Computer Simulations for Interpreting μSR Experiments: Beyond DFT

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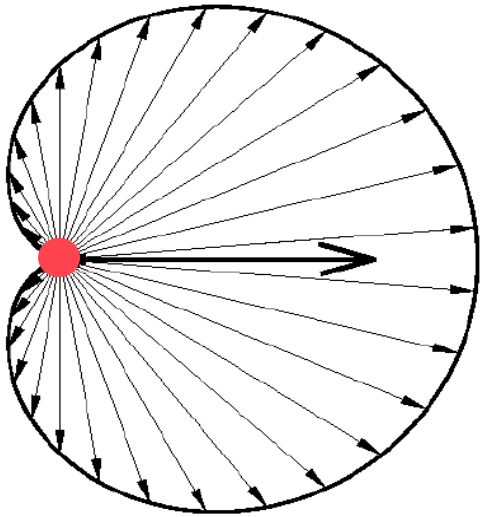

1

Where is the muon? What have been tried and how we could complement it. Our version of the UEP method.

2

DFT combined with Ab Initio Random Searching and Machine Learning. Some examples

3

How to accelerate High Throughput Calculations: CASTEP vs DFT+.

4

Conclusions. Work in progress. Future plans.

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EXPERIMENTAL APPROACH

- Muonated Fe: follow the evolution of the muon frequency shift in a transverse field experiment as a function of the applied stress in a single Fe crystal (PRB **32**, 293, 1985).

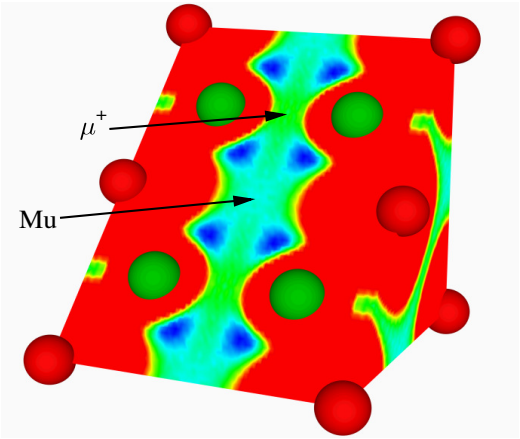
COMBINED THEORETICAL / EXPERIMENTAL APPROACH

- Muonated LiF and $Cu(pyz)(NO)_3$: the theoretical calculations are used for testing different potential muon stopping sites.

THEORETICAL APPROACH?

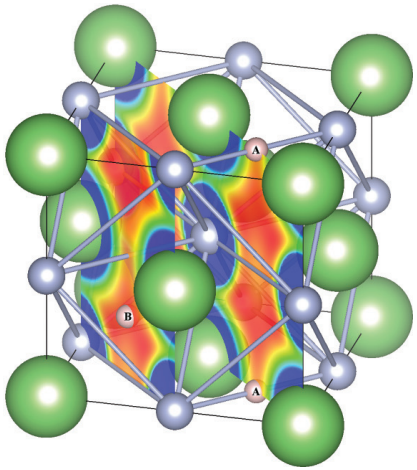
- Analysis of the DFT's electrostatic potential of the bulk material. This is know as the **Unperturbed Electrostatic Potential Method (UEP)**

μ^+ and μ^+e^- in CaF



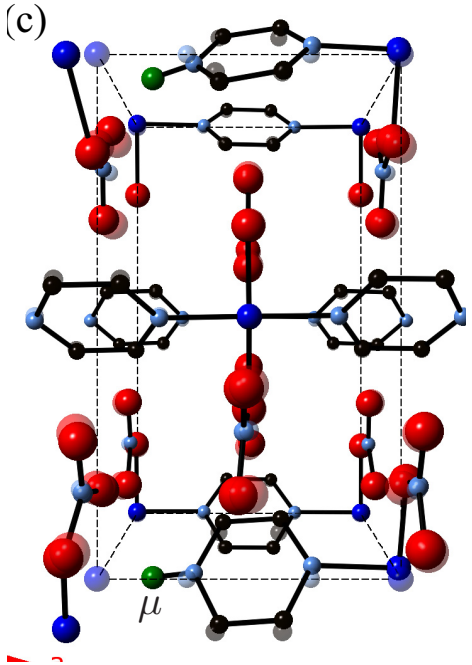
PRB **87**, 121108(R) (2013)

μ^+ in YF_3

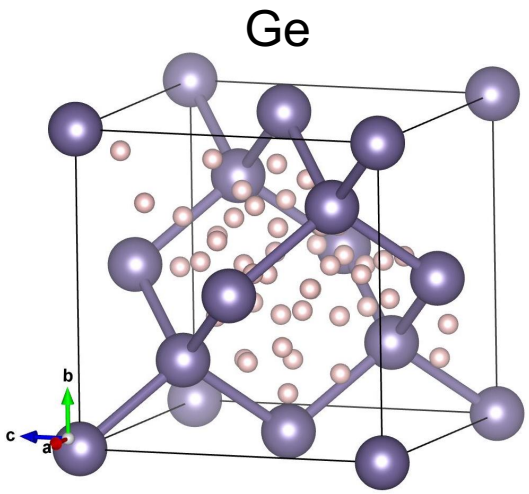


PRB **87**, 115148 (2013)

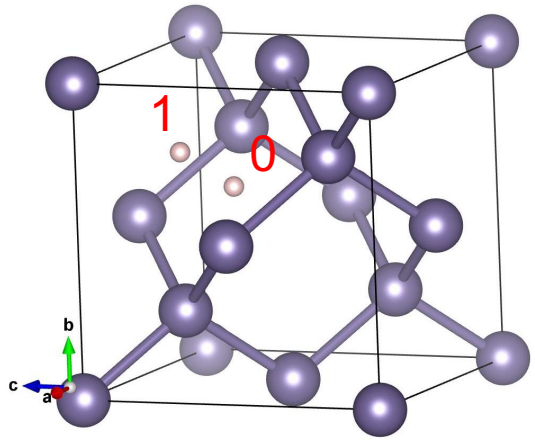
μ^+ and μ^+e^- in $Cu(pyz)(NO)_3$



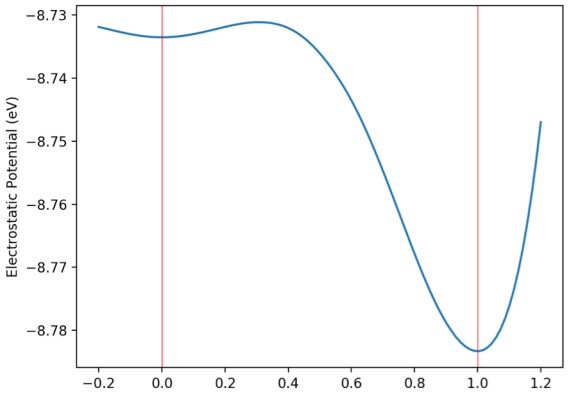
PRB **91**, 144417 (2015)



- Calculate electrostatic potential of unperturbed host material using DFT
- Randomly locate μ^+ in the host's unit cell (Ge in example)

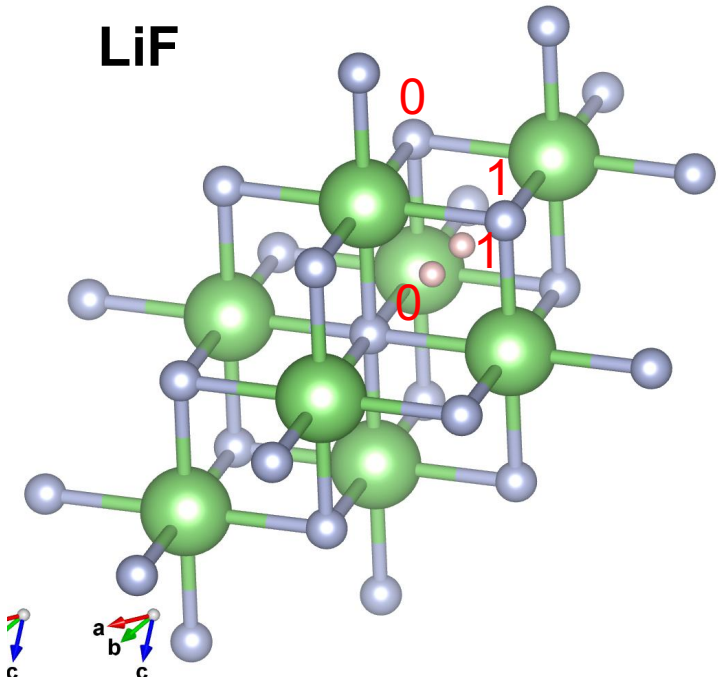


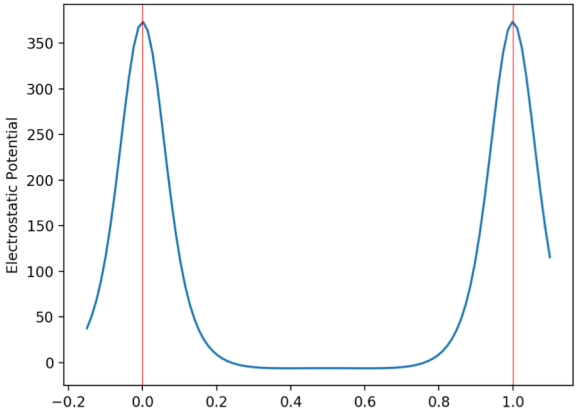
- Calculate classical forces on the μ^+ .
- Relax μ^+ to the potential minima. Identify clusters.
- Create supercell and test sites.



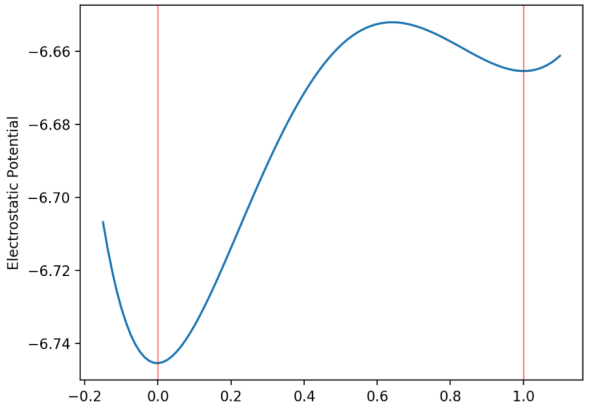
- Plot potential along the line joining 0-1.
- 1 is more likely to be an stopping site.

LiF



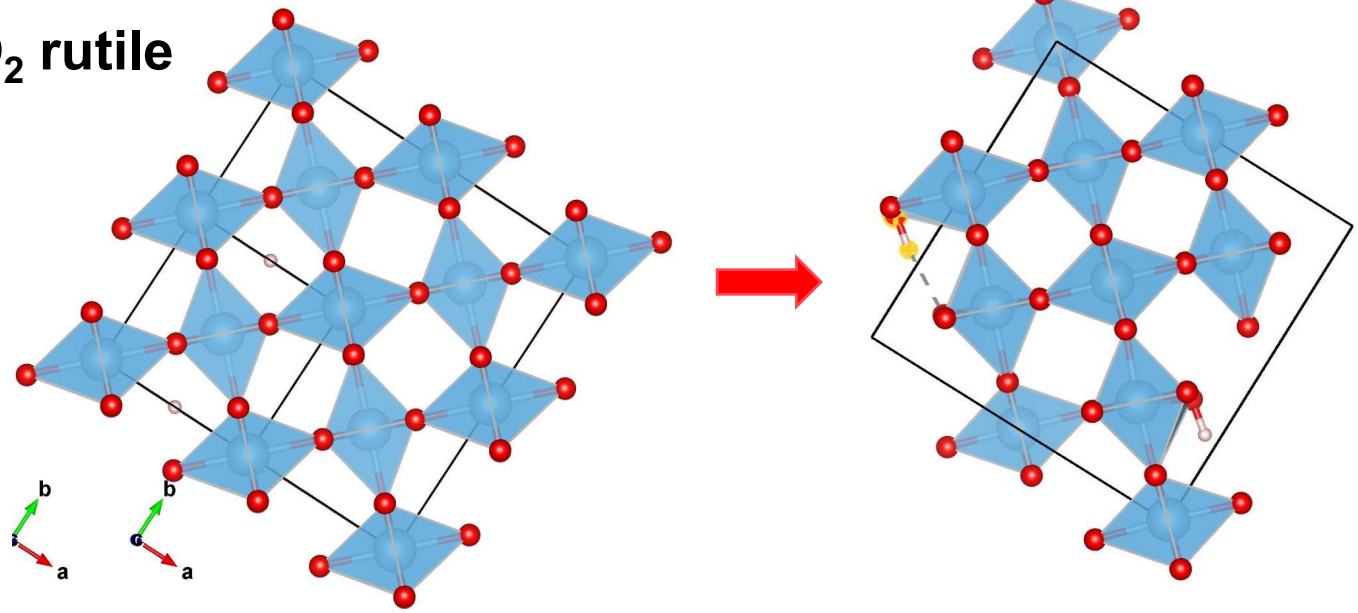


F-F potential



Mu-Mu potential

TiO_2 rutile



Testing on:
KCl
CdS
ZnO
MgO
GaAs
(**Thomas Dack**)

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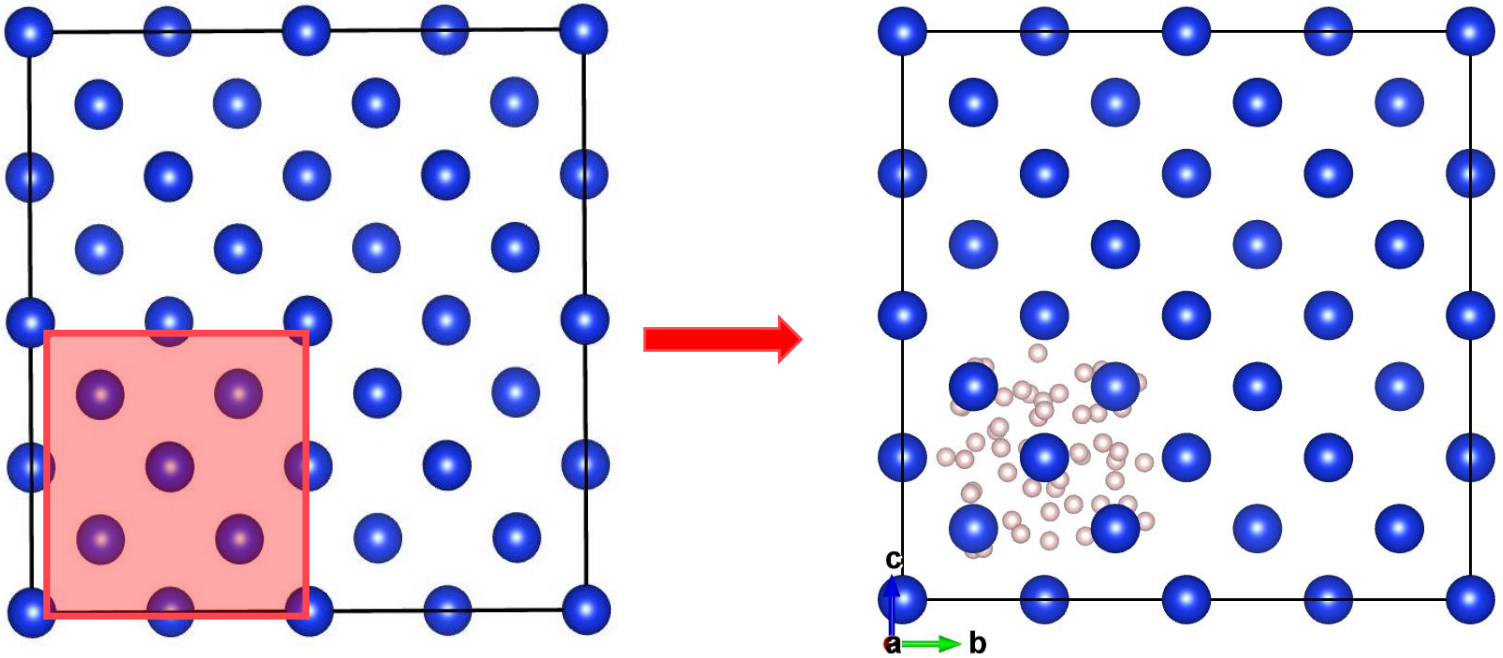
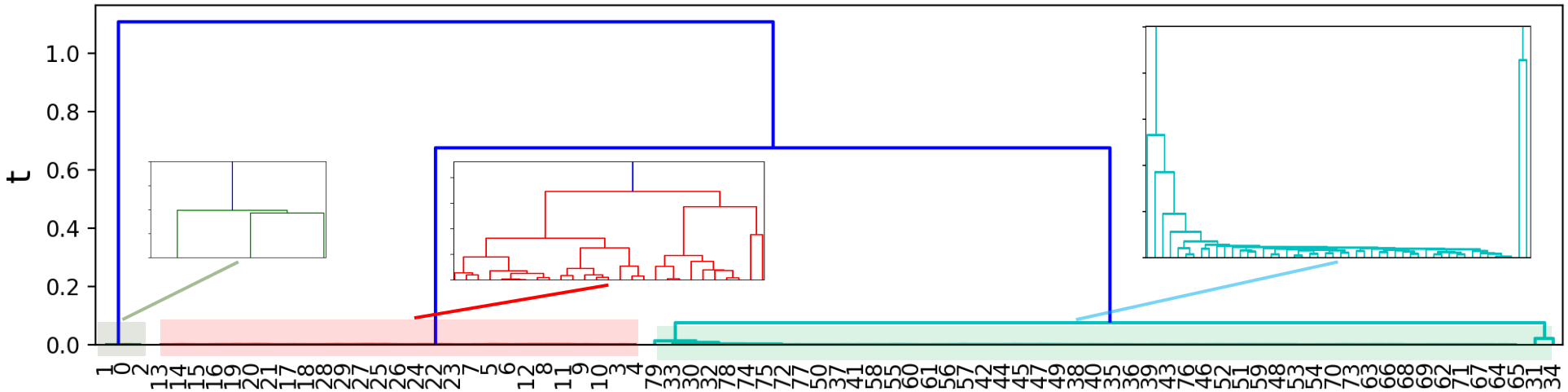
2) Define region to randomly locate muonium pseudo-atoms
3) Generate muonated structures placing muonium in randomised positions within the chosen region
4) Relax filtered structures using calculated DFT forces

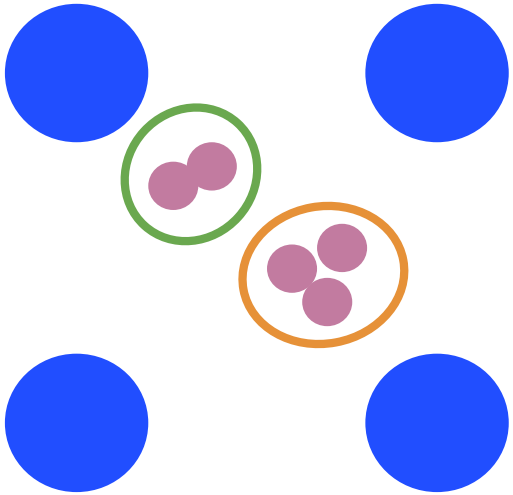
2x2x2 Si supercell

80 structures



L. Liborio, S. Sturniolo and D. Jochym, The Journal of Chemical Physics, 148, 134114 (2018)

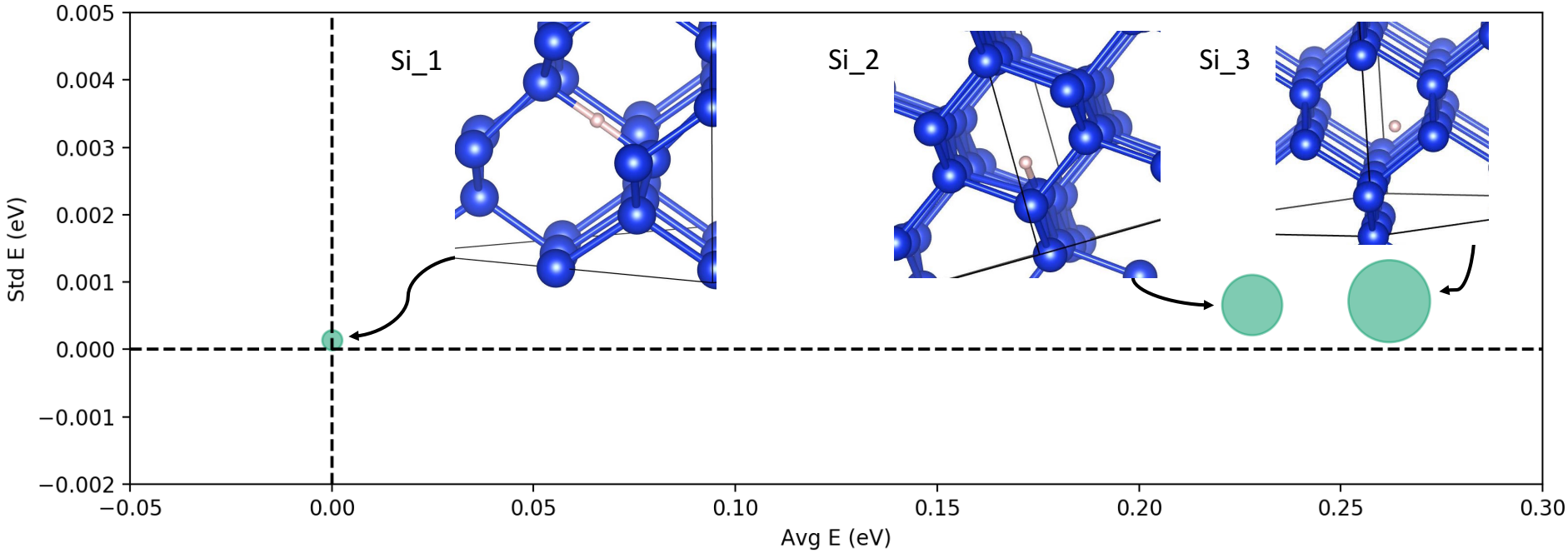


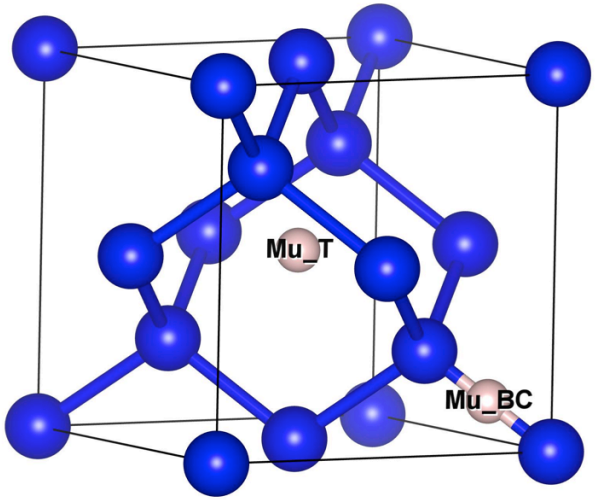


- **Define *n*D vector: (E_T, Q_1, Q_2, Q_3,…)**
- Look for “closeness” in *n*D space
- Hierarchical clustering
- 3 clusters identified

SOPRANO

Python library Soprano (CCP NC) https://github.com/CCP-NC/soprano





- Identified 3 clusters
- Use k-means clustering
- Iidentified the Mu_T and M_{BC} in Silicon.
- **High throughput method.**

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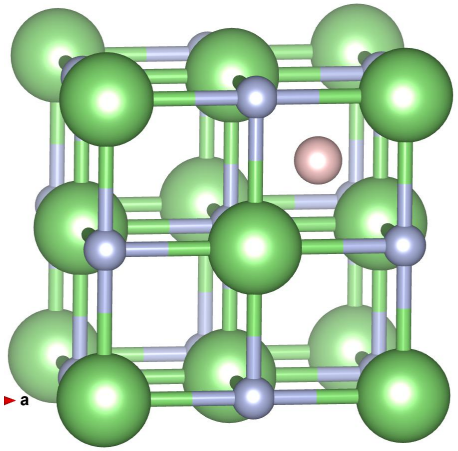
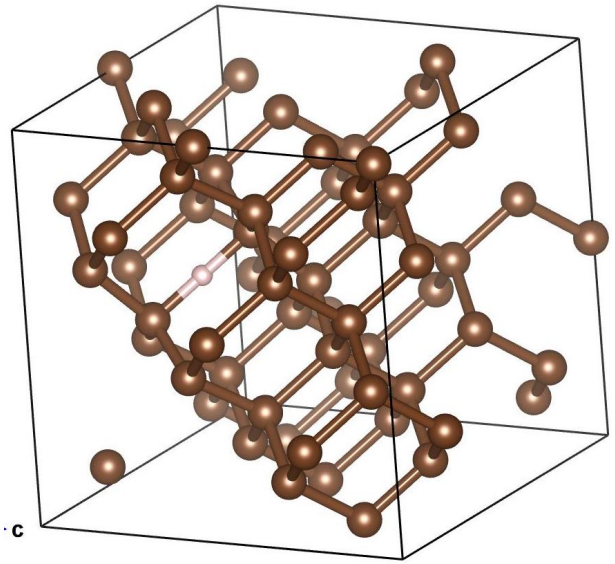
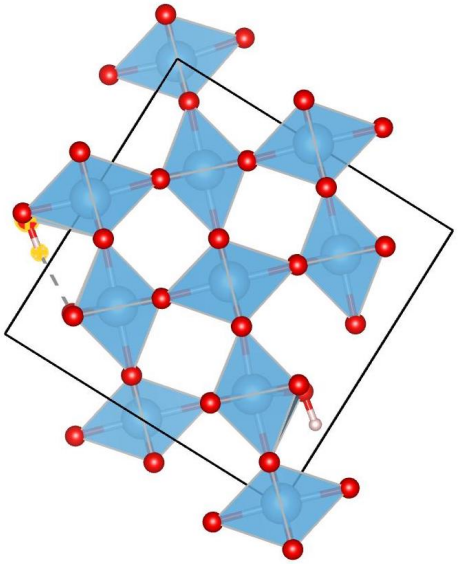


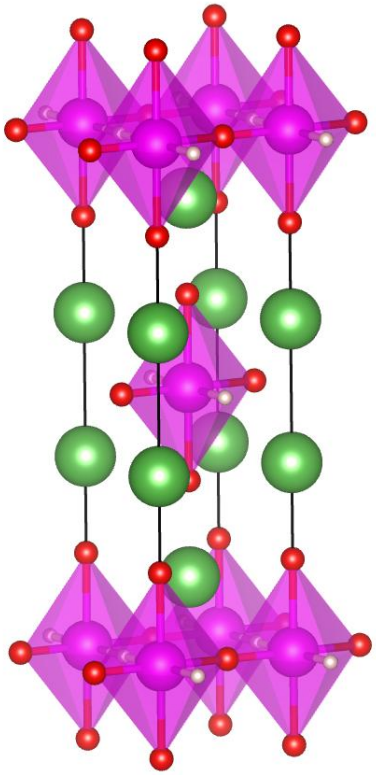
LiF



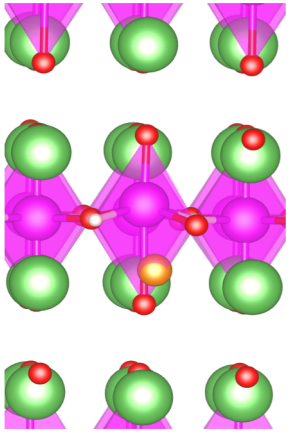
Diamond



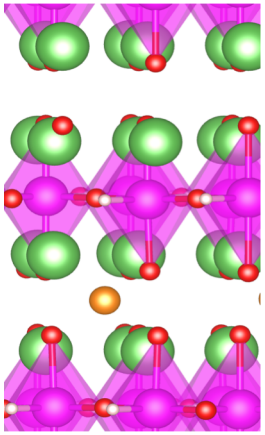
TiO_2- rutile



La_2LiHO_3



Site 1



Site 2

Collaboration with University of Oslo, Norway and ISIS

High throughput method.

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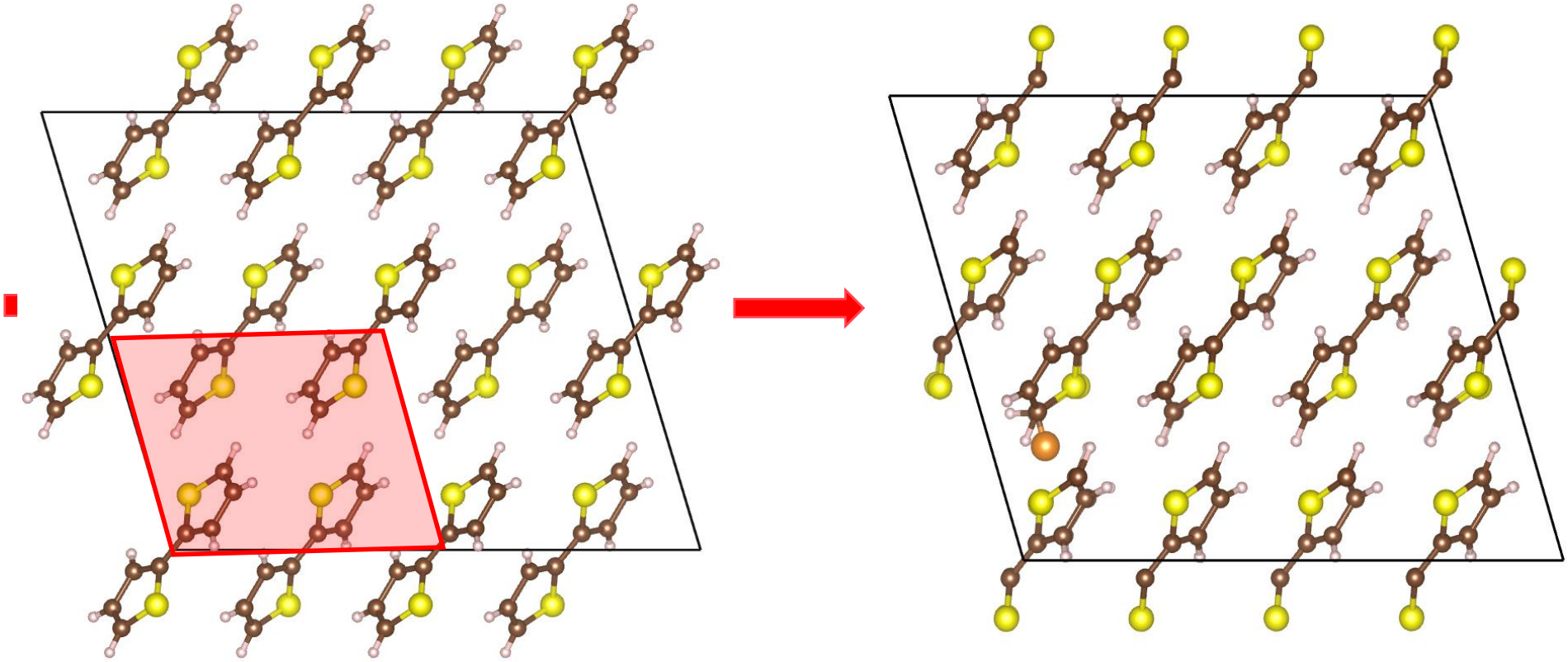
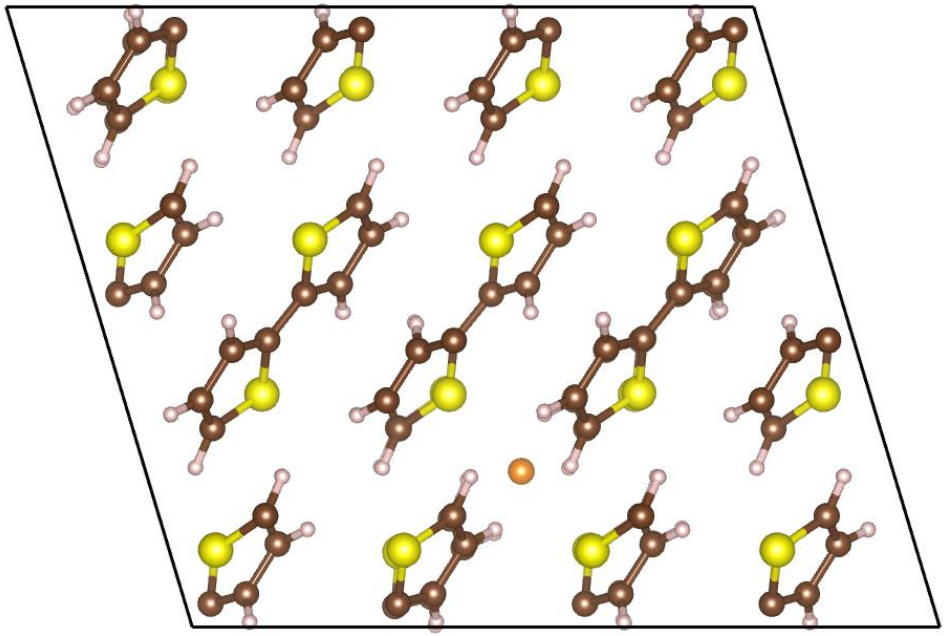
Conclusions. Work in progress. Future plans.

1) Build 2x2x2 Bithiophene supercell
2) Define region to randomly locate muonium pseudo-atoms
3) Generate muonated structures placing muonium in randomised positions within the chosen region
4) Relax filtered structures using calculated **DFTB+ forces. Reliable parameters for organic systems.**

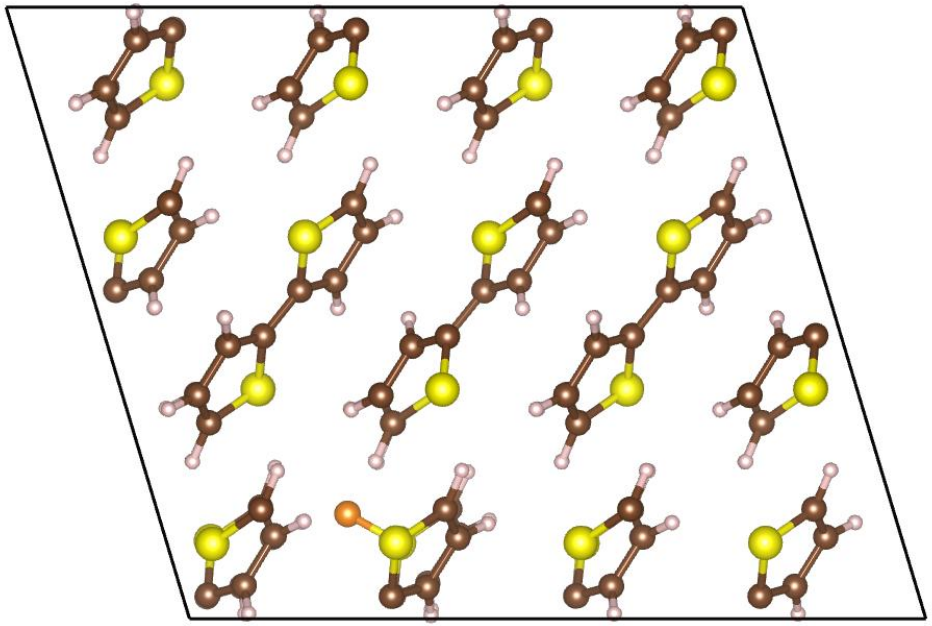


1) **Divide the sites in 'floating' and 'bounded' sites**
2) **Reduce all muonated structures to asymmetric unit cell**
3) **Define *n*D vector: (E_T, x, y, z)**
4) Look for "closeness" in *n*D space
5) Hierarchical clustering
6) Found five stopping sites

Work done with
Samuel Jackson



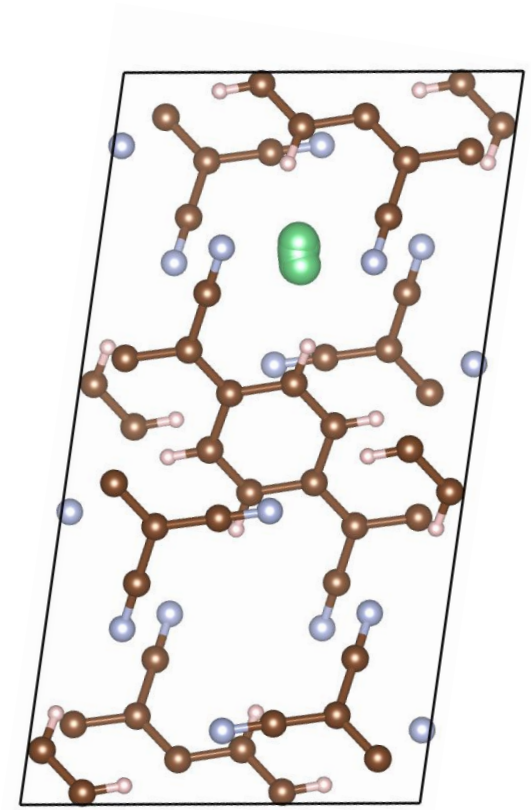
Floating site



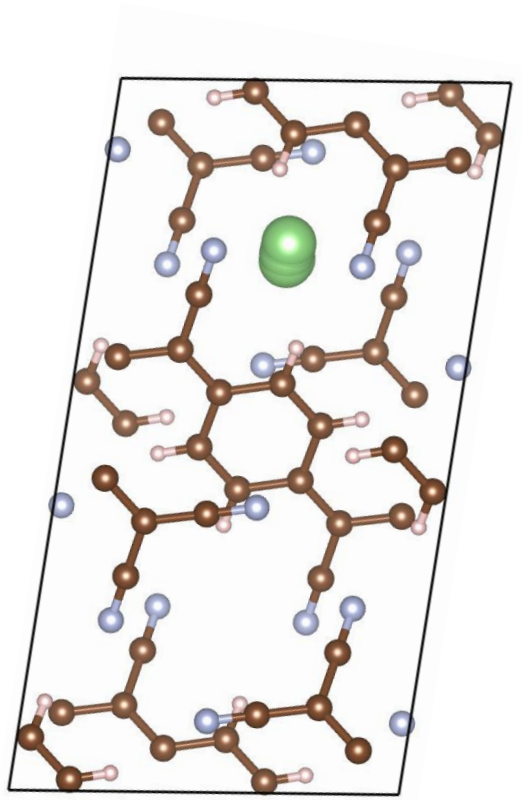
Bounded site

Sites in reasonable agreement with experiments (Except from the floating site)

- Method at least two orders of magnitude faster than the one using standard DFT.
- Tested for bithiophene and benzene and finalizing tests for TCNQ.
- Only works in organic materials composed simple atoms (Br, C, Ca, Cl, F, H, I, K, Mg, N, Na, O, P, S, Zn)
- Are floating sites real?



TCNQ CASTEP



TCNQ DFTB+

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- We are developing computational methods to **estimate the stopping sites of muons** in crystalline materials. These methods **complement** the known methodologies used for predicting the muon stopping sites. In fact, we have developed our own flavor of the UEP method.

- Our methods utilize **DFT and DFTB+ calculations,** combined with the **random generation** of potential muonated structures and the use of **machine learning techniques** to efficiently search for clusters in these structures.

- The **Python library Soprano** is used to implement the method and identify the clusters

- Our methods **predicted** muon stopping sites in Si, Ge, Diamond, LiF, TiO_2, La_2LiHO_3, Bithiophene, Bencene and TCNQ.

- We are testing the UEP method with a set of materials.

- Working on the implementation of these techniques for a general user.

- Will work on computational tools for interpreting quadrupolar level crossing resonance (QLCR) results in muSR (Beamtime requested for experiments).

- Will work on quantum tunnelling of muonium via radical states in molecular solids (Beamtime requested for experiments).

- The problem of quantum effects.

JOCHYM

STURNIOLO

LIBORIO

PRATT

JACKSON

DACK

COTTRELL