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Computer Simulations for Interpreting Muon-Spin Relaxation Experiments

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1) What is Muon-Spin Relaxation?

The STFC Rutherford Appleton Laboratory houses the ISIS Neutron and Muon Sources, which produce beams of neutrons and muons that can be used to study materials at the atomic level. The project presented in this poster is centered on the computational modelling of experiments performed with muons, which are subatomic particles produced by bombarding a graphite target with pulses of high-energy protons that originate in a synchrotron. The infrastructure required for these types of experiments includes a massive particle accelerator, tunnels for directing the particle beams and large buildings for housing the muon targets and all their corresponding scientific equipment.

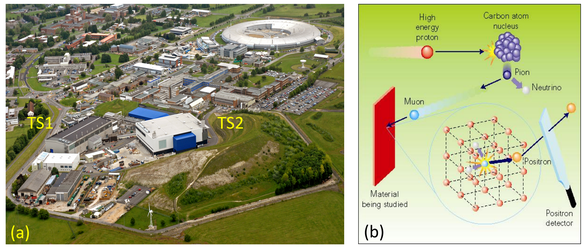


*Figure 1. (a) Aerial picture of the Rutherford Appleton Laboratory in Harwell, United Kingdom. High energy protons, extracted from a synchrotron, hit a graphite target in Target Station 2 (TS2) and produce muons which are 100% spin-polarized and are used in different μ+SR experiments. (b) These experiments involve **implanting** the muons in different material samples. Muons a have a mean life of 2.2 μs and then decay into positrons, which are emitted in the direction of the muon spin. Positrons detection allows for the measurement of the muon polarization as a function of time.*

In this project, computer simulations are used to model muon-spin relaxation (μ+SR) experiments, which can be used to study hydrogen defects in a sample, probe a sample's local magnetic structure or study the organic radicals that may result from adding muons to an organic sample.

In a muon-spin relaxation experiment (μSR) spin-polarized positive muons are implanted in a sample to probe its local properties. **The μSR technique can act as a sensitive probe, but one of its limitations is not knowing the site of implantation of the muon**, which prevents –for instance- the use μSR for measuring local magnetic moments, for comparing different magnetic structures or for accurately determining the atomic structure of organic radicals.

2) Where is the Muon Implanted?

Sometimes, the muon implantation sites can be found using experimental approaches[1]. In other cases, such as in the coordination polymer copper-pyrazine-nitrate $Cu(pyz)(NO_3)_3$, a limited number of theoretical calculations were used to test potential muon stopping sites[2]. However, whenever the candidate muon sites cannot be assigned by an educated guess, all the possible sites need to be examined using a theoretical method, such as the -so-called- Unperturbed Electrostatic Potential (UEP) method. The UEP relies on the analysis of the electrostatic potential of the host material, which is obtained from computer simulations. The key assumption is that the muon will stop in the minima of the electrostatic potential. The UEP works well in large band-gap insulators[3] and is computationally much faster than the other methods. Figure 2 shows some examples of materials where these methods were applied

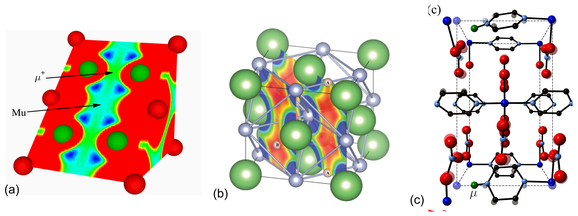
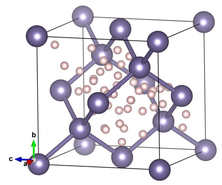


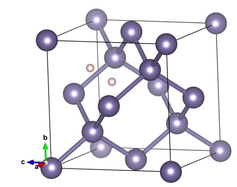
Figure 2: (a) Calculated electrostatic potential for the unperturbed [111] plane in CaF crystalline solid[4]. Blue coloring indicates regions that are attractive to a positive muon and, therefore, can be considered as potential stopping sites. (b) Possible muon implantation sites in LiF identified with labels A and B compounds[3]. (c) The green spheres represent some of the potential muon implantation sites in $Cu(pyz)(NO_3)_2$ [2]. Translucent spheres represent the ionic positions in the unit cell without the muon in it.

3) Our Computational Methods

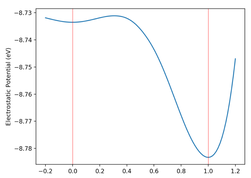
3.1) The Unperturbed Electrostatic Potential (UEP) Method



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



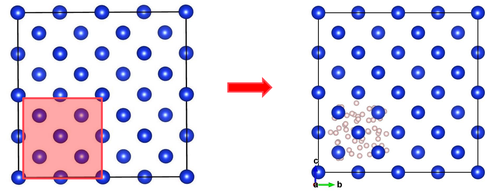
- *Calculate classical forces on the μ^+.*
- *Relax μ^+ to the potential minima. Identify clusters.*
- *Create supercell and test the implantation sites.*



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

3.2) DFT + Ab Initio Random Searching + Machine Learning[5]

- Build supercell (Si in the example)
- Define region to randomly locate muonium pseudo-atoms
- Generate structures placing muonium in randomised positions within the region [6]
- Relax structures using calculated DFT forces



- Define n-dimensional vector for each muonated structure: (E_T, Q_1, Q_2, Q_3,…)
- Look for "closeness" in the n-dimensional space
- Perform hierarchical clustering. Create dendrogram (Figure (3)).
- Three clusters identified

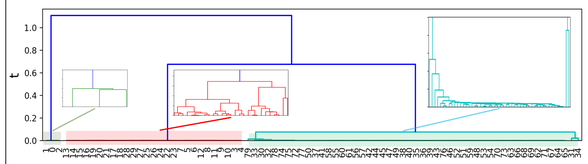


Figure 3: hierarchical clustering tree for silicon, with colours applied for truncation at t = 0.2 in the y axis. The blue lines above t = 0.2 indicates the clusters into which the structures can be classified. All the generated structures are labelled and placed along the x axis in accordance with their relative energies.

- Use k-means clustering with a guess of 3 clusters
- Iidentified the Mu_T and M_{BC} in Silicon
- **High throughput method**

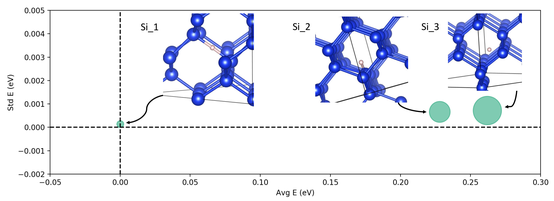
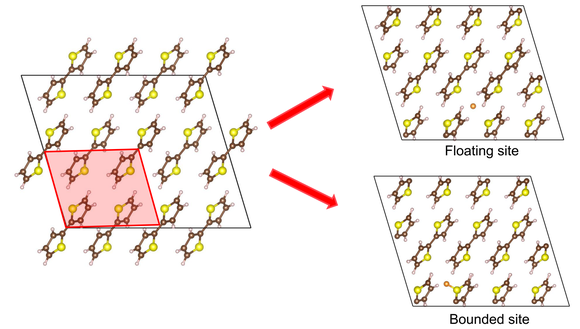


Figure (4): circles representing the clusters obtained via k-means clustering. The structures correspond to the most stable structure in each of the clusters. The diameter of each circle represents the number of structures contained in each cluster. The x coordinate of each one of the circles indicates the average energy of the corresponding cluster while the y coordinate of the centre indicates the standard deviation of the average energy of that cluster.

3.3) DFTB[7] + Ab Initio Random Searching + Machine Learning[8]

1) Build supercell (Bithiophene in the example)
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.**
5) Divide the sites in 'floating' and 'bounded' sites
6) Reduce all muonated structures to the asymmetric unit cell
7) Define n-dimensional vector: (E_T, x, y, z)
8) Look for "closeness" in n-dimensional space
9) Perform hierarchical clustering, Create dendrogram.
10) Found five stopping sites – Good agreement with experiments.
11) Method at least two orders of magnitude faster than the one using standard DFT.
12) Tested for bithiophene and benzene and finalizing tests for TCNQ.
13) Only works in organic materials composed simple atoms (Br, C, Ca, Cl, F, H, I, K, Mg, N, Na, O, P, S, Zn)



4) Conclusions

- 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.

References:

(1) PRB **32**, 293, (1985).
(2) PRB **91**, 144417, (2015).
(3) PRB **87**, 115148 (2013).
(4) PRB **87**, 121108(R) (2013)
(5) The Journal of Chemical Physics, 148, 134114 (2018)
(6) Python library Soprano (CCP NC) https://github.com/CCP-NC/soprano
(7) J. Phys. Chem. A, **111** 5678 (2007).
(8) In Preparation

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