Computer Simulations for Interpreting $\mu$SR Experiments

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2019 International Advanced School in Muon Spectroscopy, Rutherford Appleton Laboratory, UK
Some fundamental approximations involved in our computer simulations. (Or a very brief introduction to Density Functional Theory).

The use of computer simulations for μSR experiments in periodic crystalline systems. Our methods finding the muon stopping site:
• UEP
• General clustering methodology
• Clustering for organic crystals

How computer simulations can be used to assist in the interpretation of μSR experiments in hybrid molecular systems. What else can simulations be used for?

Conclusions. Work in progress. Future plans.
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Ab-initio simulations

\[ \mathcal{H} \Psi(r, \ldots r_N; R_1, \ldots R_M) = E \Psi(r, \ldots r_N; R_1, \ldots R_M) \]

\[ \hat{\mathcal{H}} |\Psi\rangle = E \hat{\mathcal{H}} |\Psi\rangle \quad \Rightarrow \quad E = \frac{\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]
• C₆H₆ has N=42 e and 3N=126 e coordinates.
• Spatial mesh M= 50 points per dimension.
• M³N=50¹²⁶ operations to find ground state.
• Powerful computers ~10²⁰ operations/second.
• Around 10⁸⁰ years to solve $E_{el} = \frac{\langle \psi | \hat{\mathcal{H}} | \psi \rangle}{\langle \psi | \psi \rangle}$ !!!!!
• Need more approximations.

Schrödinger

$$\hat{\mathcal{H}} \left[ \Psi(r, \ldots r_N; R_1, \ldots R_M) \right] = E \Psi(r, \ldots r_N; R_1, \ldots R_M)$$

Born-Oppenheimer

$$\hat{\mathcal{H}} \left[ \psi(r_1, \ldots r_N) \right] = E \psi(r_1, \ldots r_N)$$
Can solve the full Schrödinger equation by solving one-particle system equations, and obtain an approximate ground state energy for the system.
CRYSTAL14 RELEASED!

New features and performance enhancements for an improved characterization of periodic systems.

Overview

CRYSTAL is a general-purpose program for the study of crystalline solids, and the first which has been distributed publicly. The first version was released in 1988 and then six next versions have followed: CRYSTAL92, CRYSTAL95, CRYSTAL98, CRYSTAL03, CRYSTAL06 and CRYSTAL09.

The CRYSTAL program computes the electronic structure of periodic systems within Hartree Fock, density functional or various hybrid approximations (global, range-separated and double-hybrids). The Bloch functions of the periodic systems are expanded as linear combinations of atom centred Gaussian functions. Powerful screening techniques are used to exploit real space locality.

Restricted (Closed Shell) and Unrestricted (Spin-polarized) calculations can be performed with all-electron and valence-only basis sets with effective core pseudo-potentials. The program can automatically handle space symmetry (230 space groups, 80 two-sided plane groups, 99 rod groups, 45 point groups are available).

Point symmetries compatible with translation symmetry are provided for molecules. Helical symmetry is now available (up to order 48). Input tools allow the generation of a slab (2D system), or a cluster (0D system), from a 3D crystalline structure, or the creation of a supercell with a defect, or nanotubes (1D system) from a single-layer slab model (2D system).

The code may be used to perform consistent studies of the physical and chemical properties of molecules, polymers, nanotubes, ...
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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 known as the Unperturbed Electrostatic Potential Method (UEP)

\[ \mu^+ \text{ and } \mu^+e^- \text{ in CaF} \]

PRB 87, 121108(R) (2013)

\[ \mu^+ \text{ in YF}_3 \]

PRB 87, 115148 (2013)

\[ \mu^+ \text{ and } \mu^+e^- \text{ in Cu(pyz)(NO)}_3 \]

PRB 91, 144417 (2015)
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• Calculate electrostatic potential of unperturbed host material using DFT
• Randomly locate $\mu^+$ in the host’s unit cell (Ge in example)

• Calculate classical forces on the $\mu^+$.
• Relax $\mu^+$ 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

$\text{TiO}_2$ rutile

Pr$_2$Rh$_3$Ge$_5$

F-F potential

Mu-Mu potential

Work with Adroja Debashi, from ISIS
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1) Build 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**
5) Each muonated structure is a vector in data space \((E, \mu_x, \mu_y, \mu_z)\). Look for clusters in this data-space.

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

• Define 4D vector: \((E_T, \mu_x, \mu_y, \mu_z)\)
• Look for “closeness” in 4D space
• Hierarchical clustering
• 3 clusters identified

Python library Soprano (CCP NC)  [https://github.com/CCP-NC/soprano](https://github.com/CCP-NC/soprano)
Identified 3 clusters

Use k-means clustering

Identified the $\text{Mu}_T$ and $\text{M}_{\text{BC}}$ in Silicon.

High throughput method.

Python library Soprano (CCP NC)  [https://github.com/CCP-NC/soprano](https://github.com/CCP-NC/soprano)
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1) Build supercell of an organic crystal.
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
5) Each muonated structure is a vector in data space $(E, \mu_x, \mu_y, \mu_z)$. Look for clusters in this data-space.

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

Why DFTB+ is faster? Why organic systems?

- Represents the electrons as bound to the ions.
- Does not describe the full spatial electronic wavefunction.
- Uses parametrizations to describe interactions between chemical species in the system.
- These parametrizations are not easy to do. Saved in Slater-Koster sets.
- Used organic crystals because there is a well-documented Slater-Koster parameter set for organic compounds: the 3ob-3-1 set, which covers among the other elements carbon, hydrogen, oxygen, nitrogen and sulphur.

https://www.dftbplus.org/
Bithiophene

Durene

TCNQ

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Tetrakis-(2-phenyethynyl)-Silane

Phenylacetylene capped silicon nanoparticles

Collaboration with UEA, ISIS and PSI
The longitudinal field Avoided Level Crossing (ALC) muon spectrum of crystalline benzene.

- ALC spectrum for benzene at 12 K and at 210 K.
- ALC peaks narrow at 12 K by residual dynamical process.
- Further ALC peak narrowing at 210 K due to benzene rotation.

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Work in progress – Future plans

- Venturing into the field of large organic molecules.
- Working on simulations for biological systems.
- Key technical issue: flat potential surfaces, almost impossible to relax by standard DFT.
- Key technical issue: huge systems.

Plan use of machine learning to try to estimate hyperfine coupling constant tensors with DFTB+

Polipeptide – Mark Telling, ISIS
3ob-3-1 DFTB+ set
DFT is a powerful approximation that allows for the computational modelling of nanomaterials.

We developed computational methods to estimate the stopping sites of muons in crystalline materials in a fast and reliable way. These methods complement the known methodologies used for predicting the muon stopping sites. We have developed our own flavor of the UEP method.

Our new fast method utilize 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. This method predicted muon stopping sites in Bithiophene, Durene and TCNQ.

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

Computational modelling can be applied to specific problems related to muon experiments. Working on the implementation of these techniques for a general user (Software demonstrations).

We plan to start work on large organic/biological systems.