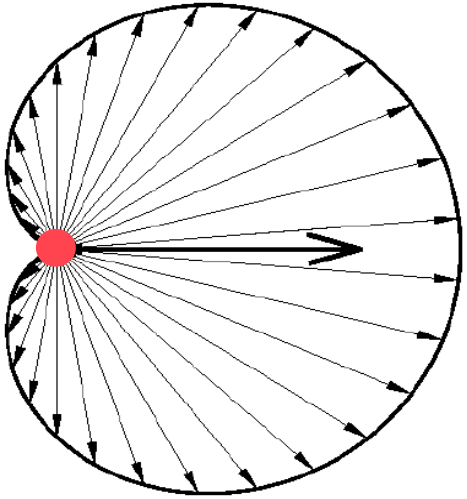
Computer Simulations for Interpreting μSR Experiments: Beyond DFT

Leandro Liborio, Simone Sturniolo, Dominik Jochym, Samuel Jackson, Thomas Dack

Theoretical and Computational Physics Group, SCD, STFC

Francis Pratt, Stephen Cottrell

ISIS Muon Group, STFC



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.

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.

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).

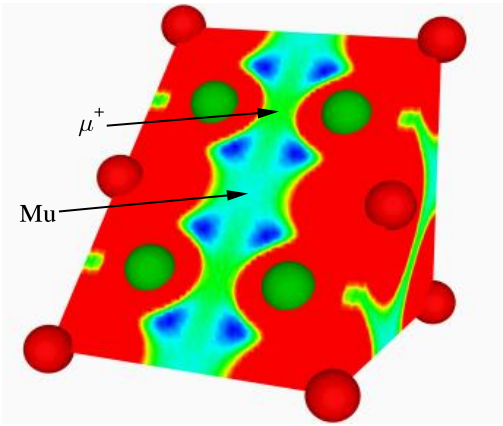
COMBINED THEORETICAL / EXPERIMENTAL APPROACH

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

THEORETICAL APPROACH?

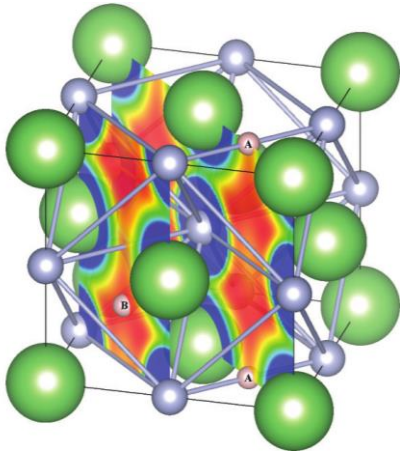
•Analysis of the DFT's electrostatic potential of the bulk material. This is know as the **Unperturbed Electrostatic Potential Method (UEP)**

μ^+ and μ^+e^- in CaF



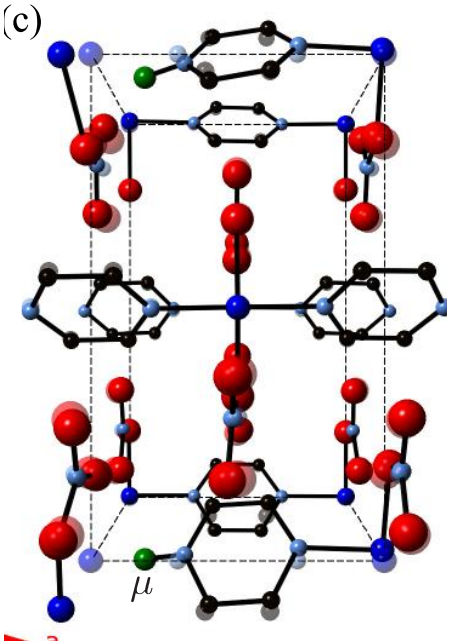
PRB **87**, 121108(R) (2013)

μ^+ in YF_3

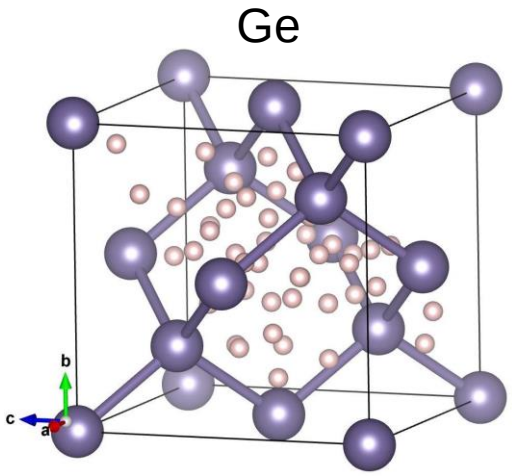


PRB **87**, 115148 (2013)

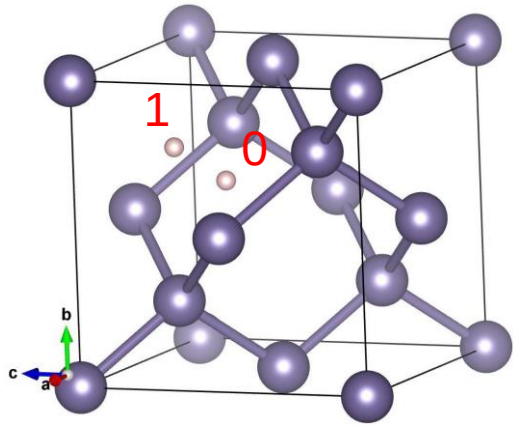
μ^+ and μ^+e^- in $Cu(pyz)(NO)_3$



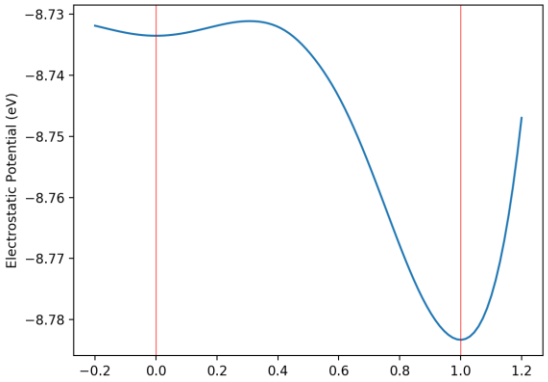
PRB **91**, 144417 (2015)



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

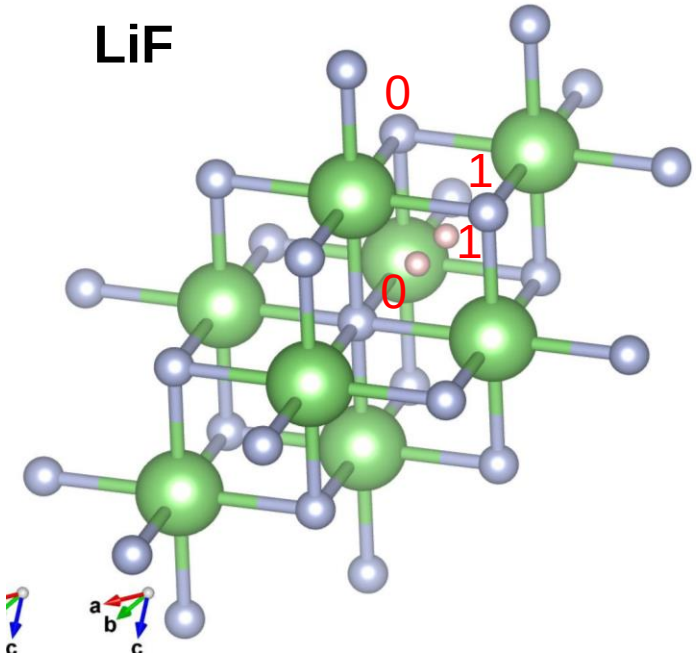


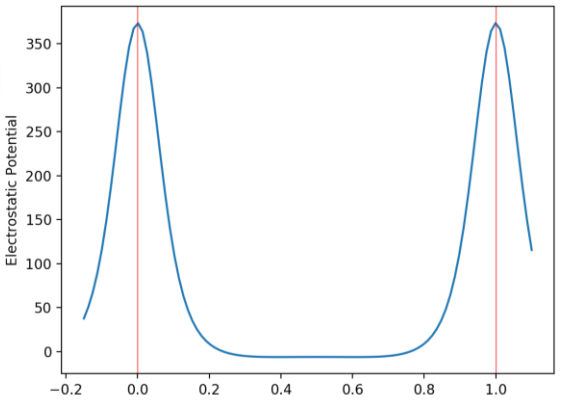
- Calculate classical forces on the μ^+ .
- Relax μ^+ to the potential minima. Identify clusters.
- Create supercell and test sites.



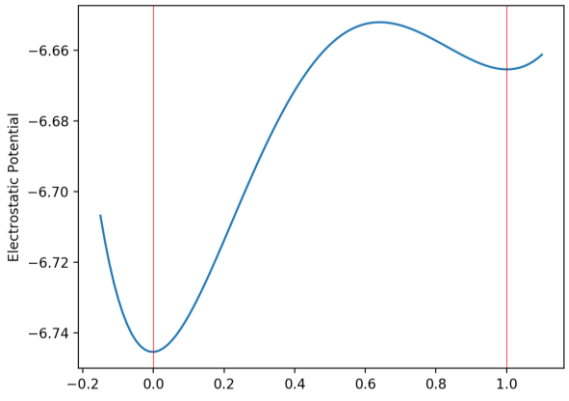
- Plot potential along the line joining 0-1.
- 1 is more likely to be an stopping site.

LiF



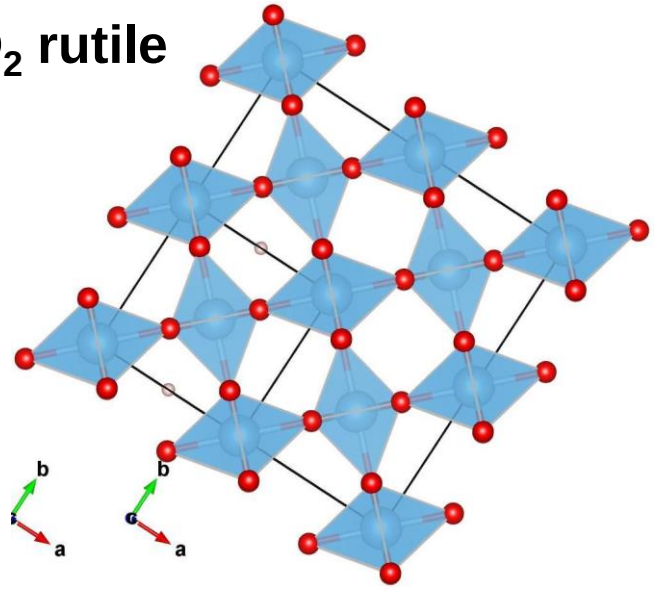


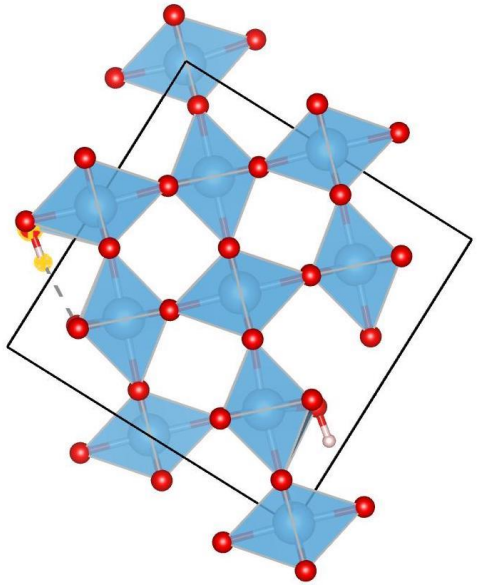
F-F potential



Mu-Mu potential

TiO_2 rutile





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

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+.

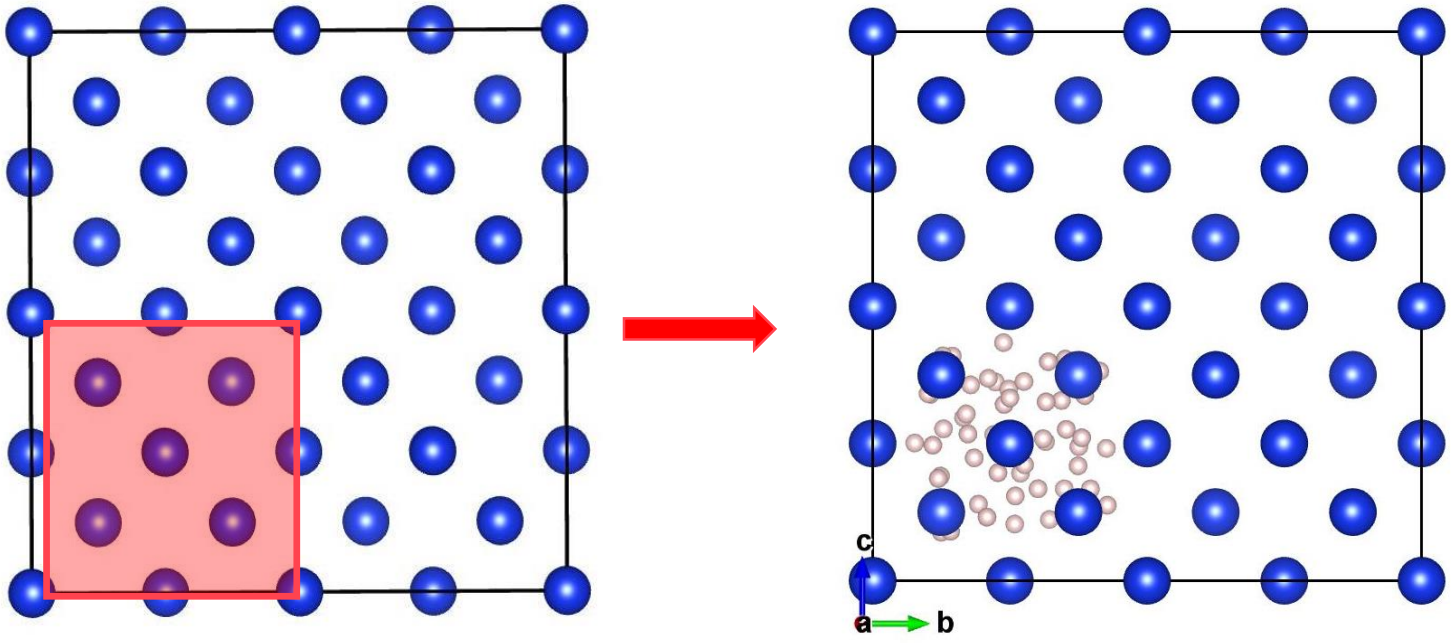
4

Conclusions. Work in progress. Future plans.

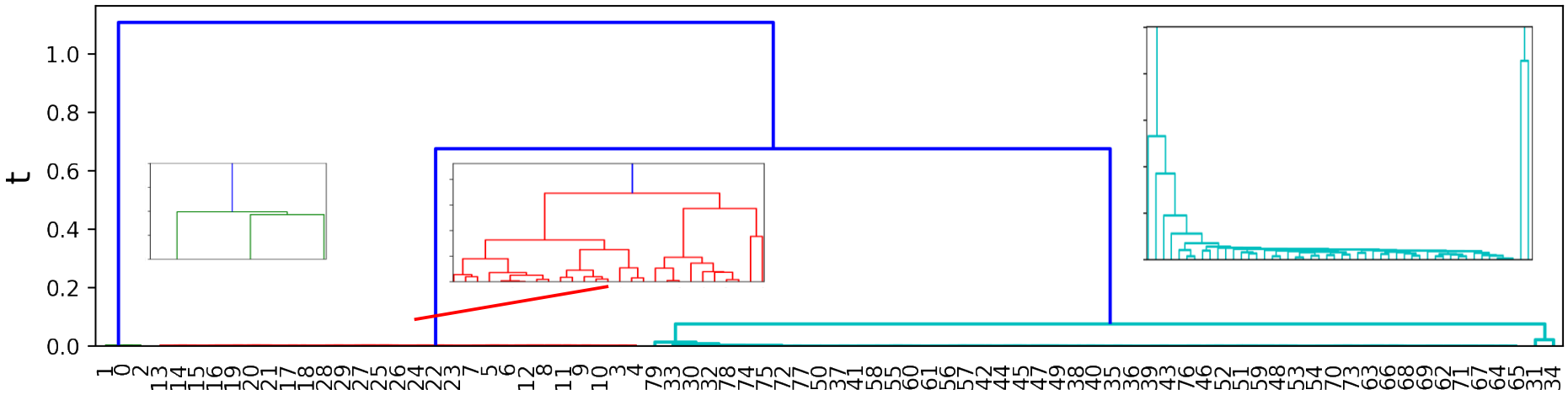
1) **Build 2x2x2 Si supercell**
2) **Define region to randomly locate muonium pseudo-atoms**
3) **Generate muonated structures placing muonium in randomised positions within the chosen region**
4) **Relax structures using calculated DFT forces**

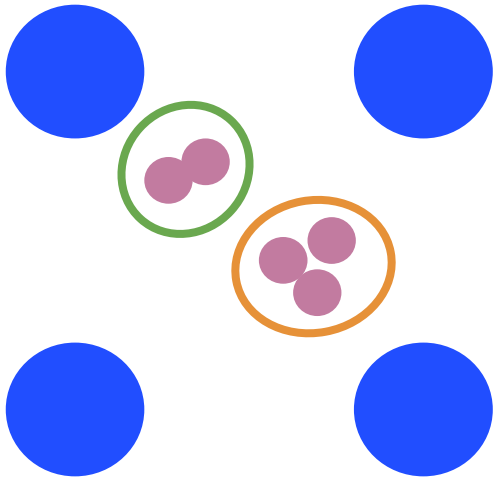
2x2x2 Si supercell

80 structures



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

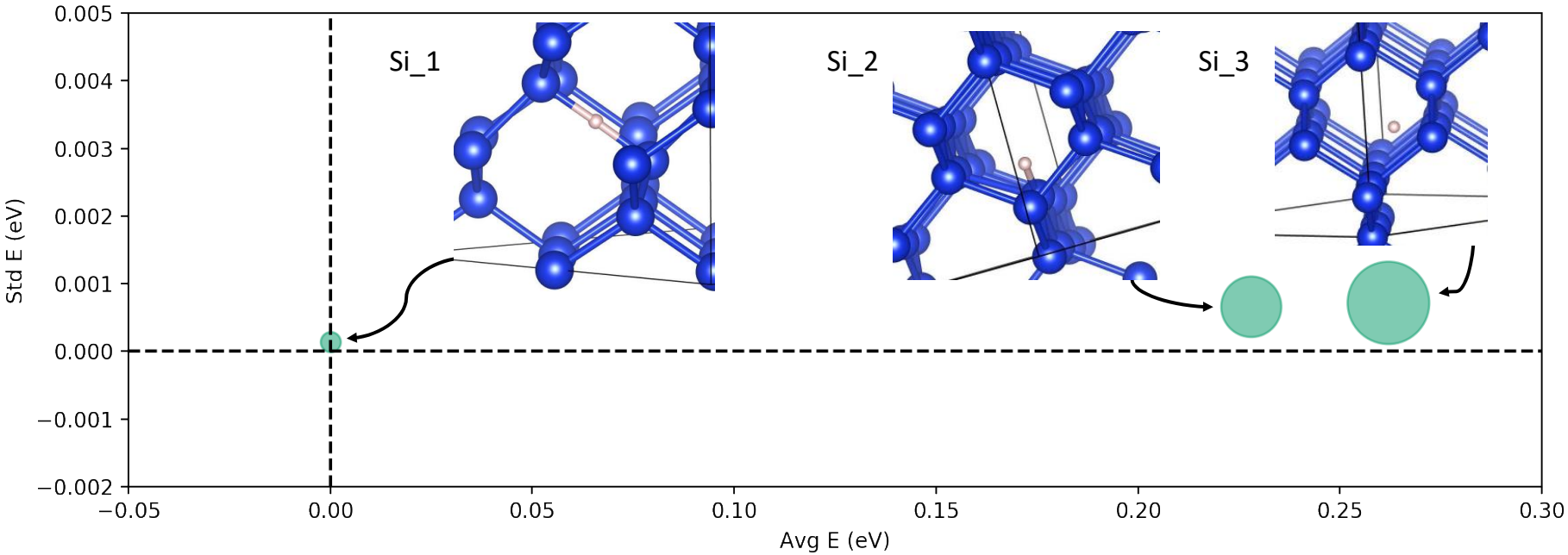


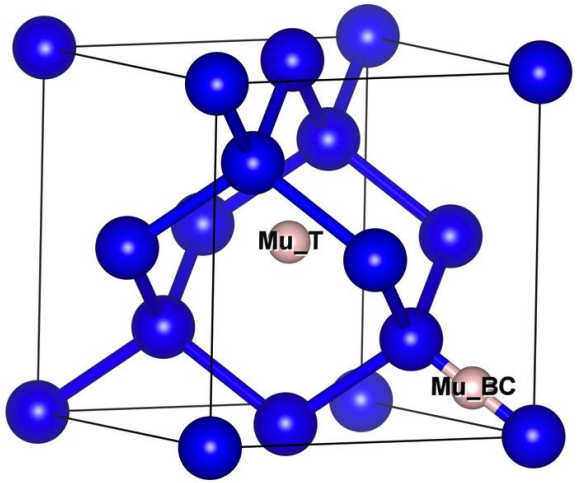


- **Define *n*D vector: (E_T, Q_1, Q_2, Q_3,…)**
- **Look for "closeness" in *n*D space**
- **Hierarchical clustering**
- **3 clusters identified**

SOPRANO

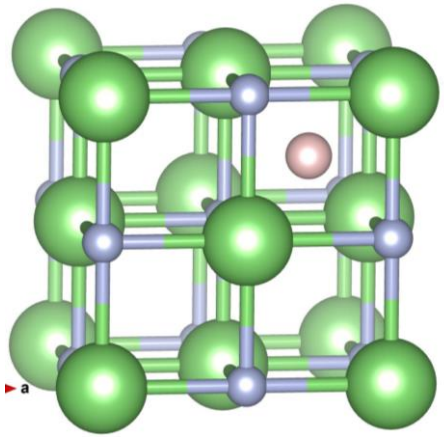
Python library Soprano (CCP NC) https://github.com/CCP-NC/soprano



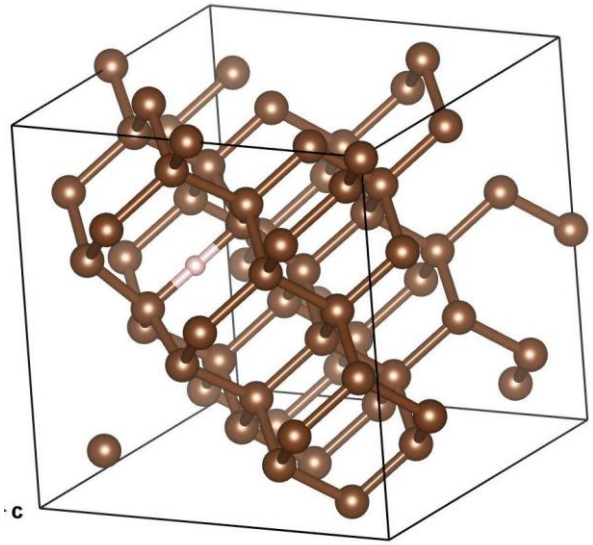


- **Identified 3 clusters**
- **Use k-means clustering**
- **Iidentified the Mu_T and M_{BC} in Silicon.**
- **High throughput method.**

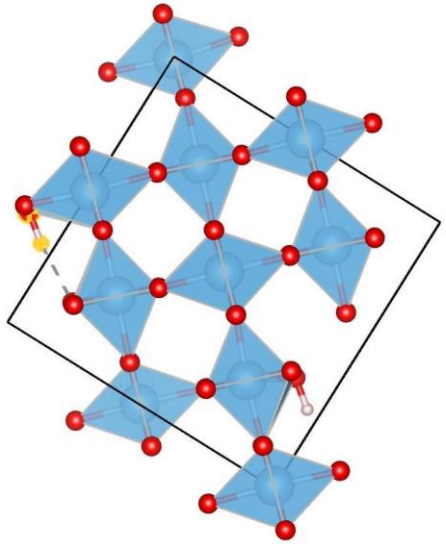
Python library Soprano (CCP NC) https://github.com/CCP-NC/soprano



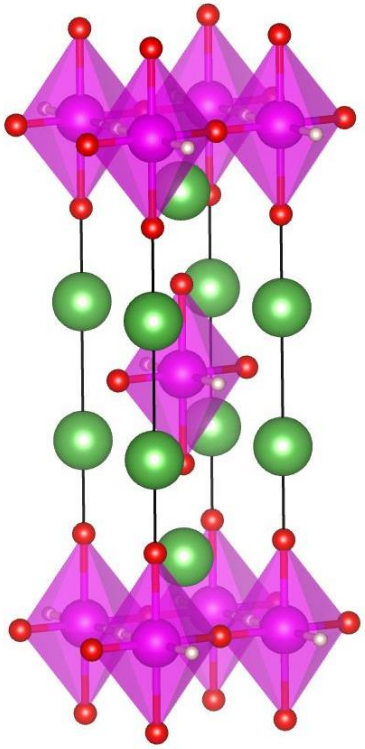
LiF



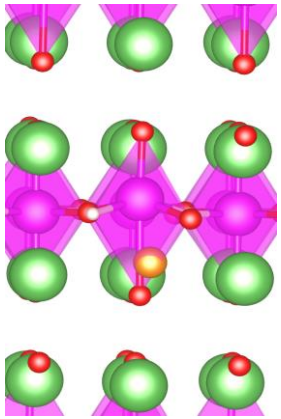
Diamond



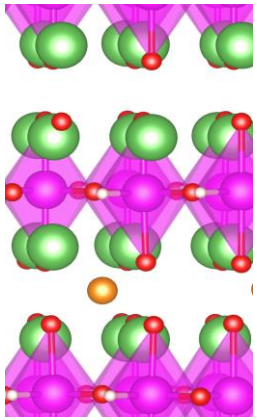
TiO_2- rutile



La_2LiHO_3



Site 1



Site 2

Collaboration with University of Oslo, Norway and ISIS

High throughput method.

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

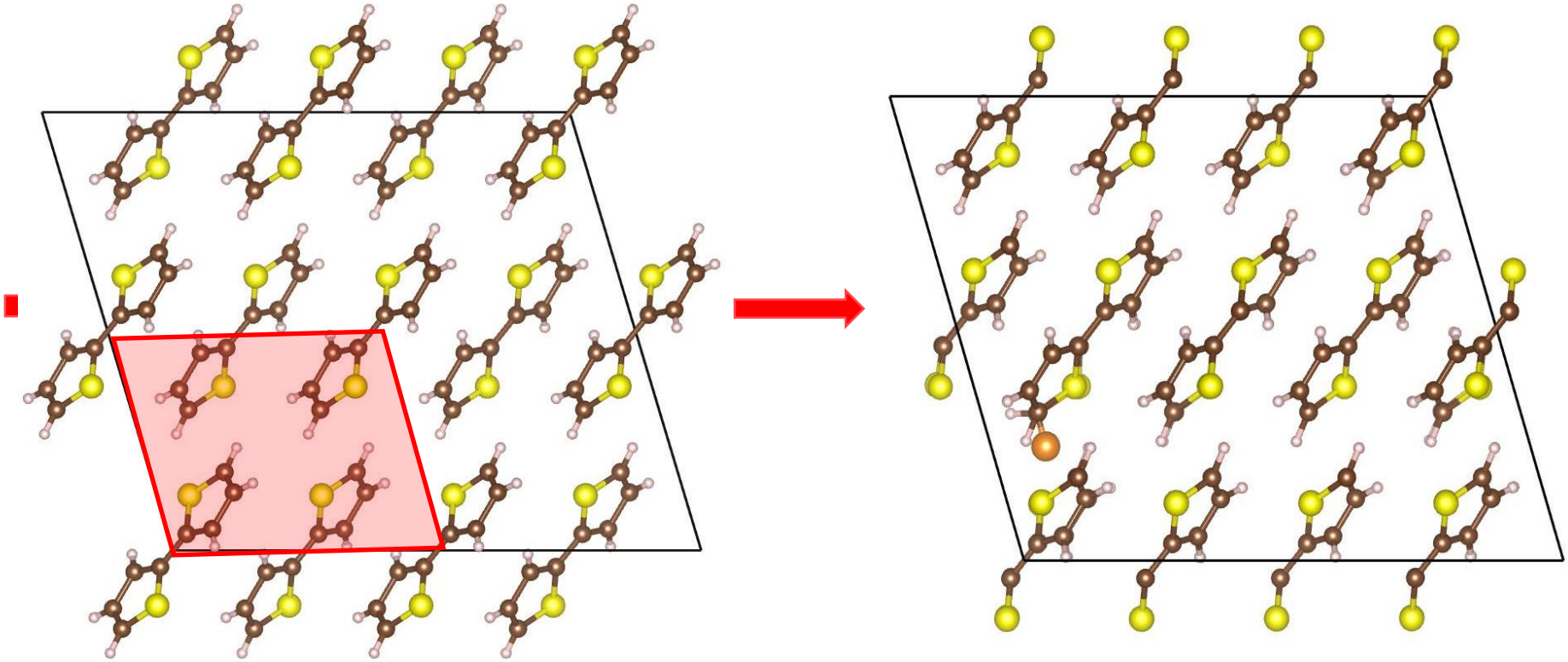
3

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

4

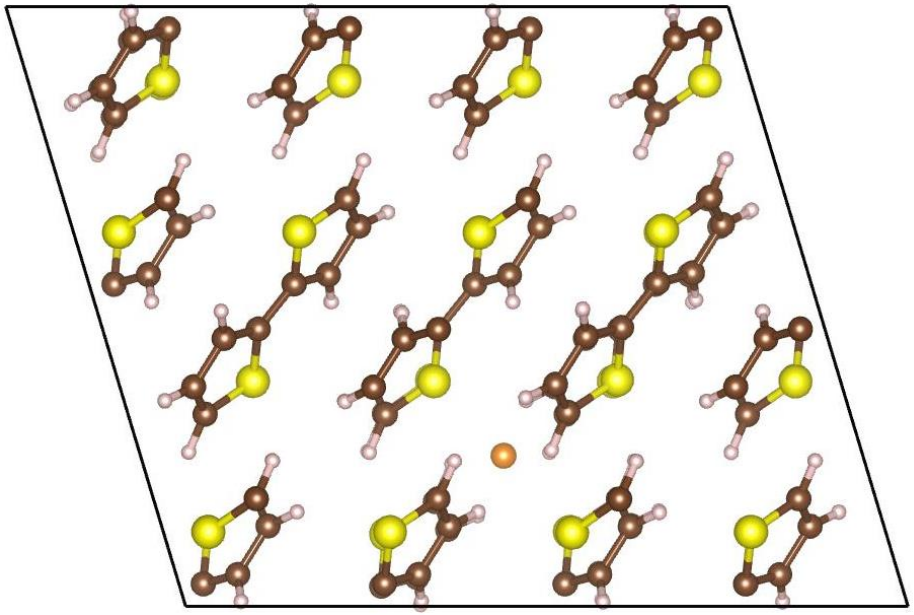
Conclusions. Work in progress. Future plans.

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 structures using calculated **DFTB+ forces. Reliable parameters for organic systems.**

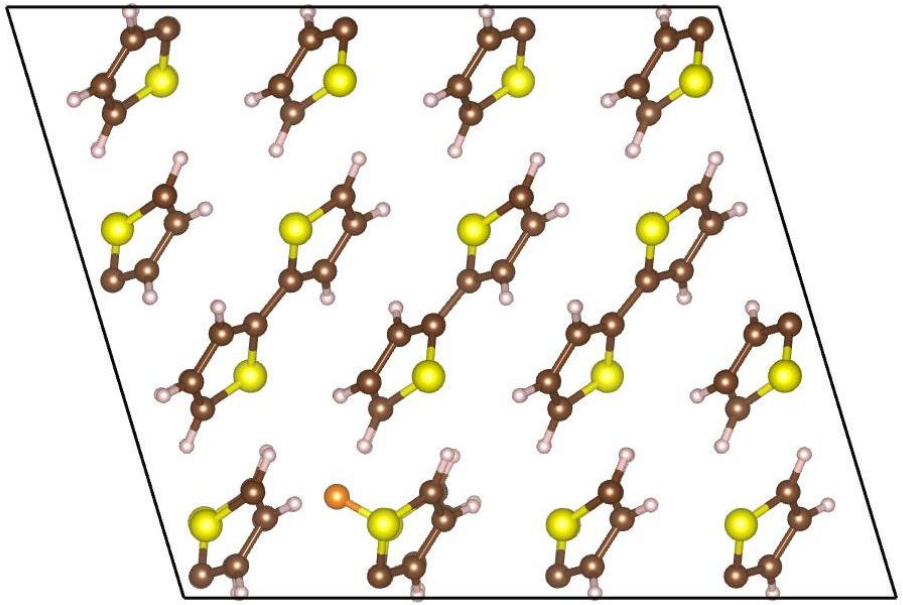


1) Divide the sites in 'floating' and 'bounded' sites
2) Reduce all muonated structures to asymmetric unit cell
3) Define *n*D vector: (E_T, x, y, z)
4) Look for "closeness" in *n*D space
5) Hierarchical clustering
6) Found five stopping sites

Work done with
Samuel Jackson



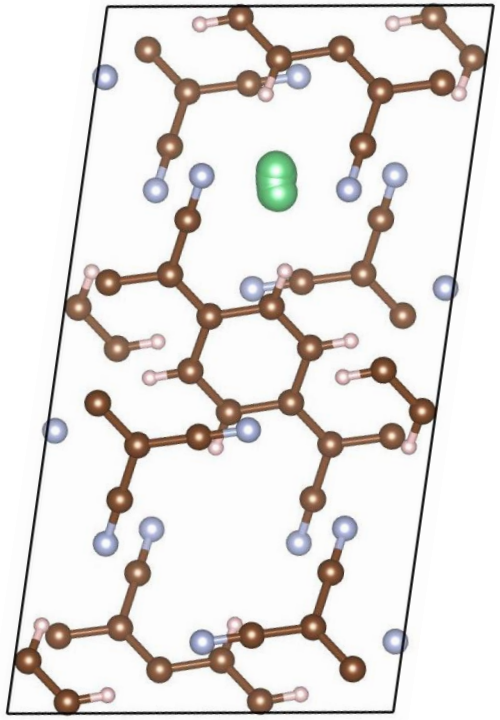
Floating site



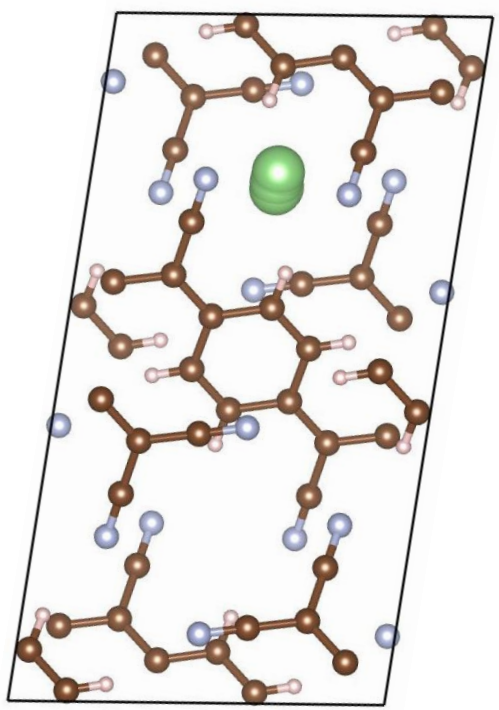
Bounded site

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+

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.

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

- 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.

- Extend the method to other DFT codes.

- 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