Computer Simulations for Interpreting μSR Experiments

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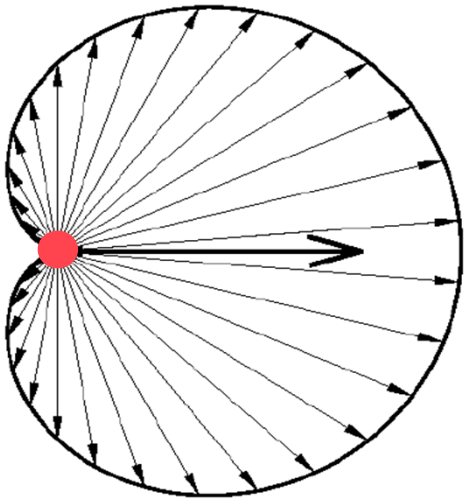

1

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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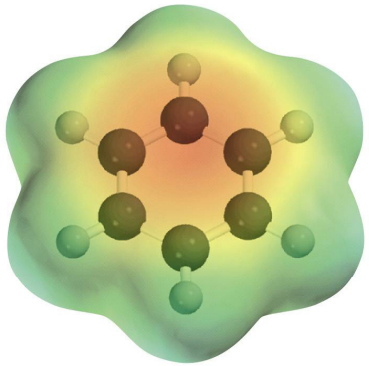
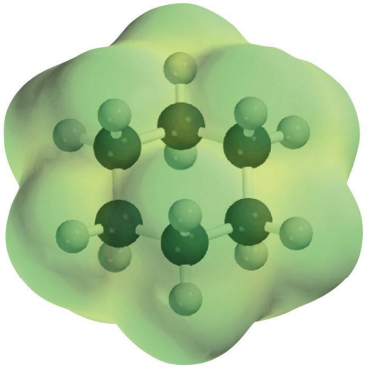
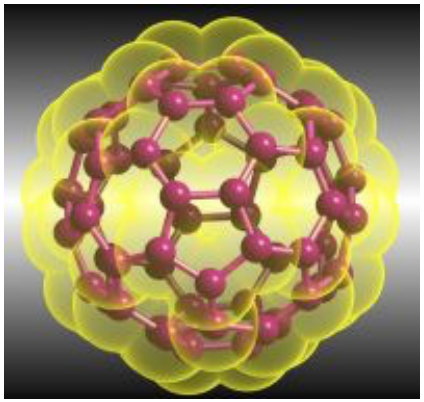






benzene

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

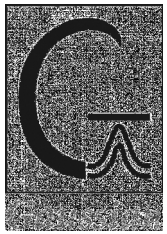
$$\hat{\mathcal{H}}_{el}[\psi(r_1,\ldots r_N)]=\mathrm{E}_{\mathrm{el}}\psi(r_1,\ldots r_N)$$

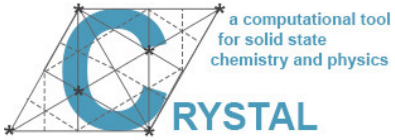
DFT

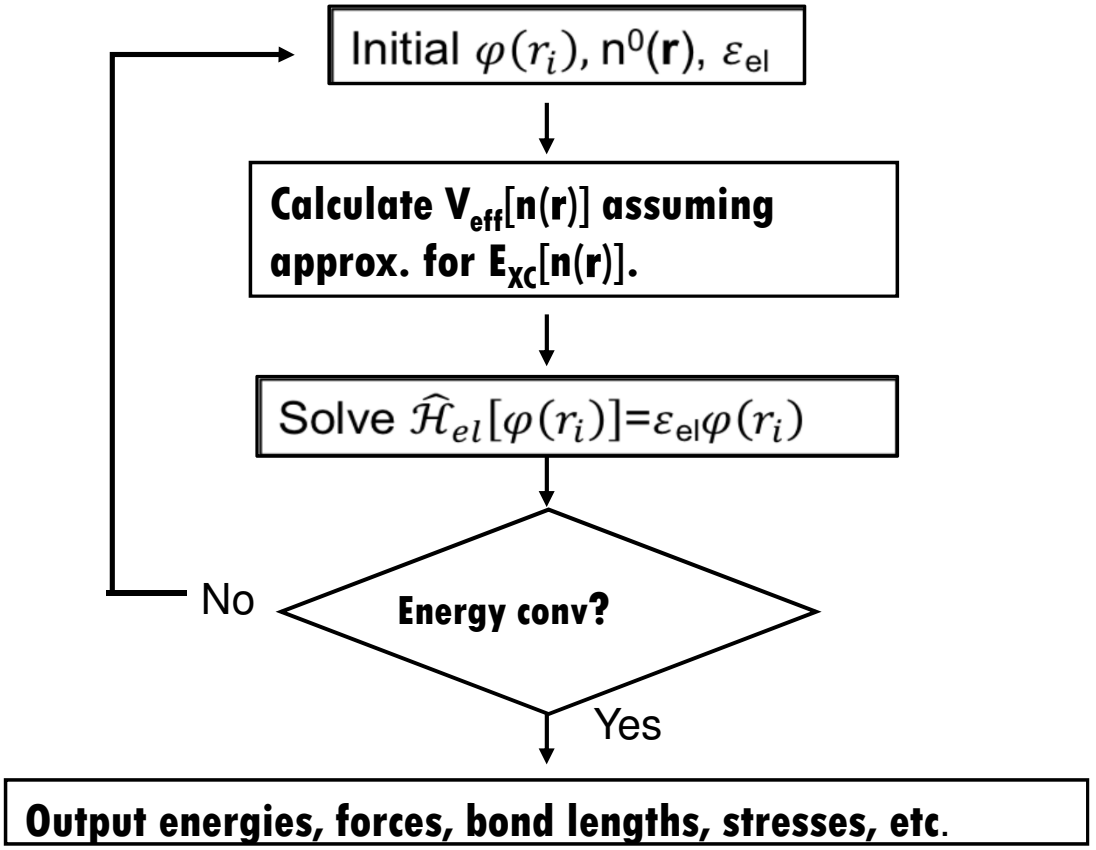
- $n(\mathbf{r})=\langle\psi(r_1,\ldots r_n)|\psi(r_1,\ldots r_N)\rangle$ electronic density.
- $E_{el}[$ PBE, B3LYP)
- $n(\mathbf{r})=\langle\varphi(r_1)\ldots\varphi(r_N)|\langle\varphi(r_1)\ldots\varphi(r_N)|\rangle$ system of fictional N-independent particles each represented by $\varphi(r_i)$.

Black Box with Suitable Approximations

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







Obtain the relax structure and the total energy of the system

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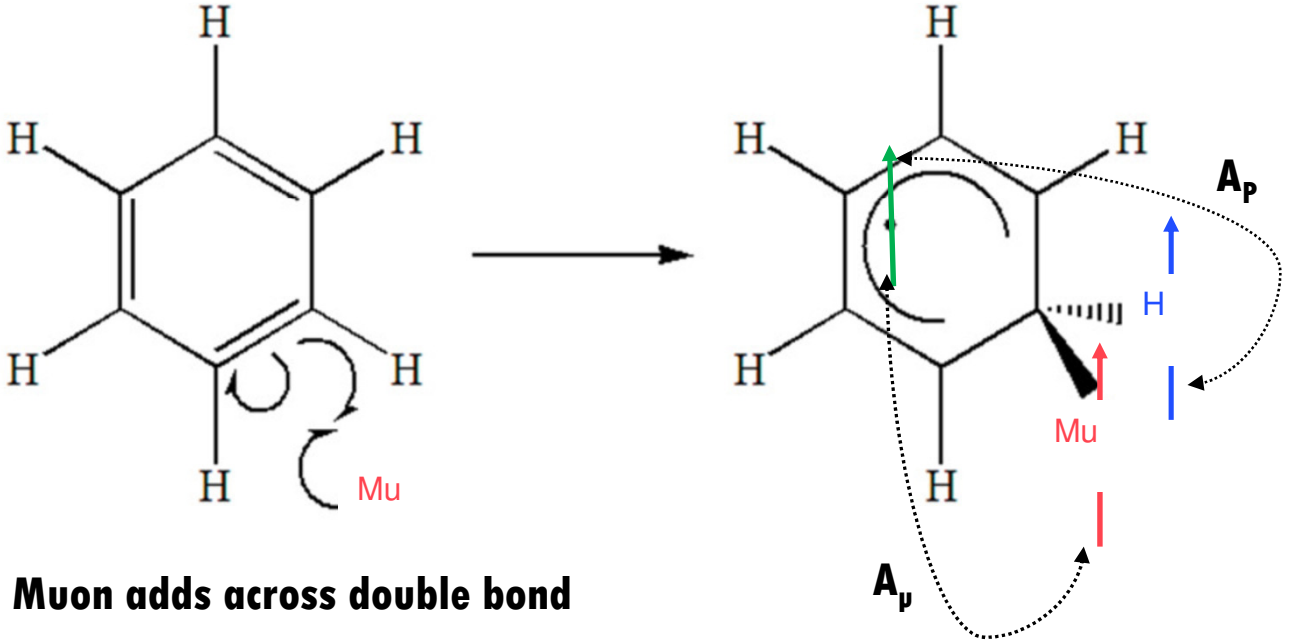
BENZENE

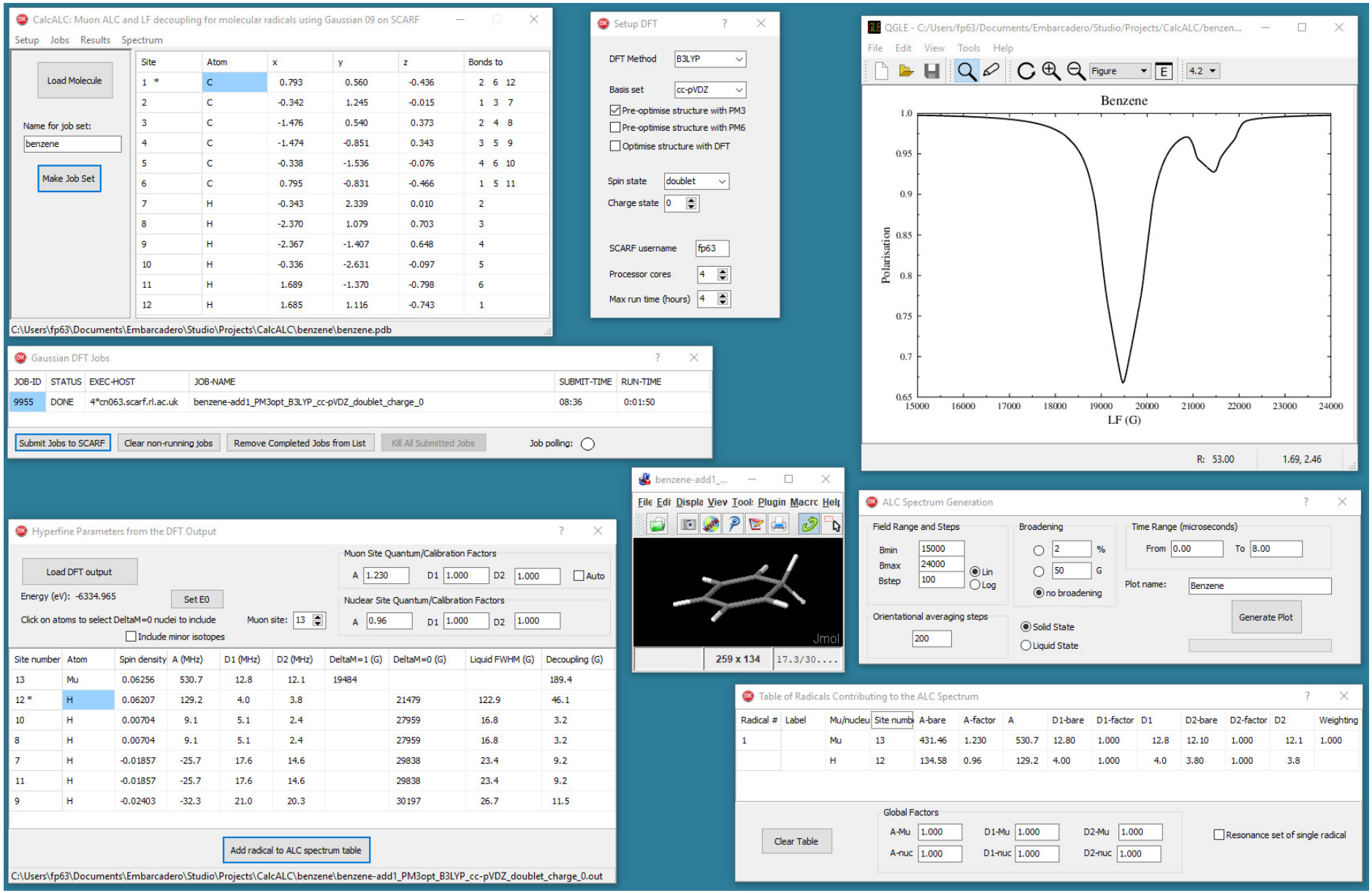
$\mu^+e^- = Mu$

Delocalized unpaired electron

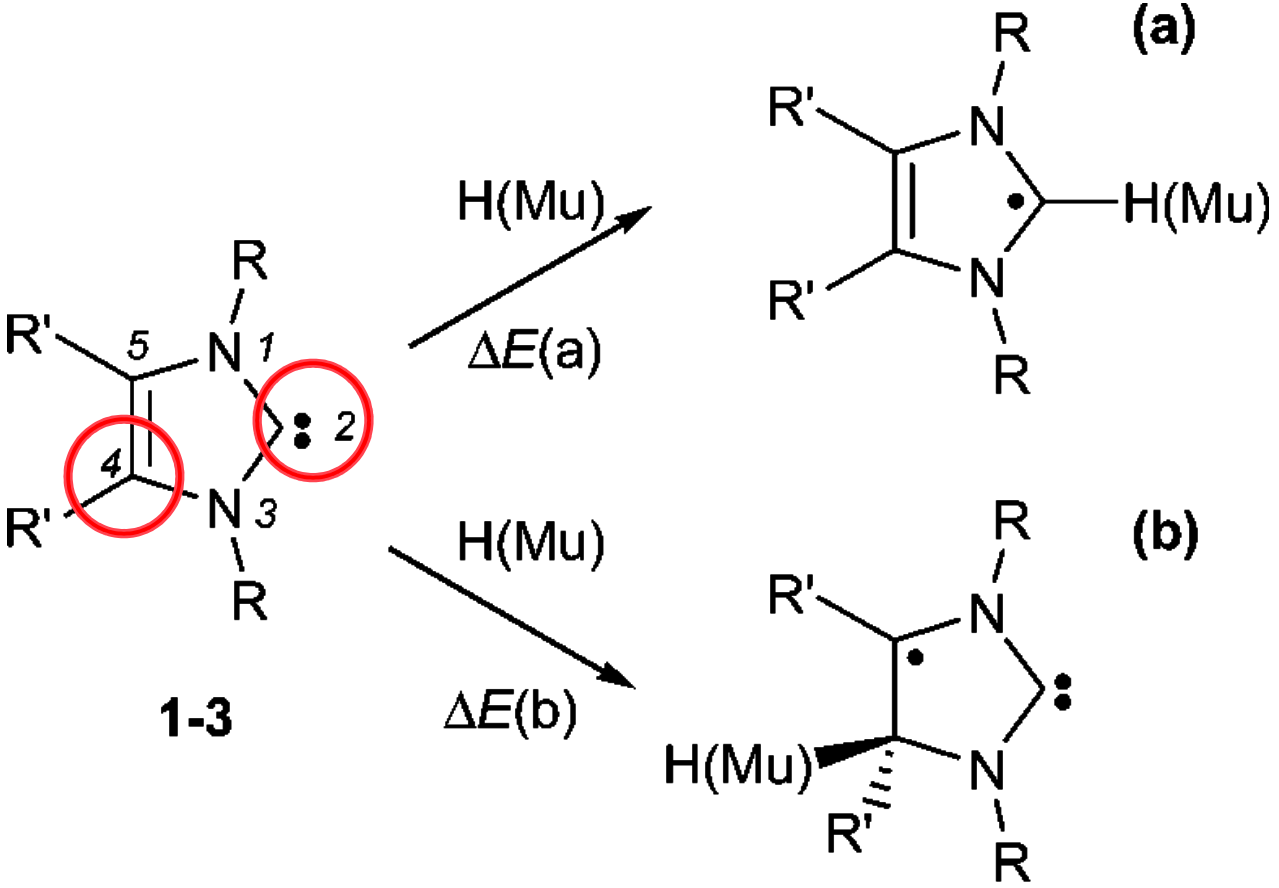


Muon adds across double bond

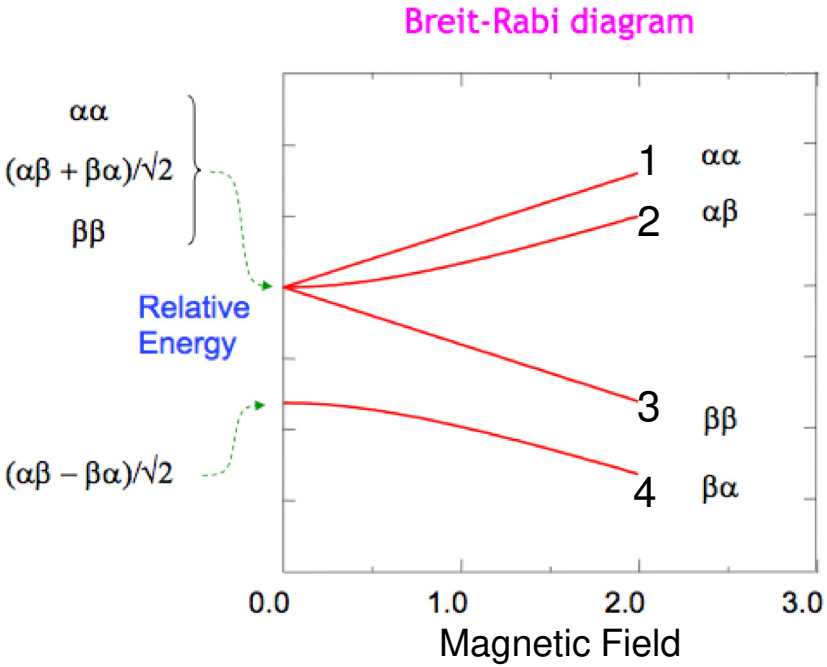
CalcALC: From Molecule to ALC Spectrum via DFT



Imidazole-type Carbene



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



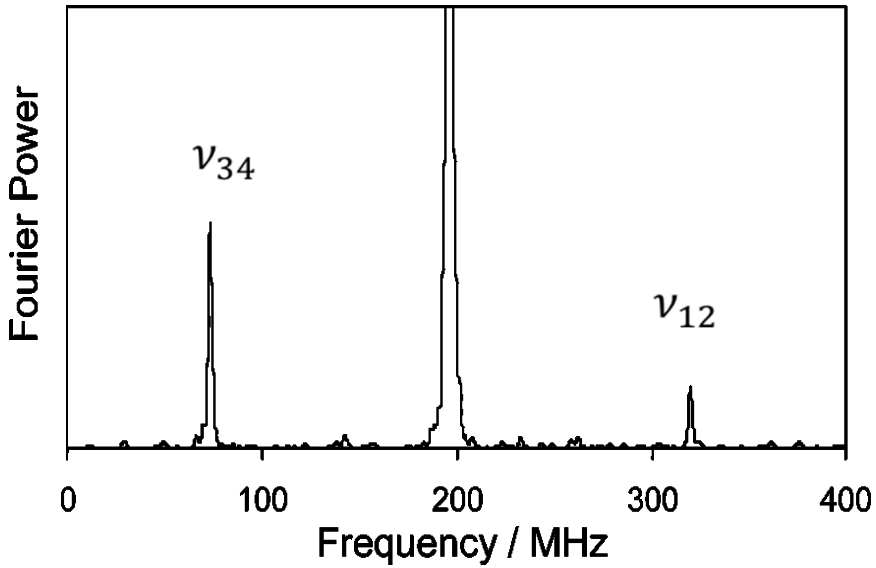


Figure 3. Transverse field μSR spectrum at 14.4 kG from **1** in THF at 298 K. The pair of peaks at ca. 73 and 320 MHz is due to a muoniated radical.

- F-μSR to calculate A_μ as

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

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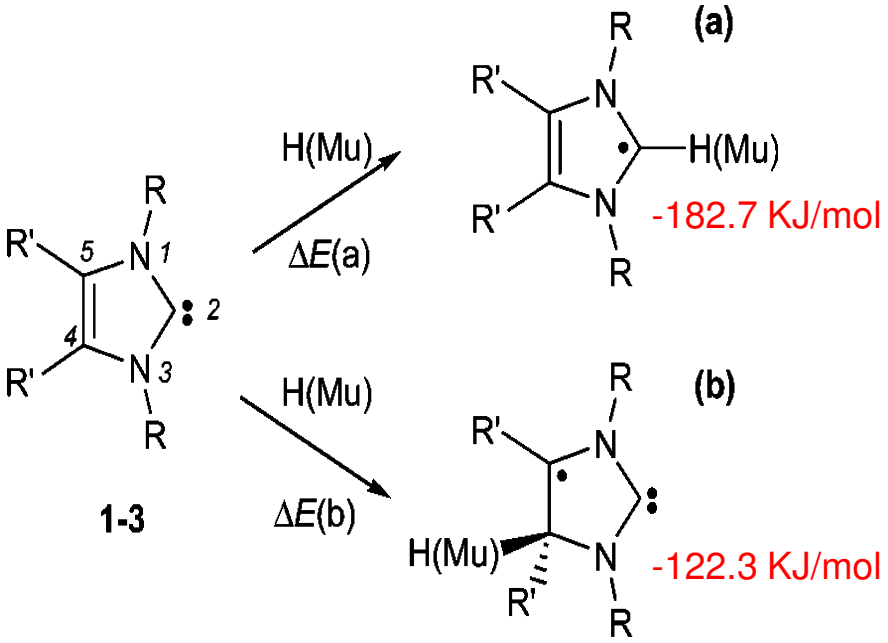
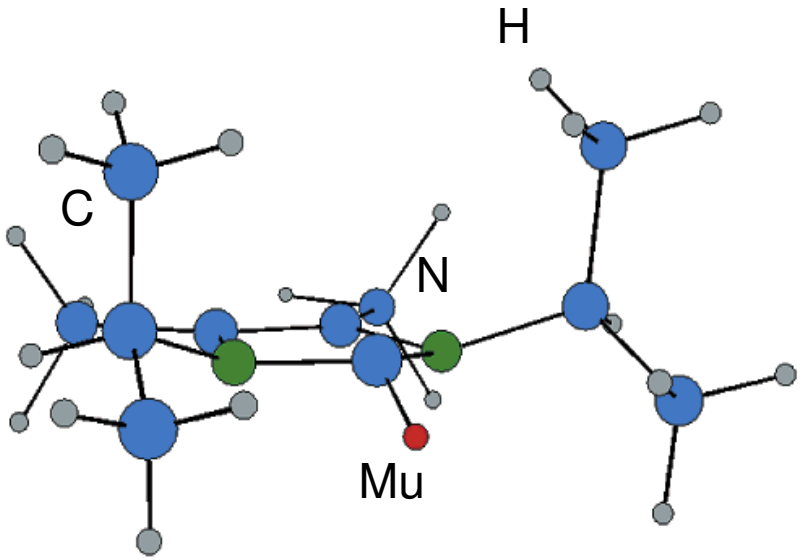


(a)



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

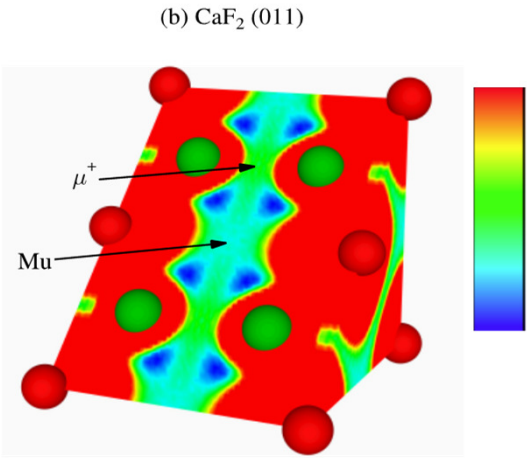
•Muonated Fe: follow the evolution of the muon frequency shift in a transverse field experiment as a function of the applied stress in a single Fe crystal[1]

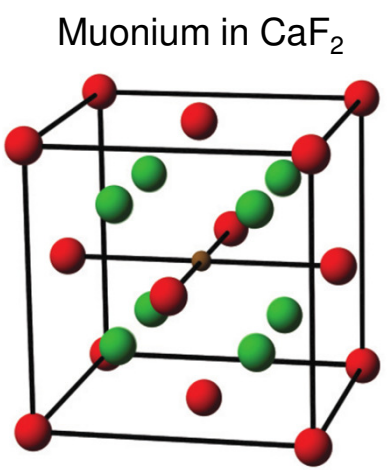
COMBINED THEORETICAL / EXPERIMENTAL APPROACH

•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)

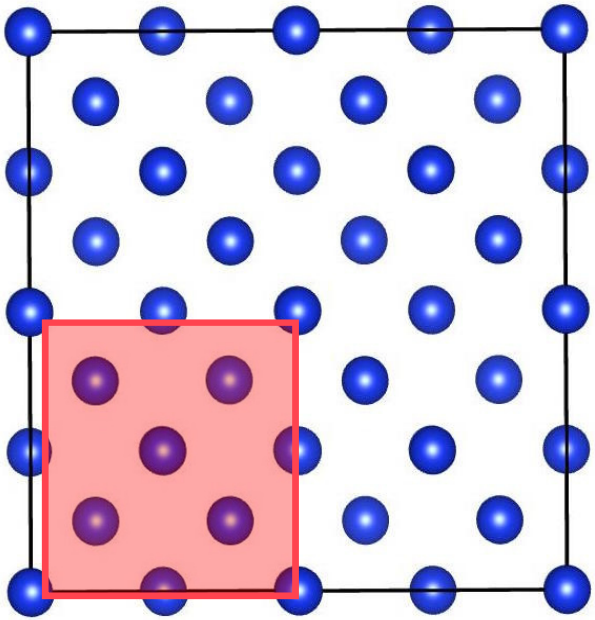




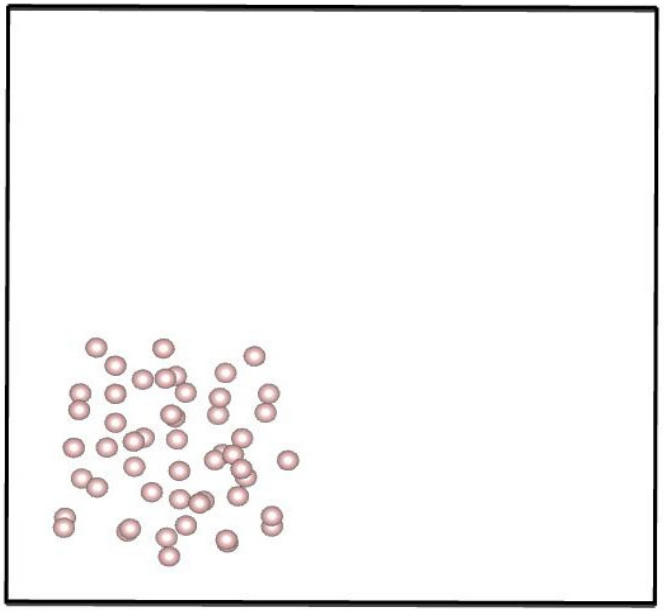
W. J. Kossler, et. al., Phys. Rev. B **32**, 293, (1985)
J. Moller, *et al.,* Phys. Rev. B **87**, 121108(R) (2013)

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

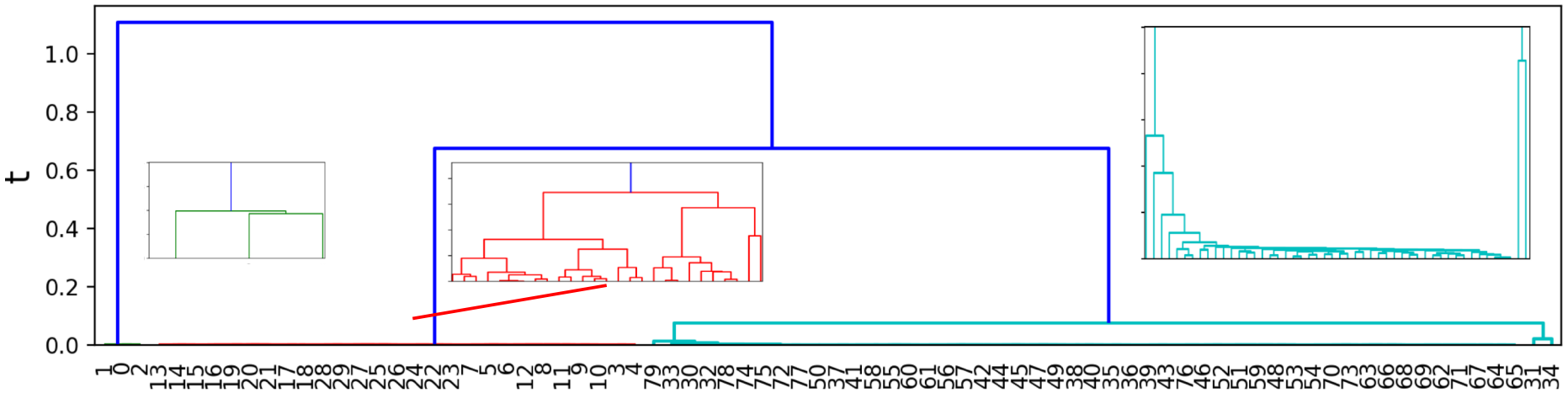
2x2x2 Si supercell

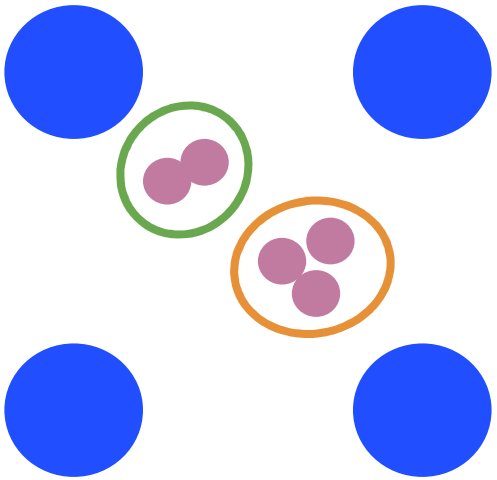


80 structures



https://arxiv.org/abs/1801.10454

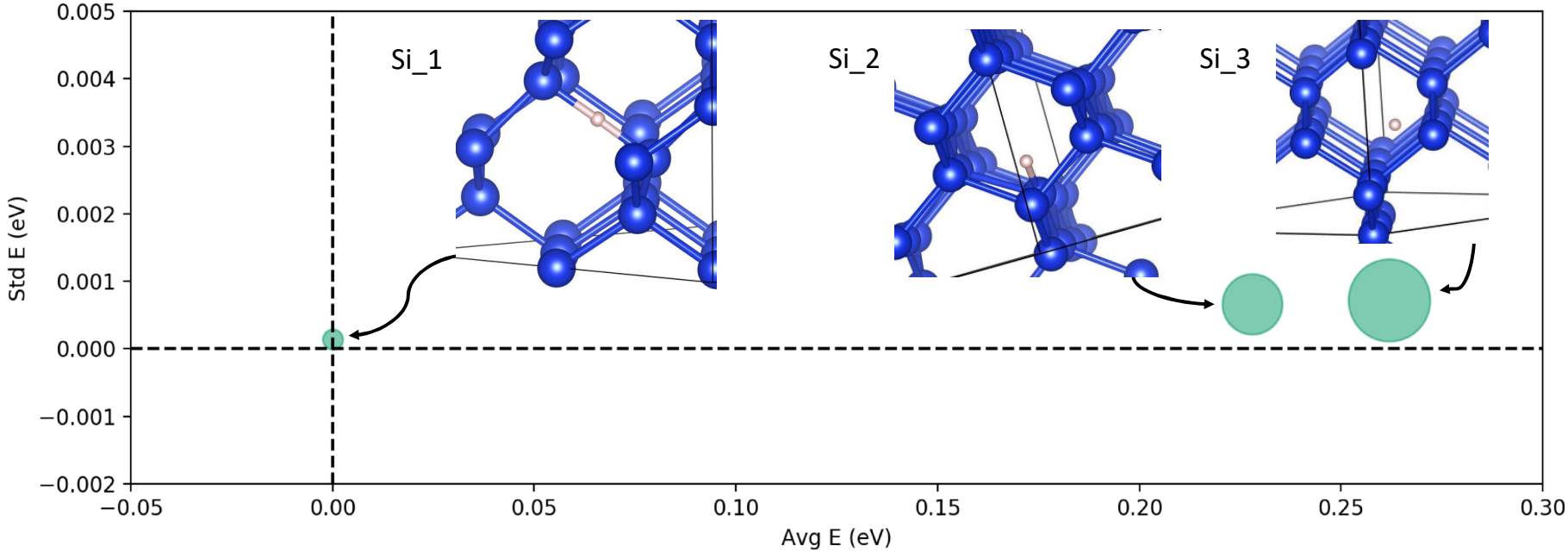


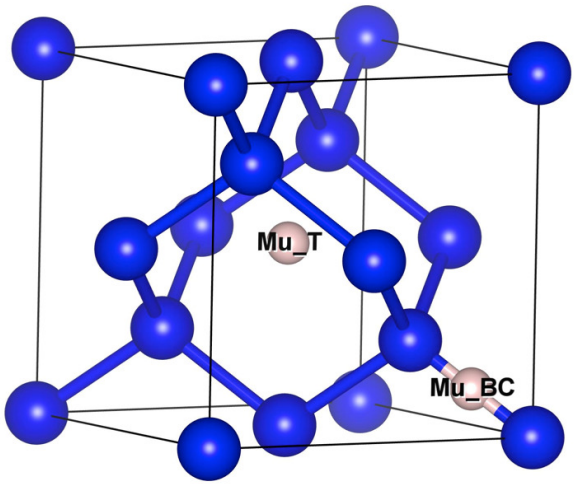


- Define *n*D vector: (E_T, Q_1, Q_2, Q_3,...)
- Look for "closeness" in *n*D space
- Hierarchical clustering
- 3 clusters identified

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.

JOCHYM

STURNIOLO

LIBORIO

PRATT

JACKSON

COTTRELL