DFT+μ : Density functional theory for muon site calculations

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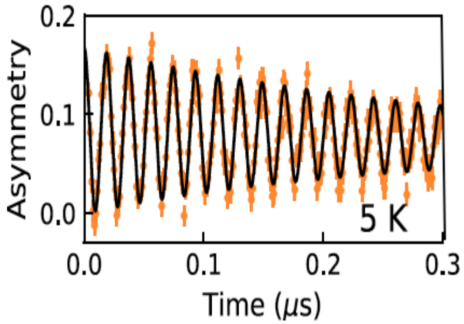
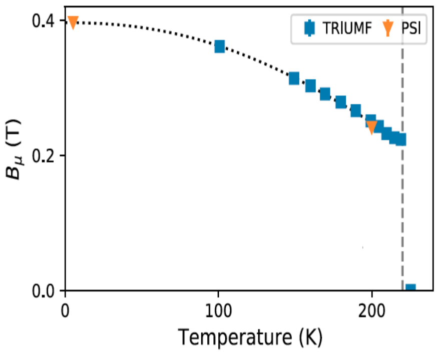
RECAP: Why do we need to know where the muon stops

- CASE I: In magnetic samples, which magnetic fields are probed?

Fe_2P





P. Bonfà et al, Phys. Rev. Materials 5, 044411 (2021)

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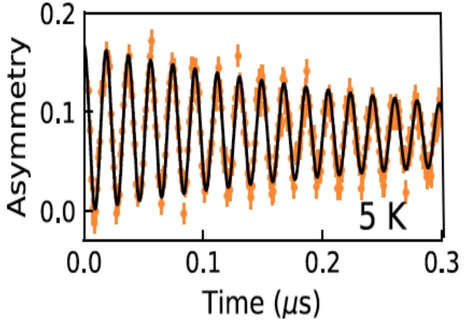

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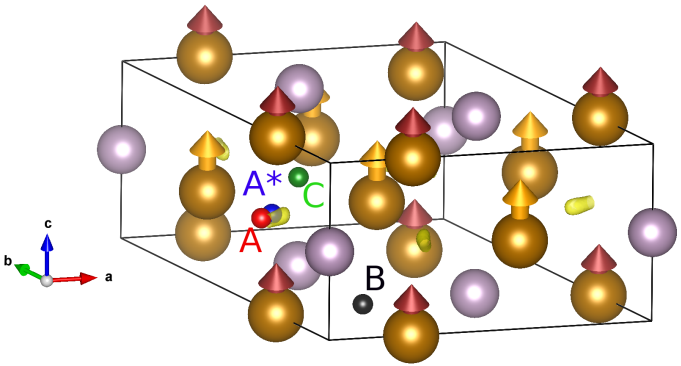
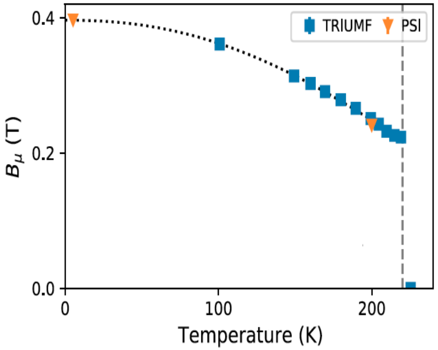
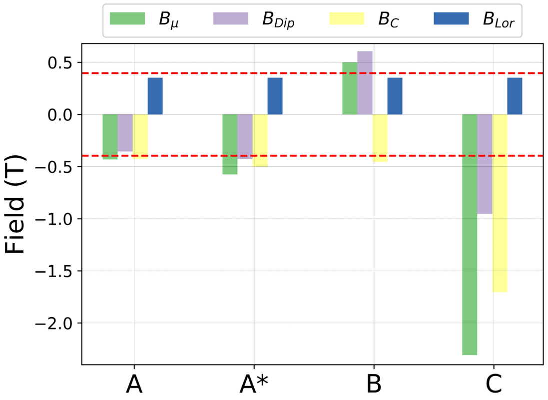


- Knowledge of the muon site required to compute the local field at the muon → obtain the size of the magnetic moment and validate the magnetic order.





$$B_\mu = B_{dip} + B_C + B_L$$

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

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

P. Bonfà et al, Phys. Rev. Materials 5, 044411 (2021)

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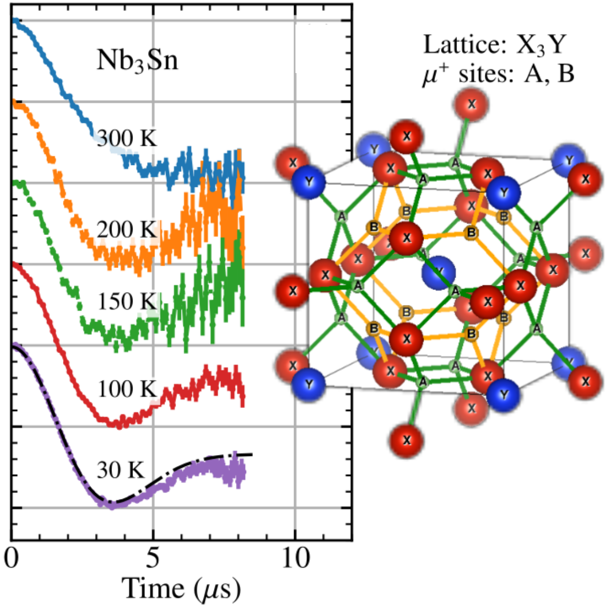
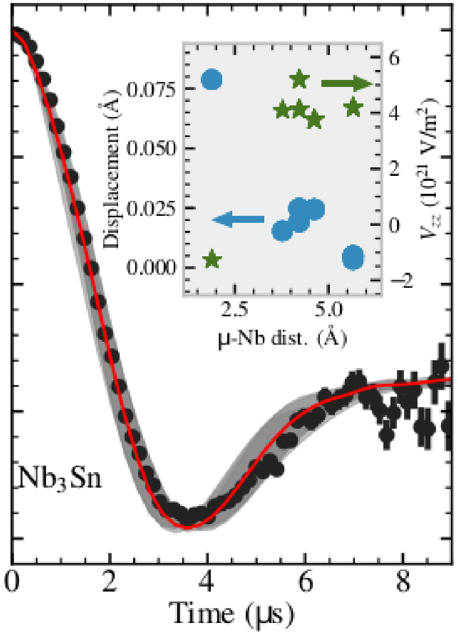
- CASE II: In non-magnetic samples what is the quadrupolar nuclei contributions to muon relaxations?

Nb_2Sn





- First we need to identify where the muon stops in the Niobium intermetallic compound,
- Allows to investigate the entangled states between the muon and the quadrupolar nuclei together with the extreme sensitivity to the local structural and electronic environments

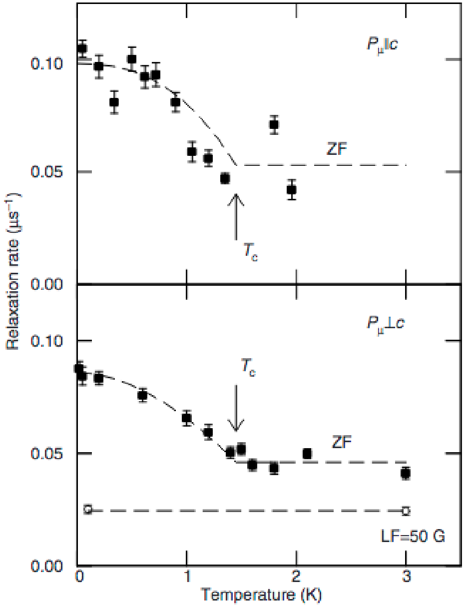
$$H=\sum_i^{N_{nuc}} \frac{\mu_0}{4\pi}\frac{\gamma_\mu \gamma_i \hbar^2}{r_i^3}\boldsymbol{S}_\mu\cdot\boldsymbol{D}^i\cdot\boldsymbol{I}^i+\frac{eQ_i}{2I(2I-1)}\boldsymbol{I}^i\cdot\boldsymbol{V}^i\cdot\boldsymbol{I}^i$$

P. Bonfà et al, Phys. Rev. Lett. 129, 097205 (2022)

RECAP: Why do we need to know where the muon stops

- CASE III: What is the effect of the muon probe in the lattice? Are some of the measured properties induced or intrinsic?

Sr_2RuO_4



- Is the Spontaneous magnetization (signature of TRSB) detected by the increase in the relaxation rate below T_c in Sr_2RuO_4, muon induced?

B.Huddart, I. J. Onuorah et al, Phys. Rev. Lett. 127, 237002 (2021)

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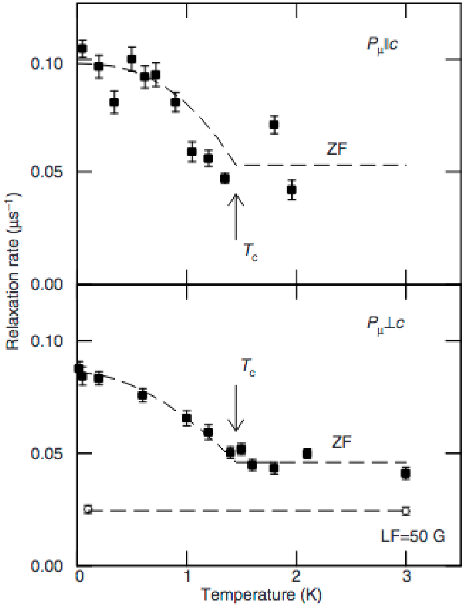

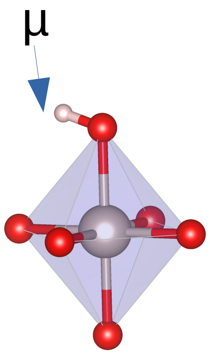

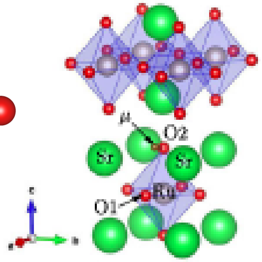

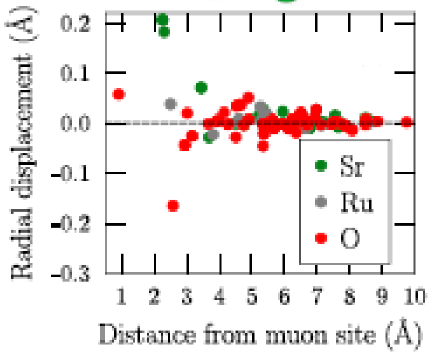

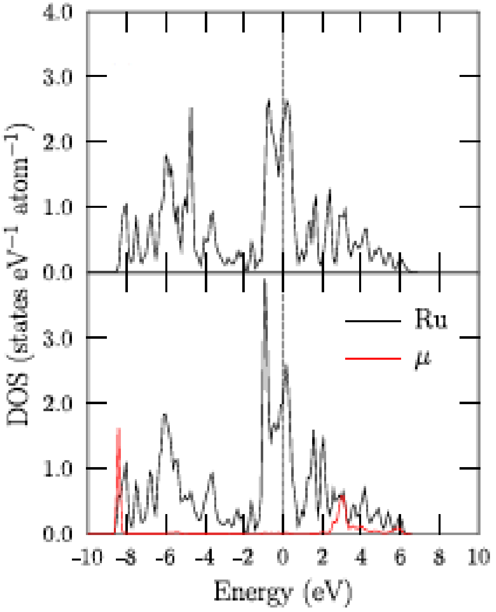

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- the muon is likely not to induce the spontaneous magnetization and that what is measured is intrinsic

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Earlier approaches to identify muon sites

- Measurement of dipolar contribution to the Knight shift in single crystals in a transverse field experiment

- Level crossing resonance method in quadrupolar nuclei

- Validation of random sites with dipolar field simulations and comparison with measured data

- Bayesian approach to determine the magnetic moment.

The Density functional theory (DFT)

… what about Density functional theory (DFT)?

The many body problem

$$\hat{H}_{tot}\Psi(\{\boldsymbol{r_i}\},\{\boldsymbol{R_I}\})=E\,\Psi(\{\boldsymbol{r_i}\},\{\boldsymbol{R_I}\})$$

$$\hat{H}_{tot}=-\sum_i\frac{\nabla_i^2}{2}-\sum_I\frac{\nabla_I^2}{2M_I}-\sum_{i,I}\frac{Z_I}{|\boldsymbol{r_i}-\boldsymbol{R_I}|}+\frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\boldsymbol{R_I}-\boldsymbol{R_J}|}+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r_i}-\boldsymbol{r_j}|}$$

Born-Oppenheimer approximation

$$\Psi(\{\boldsymbol{r_i}\},\{\boldsymbol{R_I}\})=\boxed{\psi(\boldsymbol{r_i},\boldsymbol{R_I})}\,\phi(\boldsymbol{R_I})$$

$$H=-\sum_i\frac{\nabla_i^2}{2}-\sum_{i,I}\frac{Z_I}{|\boldsymbol{r_i}-\boldsymbol{R_I}|}+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r_i}-\boldsymbol{r_j}|}$$

… the one body electronic density contains great amount of information

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

For a known energy functional form E[n(**r**)], the ground state E_o is:

$$min\, E[n(\mathbf{r})] \equiv E[n_o(\mathbf{r})] \equiv E_o$$

Figure 1. Creators of density functional theory. Walter Kohn (left, in 1962) and his two postdoctoral fellows, Pierre Hohenberg (middle, in 1965) and Lu Sham (right, undated), produced their theory in 1964 and 1965. (Photographs courtesy of Walter Kohn and the John Simon Guggenheim Memorial Foundation, Pierre Hohenberg, and Lu Sham.)

$$\frac{\delta E}{\delta n(\mathbf{r})} = \frac{\delta T_o}{\delta n(\mathbf{r})} + \underbrace{v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})}_{\tilde{v}(\mathbf{r})} = \mu$$

$$\left[\frac{-\nabla^2}{2} + \tilde{v}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r}) \longrightarrow$$

Kohn-Sham equation

… ν_{xc} is intended to capture all the not included quantum mechanical effects

$$v_{xc} \approx v_{xc}^{electron-gas}\left[n\left(\boldsymbol{r}\right)\right]$$

Different flavours LDA (LDSA), GGA, etc

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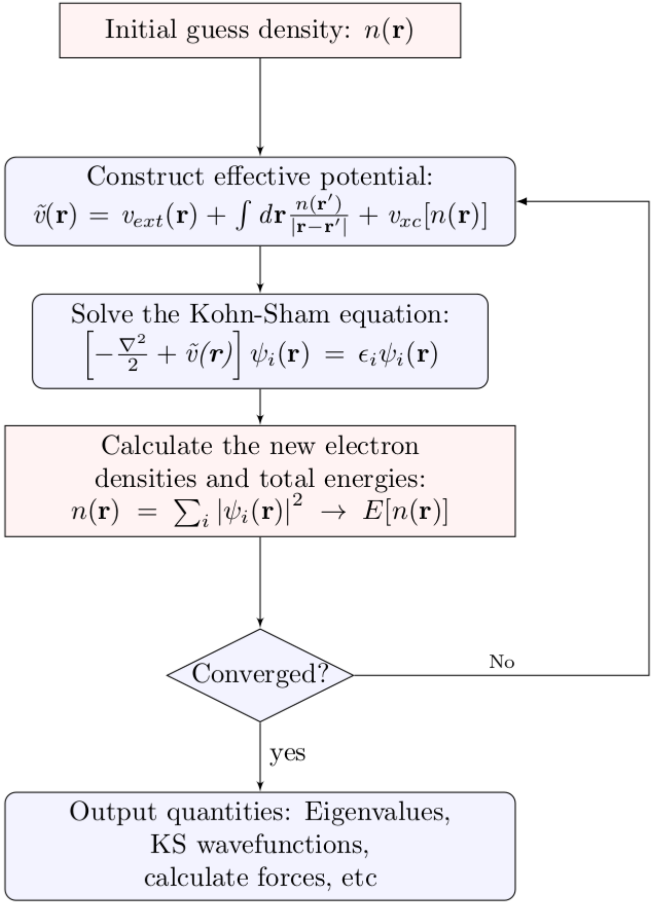
Self-consistent iterative scheme

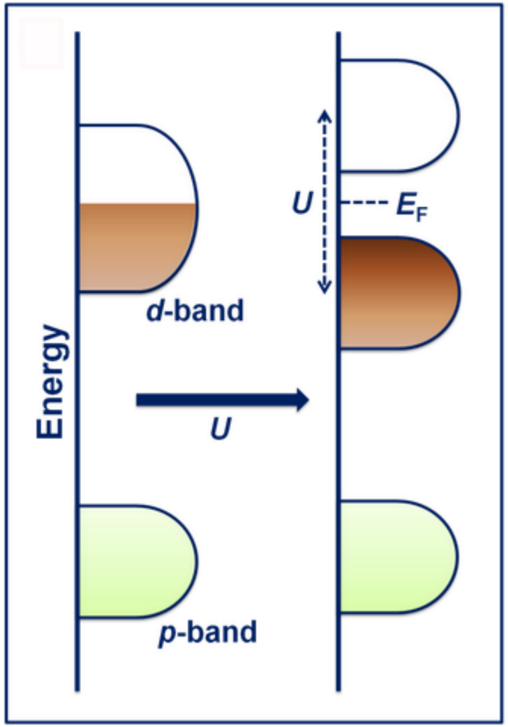


… Simple model in principle, but then the complexity can grow

In strongly correlated electron systems

- Beyond independent electrons to strong collective interactions

Hard cases: 5d, strong Coulomb repulsion (U)



Correction: DFT+U

- Coulomb *d*-*d* interaction:

$$\frac{1}{2} U \sum_{i \neq j} n_i n_j$$

- New functional:

$$E_{DFT+U}[n] = E_{DFT}[n] + E_U[n_i^{\sigma}]$$

Other details required for practical computational use of DFT

$$\psi_{i,k}(\boldsymbol{r}) = \sum_G c_{i,k+G}\, e^{(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

Plane waves basis set

QUANTUMESPRESSO

CASTEP

- The Kohn-Sham equation is computationally solved by expanding its wavefunction with basis set.
- **Flavours**: Gaussian, LCAO, LMTO, PAW, LAPW

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$$\left|\frac{\mathbf{k}+\mathbf{G}^2}{2}\right| < E_{cut}$$

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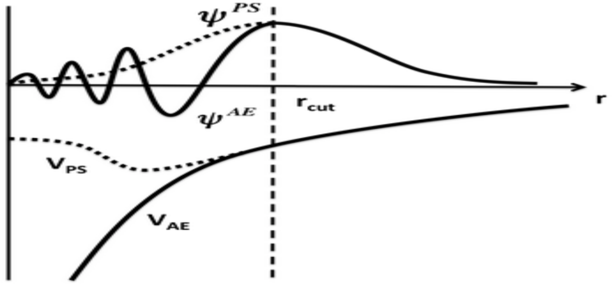

- The Kohn-Sham equation is computationally solved by expanding its wavefunction with basis set.
- **Flavours**: Gaussian, LCAO, LMTO, PAW, LAPW
- Summation truncated over a cut-off energy, This value is an input parameter.
- Plane waves → slow convergence close to the nucleus for rapidly varying functions → **Pseudopotentials.**
- **Flavours:** Norm-conserving, Ultrasoft, PAW method

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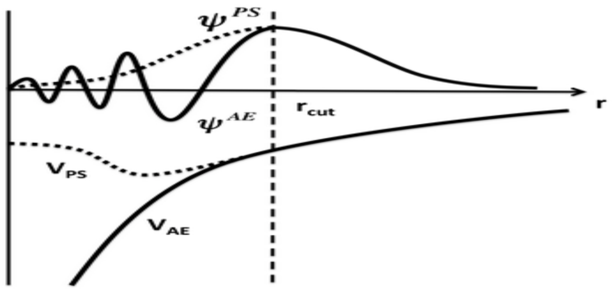

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$$F(\boldsymbol{r})=\int_{BZ} d(\boldsymbol{k})\, F(\boldsymbol{k})=\sum_{k_i\in IBZ} w_i\, F(\boldsymbol{k_i})$$

- K-points for Brillouin zone integration
- **Flavours**: Gamma point, Baldereschi points, Monkhorst-pack uniform grid

Forces: Structural optimization

- Forces + Minimization

Compute forces

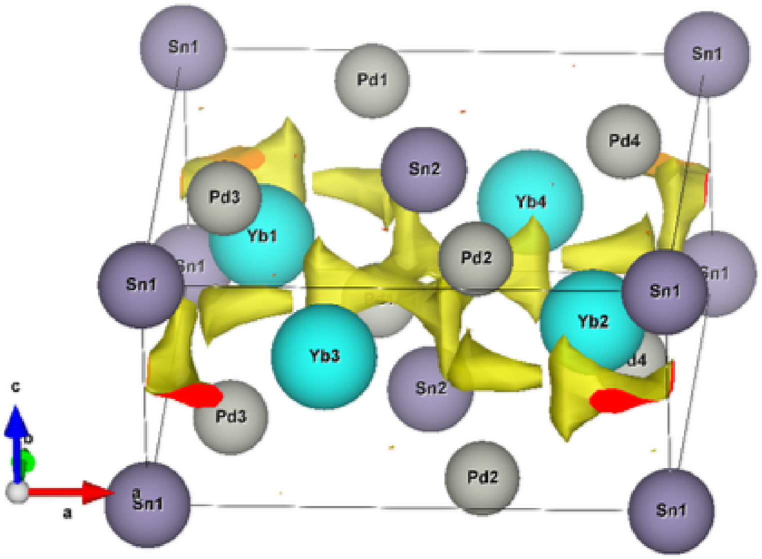
$$\boldsymbol{F}_I = -\langle \Psi(\boldsymbol{R}) | \frac{\partial H(\boldsymbol{R})}{\partial \boldsymbol{R}_I} | \Psi(\boldsymbol{R}) \rangle = \frac{-\partial E(\boldsymbol{R})}{\partial \boldsymbol{R}_I}$$

Hellmann-Feynman theorem

- Computing forces and structural optimization is crucial for finding the muon sites
- Several flavours of minimization schemes

Muon sites inferred from the **minimum of the unperturbed electrostatic potential**

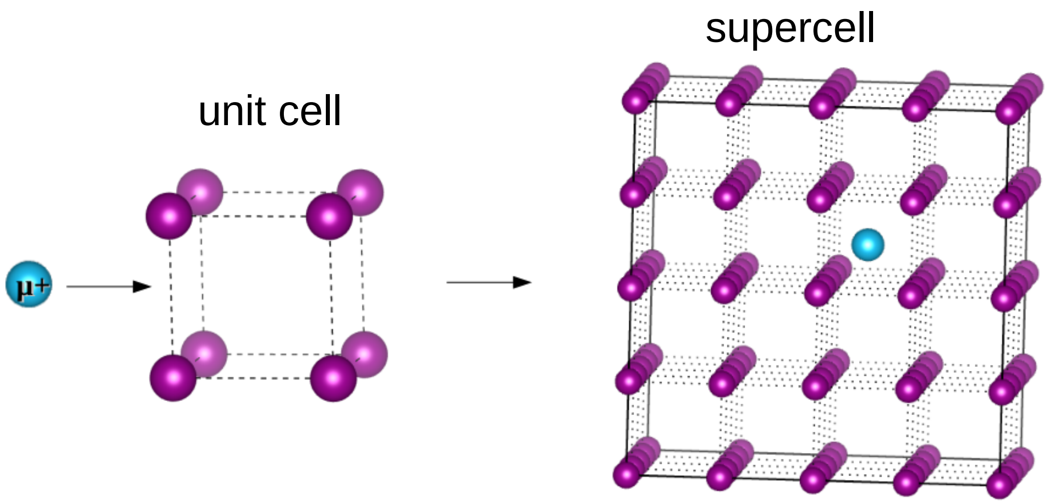
Yb_2Pd_2Sn



- Compute the electrostatic potential without introducing the muon
- The muon position(s) is assumed to be at the minima of the potential
- This method often fails not reliable!

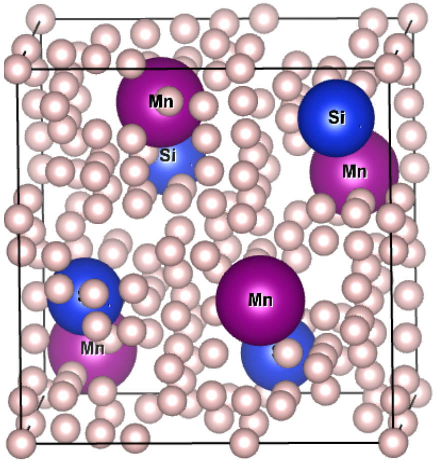
The DFT+μ approach

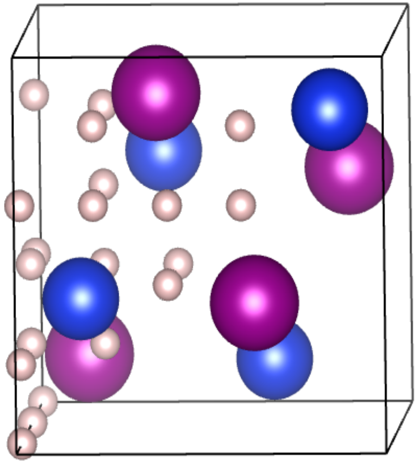
DFT+μ: Adding the muon as an impurity in the model (step I)



- The muon is treated as interstitial defect and represented with the hydrogen pseudopotential
- Supercell: Ensure muon periodic replicas do not interact with each other.
- Compromise between how far we can suppress this artificial interaction and available computational resources.
- Two cases of charge states can be considered: diamagnetic (Mu+ in charged supercell) and the paramagnetic muon (Mu° in neutral supercell).

The procedure (Step II): Initial muon positions



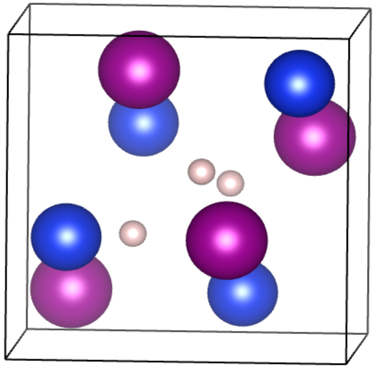


5x5x5 grid to 20 supercells to be calculated

- Where do we add the muon, how do we start?
- Sample the voids in a uniform grid
- Remove symmetry replicas

Step III & IV: Structural relaxations with DFT and analysis of muon sites

Candidate muon sites in MnSi



Candidate Sites	Position	E_I -E_A (eV)
A	(0.542,0.542,0.542)	0.0
B	(0.607, 0.477,0.220)	0.86
C	(0.329, 0.329, 0.329)	1.12

- The supercells with the muon are then relaxed by imposing that forces acting on all atoms vanish.
- Relaxed structures are clustered to eliminate symmetry equivalent muon positions
- Likely produces several different local minima, each with muon in a distinct crystallographic (candidate sites) also distinguished by DFT calculated total energy differences.
- The muon position is determined by the argument of the lowest energy site.
- Note, in some cases muons may occupy more than one site.

Might be resource intensive, high performance computers generally required!

If I now know where the muon stops: I can extract, compute and simulate other properties

Muon local magnetic field

$$B_\mu = B_{dip} + B_C + B_L$$

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

MUESR SOFTWARE

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

DFT post-processing

Nuclei and quadrupolar contributions to muon relaxation

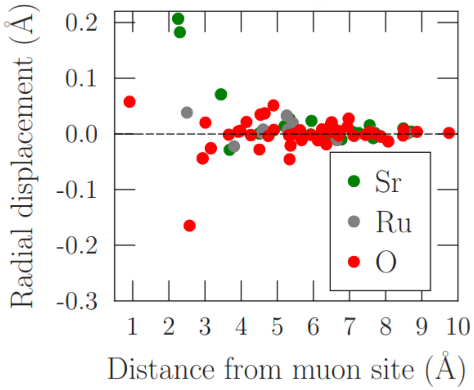
$$H = \sum_i^{N_{nuc}} \frac{\mu_0}{4\pi}\frac{\gamma_\mu \gamma_i \hbar^2}{r_i^3} \boldsymbol{S}_\mu \cdot \boldsymbol{D}^i \cdot \boldsymbol{I}^i + \frac{eQ_i}{2I(2I-1)} \boldsymbol{I}^i \cdot \boldsymbol{V}^i \cdot \boldsymbol{I}^i$$

UNDI SOFTWARE

EFG from

DFT

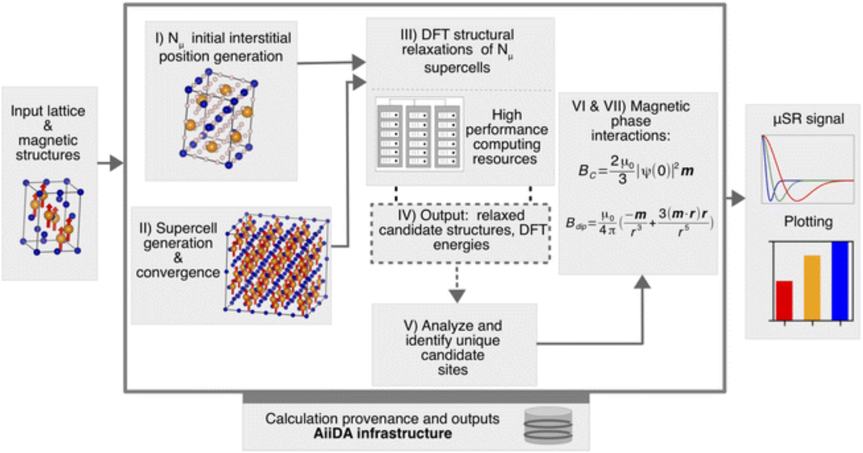
Access muon induced distortion from DFT results



Automating DFT+μ calculations

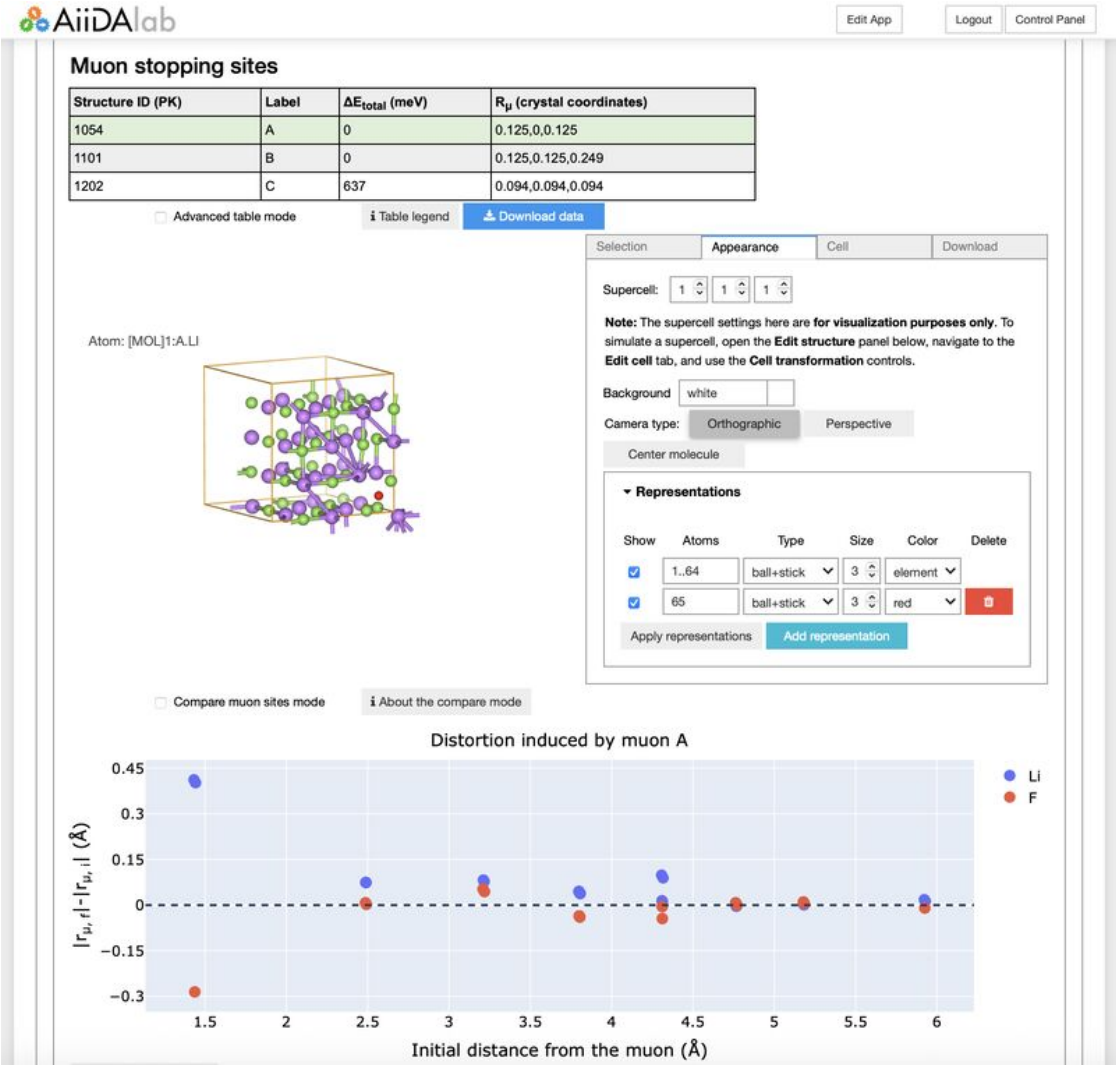
- Promotes ease of use

Build algorithms
and
workflows



- **Tool for the tutorial session**

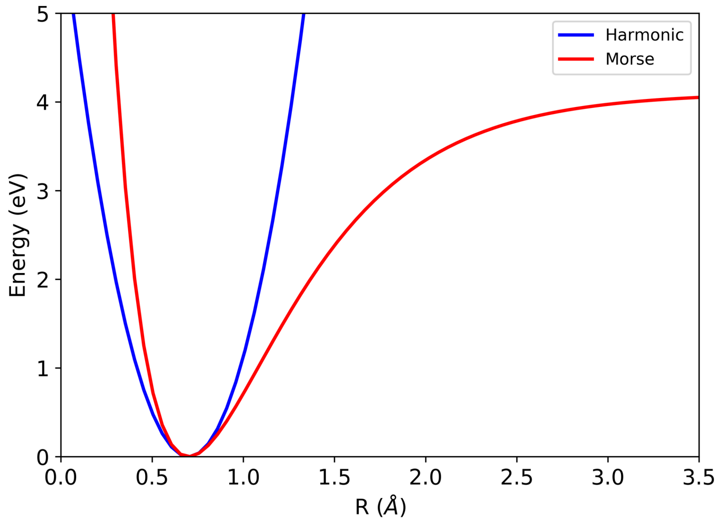
AiiDAlab: The Graphical User Interfaces



I.J. Onuorah, M. Bonacci et al...Digital Discovery, 2025,4, 523-538

More→ Quantum muon effects - The muon zero point motion.

Muon zero point motion is not harmonic



- Remember with Born-Oppenheimer approx., DFT does not treat electrons and the nuclei on same footing. Mass of the muon not considered.
- Muon has very light mass (1/9 of proton mass), vibration estimated to be of amplitude of 1 Bohr radius.
- Required in some cases to stabilize the muon positions and their interaction.
- Mostly considered post DFT within the harmonic approximation
- But the muon vibrations are anharmonic
- Can be computationally demanding!!!

P. Bonfà, F. Sartori, R. De Renzi, . Phys. Chem. C 2015, 119, 8, 4278–4285 (2015), I. J. Onuorah, et. al. Phys. Rev. Mat. 3, 073804, (2019) Thank you!

Next, hands on tutorial session with the Aiidalab-demo

DFT+μ & tools - relevant references:

[1] S. J. Blundell , R. De Renzi , T. Lancaster and F. L. Pratt , *Muon Spectroscopy: An Introduction* , Oxford University Press, (2021).

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[3] J. S Möller, P Bonfà, et al “*Playing quantum hide-and-seek with the muon: localizing muon stopping sites*” Physica Scripta 88 (6), 068510 (2013).

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[6] X. Wang, ..., M. Bonacci, et. al., “*Making atomistic materials calculations accessible with the AiiDAlab Quantum ESPRESSO app*”, in preparation, 2025.

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[8] P. Bonfà, I. J. Onuorah, & R De Renzi “Introduction and a Quick Look at MUESR, ...”, JPS Conf. Proc. 21, 011052 (2018)

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[13] Stephen J Blundell et. al, “Electronic structure calculations for muon spectroscopy” Electron. Struct. 7 023001 (2025).