Computer Simulations for Interpreting μSR Experiments

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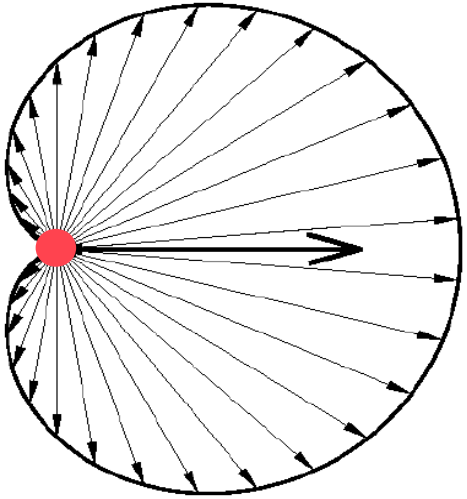

1

Some fundamental approximations involved in our computer simulations. (Or a very brief introduction to Density Functional Theory).

2

How computer simulations can be used to assist in the interpretation of μSR experiments in molecular systems.

3

The use of computer simulations for μSR experiments in periodic crystalline systems. The problem of finding the muon stopping site .

4

Conclusions. Work in progress. Future plans.

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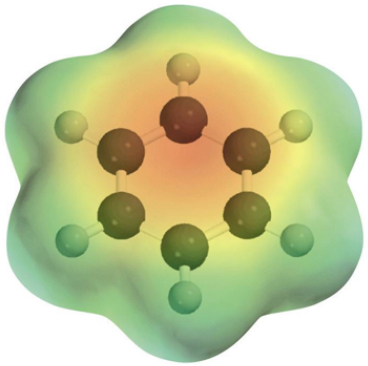
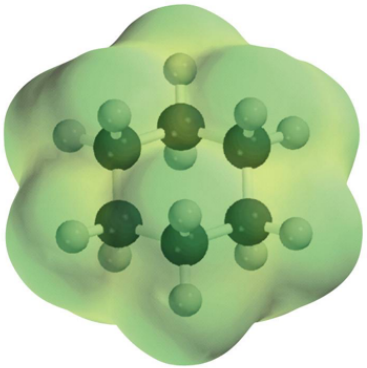
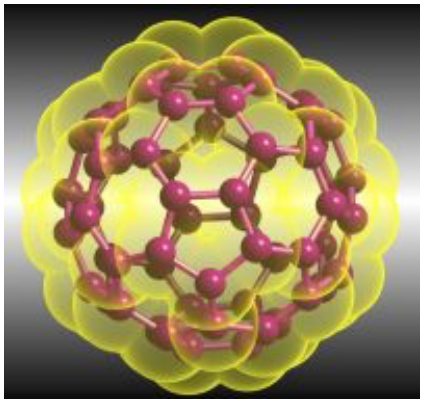






benzene

cyclohexane

buckyball

Schrödinger equation contains most of a system's chemistry:

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

Born-Oppenheimer Approximation:

Assume that electronic relaxation is much faster than nuclei motion ($m_e << m_N$).
Then can assume electrons move in the field of fixed nuclei.

$$\hat{\mathcal{H}}_{el}[\psi(r_1,\ldots r_N\,)]=\mathrm{E}_{\mathrm{el}}\psi(r_1,\ldots r_N\,)$$

WARNING: ($m_e << m_\mu$) NOT true for muons.

$$\hat{\mathcal{H}}[\,\Psi(r,\ldots r_{N;}\,R_1,\ldots R_M)]=\mathrm{E}\Psi(r,\ldots r_{N;}\,R_1,\ldots R_M)$$

Born-Oppenheimer

$$\hat{\mathcal{H}}_{el}[\psi(r_1,\ldots r_N)]=\mathrm{E}_{\mathrm{el}}\psi(r_1,\ldots r_N)$$

DFT

- $n(\mathbf{r})=\langle\psi(r_1,\ldots r_n)|\psi(r_1,\ldots r_N)\rangle$ electronic density.
- $E_{el}[$ PBE, B3LYP)
- $n(\mathbf{r})=\langle\varphi(r_1)\ldots\varphi(r_N)|\langle\varphi(r_1)\ldots\varphi(r_N)|\rangle$ system of fictional N-independent particles each represented by $\varphi(r_i)$.

Black Box with Suitable Approximations

Can solve the Schrödinger equation and obtain an approximate energy and wave function for the system.

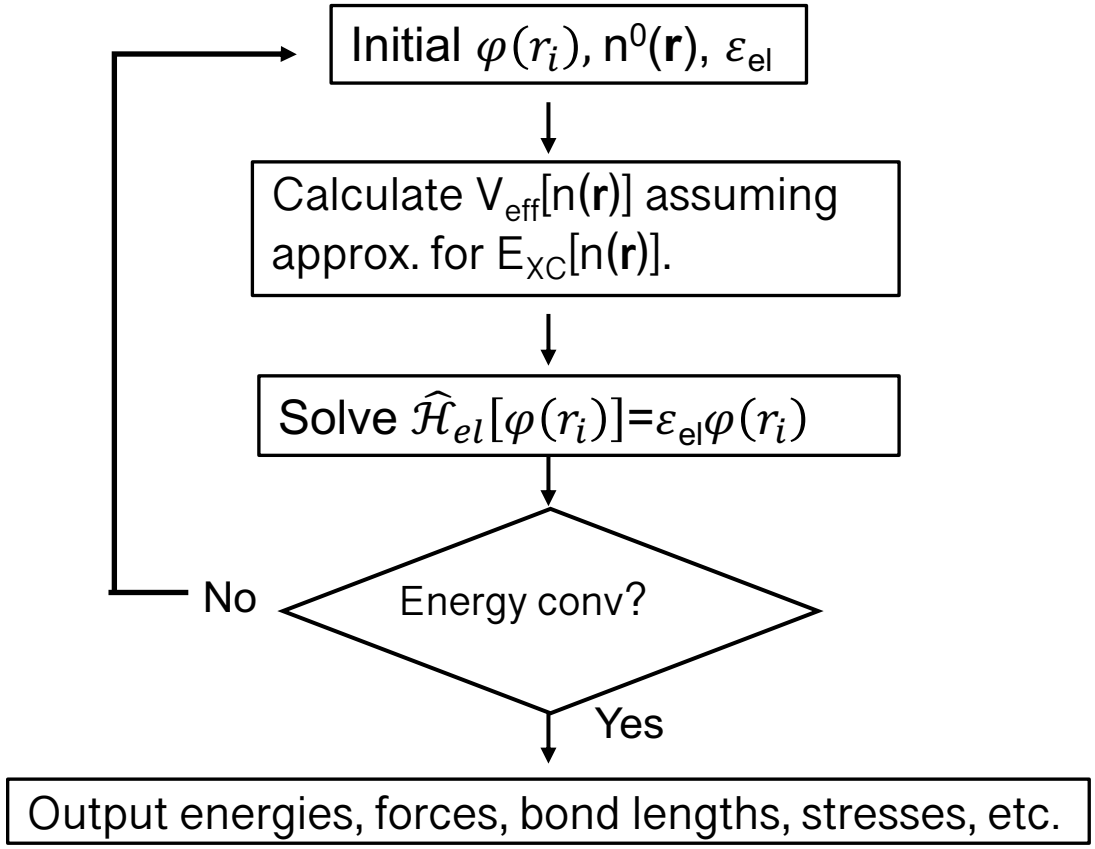
Gaussian

a computational tool for solid state chemistry and physics
CRYSTAL

DFTB

QUANTUMESPRESSO

CASTEP



Obtain the relax structure and the total energy of the system

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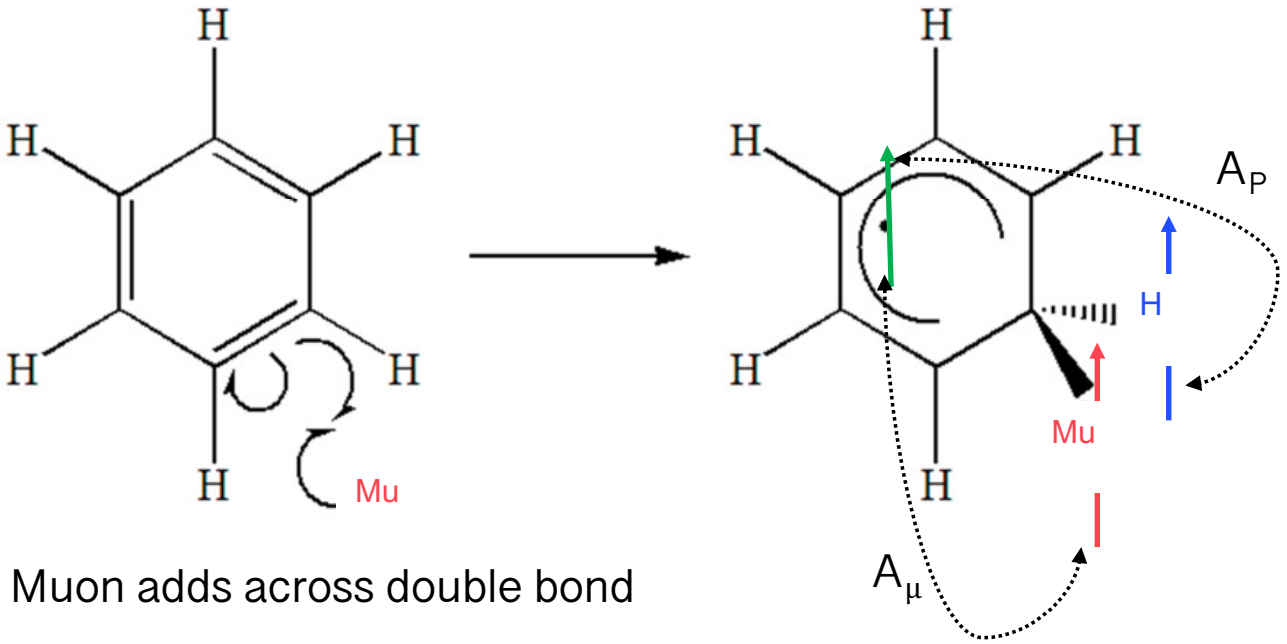
BENZENE

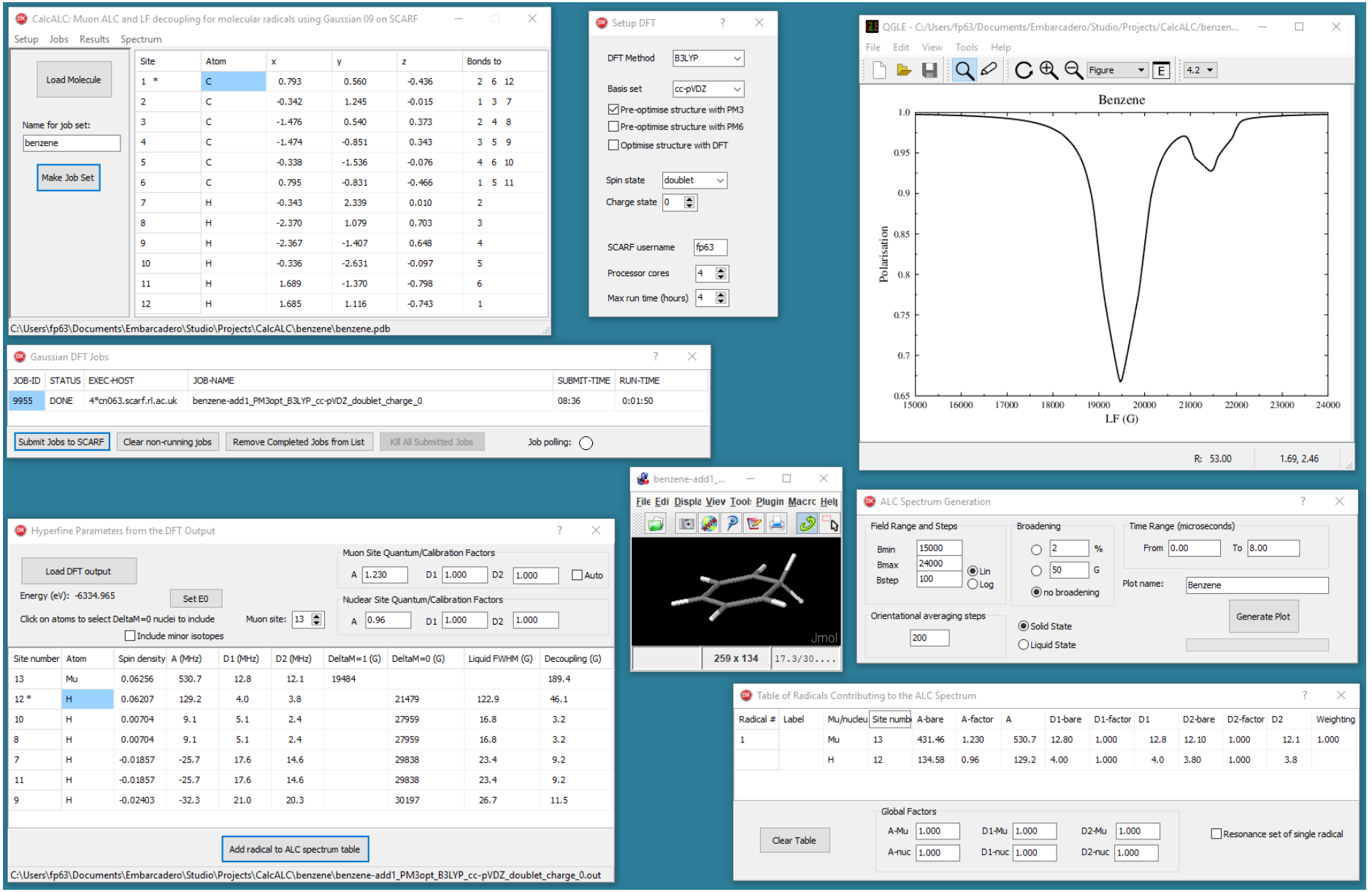
$\mu^+e^- = Mu$

Delocalized unpaired electron

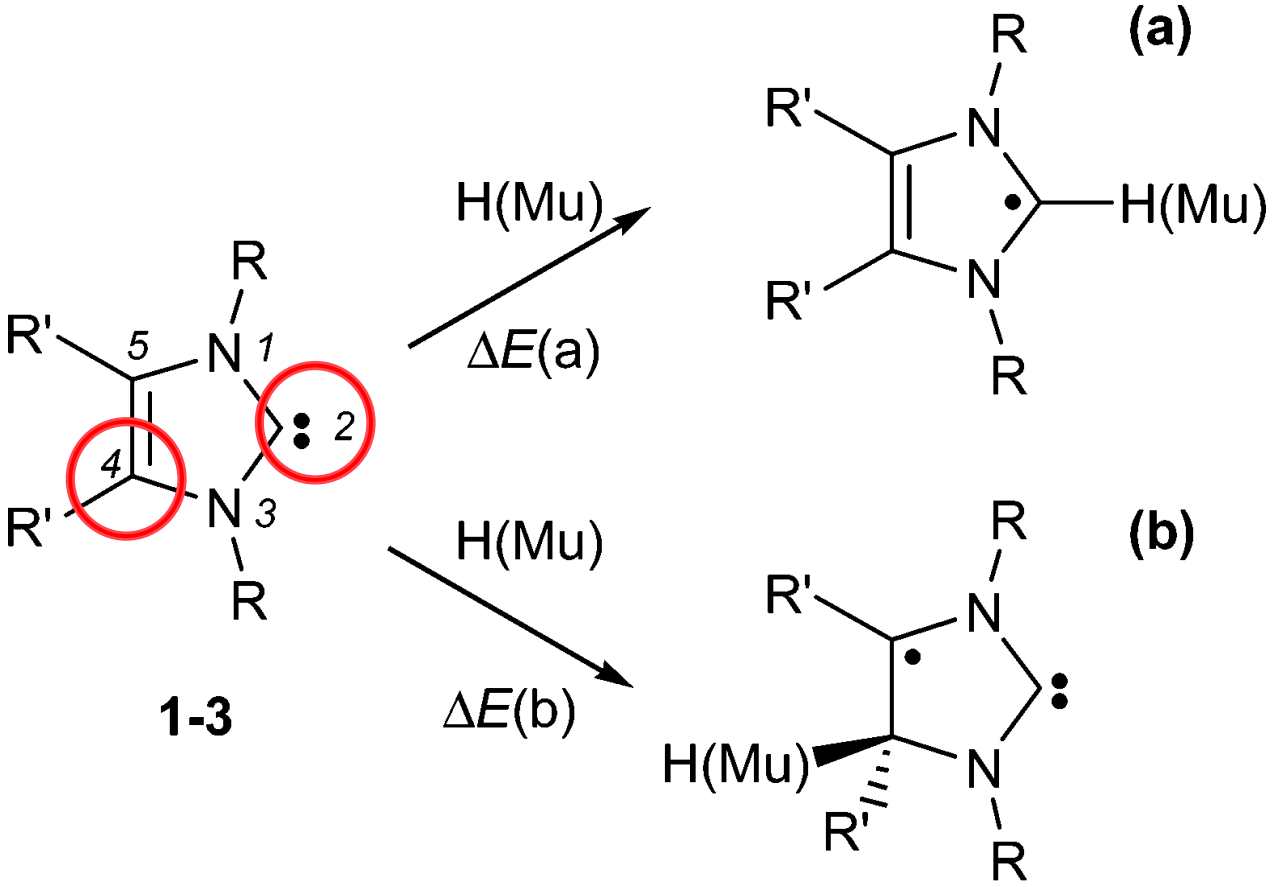


Muon adds across double bond

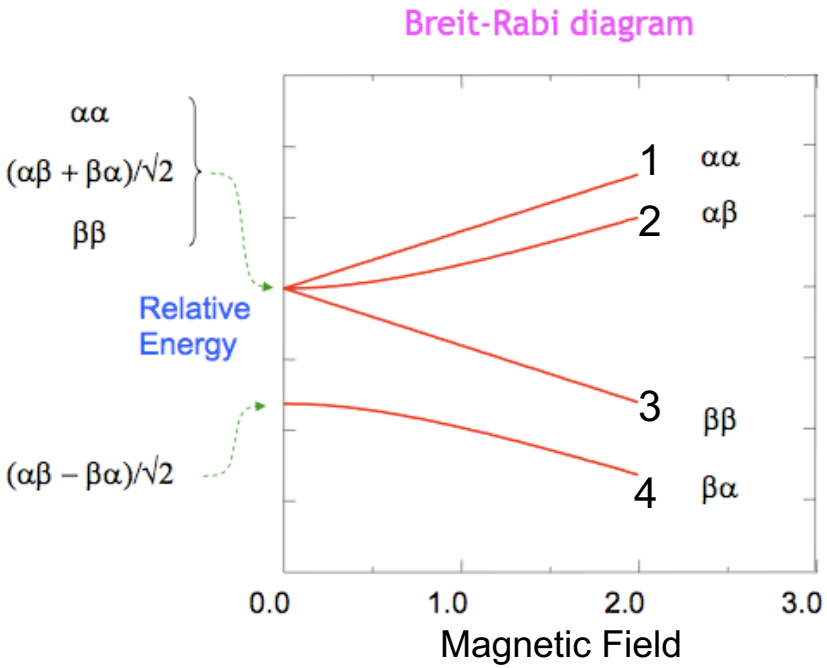
CalcALC: From Molecule to ALC Spectrum via DFT



Imidazole-type Carbene



I. McKenzie, *et al.,* **J. AM. CHEM. SOC.** VOL. 125, NO. 38, p. 11565, (2003)



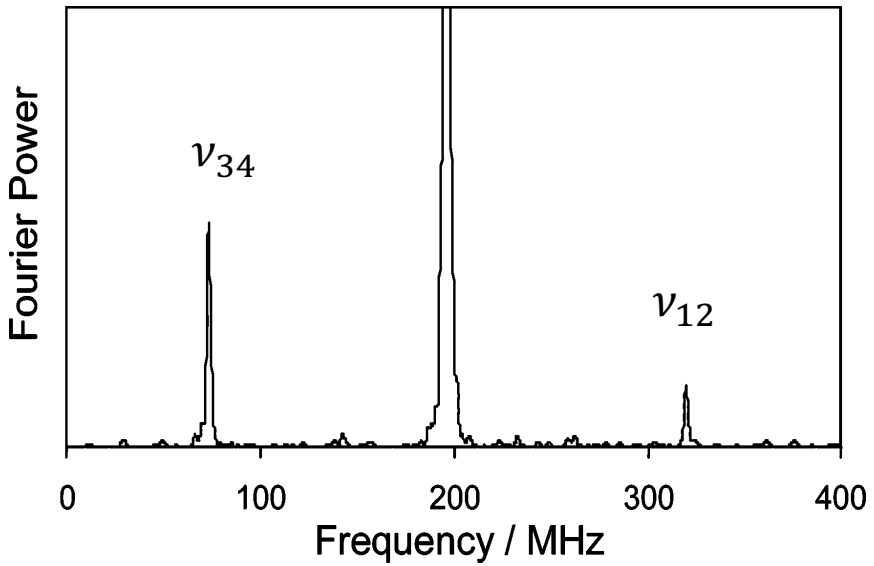


Figure 3. Transverse field μSR spectrum at 14.4 kG from **1** in THF at 298 K. The pair of peaks at ca. 73 and 320 MHz is due to a muoniated radical.

- F-μSR to calculate A_μ as

$$A_\mu = \nu_{12} - \nu_{34} = \mathbf{246.4\ MHz}$$

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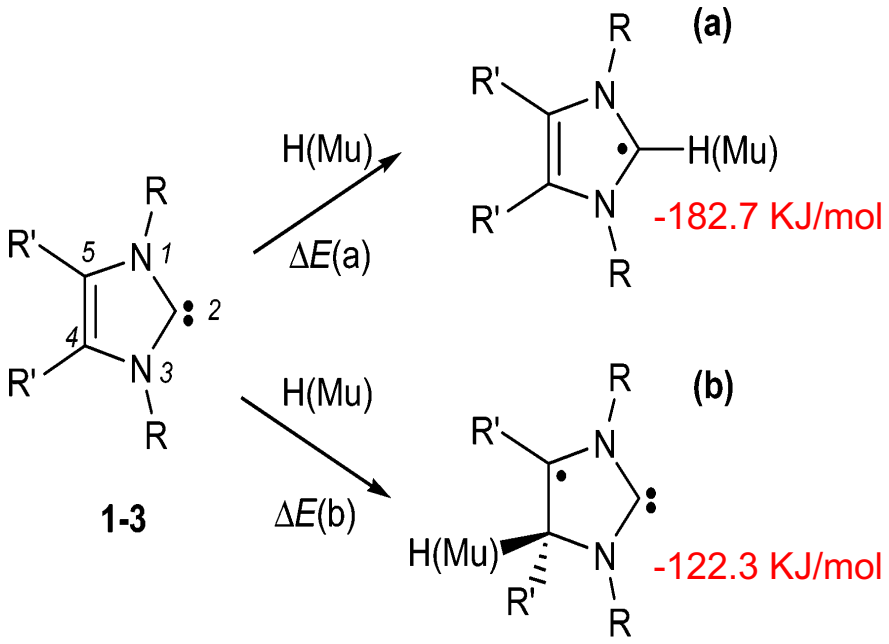

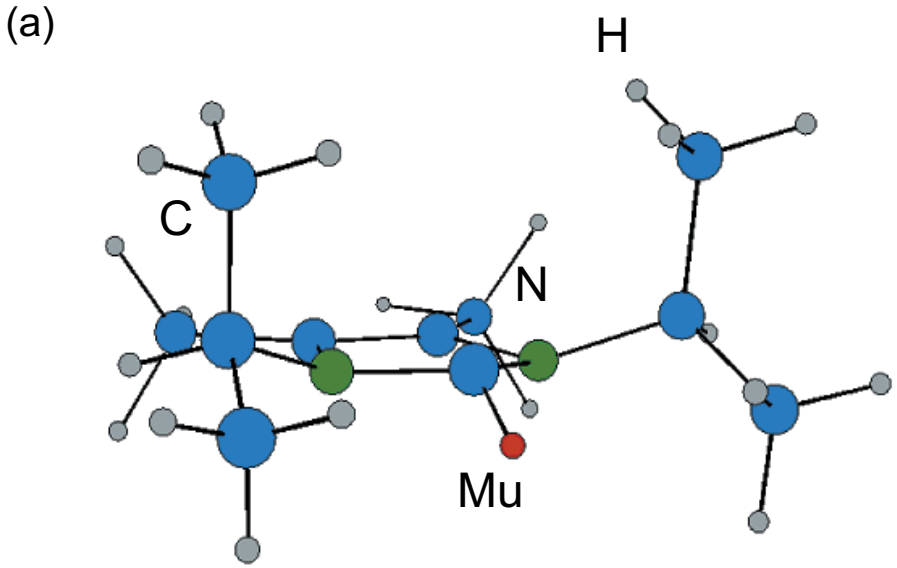

A_μ=246.4 MHz (adjusted to experiment)

- Used calculated reaction energies to place Mu in the molecule: (a) preferred site.

$$\Delta E(a) = E_{radical.} - (E_{carbene.} + E_H)$$

- Adjust the theoretical A_μ to agree with the experimental value.

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EXPERIMENTAL APPROACH

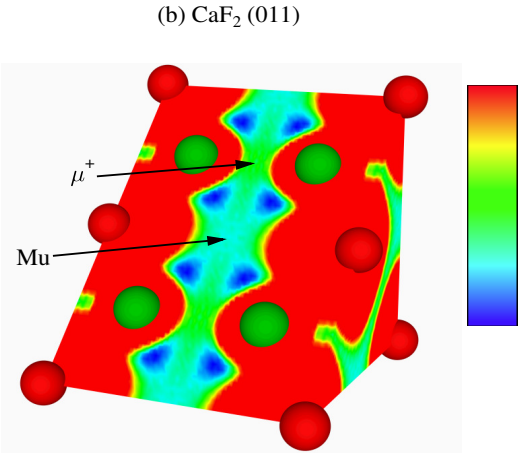
- Muonated Fe: follow the evolution of the muon frequency shift in a transverse field experiment as a function of the applied stress in a single Fe crystal[1]

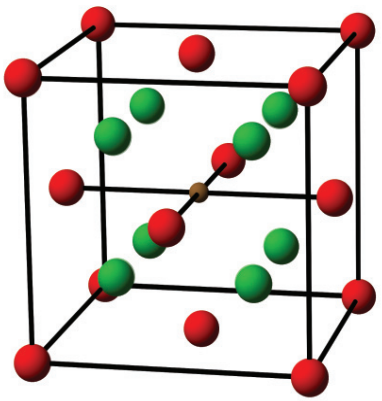
COMBINED THEORETICAL / EXPERIMENTAL APPROACH

- Muonated Fe_3O_4, ZnO and LiF: the theoretical calculations are used for testing different potential muon stopping sites

THEORETICAL APPROACH

- Approach that relies on the analysis of the electrostatic potential of the bulk material obtained from Density Functional Theory (DFT) simulations. This is know as the **Unperturbed Electrostatic Potential Method (UEP)**

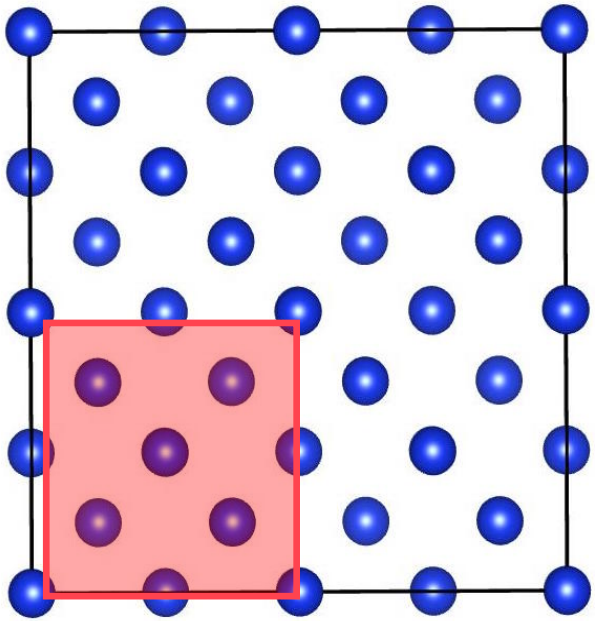




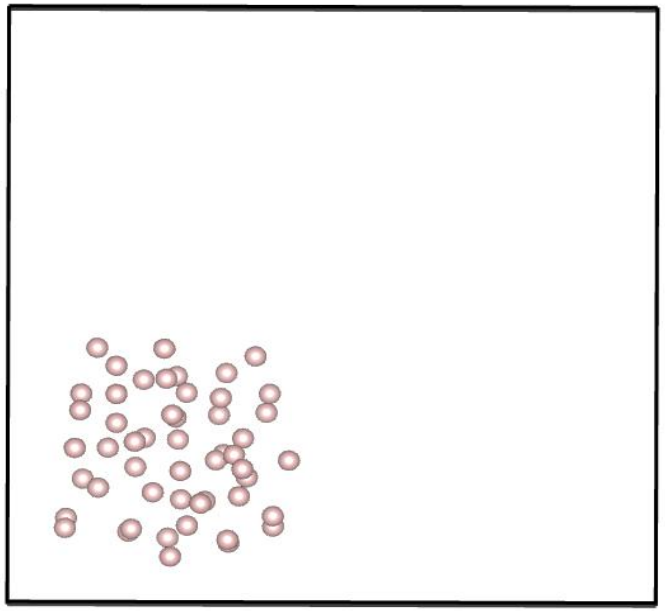
W. J. Kossler, et. al., Phys. Rev. B **32**, 293, (1985)
J. Moller, *et al.,* Phys. Rev. B **87**, 121108(R) (2013)

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 filtered structures using calculated DFT forces

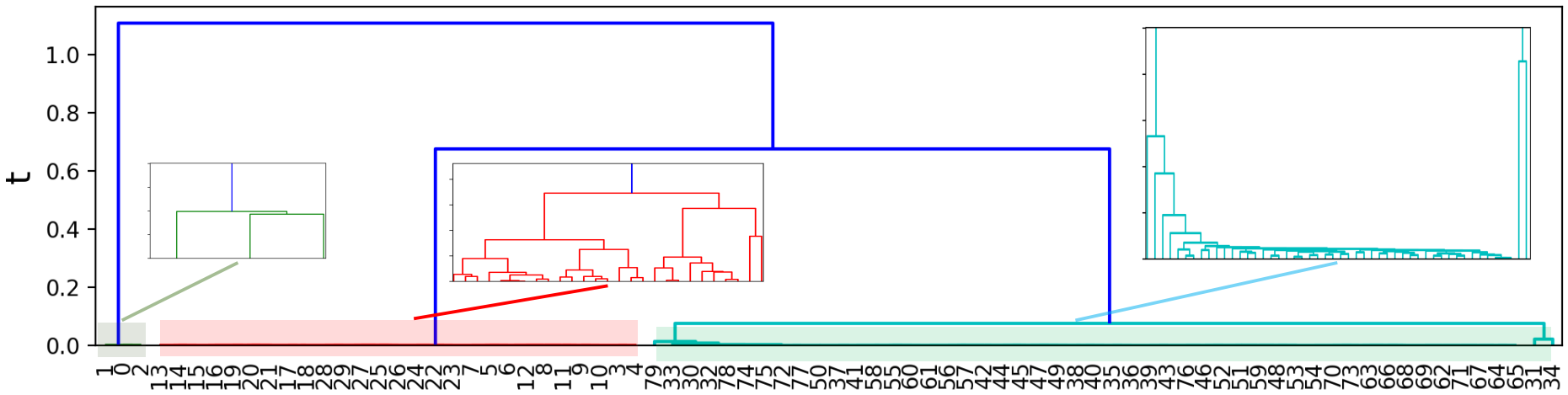
2x2x2 Si supercell

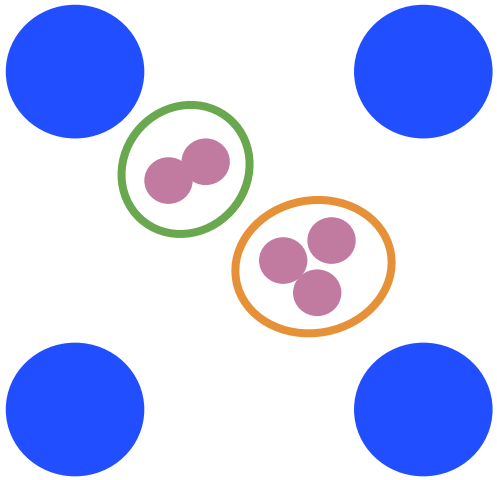


80 structures



https://arxiv.org/abs/1801.10454

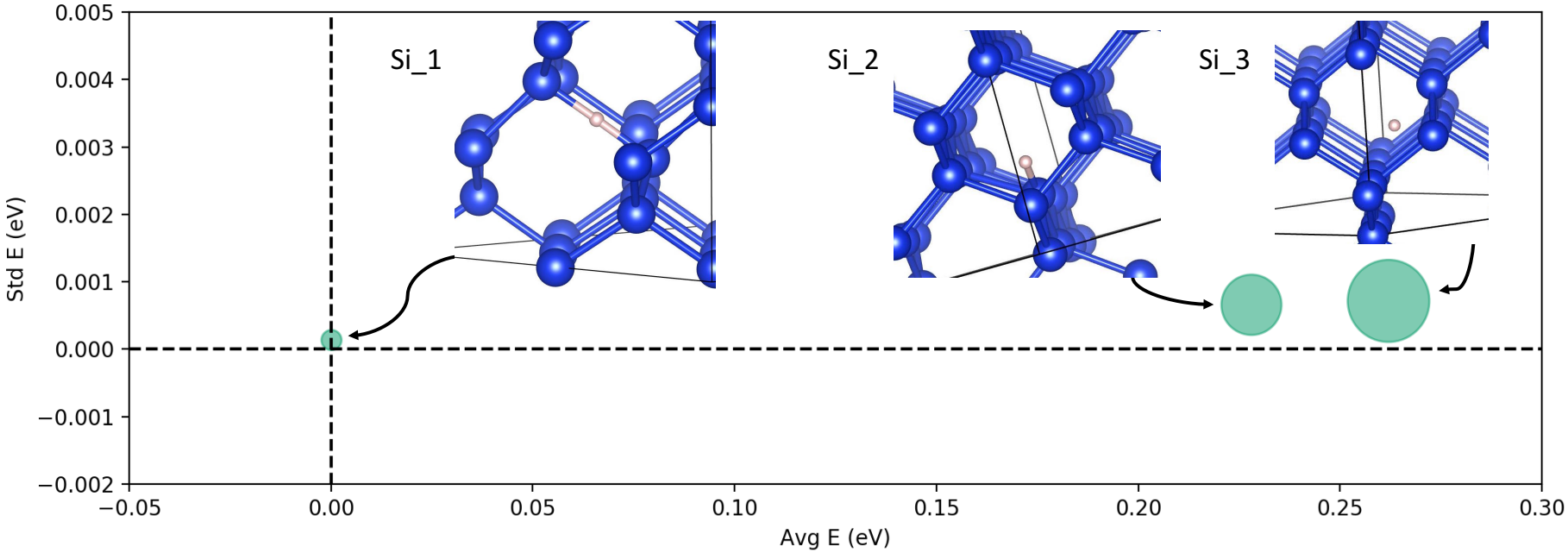


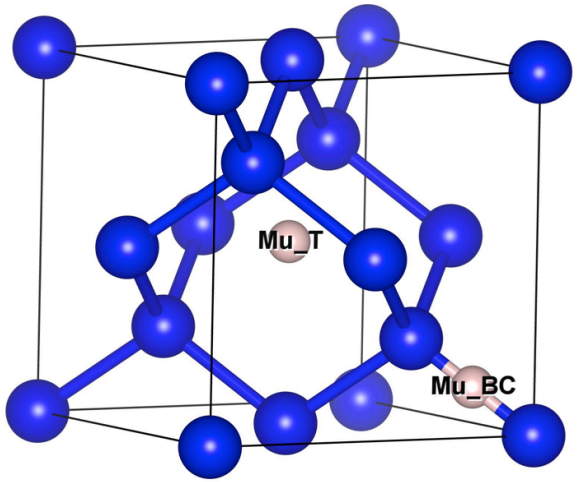


- Define *n*D vector: (E_T, Q_1, Q_2, Q_3,…)
- Look for “closeness” in *n*D space
- Hierarchical clustering
- 3 clusters identified

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.

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CONCLUSIONS

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DFT provides the basis for our computer simulations. Choose right code and XC functional for your system.

2

For molecules, standard DFT calculations can assist experiments, i.e.: help with ALC results.

3

For crystals, we can use simulations to predict the muon stopping site.

4

Working of using DFTB+, which may accelerate the calculations.
Need to estimate the quantum effects.