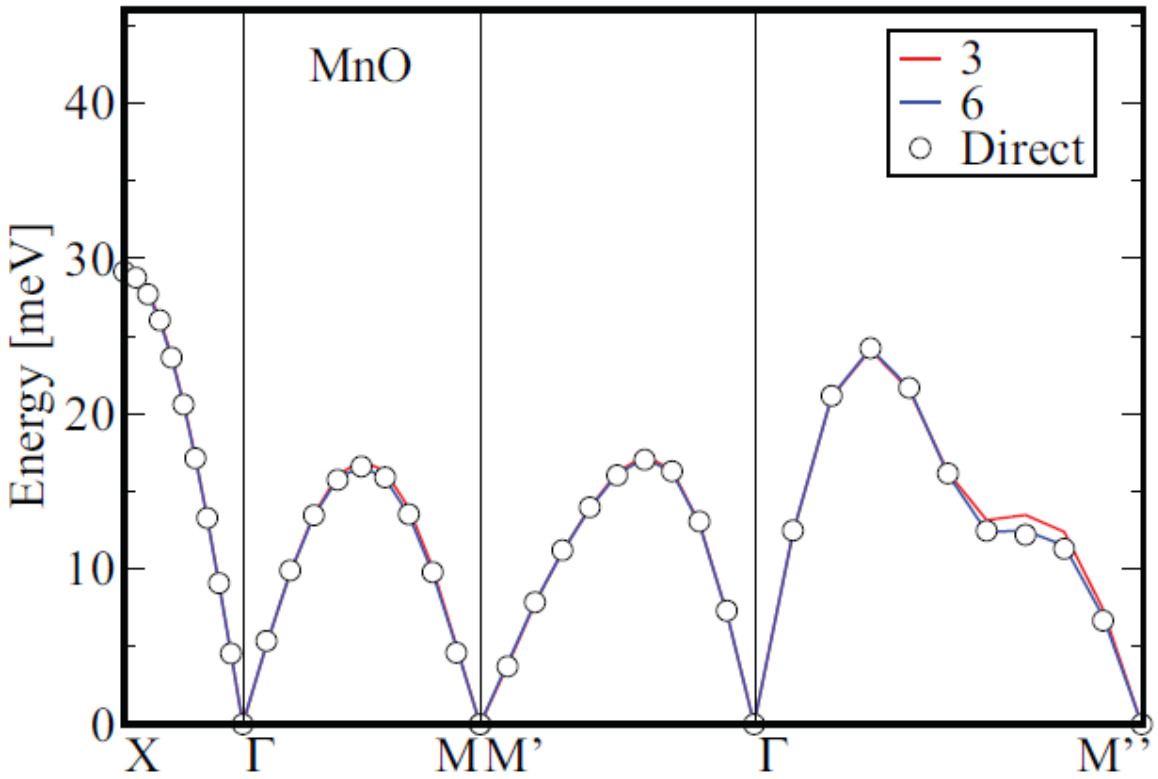
$$\begin{aligned} &\frac{2}{\sin^2(\theta)}\left(E_{\alpha\beta}^{0}[\mathbf{0},\{\theta\}] - E_{\alpha\beta}^{0}[\mathbf{q},\{\theta\}]\right) \\ &\quad = 2\sum_{n} J_{0n}^{\alpha\beta}(1-\cos\left(\mathbf{q}\cdot(\mathbf{R}_{0\alpha} - \mathbf{R}_{n\beta})\right)) \\ &\qquad + \sum_{n} J_{0n}^{\alpha\alpha}(1-\cos(\mathbf{q}\cdot\mathbf{R}_{n\alpha})) \\ &\qquad + \sum_{n} J_{0n}^{\beta\beta}(1-\cos(\mathbf{q}\cdot\mathbf{R}_{n\beta})). \end{aligned}$$

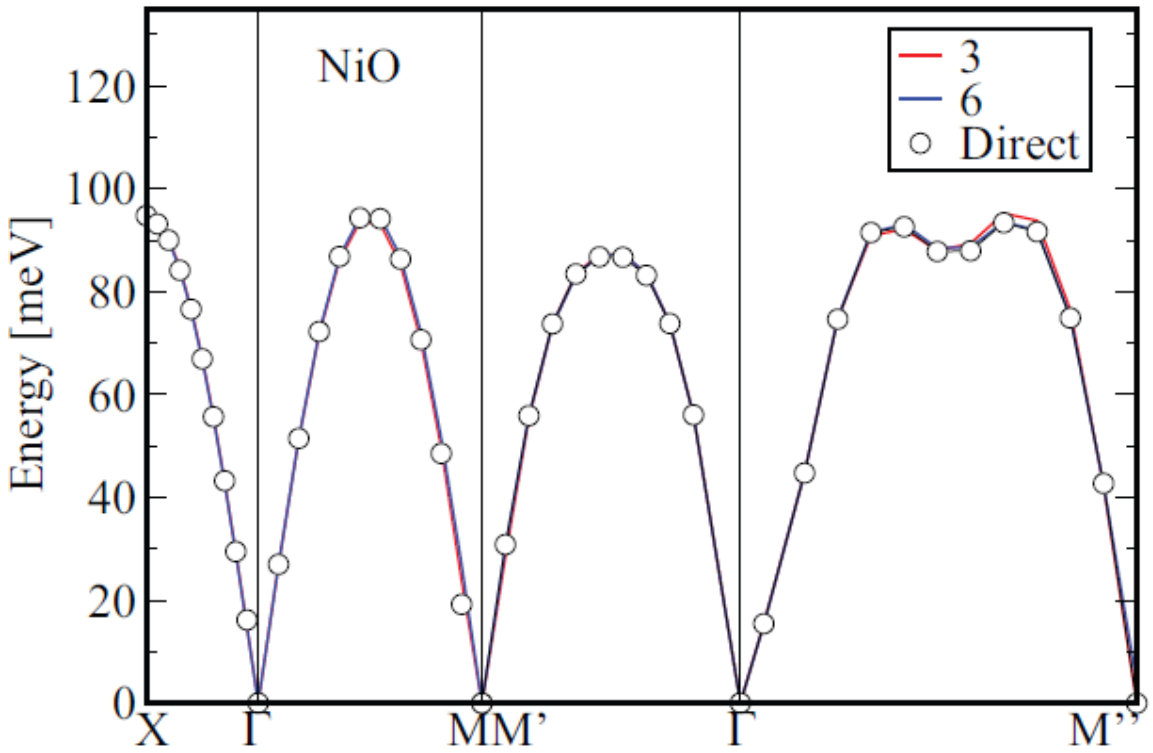
$$J^{\alpha\beta}(\mathbf{q}) = \sum_{n} J_{0n}^{\alpha\beta}\cos\left(\mathbf{q}\cdot(\mathbf{R}_{0\alpha} - \mathbf{R}_{n\beta})\right)$$

$$\omega_{\mathbf{q}} = 2\frac{J(\mathbf{0}) - J(\mathbf{q})}{M}$$

$$\omega_{\mathbf{q}} = 4\frac{E(\mathbf{q},\theta) - E(\mathbf{0},\theta)}{M\sin^2(\theta)}$$

Exchange parameters from DFT: spin spiral





https://doi.org/10.1103/PhysRevB.88.134427

Exchange parameters from DFT: Magnetic Force Theorem

- Total energy:

$$E_{\mathrm{SM}} = -\frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\mathbf{u}^{T}(\mathbf{r})\mathrm{J}(\mathbf{r},\mathbf{r}')\mathbf{u}(\mathbf{r}')$$

- Exchange tensor:

$$\mathrm{J}(\mathbf{r},\mathbf{r}') = \begin{pmatrix} J^{xx} & J^{xy} & J^{xz} \\ J^{yx} & J^{yy} & J^{yz} \\ J^{zx} & J^{zy} & J^{zz} \end{pmatrix}\Bigg|_{(\mathbf{r},\mathbf{r}')}$$

- Energy change via rotation of magnetic moment:

$$\Delta E_{\mathrm{DFT}} \simeq E_{\mathrm{SP}}[\mathbf{u}^{\mathrm{rot}}, n_0, m_0] - E_{\mathrm{SP}}[\mathbf{u}_0, n_0, m_0]$$

- Therefore:

$$J(\mathbf{r},\mathbf{r}') = -2B^{\mathrm{xc}}(\mathbf{r})\chi_{\mathrm{KS}}'^{+-}(\mathbf{r},\mathbf{r}')B^{\mathrm{xc}}(\mathbf{r}')$$

- Kohn–Sham susceptibility:

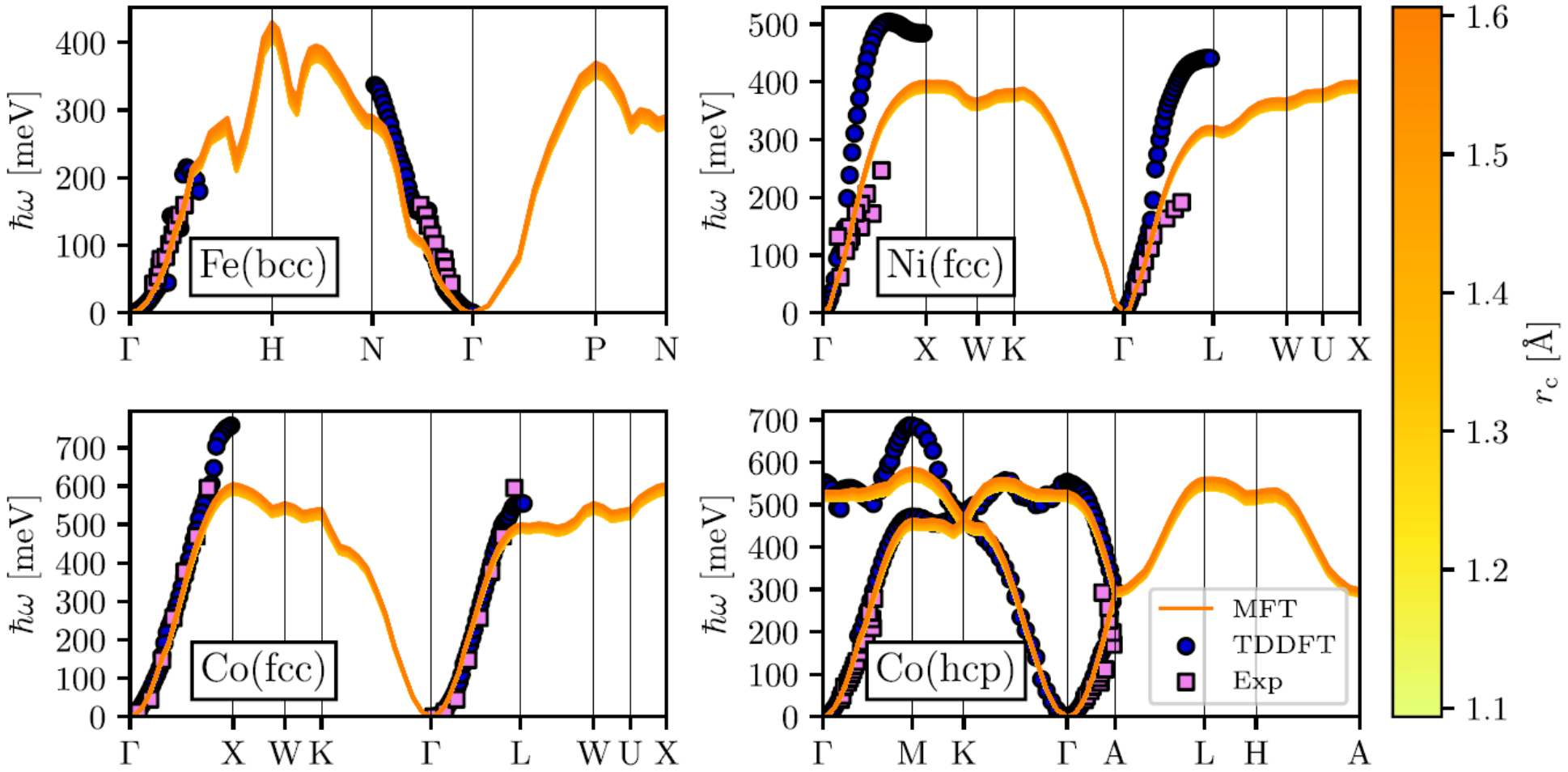
$$\chi_{\mathrm{KS}}'^{+-}(\mathbf{r},\mathbf{r}') = \sum_{n,m}\frac{f_{n\uparrow}-f_{m\downarrow}}{\varepsilon_{n\uparrow}-\varepsilon_{m\downarrow}}\psi^{*}_{n\uparrow}(\mathbf{r})\psi_{m\downarrow}(\mathbf{r})\psi^{*}_{m\downarrow}(\mathbf{r}')\psi_{n\uparrow}(\mathbf{r}')$$

- Isotropic Heisenberg model:

$$H^{ab}(\mathbf{q}) = \frac{g\mu_{\mathrm{B}}}{\sqrt{M_a M_b}}\left[\sum_{c}\bar{J}^{ac}(0)\delta_{ab} - \bar{J}^{ab}(\mathbf{q})\right]$$

$$\hbar\omega(\mathbf{q}) = \frac{g\mu_{\mathrm{B}}}{M}\left[J(0) - J(\mathbf{q})\right]$$

Exchange parameters from DFT: Magnetic Force Theorem



https://doi.org/10.1088/1361-648X/acab4b

Exchange parameters from DFT: Green functions

- Multiple Scattering Theory (KKR):

$$J_{ij} = \frac{1}{4\pi}\int d\varepsilon f(\beta(\varepsilon-\varepsilon_F))\,\mathrm{Im\,Tr}[\hat{\Delta}_i \hat{T}^{ij}_{\uparrow}\hat{\Delta}_j \hat{T}^{ji}_{\downarrow}]$$

$$J_{ij} = \frac{1}{4\pi}\int d\varepsilon f(\beta(\varepsilon-\varepsilon_F))\,\mathrm{Im\,Tr}[\hat{G}^{+}_{\uparrow}(\varepsilon)\hat{P}_i\hat{G}^{+}_{\downarrow}(\varepsilon)\hat{P}_j]$$

$$\hat{P}_i \equiv \hat{H}_{i\uparrow} - \hat{H}_{i\downarrow}$$

- KS formalism:

$$J_{i\mathbf{0},j\mathbf{R}} = \frac{1}{4\pi N^2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{n,n'}\sum_{\mu,\nu\in i}\sum_{\mu',\nu'\in j} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \times \int d\varepsilon f(\beta(\varepsilon-\varepsilon_F)) \times \mathrm{Im}\left[\frac{C_{j\mu',n\uparrow}(\mathbf{k})C^{*}_{i\nu,n\uparrow}(\mathbf{k})}{\varepsilon+i\eta-\varepsilon_{n\uparrow}(\mathbf{k})}[\hat{P}_i]_{\nu\mu} \times \frac{C_{i\mu,n'\downarrow}(\mathbf{k}')C^{*}_{j\nu',n'\downarrow}(\mathbf{k}')}{\varepsilon+i\eta-\varepsilon_{n'\downarrow}(\mathbf{k}')}[\hat{P}_j]_{\nu'\mu'}\right],$$

$$J_{i\mathbf{0},j\mathbf{R}} = \frac{1}{4\pi}\sum_{\mu,\nu\in i}\sum_{\mu',\nu'\in j}\int_{-\infty}^{\infty} dz\, f(\beta(z-\varepsilon_F)) \times \mathrm{Im}\{[\hat{P}_i]_{\nu\mu}G^{+}_{i\mu,j\nu'}(\downarrow,z,\mathbf{R}) \times [\hat{P}_j]_{\nu'\mu'}G^{+}_{j\mu',i\nu}(\uparrow,z,-\mathbf{R})\},$$

$$G^{+}_{j\mu',i\nu}(\uparrow,z,-\mathbf{R}) = \int d^3\left(\frac{ka}{2\pi}\right)e^{i\mathbf{k}\cdot\mathbf{R}}\sum_n \frac{C_{j\mu',n\uparrow}(\mathbf{k})C_{i\mu,n\uparrow}(\mathbf{k})}{z+i\eta-\varepsilon_{n\uparrow}(\mathbf{k})}$$

$$G^{+}_{i\mu,j\nu'}(\downarrow,z,\mathbf{R}) = \int d^3\left(\frac{ka}{2\pi}\right)e^{-i\mathbf{k}\cdot\mathbf{R}}\sum_{n'} \frac{C_{i\mu,n'\downarrow}(\mathbf{k})C_{j\nu',n'\downarrow}(\mathbf{k})}{z+i\eta-\varepsilon_{n'\downarrow}(\mathbf{k})}$$

Exchange parameters from DFT: Green functions

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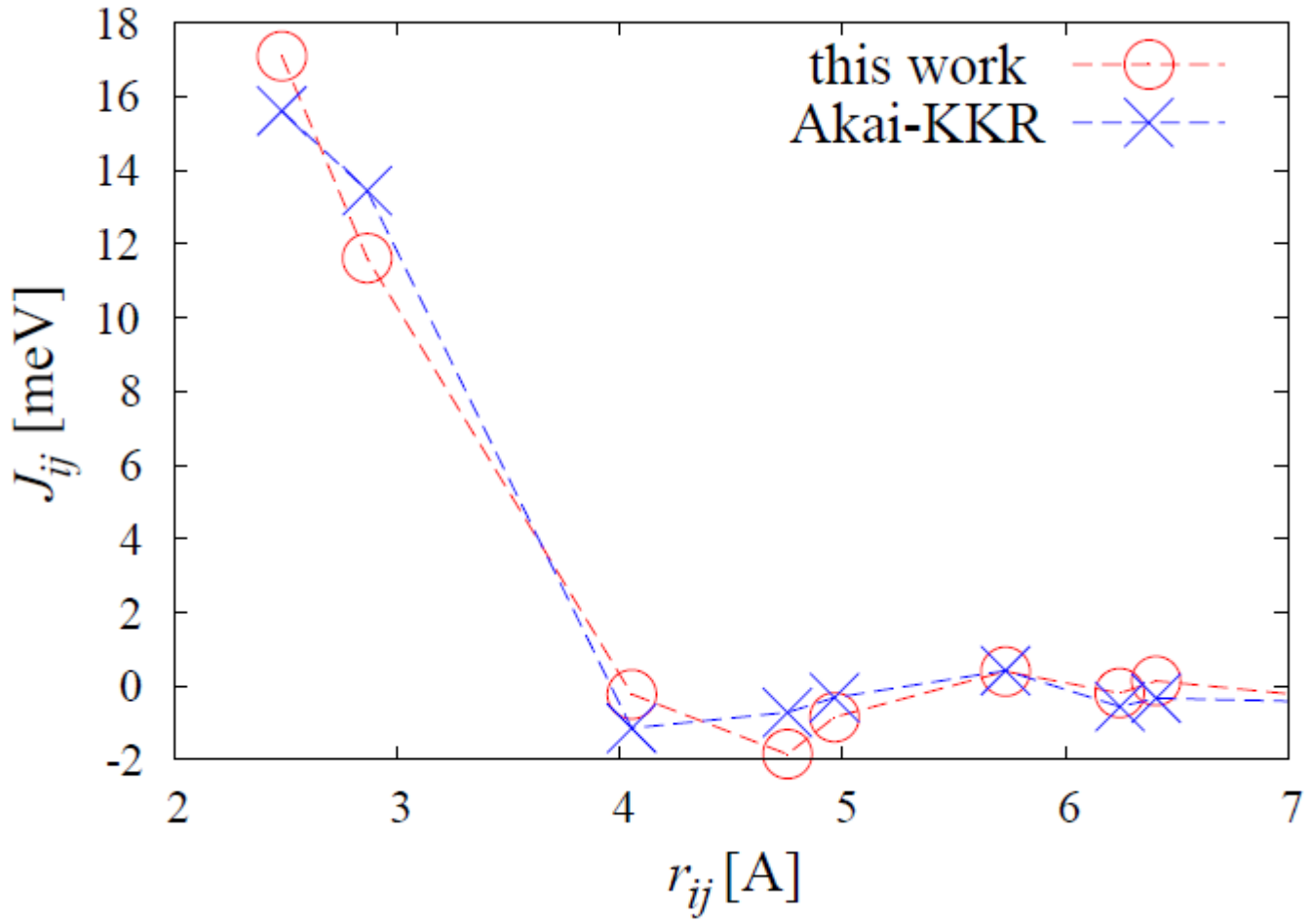

https://doi.org/10.7566/JPSJ.88.114706

Any Questions?