Ifeanyi J. Onuorah, University of Parma, Italy

Miki Bonacci, Laboratory for Materials Simulations, PSI, Switzerland

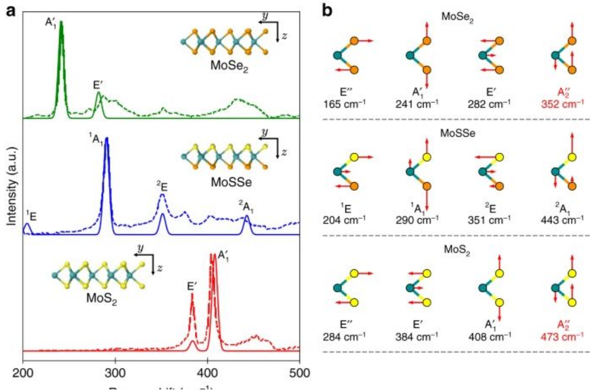
Automating ab initio modeling applied to muon spin rotation and relaxation spectroscopy

30-11-2023

Introduction

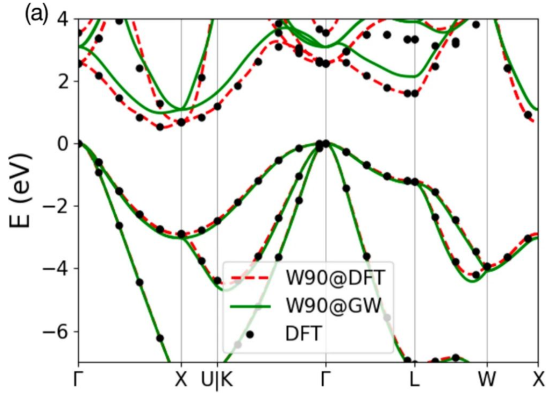
Automated first-principles simulations as a service: accelerating materials discovery via computational spectroscopies

Ab initio lattice vibration: Raman spectroscopy



Alireza Taghizadeh et al., Nat. Commun. **11**, 3011 (2020)

Many-body perturbation theory: Optical spectroscopy



Miki Bonacci et al. npj Comp. Mat. **9**, 74 (2023)

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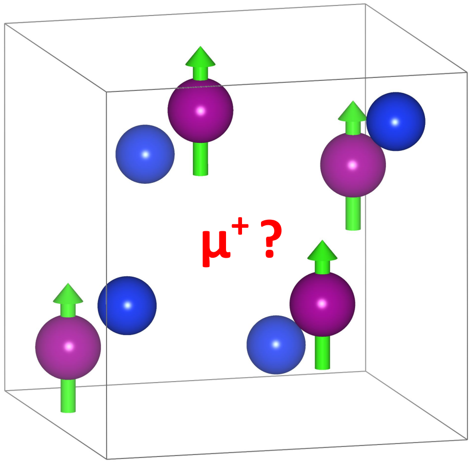
Introduction

Where does the muon stop?



Magnetic ($\sim \mathbf{S}_\mu \cdot \mathbf{A} \cdot \mathbf{S}_e$) &/or paramagnetic ($\sim \mathbf{S}_\mu \cdot \mathbf{A} \cdot \mathbf{I}$) phase interactions

Internal field at the muon

$$B_\mu \approx B_{dip} + B_{hf} + \ldots$$

$$B_{dip} = \frac{\mu_0}{4\pi}\left(\frac{-\boldsymbol{m}}{r^3} + \frac{3(\boldsymbol{m}\cdot\boldsymbol{r})\boldsymbol{r}}{r^5}\right)$$

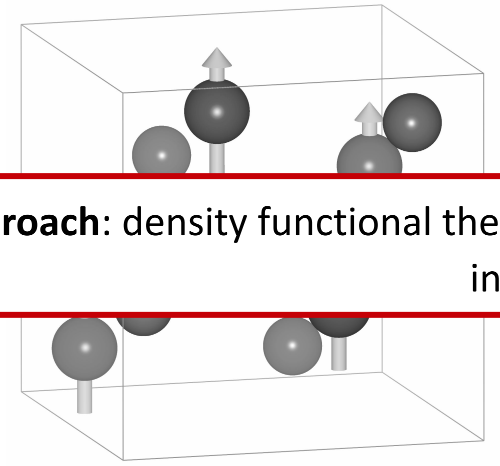
$$B_{hf} = \frac{2\mu_0}{3}|\psi(0)|^2 \boldsymbol{m}$$

P. Bonfà, R. De Renzi, J. Phys. Soc. Jpn. **85**, 091014 (2016)
S. J. Blundell, T. Lancaster, Appl. Phys. Rev. **10**, 021316 (2023)
I. J. Onuorah, et al Phys. Rev. B **97**, 174414 (2018).

Introduction

Where does the muon stop?

Magnetic (~ $S_\mu \cdot A \cdot S_e$) &/or paramagnetic (~ $S_\mu \cdot A \cdot I$) phase interactions



Internal field at the muon

$$B_\mu \approx B_{dip} + B_{hf} + \ldots$$

$$B_{hf} = \frac{2\mu_0}{3}|\psi(0)|^2 \boldsymbol{m}$$

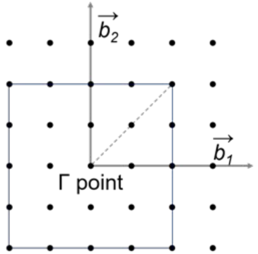
Approach: density functional theory (DFT) based simulations with μ^+ modelled as interstitial impurity.

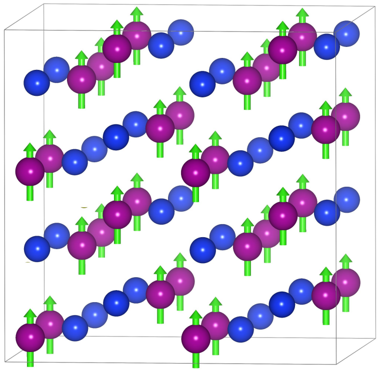
P. Bonfà, R. De Renzi, J. Phys. Soc. Jpn. **85**, 091014 (2016)
S. J. Blundell, T. Lancaster, Appl. Phys. Rev. **10**, 021316 (2023)
I. J. Onuorah, et al Phys. Rev. B **97**, 174414 (2018).

Muon calculation protocols

Challenges for a regular user within DFT-based high-throughput approaches:

- What supercell size is sufficient for impurity calculations
- Initial trial muon positions?
- Choice of optimized DFT parameters:
  - **q** point sampling of the Brillouin zone
  - Plane-wave cutoffs
  - Convergence thresholds
- Results, data handling and analysis:
  - A lot of human intervention/expertise
  - Task intensive
  - Reproducibility loss





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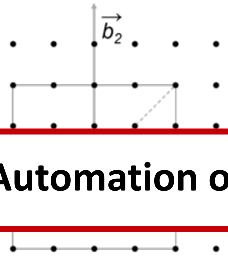
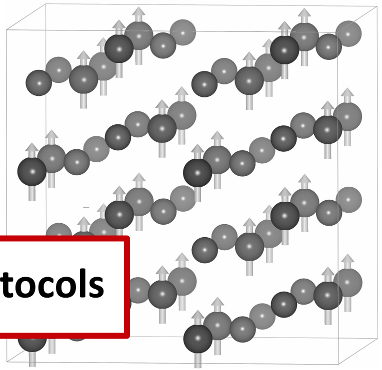
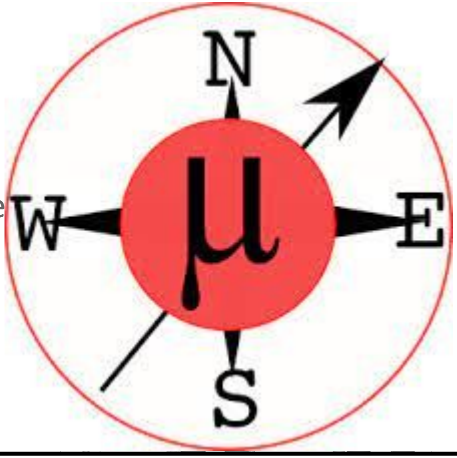




Not User friendly!!! → **Automation of the protocols**

Muon calculation protocols



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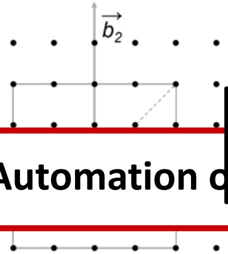

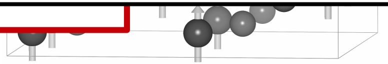

Not User friendly!!! → **Automation o**

Huddart, B. M., et al., **280**, 108488 (2022)

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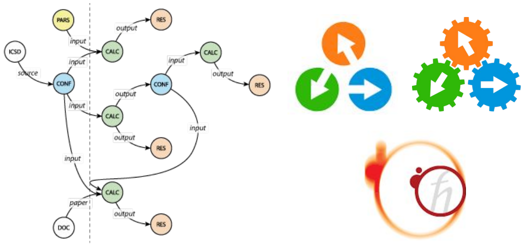
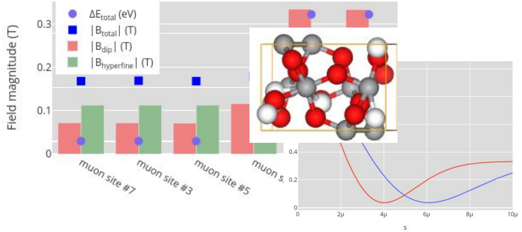
Outline

Automation Platforms



High-throughput stories

Automation protocols & validation



Outlooks and future perspectives

Automation strategy & Platforms

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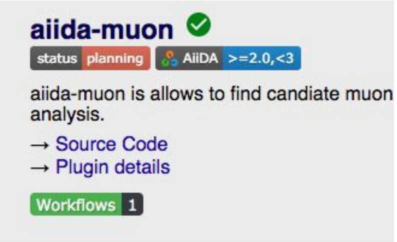
S. P. Huber et al., Sci. Data, **7**(1):300 (2020)
M. Uhrin et al., Comp. Mat. Sci. **187,** 110086 (2021)
https://www.aiida.net



https://github.com/positivemuon/aiida-muon

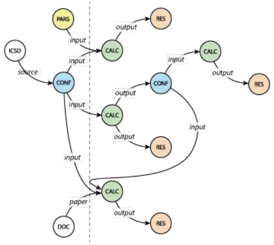
QUANTUMESPRESSO

P. Giannozzi et al., JPCM, **29**:465901 (2017)

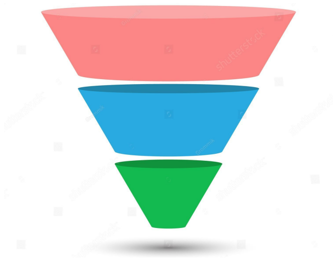
https://github.com/aiidateam/aiida-quantumespresso

Outline

Automation Platforms



High-throughput stories



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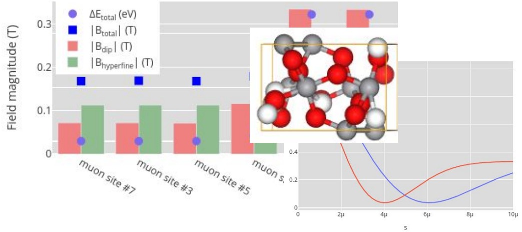
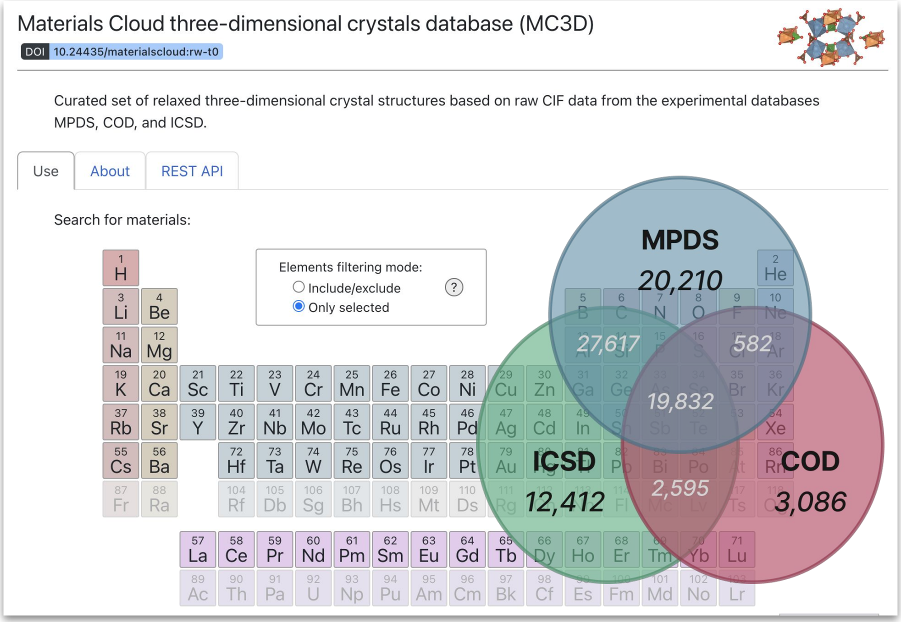


Outlooks and future perspectives

High-throughput stories

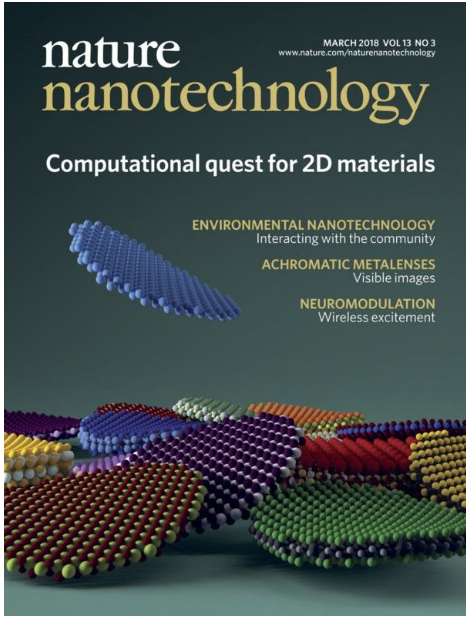
Powered by AiiDA

MC3D ~ **35 000** inorganic 3D crystals



S. Huber, M. Bercx, N. Hörmann, M. Uhrin, G. Pizzi, N. Marzari
https://archive.materialscloud.org/record/2022.38

MC2D > **2 000** layered 2D materials

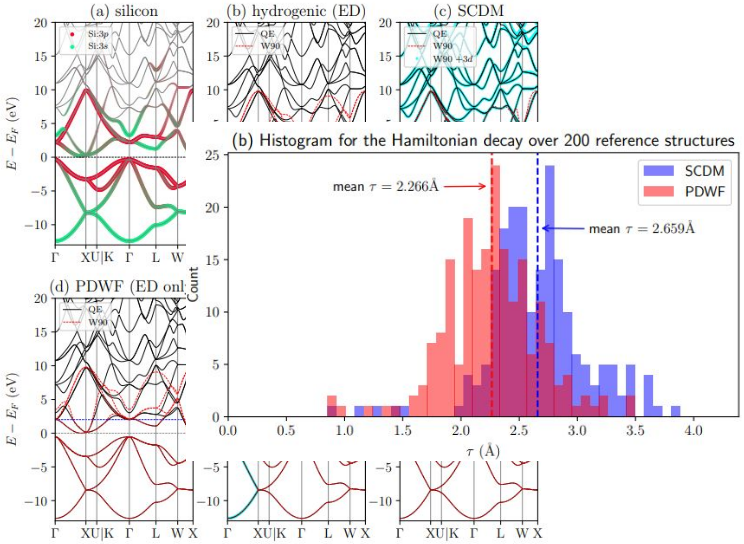


N. Mounet et al., Nat. Nanotech. **13**, 246-252 (2018)
D. Campi et al., ACS Nano, **17**, 12, 11268–11278 (2023)
https://archive.materialscloud.org/record/2020.158

High-throughput stories

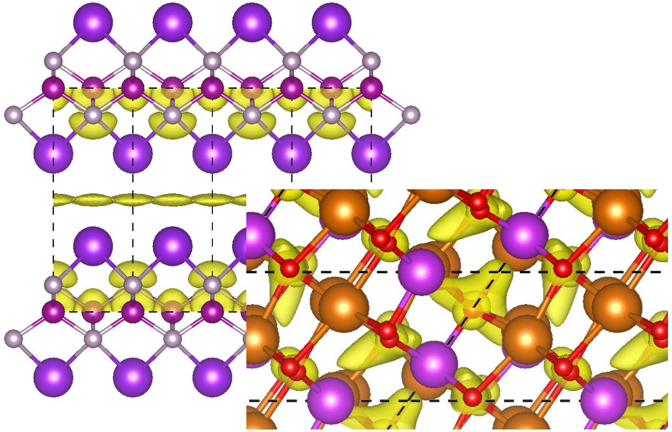
Powered by AiiDA

Automated Wannierization of **17 744** materials (**1 155 049** MLWFs)



J. Qiao, G. Pizzi, N. Marzari, npj Comp. Mat. **9**, 206 (2023)
J. Qiao, G. Pizzi, N. Marzari, npj Comp. Mat. **9**, 208 (2023)

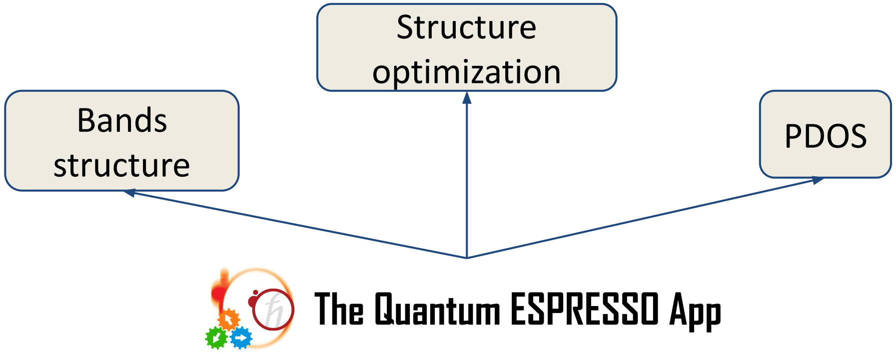
352 new electrides identified, several of which with relevant magnetic properties

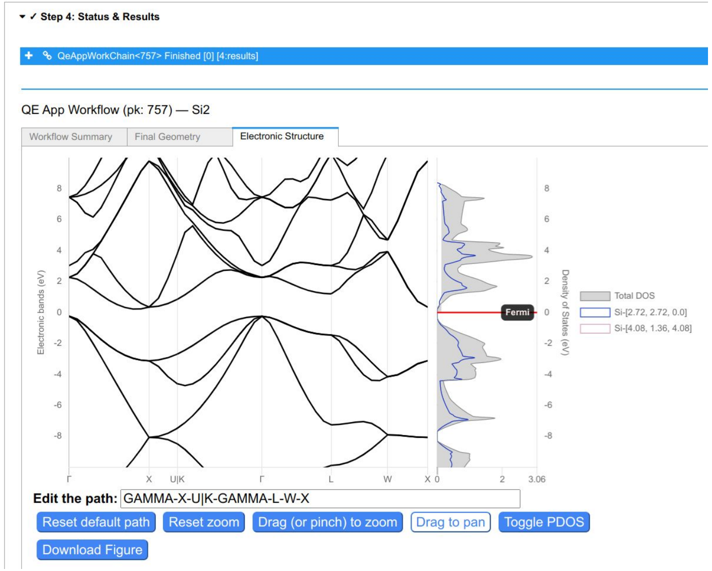


F. Ramirez, L. Ponet, M. Bercx, N. Marzari, G. Pizzi, *in preparation*

Graphical user interface (GUI)

AiiDAlab-QuantumESPRESSO: The web environment for first-principle calculations.



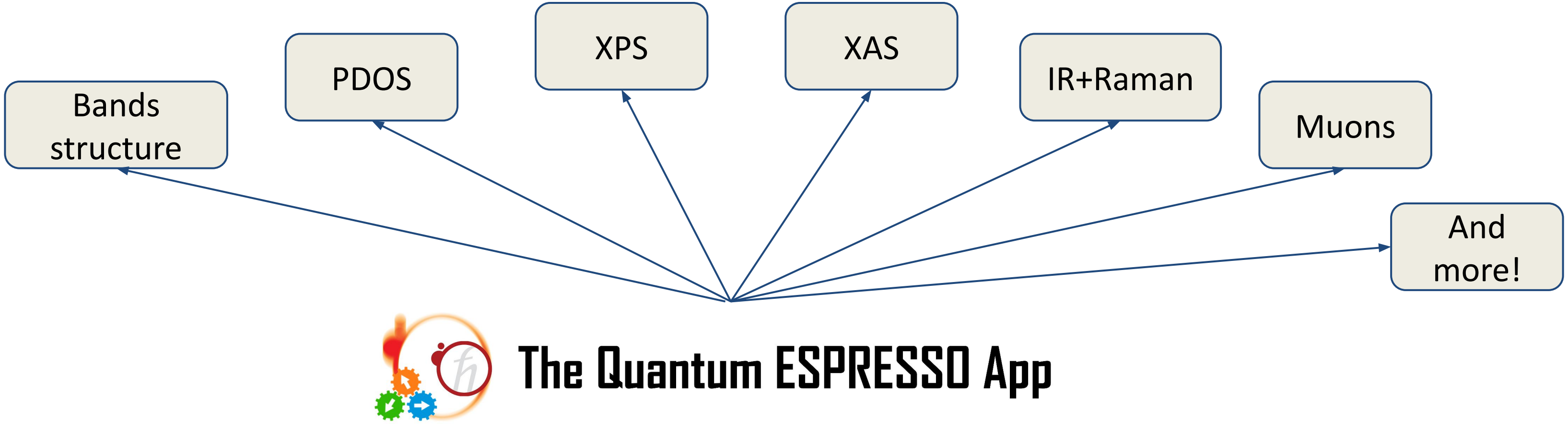


A. V. Yakutovich et al., Comp. Mat. Sci. **188**, 110165 (2021)
https://www.aiidalab.net/

Graphical user interface (GUI)

Xing Wang (LMS, PSI)
Jusong Yu (LMS, PSI)

New implementation supports multiple properties in one interface.



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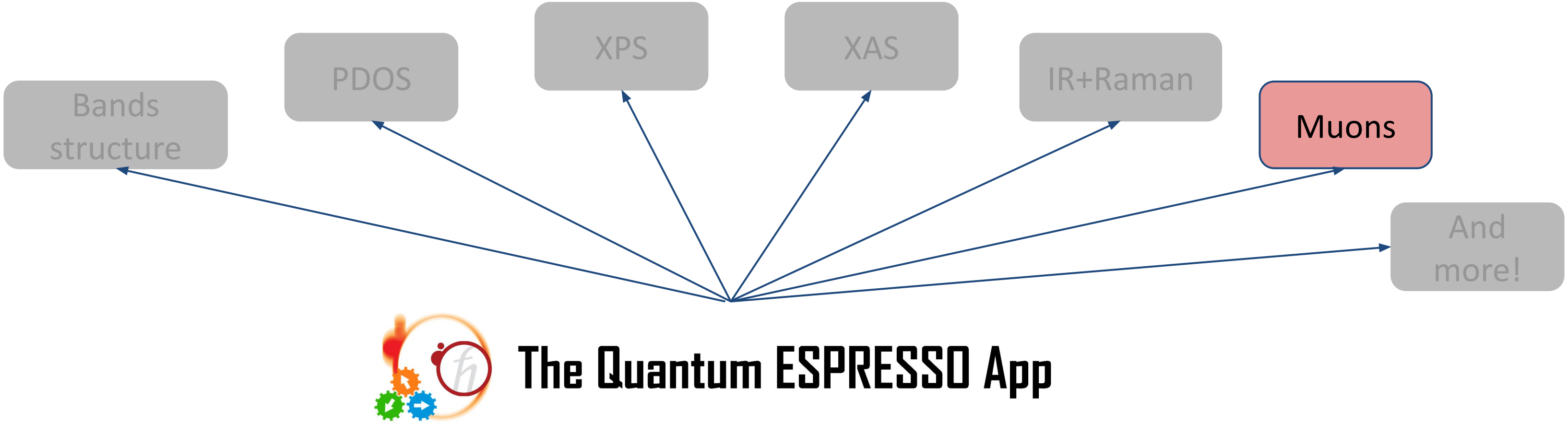

New AiiDAlab Quantum ESPRESSO app plugin for muon simulations
https://github.com/mikibonacci/aiidalab-qe-muon

Graphical user interface (GUI) AiiDAlab

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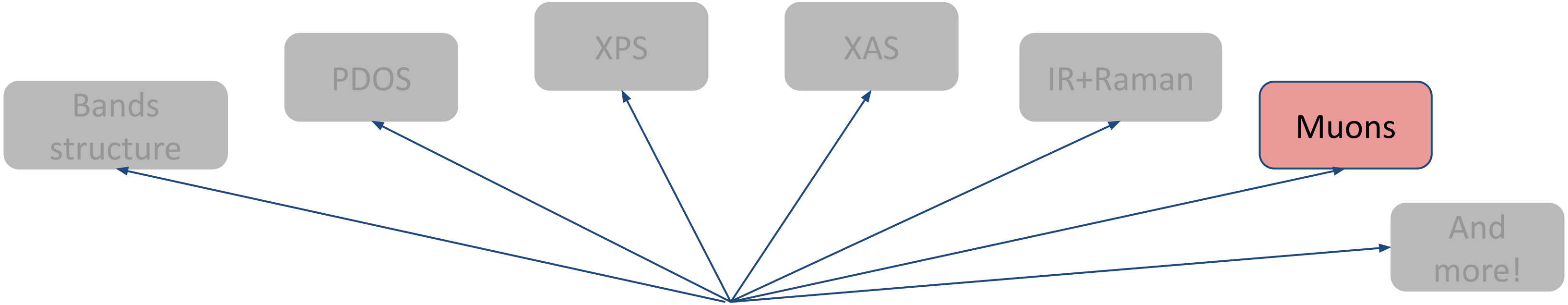

The Quantum ESPRESSO App

Available at aiidalab.psi.ch

New AiiDAlab Quantum ESPRESSO app plugin for muon simulations
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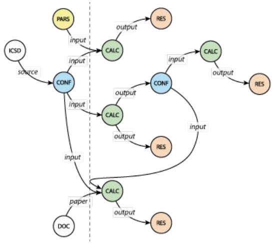
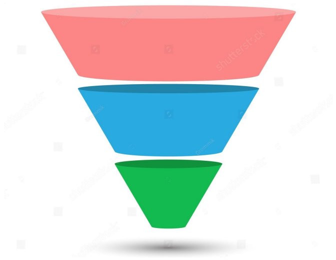
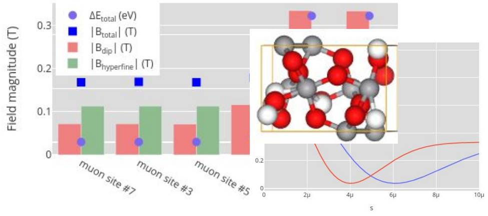


High-throughput stories

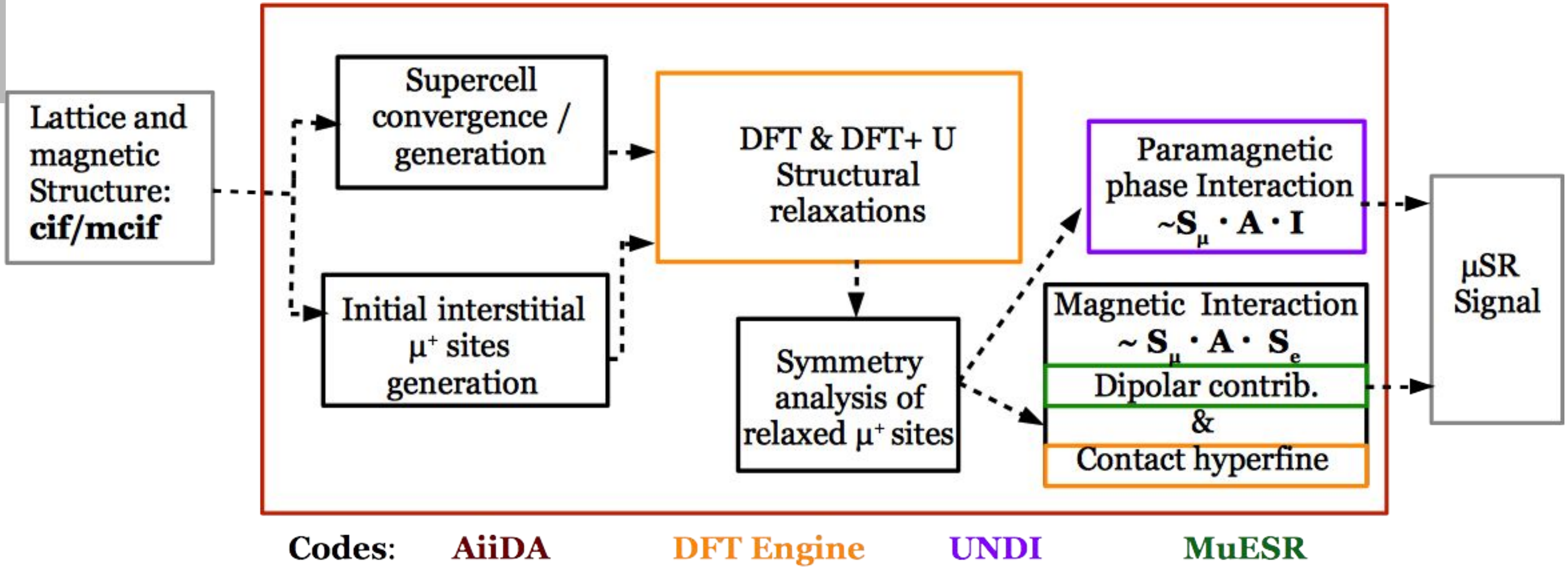


Automation protocols & validation



Outlooks and future perspectives

AiiDA-muon: workflows & implementation



Open source code: https://github.com/positivemuon/aiida-muon

AiiDA-muon: workflows & implementation

Dipolar fields using classical approximation:

$$\boldsymbol{B}_{\text{dip}} = \frac{\mu_0}{4\pi} \sum_{i=1}^{N} \left(-\frac{\boldsymbol{m}_i}{r_i^3} + \frac{(\boldsymbol{m}_i \cdot \boldsymbol{r}_i)\, \boldsymbol{r}_i}{r_i^5} \right)$$

Contact hyperfine fields using spin density at the muon site:

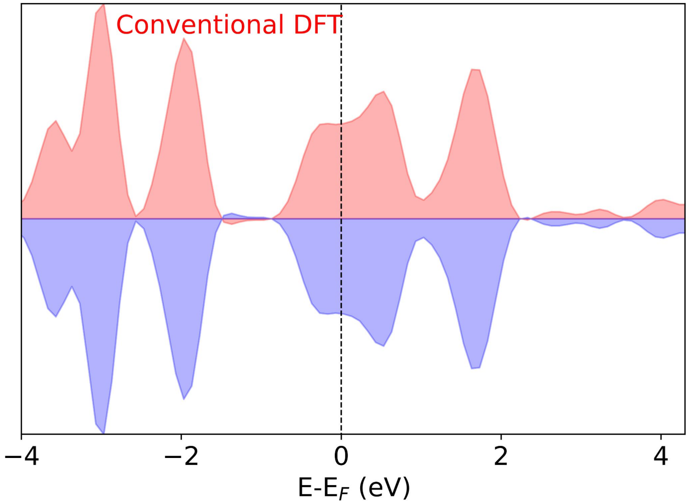
$$B_{hf} = \frac{2}{3}\mu_0 \mu_B \left[\rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})\right]$$

The variance of the field distribution at the muon site due to nuclear dipoles:

$$(\sigma/\gamma_\mu)^2 = \frac{2}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \sum_{j=1}^{M} \frac{\gamma_j^2 I_j (I_j+1)}{r_j^6} \qquad P^{KT}(t) = \frac{1}{3} + \frac{2}{3}\left(1 - \sigma^2 t^2\right) e^{-\frac{1}{2}\sigma^2 t^2}$$

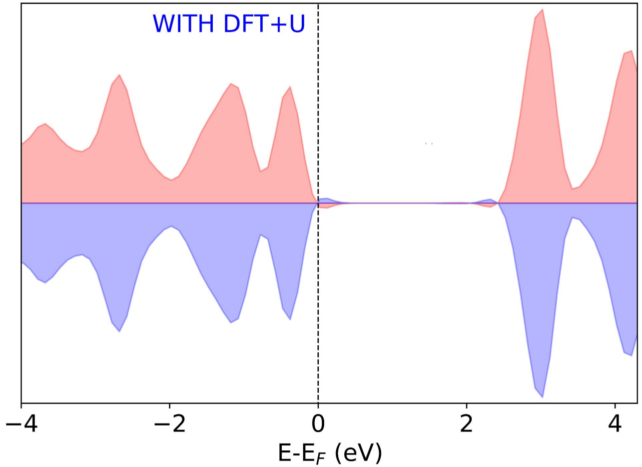
Challenges in Automation

- Move beyond DFT and introduce corrections to describe **electronic correlation effects**



Iurii Timrov et al. Phys. Rev. B 98, 085127 (2018)

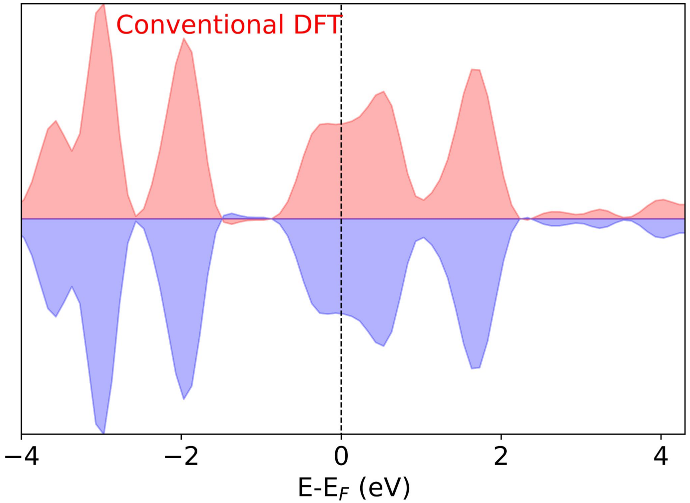
Example: FeO



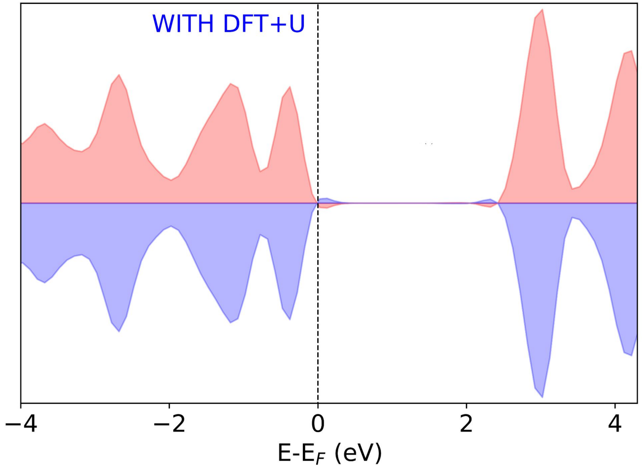
- This affects **outcomes of muon site predictions**.
- Important to get correct conducting state because of different charge screening effects.

Challenges in Automation

- Move beyond DFT and introduce corrections to describe **electronic correlation effects**



Example: FeO



This affects **outcomes of muon site predictions**.

DFT+U correction, with U values obtained from the analysis of large set of oxidation energies.

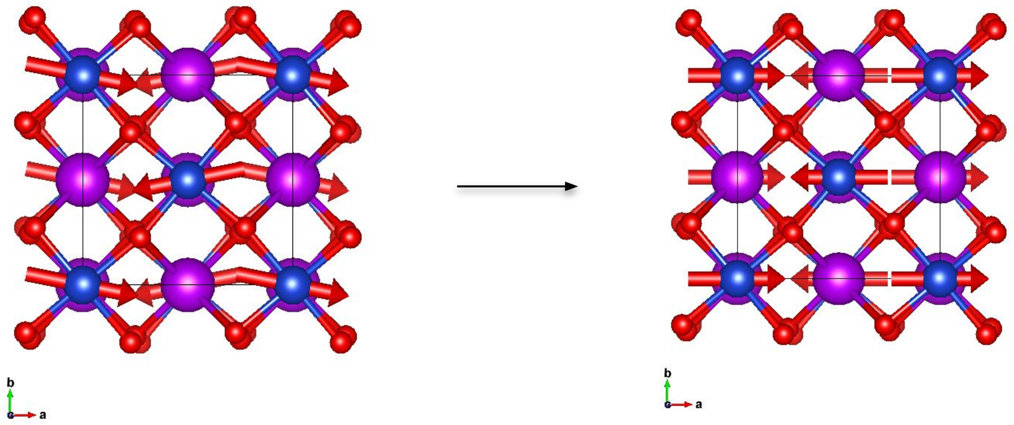
Lei Wang, *et al* Phys. Rev. **B** 73, 195107 (2006)

Co	Cr	Fe	Mn	Ni	V	Cu
3.3	3.5	4.0	4.0	6.4	3.1	4.0

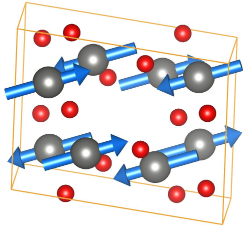
Challenges in Automation

The description of **non collinear** magnetic structures is **computationally demanding** and can be affected by numerical instabilities.

- Algorithm produces collinear spin structures (if possible) and performs collinear DFT calculations.
- Original structure is used to compute the dipolar interactions.



Muon local field in V_2O_3



B. A. Frandsen et al., Phys. Rev. B **100**, 235136 (2019)
Uemura et al., Hyperfine Interact. **17**, 339 (1984)

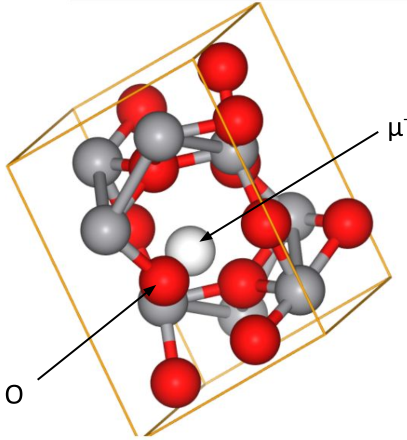
jupyter

QE App Workflow (pk: 38028) — O12V8

Workflow Summary | Muon spectroscopy | Vibrational Structure

Select view mode for muonic outputs: Summary of all unique muon s

Select muon site: 7



Data for muon site #7

Entry	Value
muon position (crystal coordinates)	[0.559, 0.316, 0.476]
ΔE_{total} (eV)	0.0
structure pk	38162
B_{total} (T)	[0.138, -0.042, 0.086]
$B_{dipolar}$ (T)	[0.03, -0.042, 0.05]
$\lvert B_{total}\rvert$ (T)	0.168
$\lvert B_{dip}\rvert$ (T)	0.072
$\lvert B_{hyperfine}\rvert$ (T)	0.113

Download table in csv format: muon_7.csv

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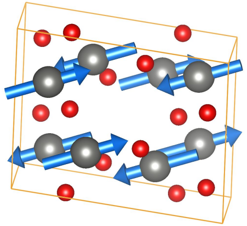
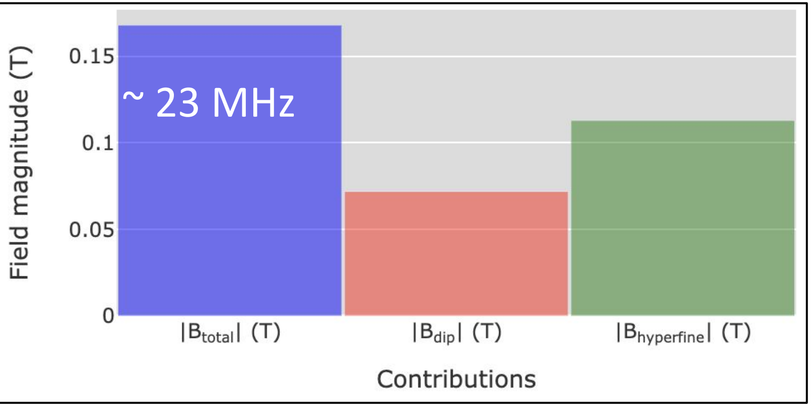
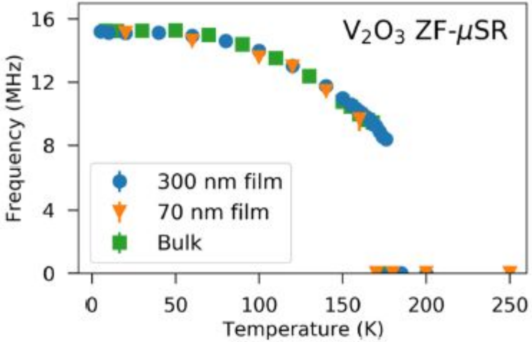


B. A. Frandsen et al., Phys. Rev. B **100**, 235136 (2019)
Uemura et al., Hyperfine Interact. **17**, 339 (1984)





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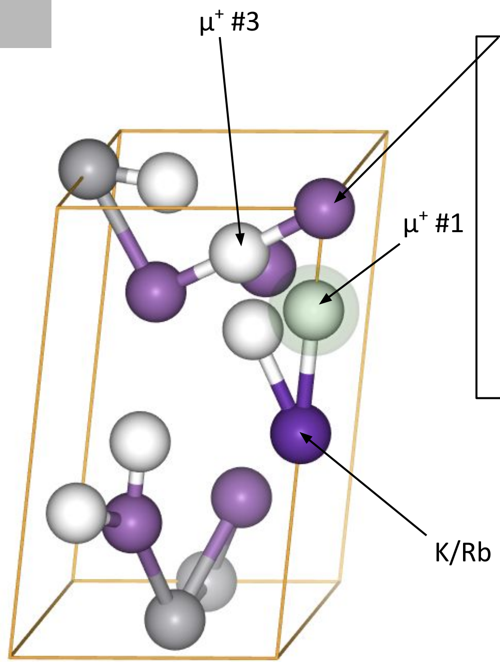
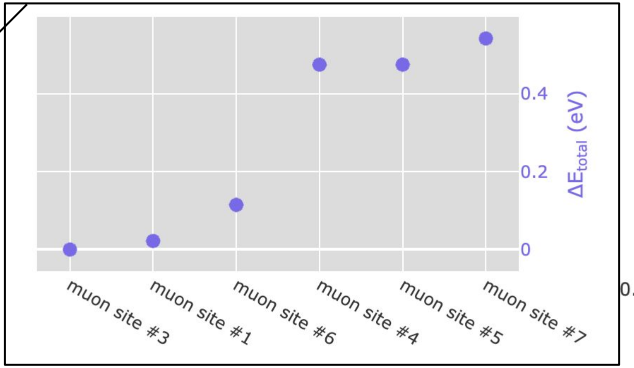
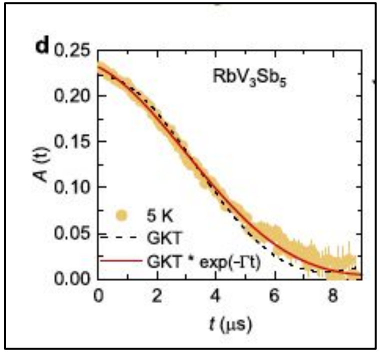
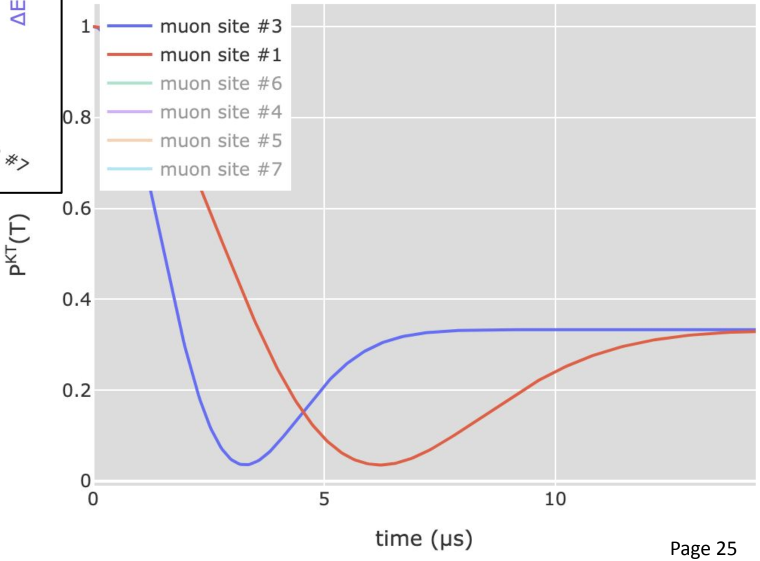
KT Polarization: KV_3Sb & RbV_3Sb_5

Mielke, C., Das, D., Yin, JX. *et al.*, *Nature* **602**, 245 (2022)



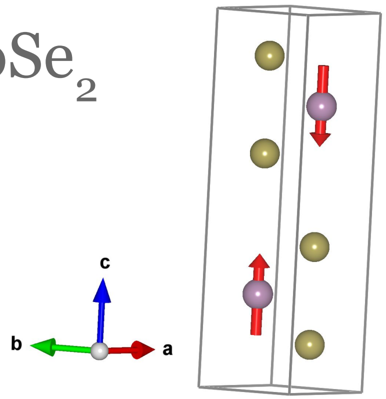






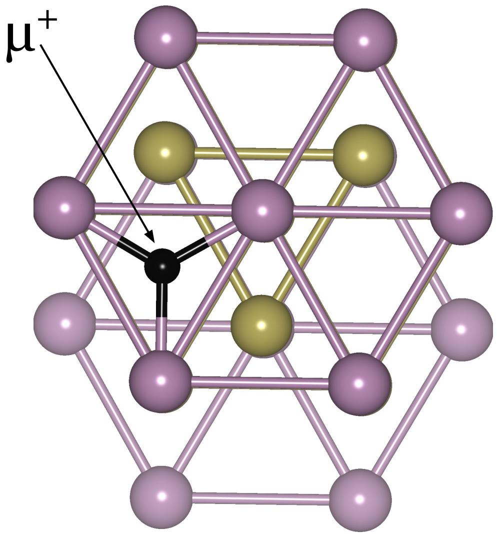
Magnetism in 2H-$MoTe_2$ & 2H-$MoSe_2$

Guguchia et al., Sci. Adv., **4**, 12: eaat3672 (2018)



- ➔ <u>Substitutional defect</u> calculations are <u>not yet implemented</u>
- ➔ Assuming an induced ~**0.4** μ_B moment at Mo sites

Muon site in the Mo site vicinity



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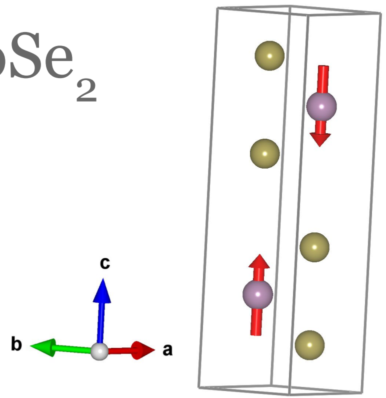
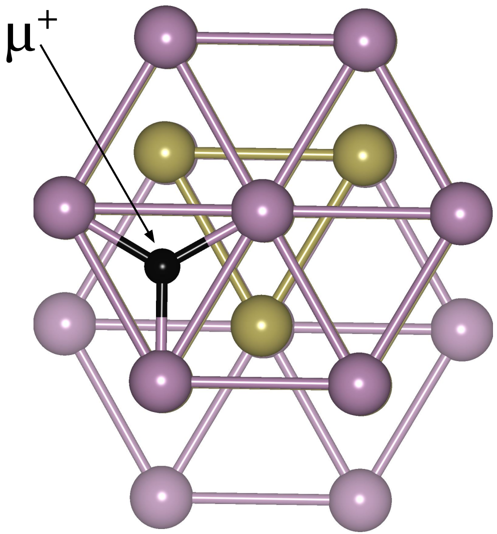
Guguchia et al., Sci. Adv., **4**, 12: eaat3672 (2018)

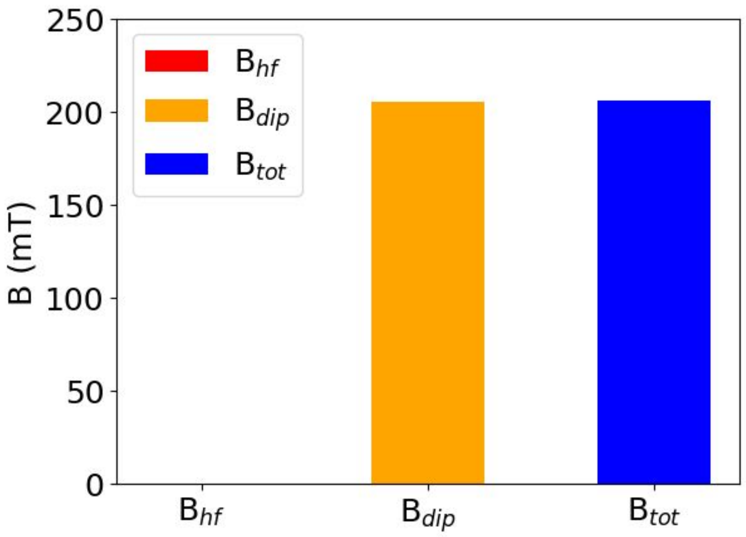


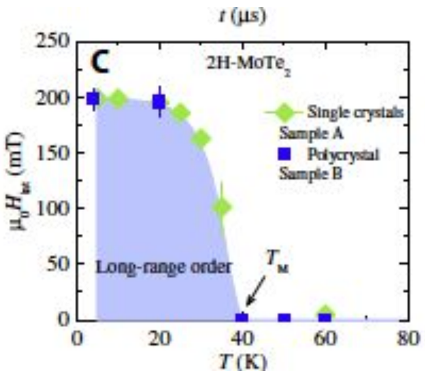
- ➔ <u>Substitutional defect</u> calculations are <u>not yet implemented</u>
- ➔ Assuming an induced ~**0.4** μ_B moment at Mo sites

Muon site in the Mo site vicinity

Local field at the muon







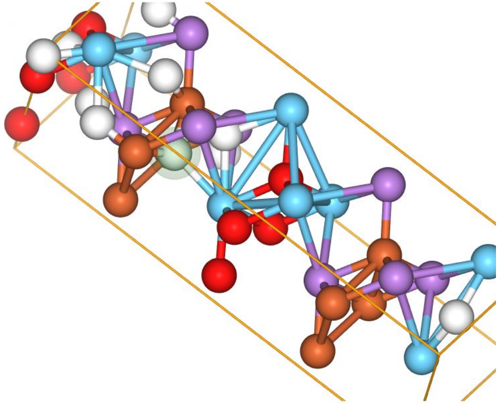
Internal field in LaFeAsO

H. Maeter, et al., Phys. Rev. B **80**, 094524 (2009)

Select view mode for muonic outputs: Summary of all ur

Select muon site: 10

Unit cell containing all the unique muon sites:



Summary for all the unique muon sites, sorted by energy:

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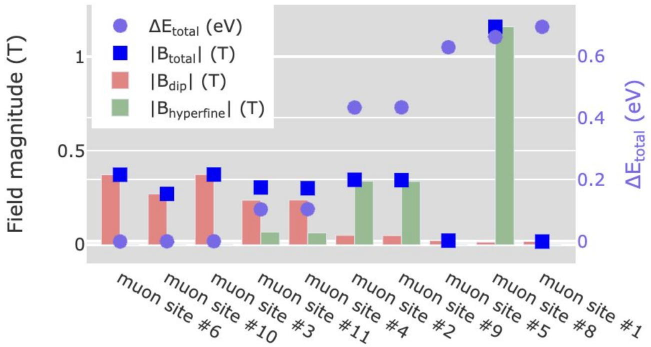

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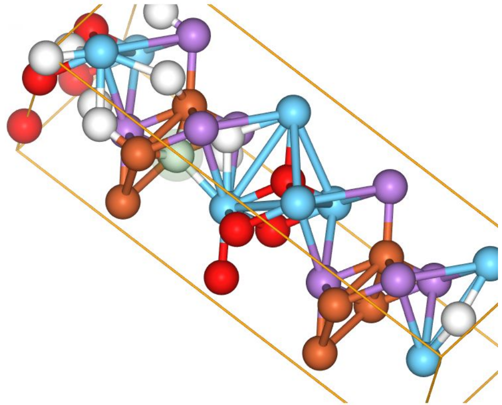

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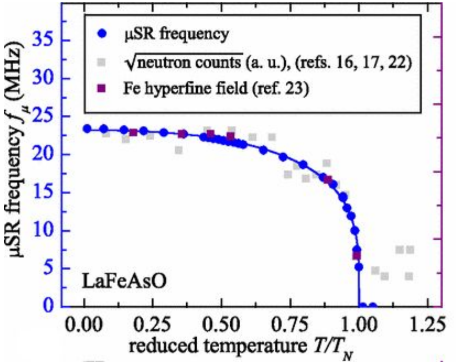
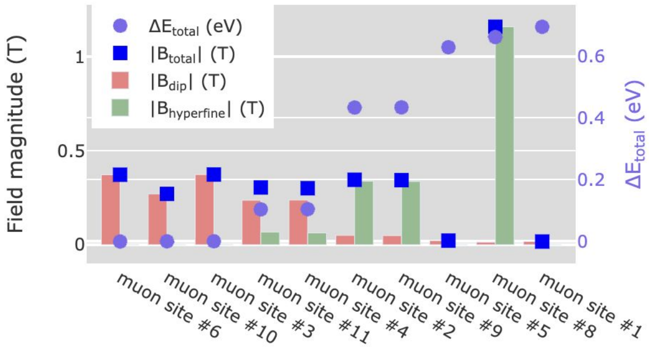


51 MHz or 37 MHz



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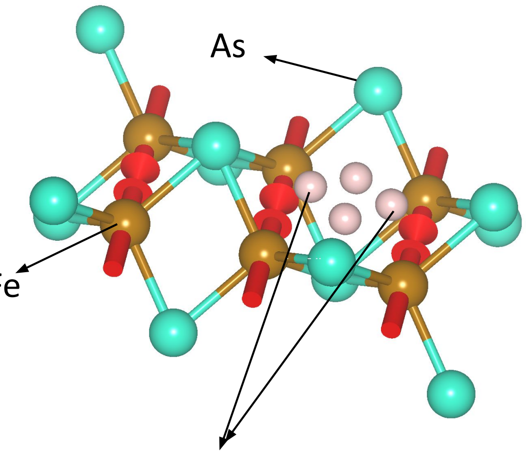

μ^+ sites 6, 10, 3

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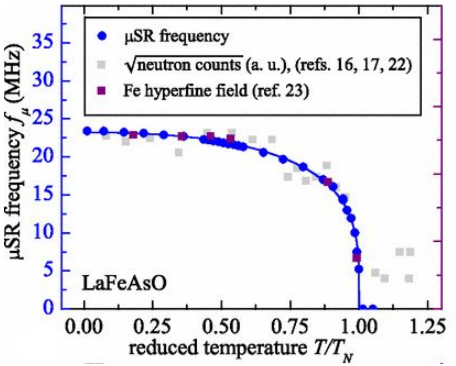

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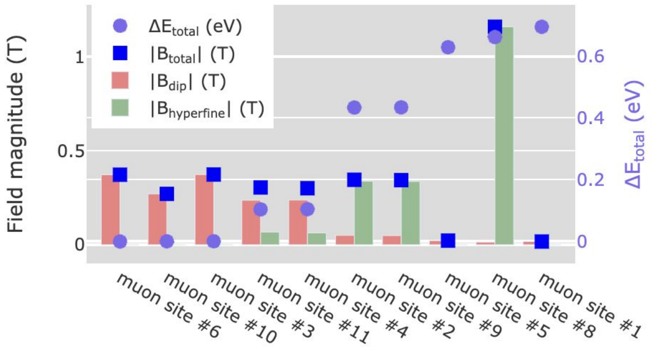
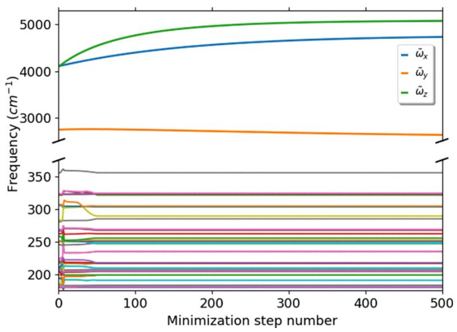
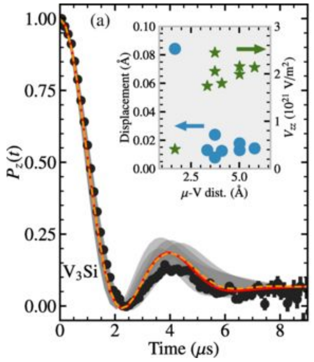


Outlook: further developments and case studies

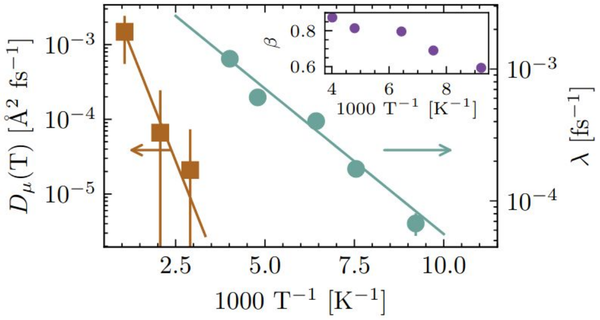
What's still missing?

- Full treatment of nuclear-muon interactions
- PES barriers (NEB and TST)
- Zero-point motion corrections

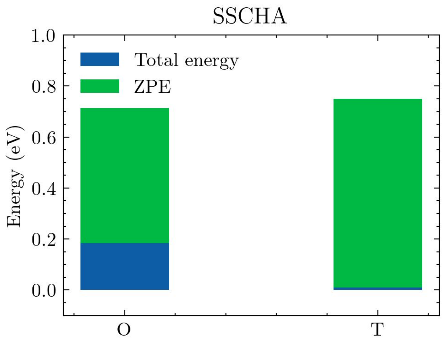




P. Bonfà *et al.*, PRL **129** 097205 (2022)

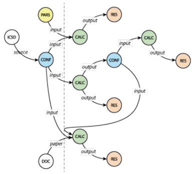


P. Bonfà *et al.*, arXiv:2305.12237 (2023)

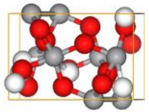


I. Onuorah *et al.*, Phys. Rev. Materials **3**, 073804 (2019)

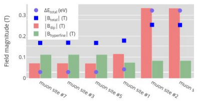
Summary and conclusions



AiiDA-muon workflows and the GUI is ready for use at aiidalab.psi.ch deployed inside PSI network for PSI users.



Already includes static DFT based muon embedding site identification for magnetic and non magnetic systems.



Computes the hyperfine interaction parameters for magnetic systems and nuclear relaxation rate based on second moment approximation.

…more to come in the near future!

Acknowledgements

People

Unipr

Muhammad Makudi Isah
Marcello Mazzani
Roberto De Renzi
Pietro Bonfà

PSI

Giovanni Pizzi
Nicola Marzari

AiiDAlab team

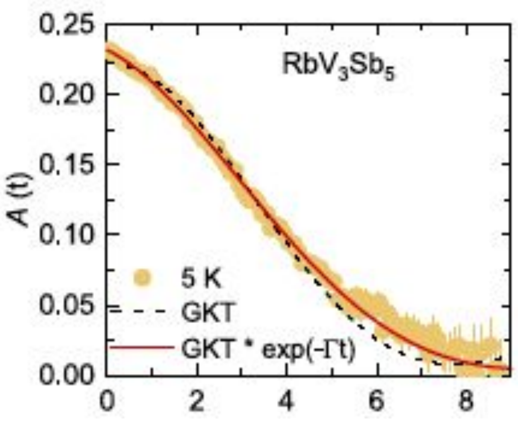
Carlo Pignedoli (Empa)
Aliaksandr Yakutovich (Empa)
Jusong Yu (PSI)
Xing Wang (PSI)
Marnik Bercx (PSI)
Dou Du (EPFL)
Daniel Hollas (Univ. of Bristol)
Andres O. Guerrero (Empa)
Edan Bainglass (PSI)

Benchmark & Validation on;

- V_2O_3
- RbV_3Sb_5 & KV_3Sb_5 & CsV_3Sb_5
- $MoTe_2$ & $MoSe_2$
- $LaRu_3Si_2$

Muon polarization function in $LaRu_3Si_2$

C. Mielke, III, et al, Phys. Rev. Mat 5, 034803 (2021)

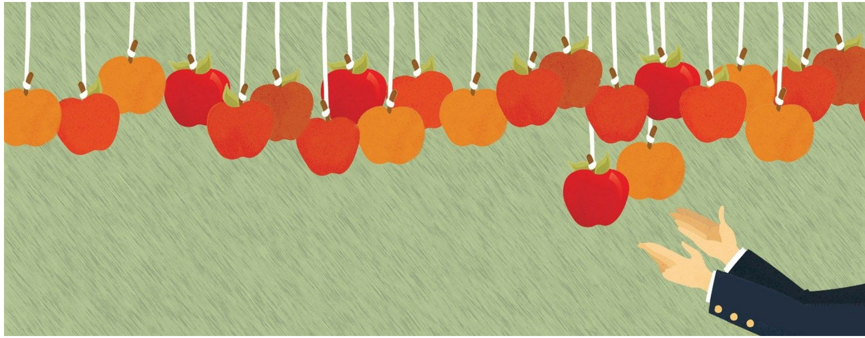


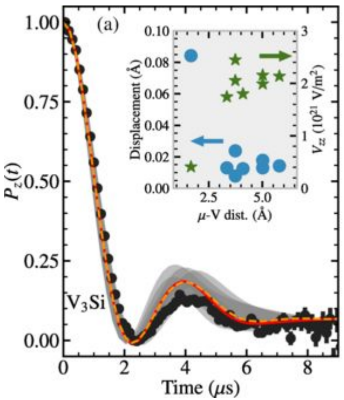
Outlooks - further developments and case studies

What's still missing?

Low-hanging fruits

- Fll treatment ofu nuclear-muon interactions
- PES barriers (NEB and TST)
- Diamagnetic or paramagnetic?
- Muonium hyperfine coupling parameters

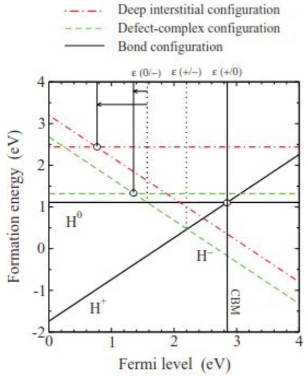




P. Bonfà *et al.*, PRL **129** 097205 (2022)

		A	E_{HA}	$\langle A\rangle_{HA}$	E_{FD}	$\langle A\rangle_{FD}$	A_{exp}
Vac.	Mu	4711					4463
	H_i^0	1480					1420
LiF	Mu	4368	0.50	4256	0.51	4238	4584[27]
	H_i^0	1372	0.18	1361	0.17	1360	1400[28]
NaF	Mu	4389	0.38	4293	0.42	4208	4642[27]
	H_i^0	1379	0.13	1371	0.14	1367	1500[29]
CaF_2	Mu	4610	0.31	4564	0.33	4564	4479[30]
	H_i^0	1448	0.10[a]	1440	0.10	1440	1464[31]
BaF_2	Mu	4605	0.20	4560	0.23	4565	
	H_i^0	1447	0.07	1440	0.07	1440	1424[32]
CoF_2	Mu	1281	0.62	1397	0.59	1535	[b]
	H_i^0	403	0.21	420	0.20	441	

J. S. Möller *et al.*, PRB **87**, 121108R (2013)



$$E_{\rm form}(H^q) = E_{\rm tot}(H^q) - E_{\rm tot}({\rm bulk}) - \mu_H + q(E_F + E_{\rm VBM}).$$

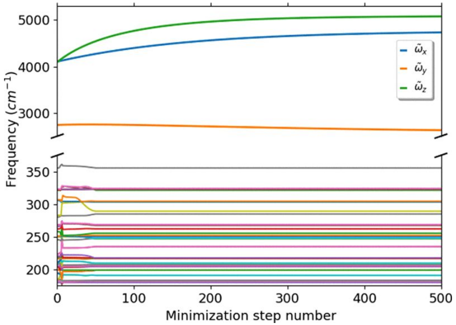
R. C. Vilão *et al.*, PRB **84**, 045201 (2011)

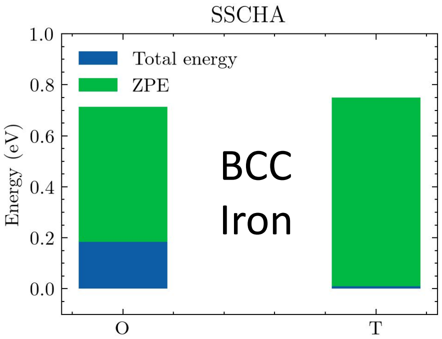
Outlooks - further developments and case studies

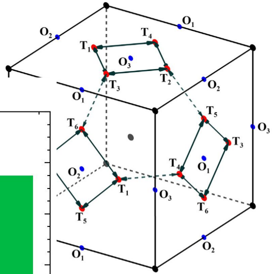
What's still missing?

After low-hanging fruits

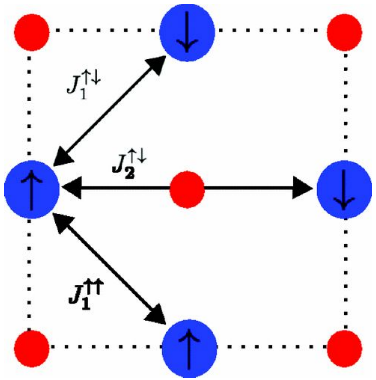
- Zero point motion correction
- Muon site population
- Magnetic fluctuations
  (magnons, crystal-field transitions, …)







I. Onuorah *et al.*, Phys. Rev. Materials **3**, 073804 (2019)



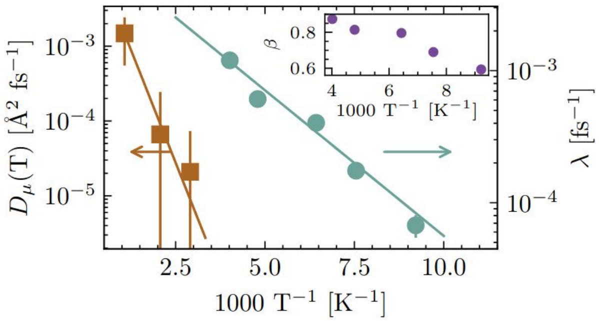
Jacobsson *et al.*, Phys. Rev. B **88**, 134427 (2013)

Outlooks - further developments and case studies

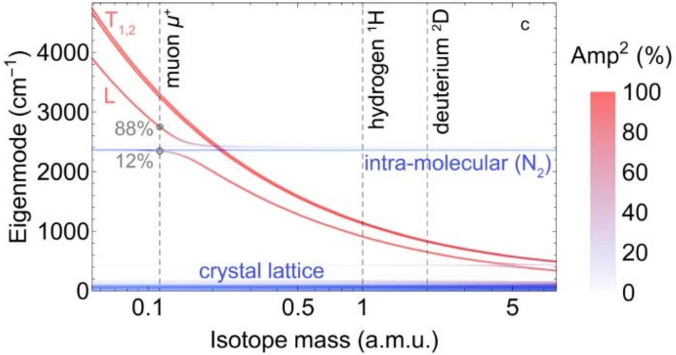
What's still missing?

High-hanging fruits

- Dynamical effects and muon diffusion (classical)
- Quantum motion
- Superfluid density (BCS)



P. Bonfà *et al.*, arXiv:2305.12237 (2023)



M. Gomilšek et al. Commun. Phys. **6**, 142 (2023)

Muon local field in LaFeAsO

H. Maeter, et al., Phys. Rev. B **80**, 094524 (2009)

Summary for all the unique muon sites, sorted by energy:

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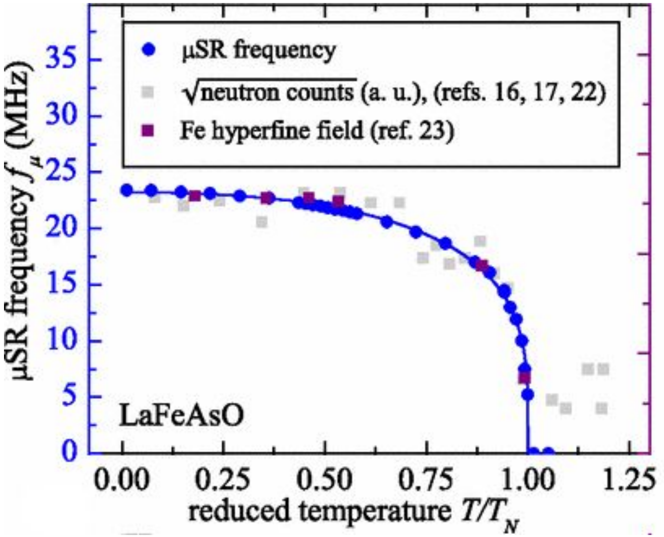
51 MHz or 37 MHz?
Or both?



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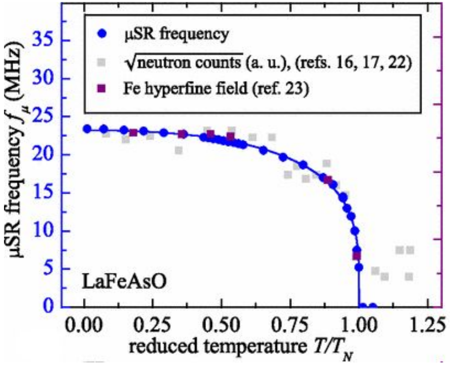

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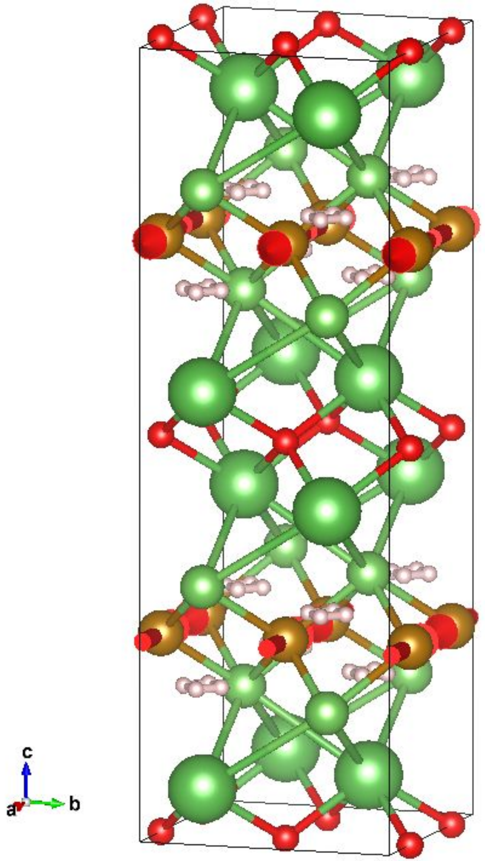

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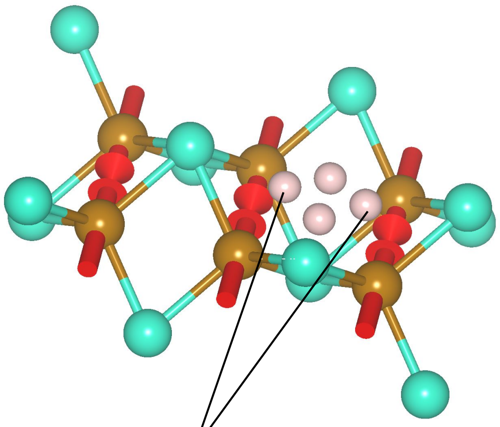

μ^+ site 6, 10, 3

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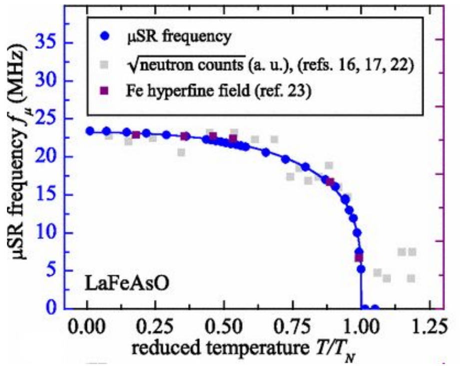

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