Magnetic molecules and ferroelectric solids: material properties from advanced simulations based on density-functional theory.

Elia Stocco

NOVEL MATERIALS DISCOVERY

Coffee Talk
February 6th, 2023
Berlin

DFT study of octonuclear molecular nano-magnets

Supervisors: Matteo Cococcioni[1]
Andrea Floris[2]
Institute: University of Pavia (Italy)
Project: Master Thesis (Physics)
Period: Academic Year 2020-2021

UNIVERSITÀ DI PAVIA

Theoretical investigation of light-matter coupling on nuclear dynamics

Supervisors: Christian Carbogno[3]
Mariana Rossi[4]
Institute: NOMAD, Fritz Haber Institute
Role: Scientific Assistant
Period: October 2022 - present

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

NOMAD
NOVEL MATERIALS DISCOVERY

[1] University of Pavia , Physics Department
[2] University of Lincoln (UK), School of Chemistry
[3] NOMAD Laboratory, Fritz Haber Institute, of the Max-Planck Gesellschaft (Berlin)
[4] Max Planck Institute for the Structure and Dynamics of Matter (Hamburg)

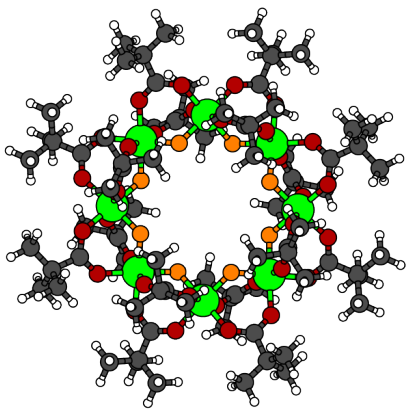
DFT study of octonuclear molecular nano-magnets

Plan of the work

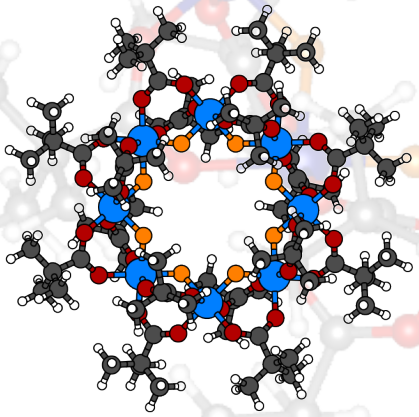
Work typology: computational study,
based on Density Functional Theory (DFT)

Case studies: three Molecular Nano-Magnets (MNMs):
Cr_8, V_8, and V_7Ni

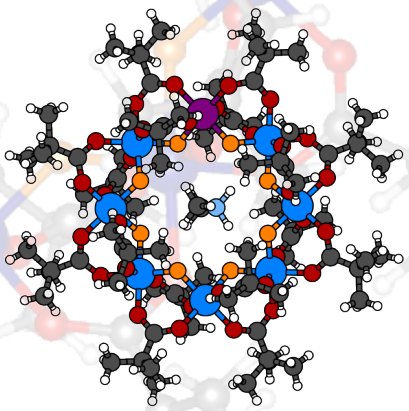
Objectives: magnetic properties of these MNMs



Cr_8



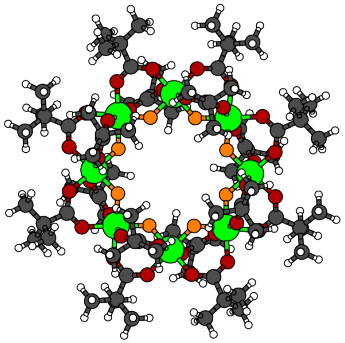
V_8



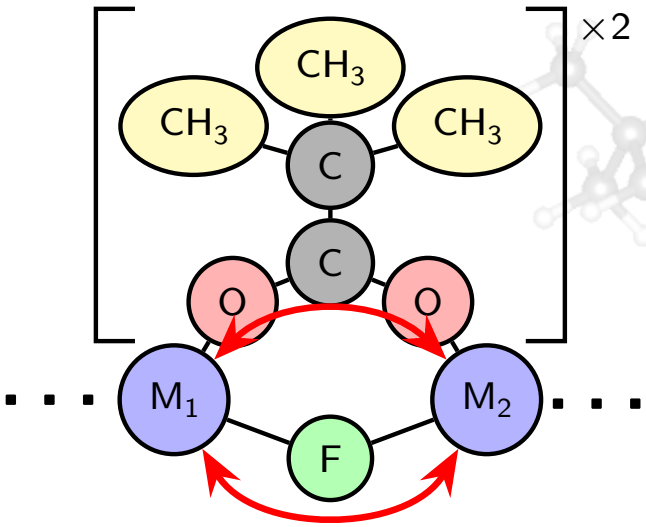
V_7Ni

DFT study of octonuclear molecular nano-magnets

Superexchange interactions



molecular structure

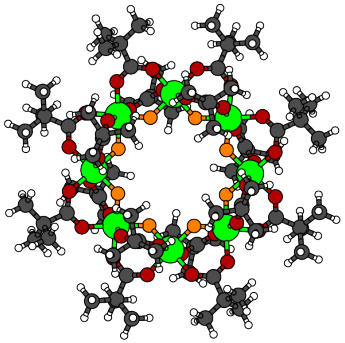


M_1, M_2 = Cr, V, and Ni

Anderson, Philip W., Journal of Physics C: Solid State Physics 14 (1963): 99-214.

DFT study of octonuclear molecular nano-magnets

Superexchange interactions



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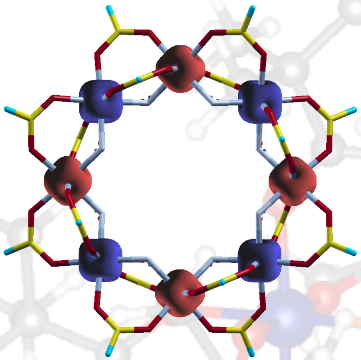
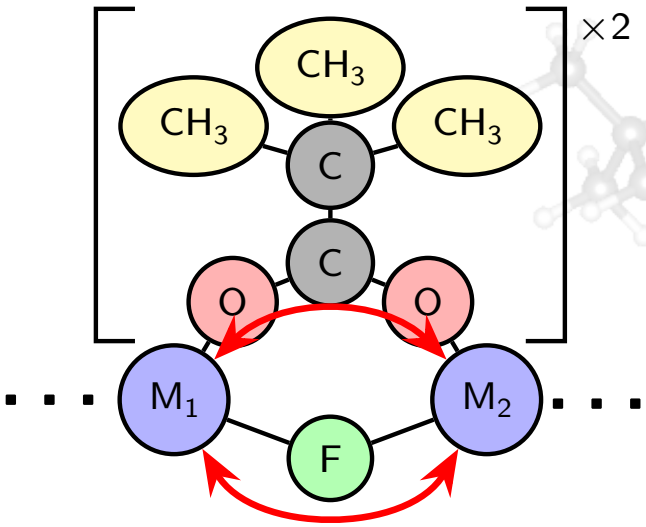


magnetization



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DFT study of octonuclear molecular nano-magnets

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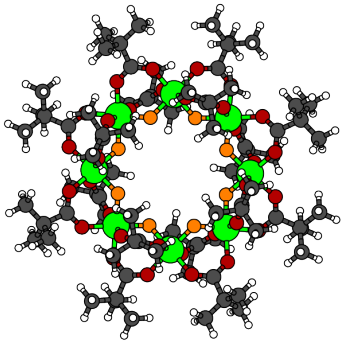

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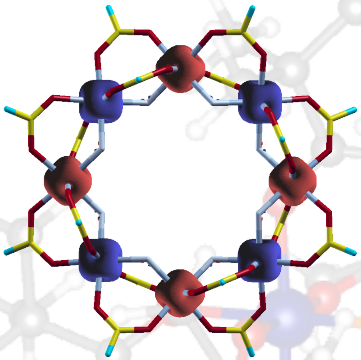

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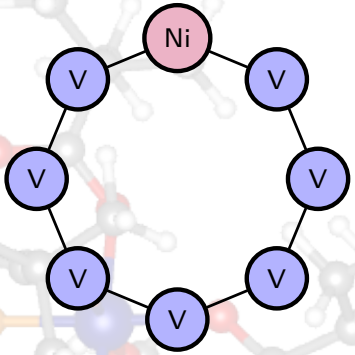
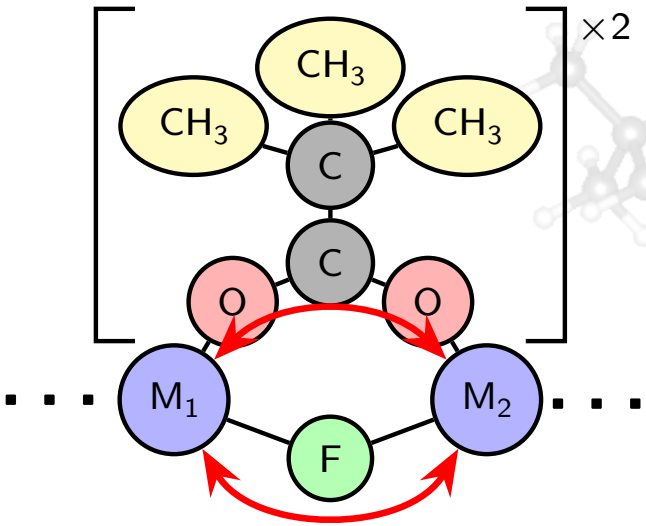


spin chain



M_1, M_2 = Cr, V, and Ni

Model spin Hamiltonian:

$$\hat{\mathcal{H}} = \sum_{i=1}^{8} \hat{\mathbf{S}}_i \cdot \underline{\underline{J}}_i \cdot \hat{\mathbf{S}}_{i+1} + \hat{\mathbf{S}}_i \cdot \underline{\underline{D}}_i \cdot \hat{\mathbf{S}}_i$$

Anderson, Philip W., Journal of Physics C: Solid State Physics 14 (1963): 99-214.

DFT study of octonuclear molecular nano-magnets

Computational details

- **spin-polarized** DFT
- **non-collinear** formulation
- **Hubbard-corrections**/DFT+U (to capture electron localization)

$$E_{\mathrm{DFT+U}}\left[n,\mathbf{m}\right] = E_{\mathrm{DFT}}\left[n,\mathbf{m}\right] + \sum_{I,\sigma} \frac{U^I}{2} \mathrm{Tr}\left[\mathbf{n}^{I\sigma}\left(1-\mathbf{n}^{I\sigma}\right)\right]$$

$$\text{with} \quad n^{I\sigma}_{mm'} = \sum_{i=1}^{N} \langle \phi_i^\sigma \,|\, \psi^I_{m\sigma} \rangle \langle \psi^I_{m'\sigma} \,|\, \phi_i^\sigma \rangle \qquad \textit{(atomic occupations)}$$

- **Linear Response** approach

$$U^I = \frac{\partial^2 E}{\partial n^I \partial n^I} \qquad \text{with} \quad n^I = \sum_{\sigma=\uparrow,\downarrow} \mathrm{Tr}\left[\mathbf{n}^{I\sigma}\right]$$

International Journal of Quantum Chemistry, 114.1 (2013), pp. 14–49
Phys. Rev. B 71, 035105 (2005)

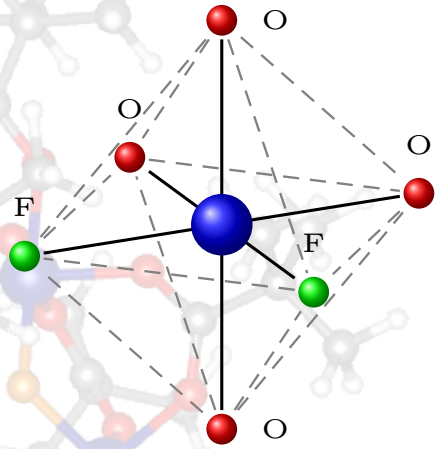
DFT study of octonuclear molecular nano-magnets

Anisotropic interactions

Anisotropic spin Hamiltonian:

$$\hat{\mathcal{H}} = \sum_{i=1}^{8} \hat{\mathbf{S}}_i \cdot \underline{\underline{J}} \cdot \hat{\mathbf{S}}_{i+1} + \hat{\mathbf{S}}_i \cdot \underline{\underline{D}} \cdot \hat{\mathbf{S}}_i$$

$$\underline{\underline{J}} = \begin{array}{c} \begin{array}{ccc} t & r & z \end{array} \\ \begin{bmatrix} J_t & 0 & 0 \\ 0 & J_r & 0 \\ 0 & 0 & J_z \end{bmatrix} \end{array} \begin{array}{c} t \\ r \\ z \end{array} \qquad \underline{\underline{D}} = \begin{array}{c} \begin{array}{ccc} t & r & z \end{array} \\ \begin{bmatrix} E & 0 & 0 \\ 0 & -E & 0 \\ 0 & 0 & D \end{bmatrix} \end{array} \begin{array}{c} t \\ r \\ z \end{array}$$



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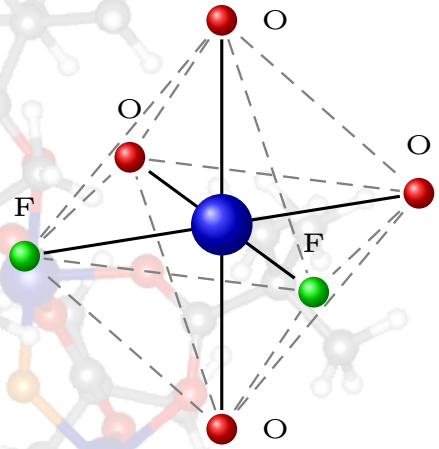

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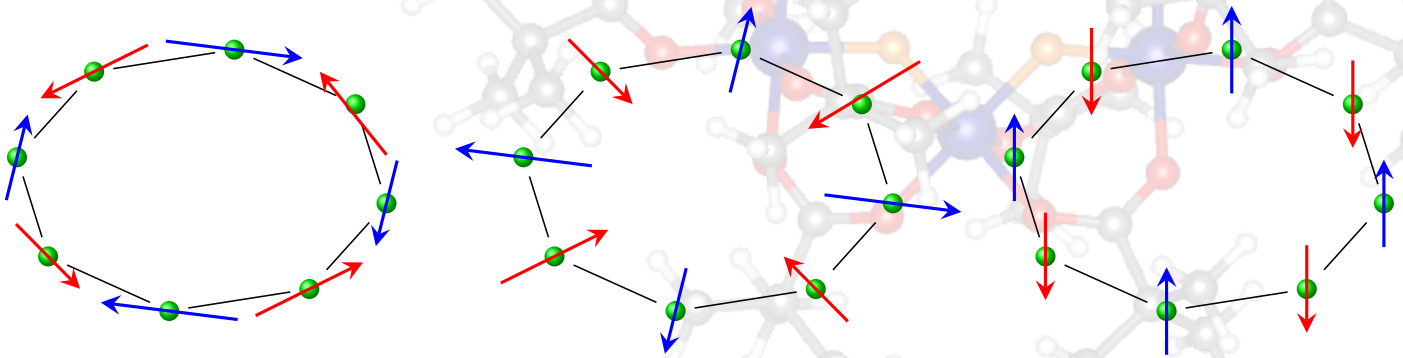
Non-collinear DFT calculation of the following configurations:

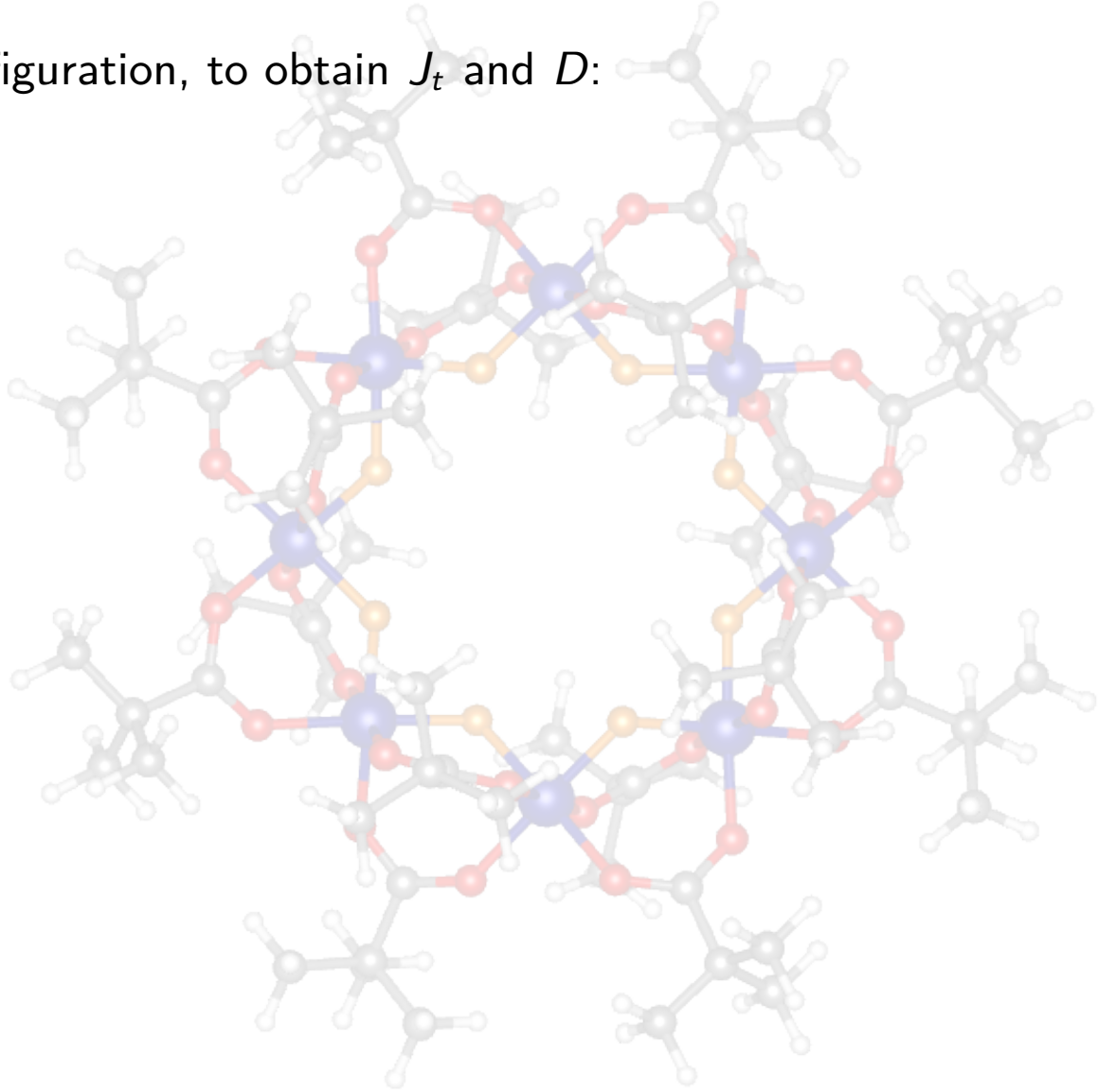


tangential$\rightarrow J_t, D$ radial$\rightarrow J_r, D$ axial$\rightarrow J_z, D, E$

DFT study of octonuclear molecular nano-magnets

Anisotropic interactions

Example: tangential configuration, to obtain J_t and D:



DFT study of octonuclear molecular nano-magnets

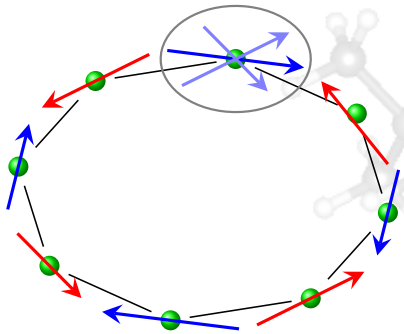
Anisotropic interactions

Example: tangential configuration, to obtain J_t and D:

- express the **energy** as a function of the spin **angle** ϕ

$$E_t(\phi) = S^2\left(-2J^t \sin\phi + E'\right) + c_t$$

where $E' = S\left(S - \frac{1}{2}\right)E$, $S = 1$ for V, Ni and $S = 3/2$ for Cr.



Tangential configuration: only J_t and D contribute.

DFT study of octonuclear molecular nano-magnets

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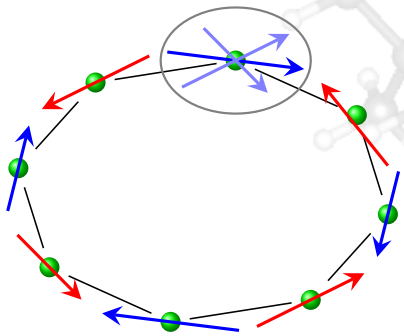
- **compute** the energy at different angles ϕ



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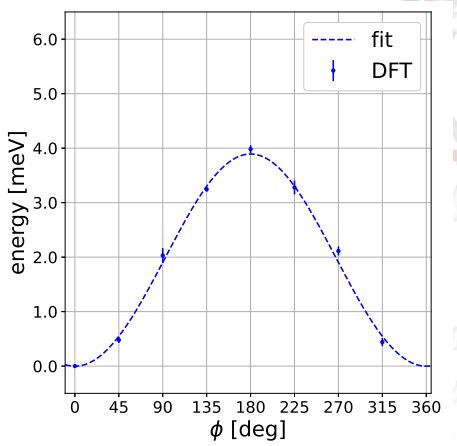

Energy (y-axis) at varying spin angle (x-axis): DFT energy values are fitted with the expression $E_t(\phi)$.

DFT study of octonuclear molecular nano-magnets

Anisotropic interactions

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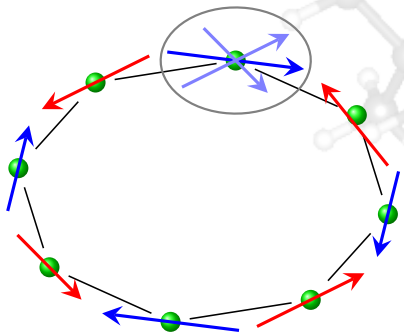
- **compute** the energy at different angles ϕ
- **fit** the energies with the expression $E_t(\phi)$ to get the couplings J_t and D



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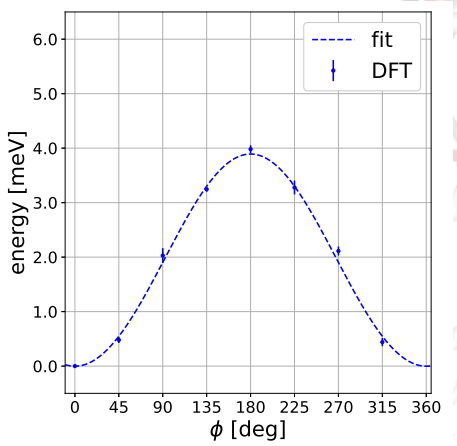

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- **compute** the energy at different angles ϕ
- **fit** the energies with the expression $E_t(\phi)$ to get the couplings J_t and D

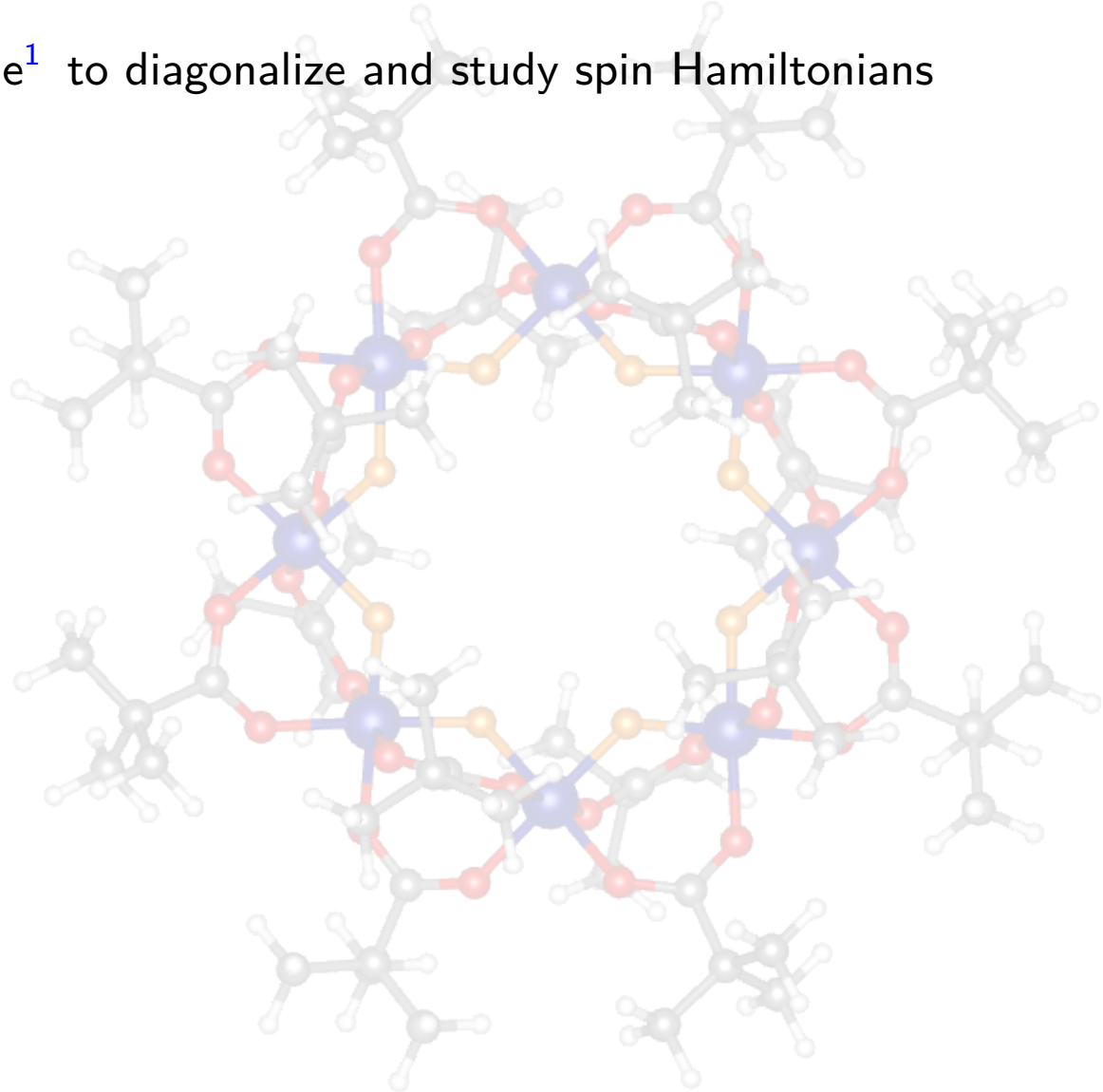
Repeat the same procedure for the radial and axial configurations too.

parameters	Cr_8	V_8	V_7Ni (Ni only)
J^t [meV]	0.433(3)	−0.67(5)	1.26(9)
J^r [meV]	0.437(2)	−0.65(2)	1.30(7)
J^z [meV]	0.629(3)	−0.77(5)	1.78(3)
D [meV]	−0.585(7)	−0.70(9)	−0.27(4)
E [meV]	−0.005(9)	−0.03(6)	−0.11(7)

DFT study of octonuclear molecular nano-magnets

Magnetic properties

Developed a `python` code[1] to diagonalize and study spin Hamiltonians



[1] https://github.com/EliaStocco/QuantumSparse

DFT study of octonuclear molecular nano-magnets

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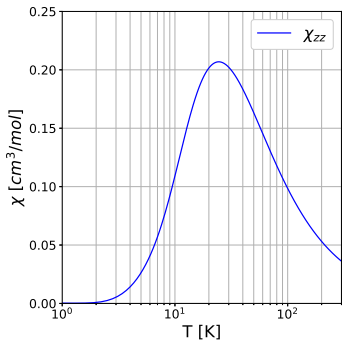
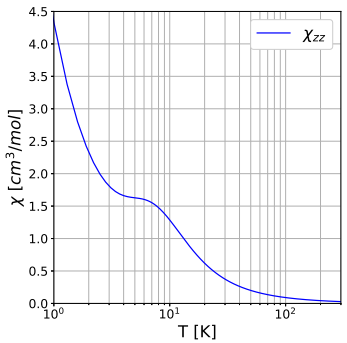
Magnetic susceptibility from the fluctuation-dissipation theorem ($\beta = 1/Tk_B$):

$$\chi_{ab}(\beta) = \frac{1}{\beta}\frac{\partial^2 \ln Z}{\partial B_a \partial B_b}\bigg|_{\mathbf{B}=\mathbf{0}} = \beta\mu_B^2 g^2\left[\langle \hat{S}_a\hat{S}_b\rangle_\beta - \langle \hat{S}_a\rangle_\beta \langle \hat{S}_b\rangle_\beta\right]$$

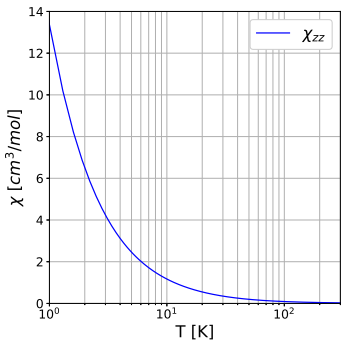
Cr_8



V_8



V_7Ni



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DFT study of octonuclear molecular nano-magnets

Conclusions and outlook

Conclusions:

- outlined a self-consistent DFT-based approach to study MNMs
- applied (and extended) a method to construct spin Hamiltonians
- developed a code to study the magnetic properties of a spin Hamiltonian

DFT study of octonuclear molecular nano-magnets

Conclusions and outlook

Conclusions:

- outlined a self-consistent DFT-based approach to study MNMs
- applied (and extended) a method to construct spin Hamiltonians
- developed a code to study the magnetic properties of a spin Hamiltonian

Outlook:

- need of a rigorous theory to understand the nature of the spin-spin interactions
- better understanding of the role of a doping ion (Ni in V_7Ni)
- need of a more efficient method to study these systems

Theoretical investigation of light-matter coupling on nuclear dynamics

Supervisors: Mariana Rossi
Christian Carbogno
Period: October 2022 - present

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Theoretical investigation of light-matter coupling on nuclear dynamics

Experiments

Experimental results:

- light-induced superconductivity in cuprates
- state manipulation/control in gas and liquid phase systems
- polarization reversal in ferroelectric solids

Light-Induced Superconductivity in a Stripe-Ordered Cuprate

D. Fausti,[1,2*]†‡ R. I. Tobey,[2]†§ N. Dean,[1,2] S. Kaiser,[1] A. Dienst,[2] M. C. Hoffmann,[1] S. Pyon,[3] T. Takayama,[3] H. Takagi,[3,4] A. Cavalleri[1,2*]

Molecular Orientation and Alignment by Intense Single-Cycle THz Pulses

Sharly Fleischer, Yan Zhou, Robert W. Field, and Keith A. Nelson

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 19 April 2011; published 12 October 2011)

Transient birefringence of liquids induced terahertz electric-field torque on perman molecular dipoles

Mohsen Sajadi[1], Martin Wolf[1] & Tobias Kampfrath[1]

Ultrafast Reversal of the Ferroelectric Polarization

R. Mankowsky,[1] A. von Hoegen,[1] M. Först,[1] and A. Cavalleri[1,2]

[1]*Max Planck Institute for the Structure and Dynamics of Matter, 22761 Hamburg, Germany*

[2]*Department of Physics, University of Oxford, Clarendon Laboratory, Oxford OX1 3PU, United Kingdom*

(Received 21 January 2017; published 10 May 2017)

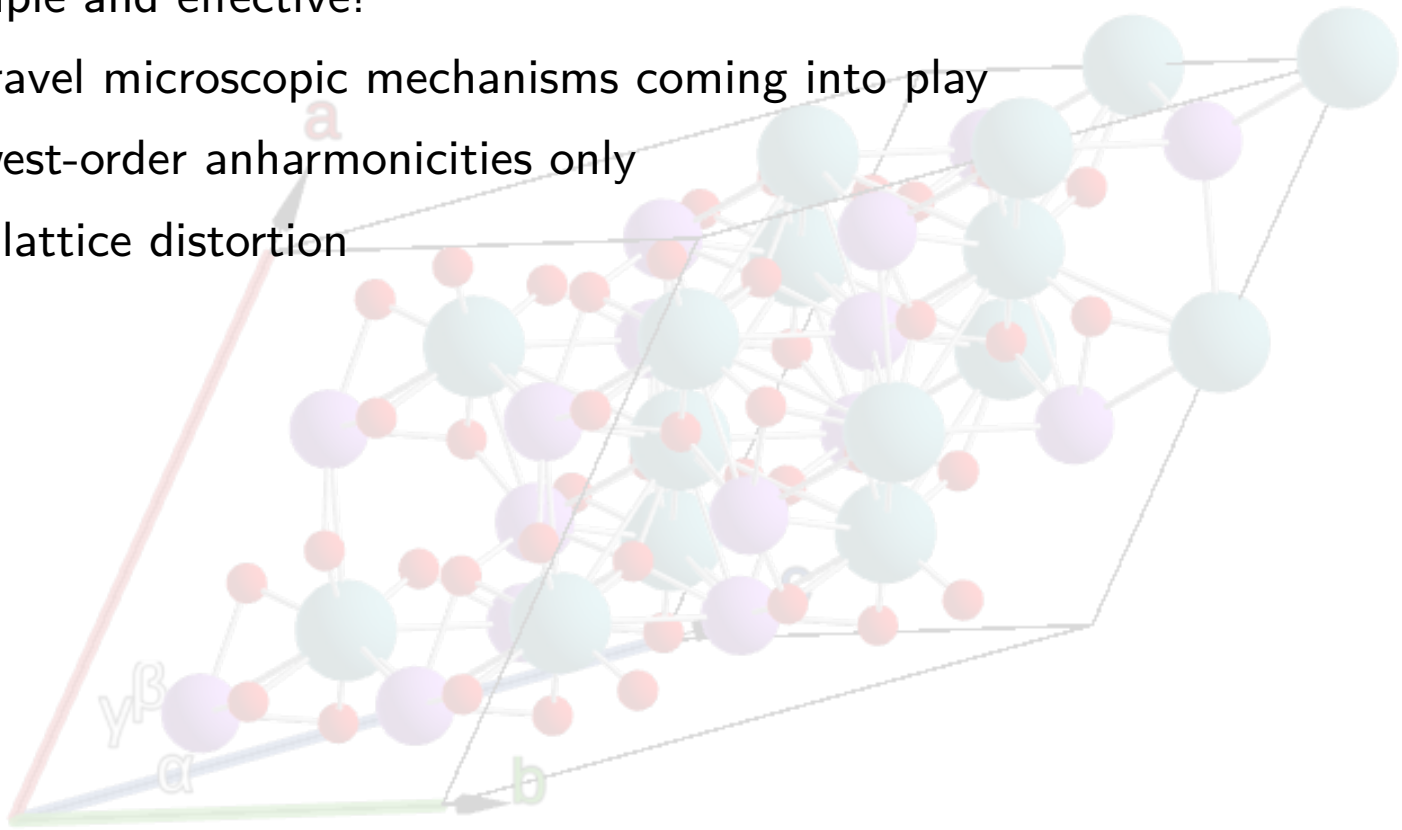
Science 331, 189–191 (2011)
Phys. Rev. Lett. 107, 163603
Nature Communications volume 8, Article number: 14963 (2017)
Phys. Rev. Lett. 118, 197601

Theoretical investigation of light-matter coupling on nuclear dynamics

Theoretical studies

Previous approach: recast the nuclear motion into a driven harmonic oscillator equations:

- simple and effective!
- unravel microscopic mechanisms coming into play
- lowest-order anharmonicities only
- no lattice distortion



Nature Physics 7, 854–856 (2011)
Phys. Rev. B 89, 220301(R)

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Theoretical studies

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The aim of this project is to develop a fully *ab initio* approach to study light-driven nuclear dynamics:

- approach based on Molecular Dynamics
- light-driven control of the system state (possibly out-of-equilibrium)
- induce (structural) phase transitions
- focus on anharmonic solids, and liquid systems

Nature Physics 7, 854–856 (2011)
Phys. Rev. B 89, 220301(R)

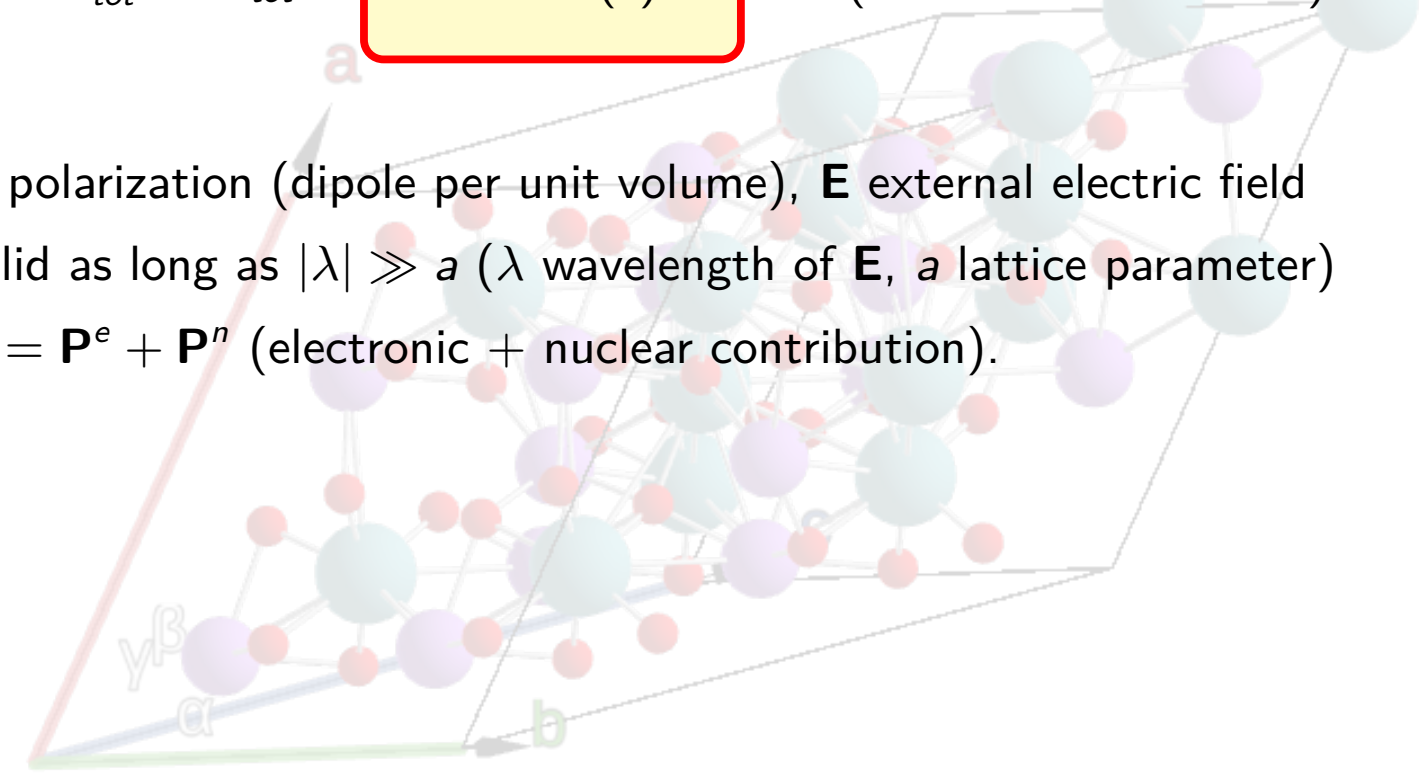
Theoretical investigation of light-matter coupling on nuclear dynamics

Dipole approximation

Light-matter coupling using the electric dipole approximation:

$$\hat{\mathcal{H}}^{\mathbf{E}}_{tot} = \hat{\mathcal{H}}_{tot} - \boxed{\Omega \mathbf{P} \cdot \mathbf{E}(t)} \qquad (\Omega = \text{unit cell volume})$$

- $\mathbf{P}$ polarization (dipole per unit volume), $\mathbf{E}$ external electric field
- valid as long as $|\lambda| \gg a$ (λ wavelength of $\mathbf{E}$, a lattice parameter)
- $\mathbf{P} = \mathbf{P}^e + \mathbf{P}^n$ (electronic + nuclear contribution).



New J. Phys. 20 (2018) 073040
Lett Math Phys (2018) 108:185–193
Phys. Rev. Lett. 89, 117602

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Periodic systems:

- $\mathbf{P}^e$ and $\mathbf{P}^n$ are expressed using the **Modern Theory of Polarization**
- $\mathbf{P}^e$ and $\mathbf{P}^n$ are no longer single-valued

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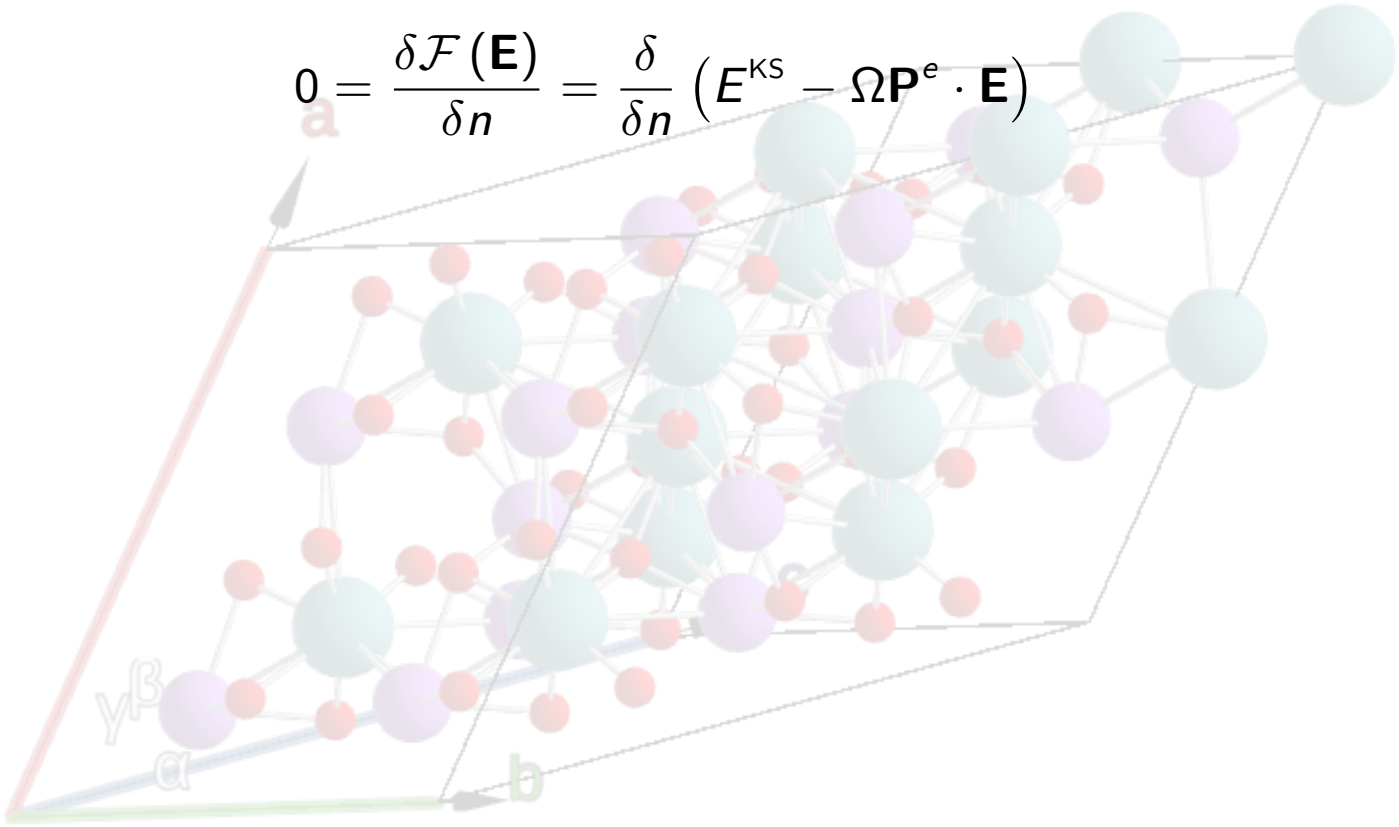
Theoretical investigation of light-matter coupling on nuclear dynamics

aiMD: DFT with external electric field

The **Born-Oppenheimer** approximation is assumed.
The electronic eqs. are solved using DFT $\rightarrow$ minimization of the enthalpy $\mathcal{F}_{\mathbf{E}}$:

$$0 = \frac{\delta \mathcal{F}(\mathbf{E})}{\delta n} = \frac{\delta}{\delta n}\left(E^{\mathrm{KS}} - \Omega \mathbf{P}^{e} \cdot \mathbf{E}\right)$$



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$$0 = \frac{\delta \mathcal{F}(\mathbf{E})}{\delta n} = \frac{\delta}{\delta n}\left(E^{\mathrm{KS}} - \Omega \mathbf{P}^{e} \cdot \mathbf{E}\right)$$

Problems:

- convergence issues, since $\mathbf{P}^{e}$ is not single-valued
- $\mathbf{P}^{e}$ is computationally expensive
- $\mathbf{P}^{e} \cdot \mathbf{E}$ breaks translational symmetry: no parallelization on $\mathbf{k}$-vectors

Phys. Rev. Lett. 89, 117602
Nature Phys 5, 304–308 (2009)

Theoretical investigation of light-matter coupling on nuclear dynamics

aiMD: DFT with external electric field

The **Born-Oppenheimer** approximation is assumed.
The electronic eqs. are solved using DFT $\rightarrow$ minimization of the enthalpy $\mathcal{F}_{\mathbf{E}}$:

$$0 = \frac{\delta \mathcal{F}(\mathbf{E})}{\delta n} = \frac{\delta}{\delta n}\left(E^{\mathrm{KS}} - \Omega \mathbf{P}^{e} \cdot \mathbf{E}\right)$$

Problems:

- convergence issues, since $\mathbf{P}^{e}$ is not single-valued
- $\mathbf{P}^{e}$ is computationally expensive
- $\mathbf{P}^{e} \cdot \mathbf{E}$ breaks translational symmetry: no parallelization on $\mathbf{k}$-vectors

Adopted way out:

- solve KS equation for $\mathbf{E} = \mathbf{0}$
- approximate the enthalpy with a 1st order expansion in $\mathbf{E}$:

$$\mathcal{F}(\mathbf{E}) \simeq E^{\mathrm{KS}}\Big|_{\mathbf{0}} - \mathbf{E} \cdot \mathbf{P}^{e}\big|_{\mathbf{0}}$$

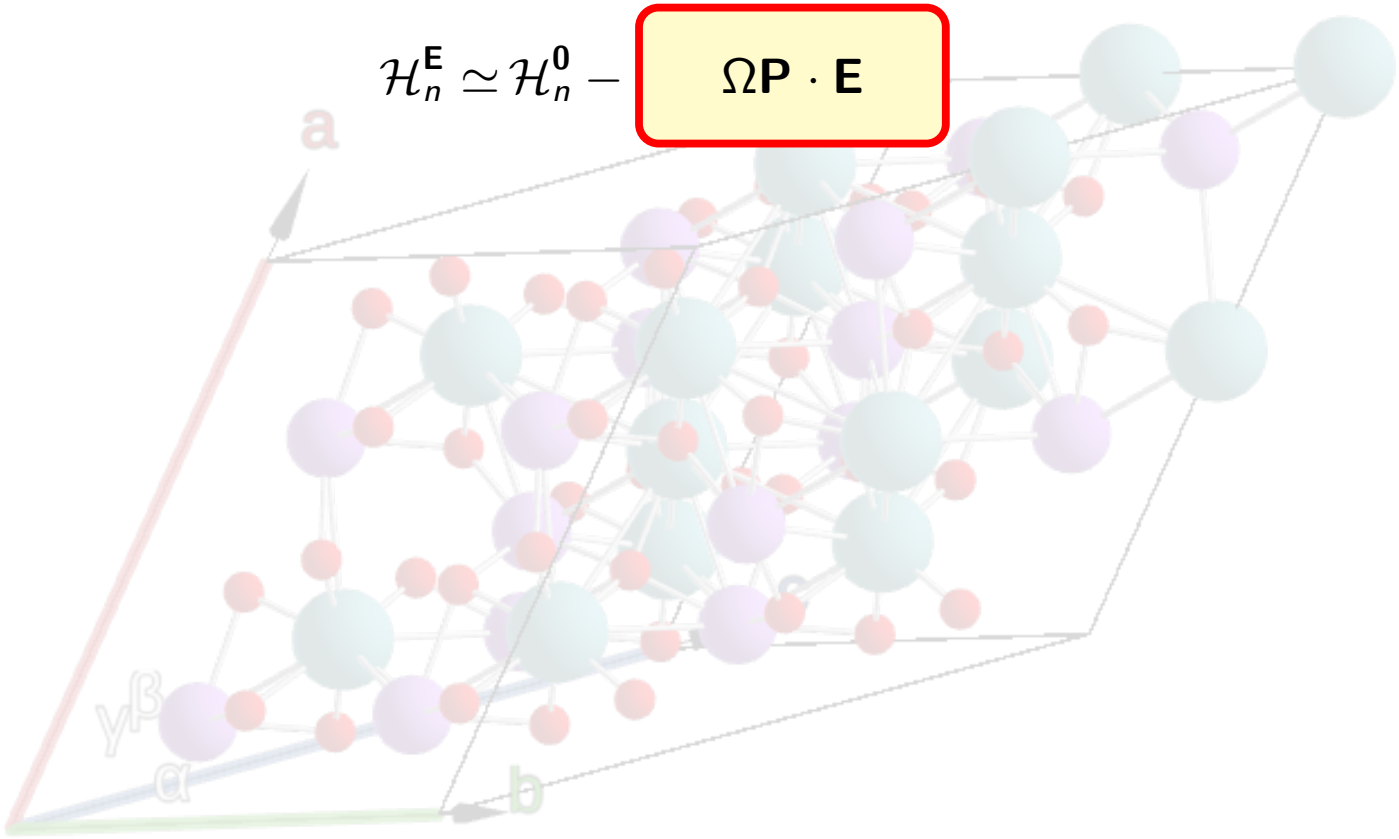
Phys. Rev. Lett. 89, 117602
Nature Phys 5, 304–308 (2009)

Theoretical investigation of light-matter coupling on nuclear dynamics

aiMD: forces

The nuclear Hamiltonian is approximated with a linear expression in **E**:

$$\mathcal{H}_n^{\mathbf{E}} \simeq \mathcal{H}_n^{\mathbf{0}} - \boxed{\Omega \mathbf{P} \cdot \mathbf{E}}$$



Theoretical investigation of light-matter coupling on nuclear dynamics

aiMD: forces

The nuclear Hamiltonian is approximated with a linear expression in **E**:

$$\mathcal{H}_n^{\mathbf{E}} \simeq \mathcal{H}_n^{\mathbf{0}} - \boxed{\Omega \mathbf{P} \cdot \mathbf{E}}$$

The forces gain just a simple term:

$$-\mathbf{F}^{\mathbf{E}I} = \frac{\partial \mathcal{H}_n^{\mathbf{E}}}{\partial \mathbf{R}^I} \simeq -\mathbf{F}^{\mathbf{0}I} + \boxed{\Omega \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{R}^I}}$$

Theoretical investigation of light-matter coupling on nuclear dynamics

aiMD: forces

The nuclear Hamiltonian is approximated with a linear expression in **E**:

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We need to know the Born Effective Charge (BEC) tensors Z_{ij}^{*I} of each ion I:

$$\frac{\partial P_i^e}{\partial R_j^I} = \frac{q_e}{\Omega} Z_{ij}^{*I}$$

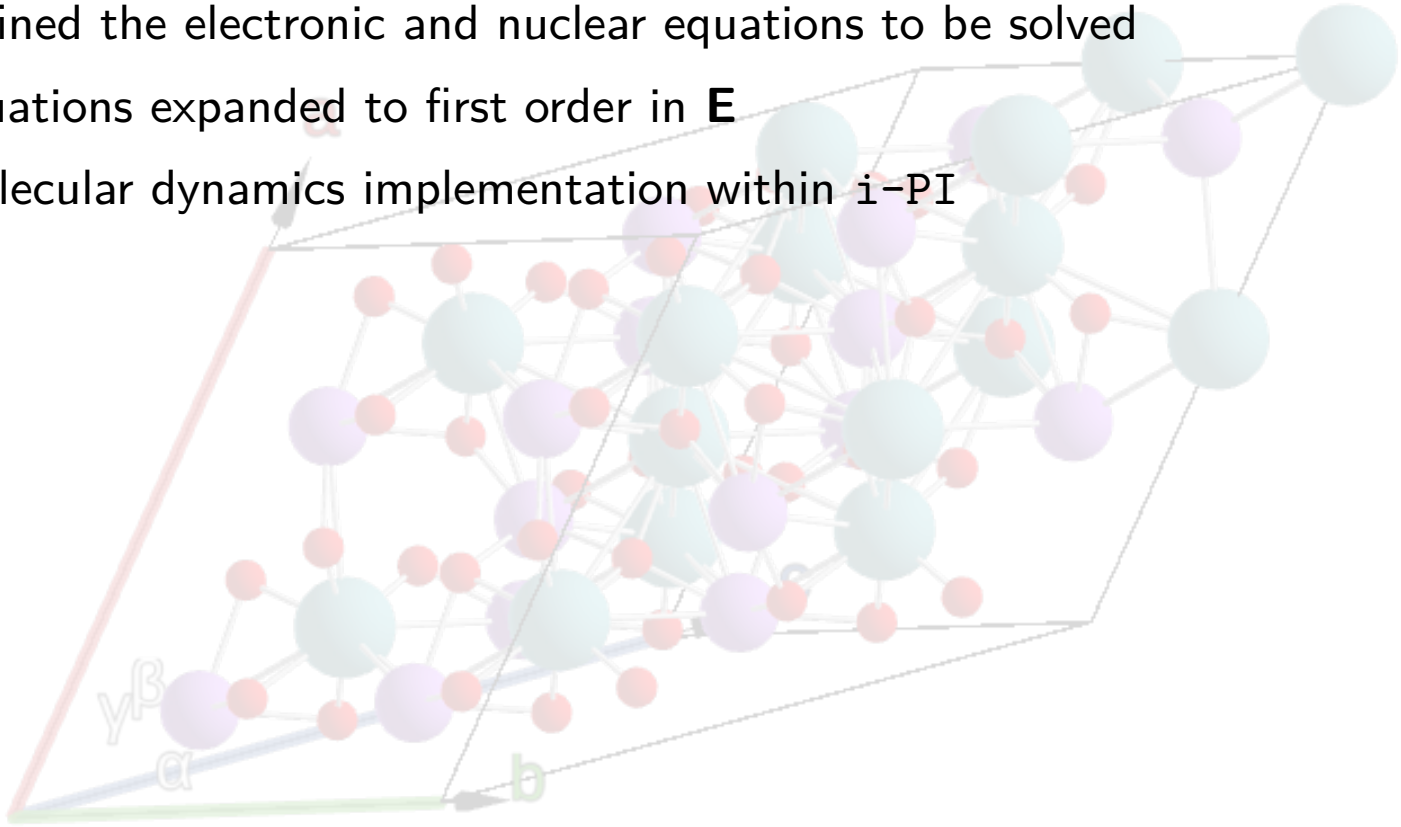
(q_e is the elementary charge)

Theoretical investigation of light-matter coupling on nuclear dynamics

Conclusions and outlook

Conclusions:

- defined the electronic and nuclear equations to be solved
- equations expanded to first order in **E**
- molecular dynamics implementation within `i-PI`



Kapil et al., Comp. Phys. Comm. 236, 214–223 (2018)

Theoretical investigation of light-matter coupling on nuclear dynamics

Conclusions and outlook

Conclusions:

- defined the electronic and nuclear equations to be solved
- equations expanded to first order in $\mathbf{E}$
- molecular dynamics implementation within `i-PI`

Outlook:

- compute the BEC tensors from machine-learned $\mathbf{P}^e$ values
- expand the equations of motion to further orders in $\mathbf{E}$
- first case study: $LiNbO_3$

Kapil et al., Comp. Phys. Comm. 236, 214–223 (2018)

Summary

DFT study of octonuclear molecular nano-magnets

Summary:

- developed a fully ab initio approach to study magnetic properties of MNMs

Outlook:

- deeper understanding of spin-spin interactions and doping ion influences
- implement of a more computationally efficient approach

Theoretical investigation of light-matter coupling on nuclear dynamics

Summary:

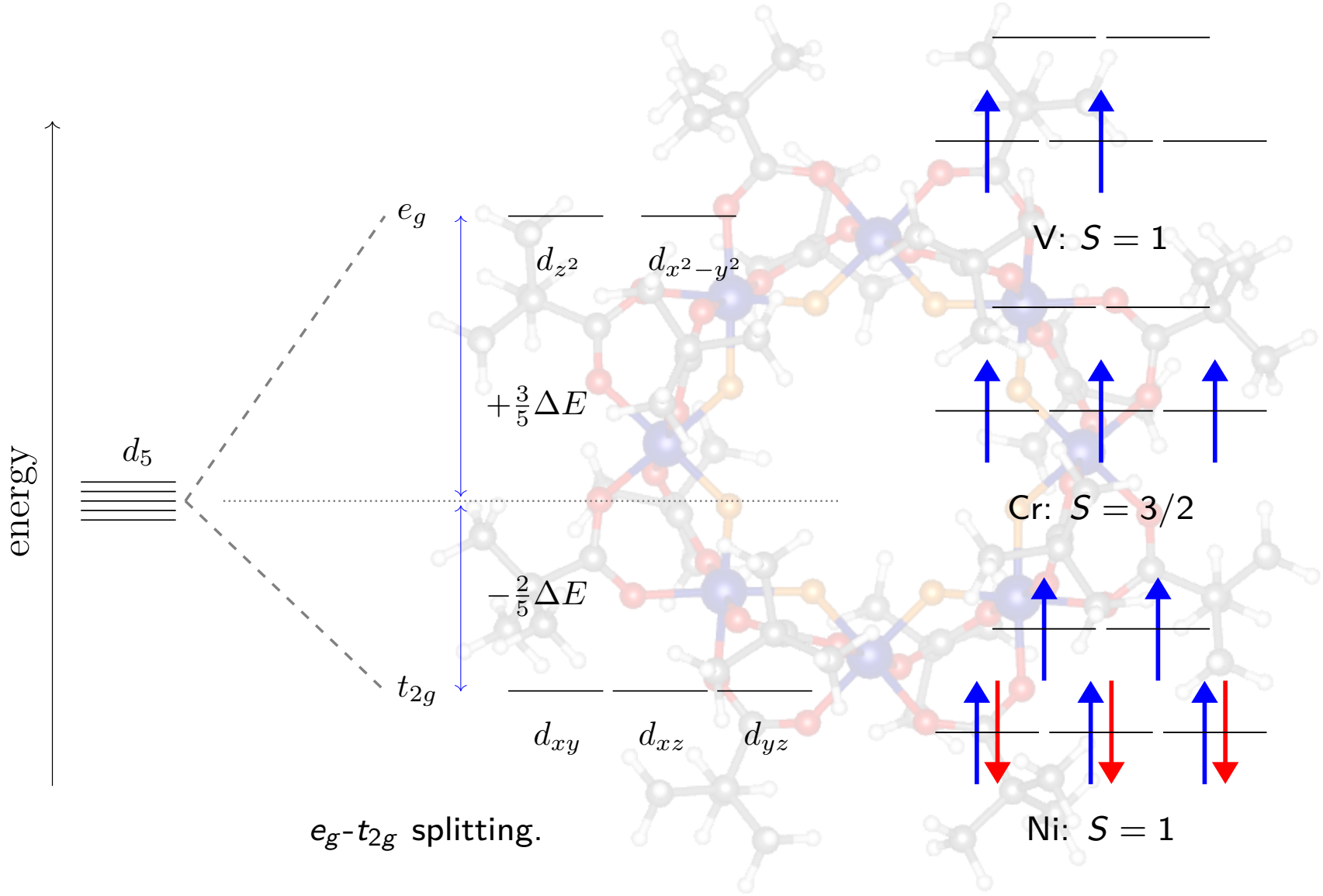
- ab initio approach to study light-driven nuclear dynamics

Outlook:

- expand the equations of motion to further orders in $\mathbf{E}$
- speed up the simulation protocol (compute BEC tensors on the fly)

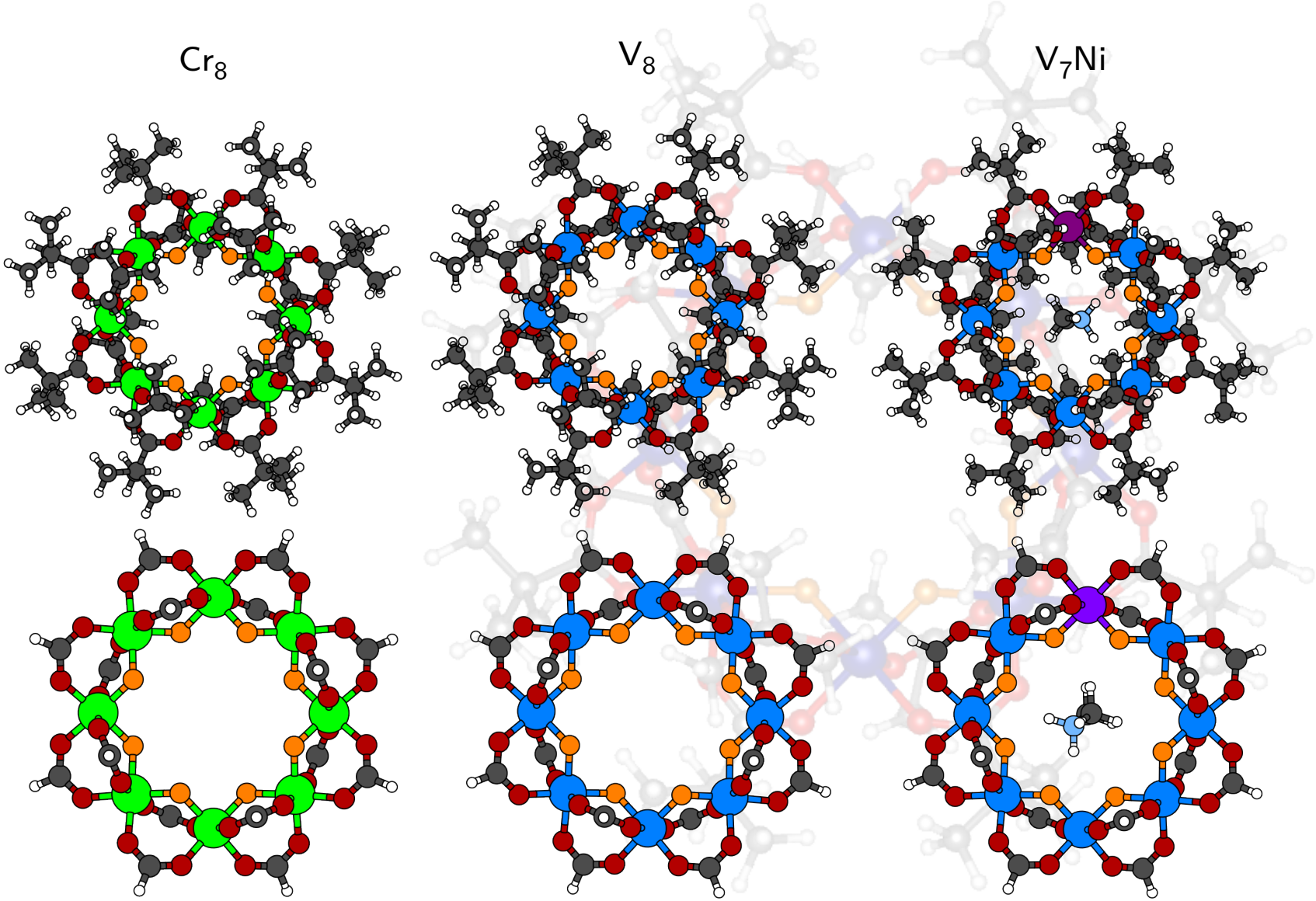
Supplementary material

d-orbitals splitting



e_g-t_{2g} splitting.

Reduced molecules



Number of electrons

system	real molecule			reduced molecule		
	# atoms	# all el.	# val. el.	# atoms	# all el.	# val. el.
Cr_8	272	1144	824	80	632	440
V_8	272	1136	816	80	624	432
V_7Ni	283	1168	830	91	656	458

Kohn-Sham DFT

Hohenberg–Kohn functional:

$$E_v[n] = \langle \psi[n] | \hat{\mathrm{T}}_+ \hat{\mathrm{V}}_{ee} + \hat{\mathrm{V}} | \psi[n] \rangle$$

$$\langle \psi[n] | \hat{\mathrm{T}}_+ \hat{\mathrm{V}}_{ee} | \psi[n] \rangle = F[n]$$

$$\langle \psi[n] | \hat{\mathrm{V}} | \psi[n] \rangle = \int d^3\mathbf{x}\, n(\mathbf{x})\, v(\mathbf{x})$$

Kohn-Sham equations:

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{x}) \right] \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}) \quad \forall i = 1, \ldots, N$$

$$v_s(\mathbf{x}) = v_H(\mathbf{x}) + v_{xc}(\mathbf{x}) + v(\mathbf{x})$$

with

$$v(\mathbf{x}) = \sum_{j=1}^{N_{ions}} \frac{-Z_i e^2}{|\mathbf{x} - \mathbf{R}_j|} \qquad v_H(\mathbf{x}) = \frac{\delta E_{Hartree}[n]}{\delta n(\mathbf{x})} = \int d^3\mathbf{y}\, \frac{n(\mathbf{y})\, e^2}{|\mathbf{x} - \mathbf{y}|}$$

$$v_{xc}(\mathbf{x}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{x})} = \frac{\delta}{\delta n(\mathbf{x})} \left[F[n] - E_{Hartree}[n] - \sum_{i=1}^{N} \langle \phi_i | \frac{-\hbar^2 \nabla^2}{2m} | \phi_i \rangle \right]$$

Spin-polarized Kohn-Sham equations

Collinear (spin-polarized) KS equations:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu_B B_s(\mathbf{x})\sigma_z\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}) \quad \text{with} \quad i = 1,\ldots,N$$

$$\text{with} \quad v_s(\mathbf{x}) = v_H(\mathbf{x}) + \frac{\delta E_{xc}[n,|\mathbf{m}|]}{\delta n} + v(\mathbf{x})$$

$$\text{and} \quad B_s(\mathbf{x}) = B_z(\mathbf{x}) - \frac{\delta E_{xc}[n,|\mathbf{m}|]}{\delta|\mathbf{m}|}\text{sign}(m_z)$$

Non-collinear (spin-polarized) KS equations:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu_B\mathbf{B}_s(\mathbf{x})\cdot\boldsymbol{\sigma}\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}) \quad \text{with} \quad i = 1,\ldots,N$$

$$v_s(\mathbf{x}) = v_H(\mathbf{x}) + \frac{\delta E_{xc}[n,|\mathbf{m}|]}{\delta n} + v(\mathbf{x})$$

$$\mathbf{B}_s(\mathbf{x}) = \mathbf{B}(\mathbf{x}) - \frac{\delta E_{xc}[n,|\mathbf{m}|]}{\delta\mathbf{m}(\mathbf{x})}\frac{\delta\mathbf{m}}{\delta|\mathbf{m}|}$$

Hubbard corrected DFT

Hubbard correction: projectors on atomic orbitals $\psi^I_{m\sigma}$

$$E_{\text{DFT+U}}[n, \mathbf{m}] = E_v[n, \mathbf{m}] + \sum_{I,\sigma} \frac{U^I}{2} \text{Tr}\left[\mathbf{n}^{I\sigma}\left(1 - \mathbf{n}^{I\sigma}\right)\right]$$

$$\text{with} \quad n^{I\sigma}_{mm'} = \sum_{i=1}^{N} \langle \phi^\sigma_i \,|\, \psi^I_{m\sigma} \rangle \langle \psi^I_{m'\sigma} \,|\, \phi^\sigma_i \rangle \qquad \textit{(atomic occupations)}$$

Linear Response approach: U^I is the curvature E w.r.t. n^I

$$U^I = \frac{\partial^2 E}{\partial n^I \partial n^I} \qquad \text{with} \quad n^I = \sum_{\sigma=\uparrow,\downarrow} \text{Tr}\left[\mathbf{n}^{I\sigma}\right]$$

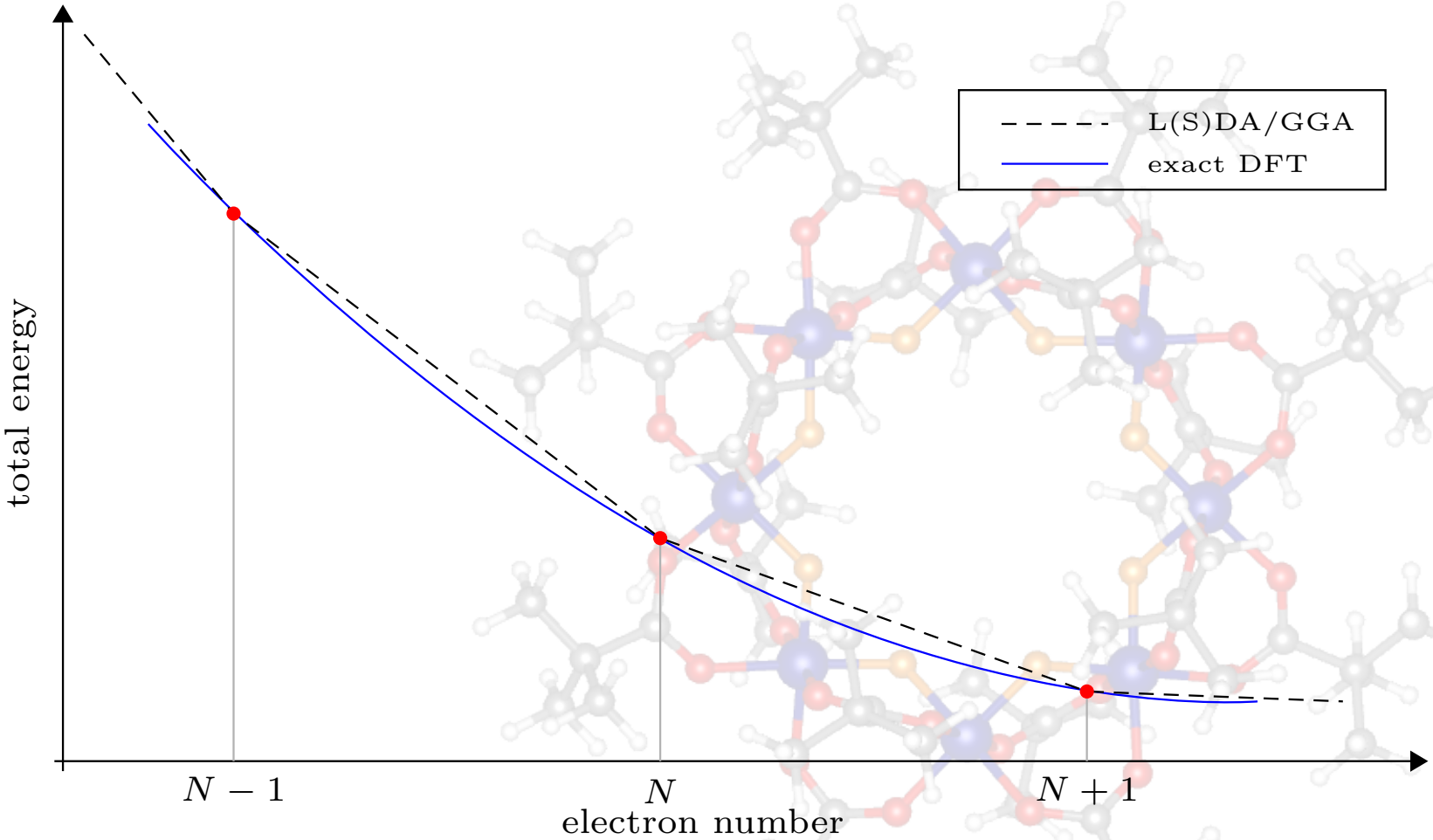
Extended Hubbard correction: intersite interactions too

$$E_{\text{DFT+U}}[n, \mathbf{m}] = E_v[n, \mathbf{m}] + \sum_{I,\sigma} \frac{U^I}{2} \text{Tr}\left[\mathbf{n}^{II\sigma}\left(1 - \mathbf{n}^{II\sigma}\right)\right] - \sum_{IJ,\sigma} \frac{V^{IJ}}{2} \text{Tr}\left[\mathbf{n}^{IJ\sigma}\mathbf{n}^{IJ\sigma}\right]$$

$$n^{IJ\sigma}_{mm'} = \sum_{i=1}^{N_{occ}} \langle \phi^\sigma_i | \psi^I_{m\sigma} \rangle \langle \psi^J_{m'\sigma} | \phi^\sigma_i \rangle$$

International Journal of Quantum Chemistry 114.1 (2013), pp. 14–49
Phys. Rev. B 71, 035105 (2005)

Hubbard corrected DFT



Schematic representation of the energy at varying number of electrons n as computed from exact Density Functional Theory (DFT) functional (blue), and an approximated functional (black). This image shows the necessity for the DFT+U correction to remove a linear term (in n) and add a quadratic term to the approximated functional.

Energy mapping

- compute the DFT total energy E_{DFT} of various spin configurations with the atomic spins $\mathbf{S}_i$ oriented differently
- map the converged spin configurations into the states $|\{\mathbf{n}_i\}\rangle$:

$$|\{\mathbf{n}_i\}\rangle = |\mathbf{n}_1\rangle \otimes |\mathbf{n}_2\rangle \otimes \cdots \otimes |\mathbf{n}_8\rangle$$

$$\text{such that} \quad \mathbf{S}_i = \langle \mathbf{n}_i \,|\, \hat{\mathbf{S}}_i \,|\, \mathbf{n}_i \rangle$$

- map the energy E_{DFT} into the exp. value $\langle \{\mathbf{n}_i\} \,|\, \hat{\mathcal{H}} \,|\, \{\mathbf{n}_i\} \rangle$:

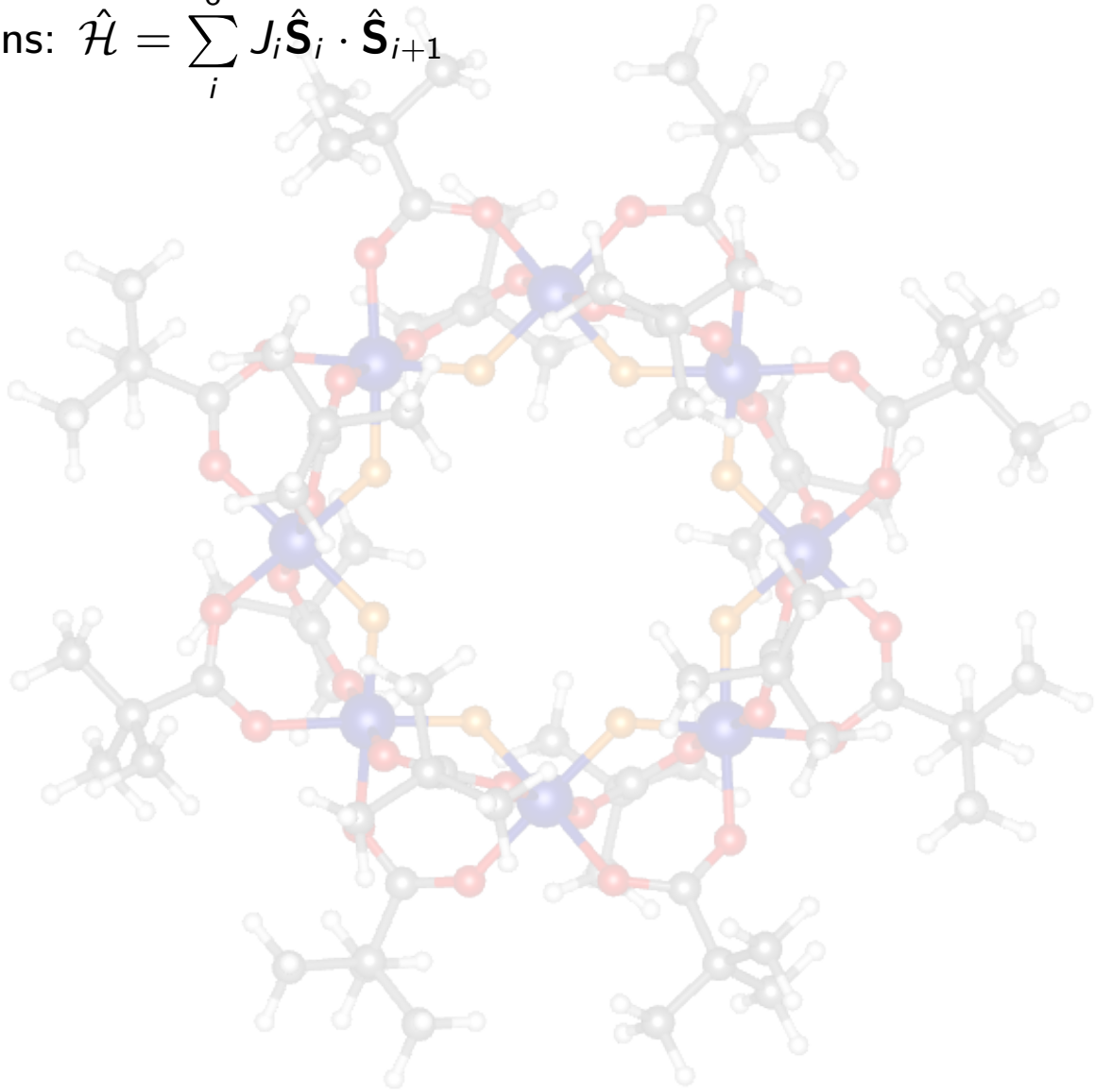
$$\begin{aligned} E_{\mathrm{DFT}} &= \langle \{\mathbf{n}_i\} \,|\, \hat{\mathcal{H}} \,|\, \{\mathbf{n}_i\} \rangle \\ &= \sum_{i=1}^{N} \mathbf{S}_i \cdot \underline{\underline{J}}_i \cdot \mathbf{S}_{i+1} + S_i \left(S_i - \frac{1}{2} \right) \mathbf{n}_i \cdot \underline{\underline{D}}_i \cdot \mathbf{n}_i \end{aligned}$$

$$\text{with} \quad \hat{\mathcal{H}} = \sum_{i=1}^{8} \hat{\mathbf{S}}_i \cdot \underline{\underline{J}}_i \cdot \hat{\mathbf{S}}_{i+1} + \hat{\mathbf{S}}_i \cdot \underline{\underline{D}}_i \cdot \hat{\mathbf{S}}_i$$

- fit the energies to get the couplings $\underline{\underline{J}}_i$, and $\underline{\underline{D}}_i$

Isotropic interactions

Isotropic spin Hamiltonians: $\hat{\mathcal{H}} = \sum_{i}^{8} J_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1}$

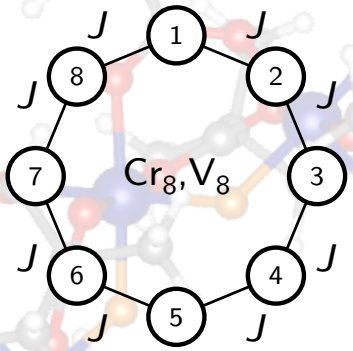


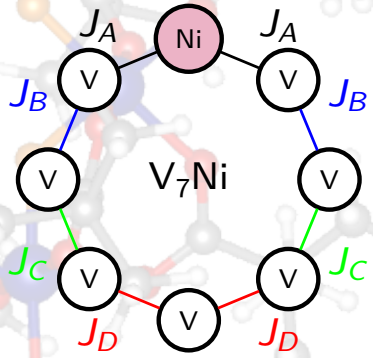
Isotropic interactions

Isotropic spin Hamiltonians: $\hat{\mathcal{H}} = \sum_{i}^{8} J_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1}$

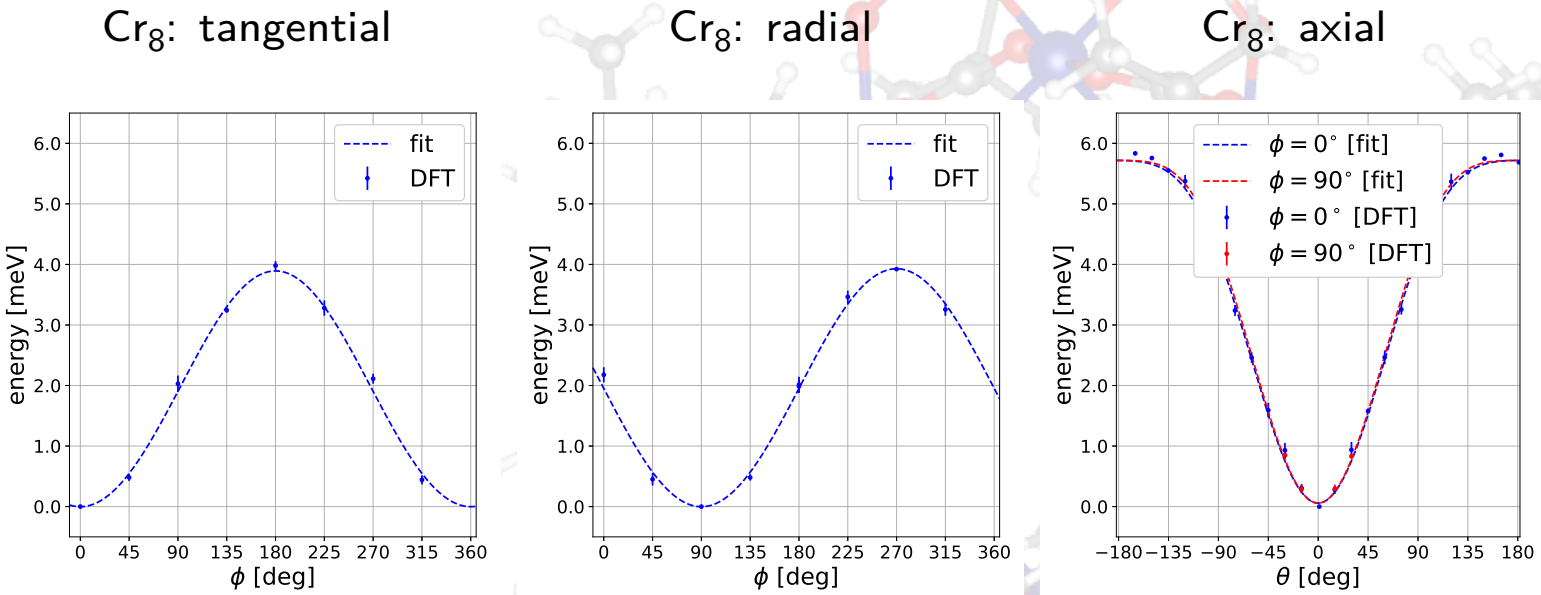
system	J [meV]
Cr_8	0.633(1)
V_8	−0.783(3)

V_7Ni coupling	J_i [meV]
J_A	1.85(2)
J_B	−0.56(2)
J_C	−0.58(2)
J_D	−0.59(2)

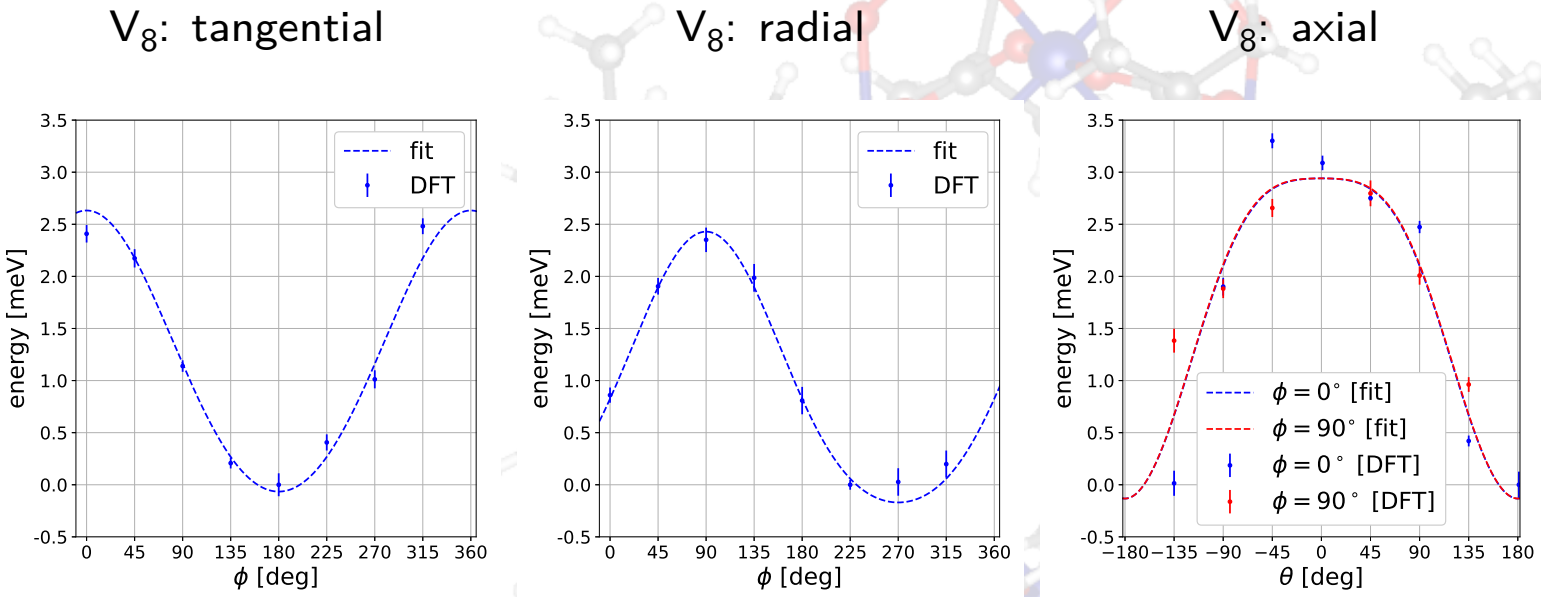




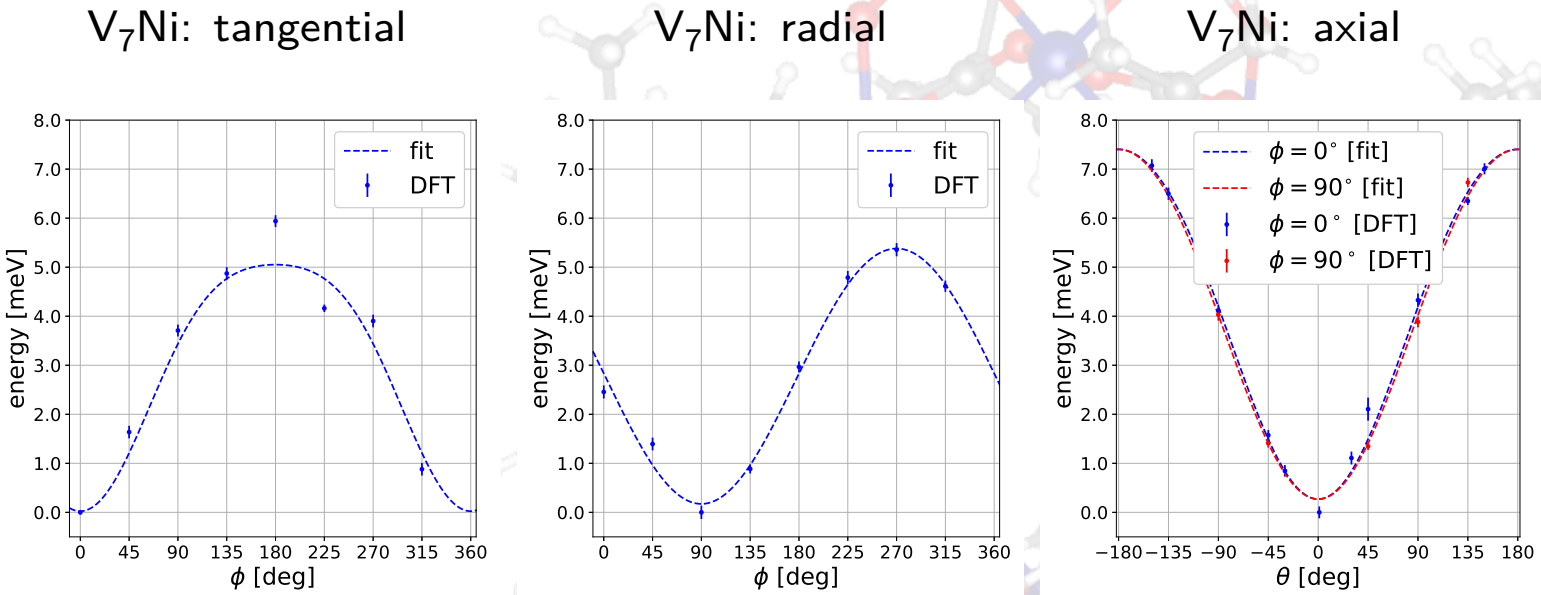
Non-colllinear calculations: Cr_8



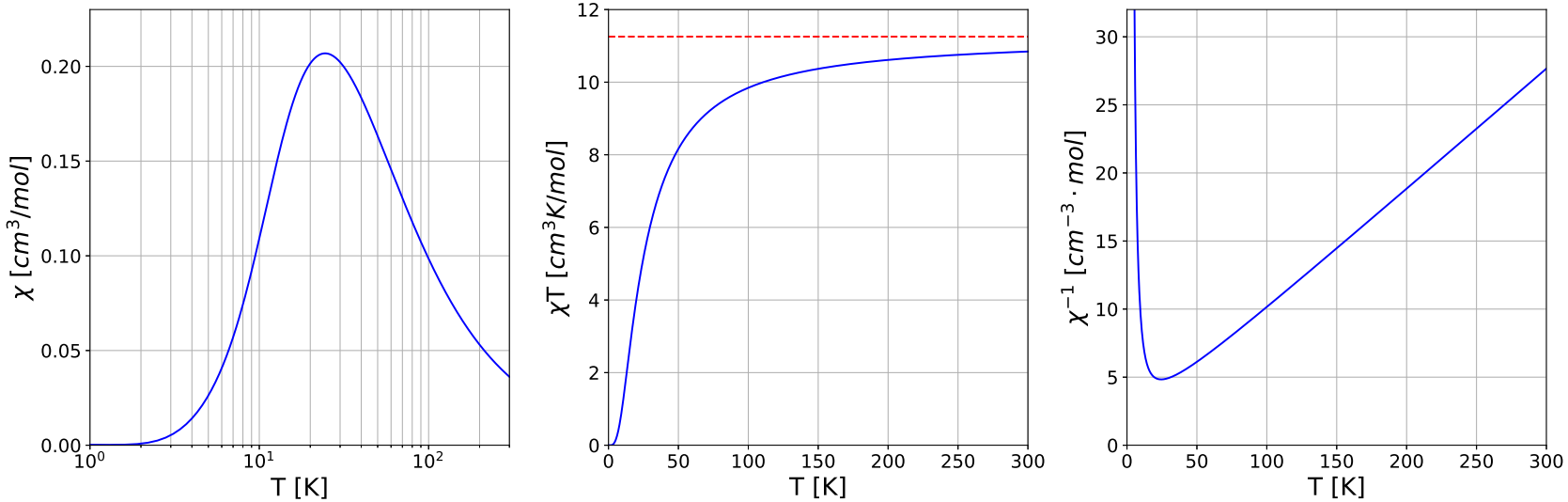
Non-colllinear calculations: V_8



Non-colllinear calculations: V_7Ni

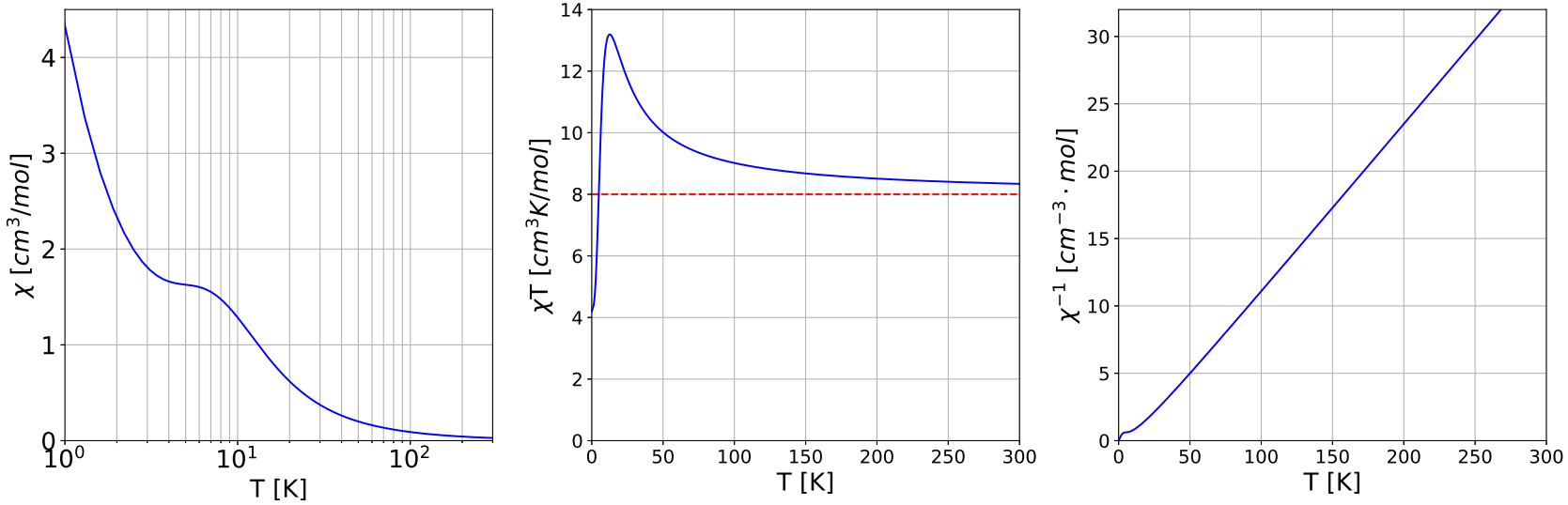


Magnetic susceptibility: Cr_8



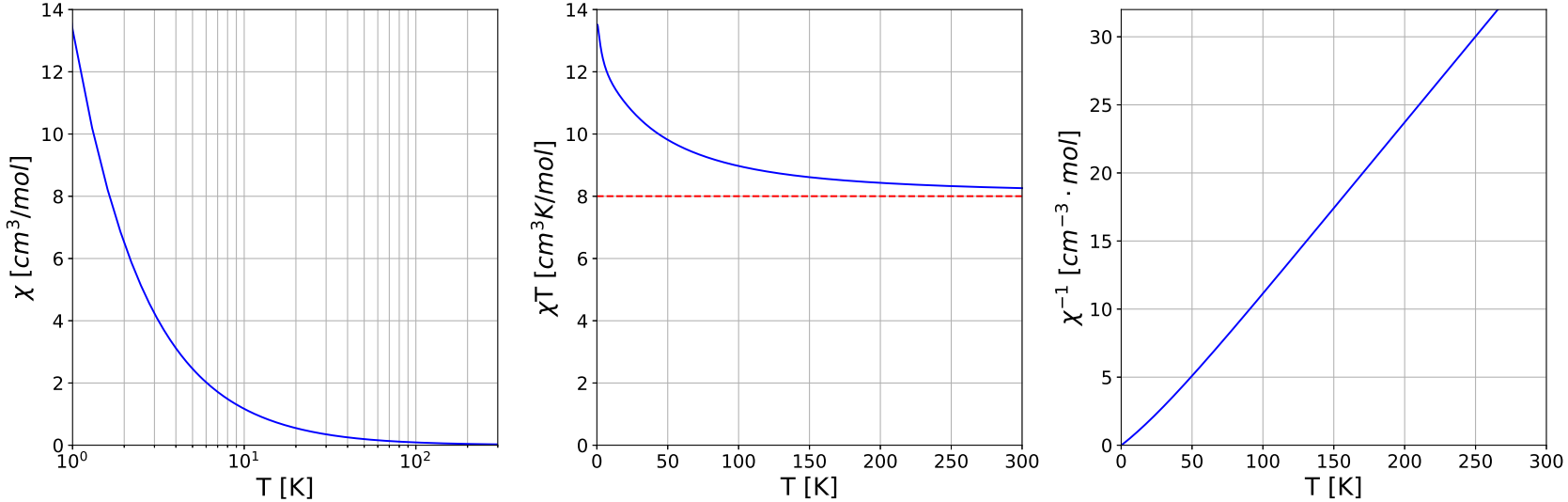
Susceptibility of Cr_8 (proxy Cr_6). At high temperatures the susceptibility approaches the Curie law, represented with with a dotted red line.

Magnetic susceptibility: V_8



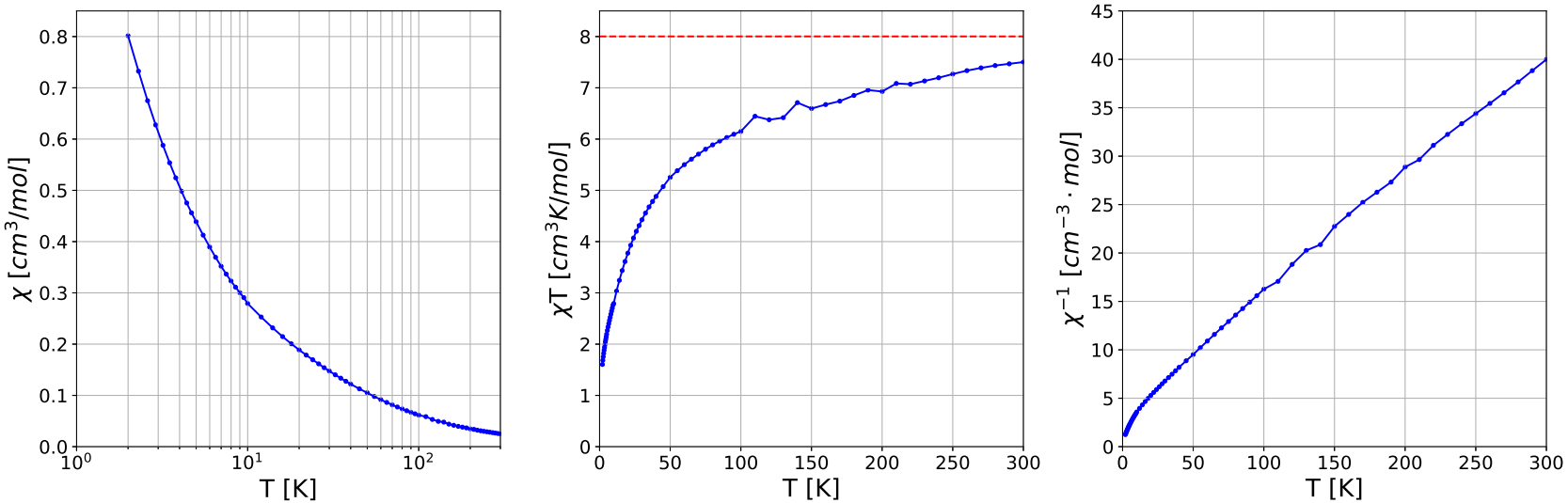
Susceptibility of V_8. At high temperatures the susceptibility approaches the Curie law, represented with with a dotted red line.

Magnetic susceptibility: V_7Ni



Susceptibility of V_7Ni. At high temperatures the susceptibility approaches the Curie law, represented with with a dotted red line.

Magnetic susceptibility (experimental): V_7Ni



Susceptibility of V_7Ni measured with a SQUID magnetometer with an applied field of 0.1 T perpendicular to the molecular plane. The red line represent the high temperature limit of χT, i.e. the Curie constant. Data are from Ref. F. Adelnia et al., "NMR Study of Spin Dynamics in V_7Zn and V_7Ni Molecular Rings", Appl. Magn. Reson. 51, 1277–1293 (2020).

Polarization

Classical formulas for the polarization of a for point charge and continuous system:

$$(nuc.\ pol.) \quad \mathbf{P}^n = \frac{q_e}{\Omega} \sum_I^{N_n} Z^I \mathbf{R}^I \qquad \text{with} \qquad \mathbf{R}^I \in \text{u.c.}$$

$$(elec.\ pol.) \quad \mathbf{P}^e = \cancel{\frac{1}{u.c.} \int_\Omega d^3\mathbf{r}\, n(\mathbf{r})\, \mathbf{r}}$$

ill-defined with pbc

The **Modern Theory of Polarization** relies on a single-particle formalism (KS orbitals in Bloch-like form):

$$\partial_\lambda \mathbf{P}^e = \frac{q_e}{(2\pi)^3} \sum_n^{occ} \int_{\text{BZ}} d^3\mathbf{k}\, 2\text{Im} \langle \partial_\lambda u_{n\mathbf{k}} | \partial_\mathbf{k} u_{n\mathbf{k}} \rangle$$

In `FHI-aims` the integral is performed along the direction of a reciprocal lattice vector $\mathbf{n}_i = \mathbf{b}_i / |\mathbf{b}_i|$:

$$P_i^e(1) - P_i^e(0) = \int_0^1 d\lambda \frac{\partial P_i^e}{\partial \lambda} \quad \xrightarrow[P_i^e(0)=0]{\text{assume that}} \quad P_i^e = \oint_{\mathbb{T}^1} d\mathbf{n}_i \frac{\partial P_i^e}{\partial \mathbf{n}_i}$$

Variable lattice parameters

A time-dependent **E**-field can induce **structural distorsions**.
Promote the lattice parameters $\mathbf{a}_i$ to dynamical variables:

$$\mathcal{H}^{\mathbf{E}}_{n,\mathbf{a}_i}\left(\mathbf{R}^l, \mathbf{p}^l\right) \quad \longrightarrow \quad \mathcal{H}^{\mathbf{E}}_{n}\left(\boldsymbol{\theta}^l, \boldsymbol{\omega}^l, \mathbf{a}_i, \boldsymbol{\kappa}_i\right)$$

where $\boldsymbol{\theta}^l$ are the fractional coordinates, $\boldsymbol{\omega}^l$ the corresponding conjugate variables, and $\boldsymbol{\kappa}_i$ the conjugate variables to the lattice parameters $\mathbf{a}_i$:

$$\mathbf{A} \stackrel{\text{def}}{=} [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] = \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} \rightarrow \begin{array}{ll} \mathbf{R}^l = & \mathbf{A} \cdot \boldsymbol{\theta}^l \\ \mathbf{p}^l = & \mathbf{B} \cdot \boldsymbol{\omega}^l \end{array}$$

with $\mathbf{B} = \left(\mathbf{A}^{-1}\right)^t$

References:
J. Phys. Chem. Solids Vol. 56, No. 3/4. pp. 501-505. 1995

Equations of motion

From the Hamilton equations of motion of $\mathcal{H}_n^{\mathbf{E}}$ we obtain:

$$\frac{d\mathbf{R}^I}{dt} = \frac{\mathbf{p}^I}{M^I} + \boxed{\frac{d\mathbf{A}}{dt} \cdot \boldsymbol{\theta}^I}$$

$$\frac{d\mathbf{p}^I}{dt} = \mathbf{F}^{0I} + \mathbf{F}^{\mathbf{E}I} - \boxed{\mathbf{B} \cdot \frac{d\mathbf{A}}{dt} \cdot \mathbf{p}^I}$$

with

$$\mathbf{F}^{0I} = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{R}^I} \quad \text{and} \quad \mathbf{F}^{\mathbf{E}I} = -\Omega \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{R}^I}$$

Equations of motion

From the Hamilton equations of motion of $\mathcal{H}_n^{\mathbf{E}}$ we obtain:

$$\frac{d\mathbf{R}^I}{dt} = \frac{\mathbf{p}^I}{M^I} + \boxed{\frac{d\mathbf{A}}{dt} \cdot \boldsymbol{\theta}^I}$$

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with

$$\mathbf{F}^{0I} = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{R}^I} \quad \text{and} \quad \mathbf{F}^{\mathbf{E}I} = -\Omega \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{R}^I}$$

Attention! We need to know the following term:

$$\frac{d\boldsymbol{\kappa}_i}{dt} = -\frac{\partial \mathcal{H}_n^{\mathbf{E}}}{\partial \mathbf{a}_i} = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{a}_i} - \boxed{\frac{\partial}{\partial \mathbf{a}_i}(\Omega \mathbf{P} \cdot \mathbf{E})}$$

Stress tensor

To perform MD simulations at fixed pressure, we need to evaluate the stress tensor $\sigma^{\mathbf{E}}_{\alpha\beta}$ at finite electric field:

$$\sigma^{\mathbf{E}}_{\alpha\beta} = \frac{1}{\Omega}\frac{d\mathcal{H}^{\mathbf{E}}_n}{d\eta_{\alpha\beta}} = \frac{1}{\Omega}\frac{d}{d\eta_{\alpha\beta}}\left(\mathcal{H}^{\mathbf{0}}_n - \Omega\mathbf{P}\cdot\mathbf{E}\right) = \sigma^{\mathbf{0}}_{\alpha\beta} + \boxed{\sigma^{\mathbf{P}}_{\alpha\beta}}$$

where $\sigma^{\mathbf{0}}_{\alpha\beta}$ is already implemented in the code, and the new term is

$$-\sigma^{\mathbf{P}}_{\alpha\beta} = \frac{1}{\Omega}\frac{d\left(\Omega\mathbf{P}\cdot\mathbf{E}\right)}{d\eta_{\alpha\beta}} = \delta_{\alpha\beta}\mathbf{P}\cdot\mathbf{E} + \left(\frac{d\mathbf{P}^n}{d\eta_{\alpha\beta}} + \frac{d\mathbf{P}^e}{d\eta_{\alpha\beta}}\right)\cdot\mathbf{E}$$

The nuclear and electronic contributions are

$$\frac{d\mathbf{P}^n}{d\eta_{\alpha\beta}}\cdot\mathbf{E} = \sum_I \frac{q_e}{\Omega} Z^I E_\alpha R^I_\beta$$

$$\frac{d\mathbf{P}^e}{d\eta_{\alpha\beta}}\cdot\mathbf{E} = \sum_i E_i\left(\sum_I \frac{q_e}{\Omega} Z^{*I}_{i\alpha} R^I_\beta + \sum_j \frac{\partial P^e_i}{\partial a_{j\alpha}} a_{j\beta}\right)$$

Computer Physics Communications, 190 (2015), 33-50