Combining μSR and Density Functional Theory

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ISIS Facility, STFC Rutherford Appleton Laboratory, UK

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Science & Technology
Facilities Council

Organization of the Talk

SECTION 1:

Key concepts, approximations and computer implementations of DFT.

SECTION 2:

How DFT results can be related to muon results in molecular systems: the case of Carbene, C_6H_6-Mu and C_6H_7

SECTION 3:

How DFT results can be related to muon results in periodic systems: the case of fluorides.

SECTION 4:

How to improve the approximations used in DFT: Treatment of the vibrational contributions and the location of the muon stopping sites.

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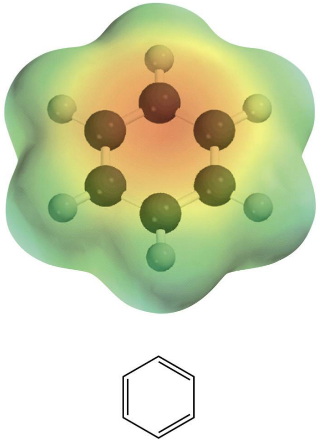
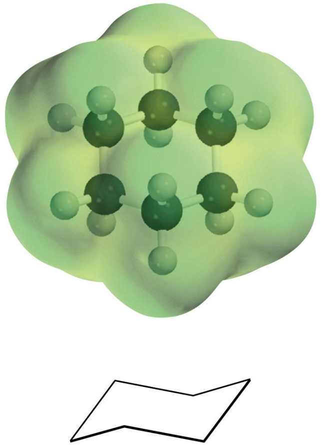
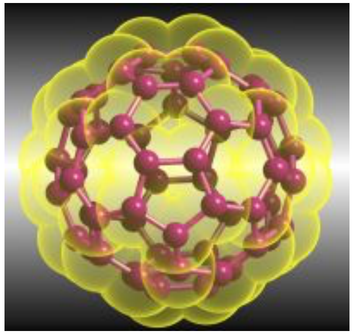
Quantum Mechanical Approach to Systems



benzene



cyclohexane



buckyball

Non-relativistic, time independent Schrödinger equation contains most of a system’s chemistry:

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

$$\hat{\mathcal{H}}=\underbrace{\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}\right)}_{\mathrm{T_e}}+\underbrace{\sum_{i=1}^{M}\left(-\frac{\nabla_I^2}{2M_I}\right)}_{\mathrm{T_N}}+\underbrace{\sum_{i,I=1}^{N,M}\left(\frac{Z_I}{|r_i-R_I|}\right)}_{\mathrm{V_{eN}}}+\underbrace{\sum_{\substack{i,j=1\\ i\neq j}}^{N,N}\left(\frac{1}{|r_i-r_j|}\right)}_{\mathrm{V_{ee}}}+\underbrace{\sum_{\substack{I,J=1\\ I\neq J}}^{M,M}\left(\frac{Z_IZ_J}{|R_I-R_J|}\right)}_{\mathrm{V_{NN}}}$$

Full quantum mechanical equations need to be simplified.

Born-Oppenheimer Approximation

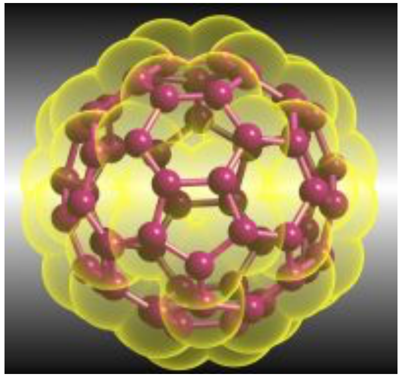
$$\hat{\mathcal{H}}\,[\,\Psi(r_1,\dots rR_1,\dots R_M)]=\mathrm{E}\Psi(r_1,\dots r_{N;}\,R_1,\dots R_M)$$

$$\hat{\mathcal{H}}=\underbrace{\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}\right)}_{\mathrm{T_e}}+\underbrace{\sum_{i=1}^{M}\left(-\frac{\nabla_I^2}{2M_I}\right)}_{\mathrm{T_N}}+\underbrace{\sum_{i,I=1}^{N,M}\left(\frac{Z_I}{|r_i-R_I|}\right)}_{\mathrm{V_{eN}}}+\underbrace{\sum_{\substack{i,j=1\\ i\neq j}}^{N,N}\left(\frac{1}{|r_i-r_j|}\right)}_{\mathrm{V_{ee}}}+\underbrace{\sum_{\substack{I,J=1\\ I\neq J}}^{M,M}\left(\frac{Z_I Z_J}{|R_I-R_J|}\right)}_{\mathrm{V_{NN}}}$$

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 ➡ Then T_{NN} is a parameter and the wave-function is separable. Hence, the new Schrödinger equation will be given by:

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

$$\hat{\mathcal{H}}_{el}=\underbrace{\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}\right)}_{\mathrm{T_e}}+\underbrace{\sum_{i,I=1}^{N,M}\left(\frac{Z_I}{|r_i-R_I|}\right)}_{\mathrm{V_{eN}}}+\underbrace{\sum_{\substack{i,j=1\\ i\neq j}}^{N,N}\left(\frac{1}{|r_i-r_j|}\right)}_{\mathrm{V_{ee}}}$$



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

The Trick of Density Functional Theory (DFT)

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

$$\widehat{\mathcal{H}}_{el}=\underbrace{\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}\right)}_{\mathrm{T_e}}+\underbrace{\sum_{i,I=1}^{N,M}\left(\frac{Z_I}{|r_i-R_I|}\right)}_{\mathrm{V_{eN}}}+\underbrace{\sum_{\substack{i,j=1\\ i\neq j}}^{N,N}\left(\frac{1}{|r_i-r_j|}\right)}_{\mathrm{V_{ee}}}$$

- $\mathrm{n}(\mathbf{r})=\langle\psi(r_1,\dots r_n)|\psi(r_1,\dots r_N)\rangle$ electronic density.
- $\mathrm{E_{el}}[\mathrm{n}(\mathbf{r})] = \mathrm{T_e}[\mathrm{n}(\mathbf{r})] + \underbrace{\mathrm{V_{eN}}[\mathrm{n}(\mathbf{r})] + \mathrm{V_H}[\mathrm{n}(\mathbf{r})] + \mathbf{E_{xc}[n(r)]}}_{\mathrm{V_{eff}}}.$
- $\mathrm{n}(\mathbf{r})=\langle\varphi(r_1)\dots\varphi(r_N)|\langle\varphi(r_1)\dots\varphi(r_N)|\rangle$ system of fictional N-independent particles each represented by $\varphi(r_i)$. $\mathrm{E_{el}}[\mathrm{n}(\mathbf{r})] = \mathrm{T^0_e}[\mathrm{n}(\mathbf{r})] + \mathrm{V_{eff}}[\mathrm{n}(\mathbf{r})]$, with $\mathrm{H_{el}}=\mathrm{T_{el}}+\mathrm{V_{eff}}$.

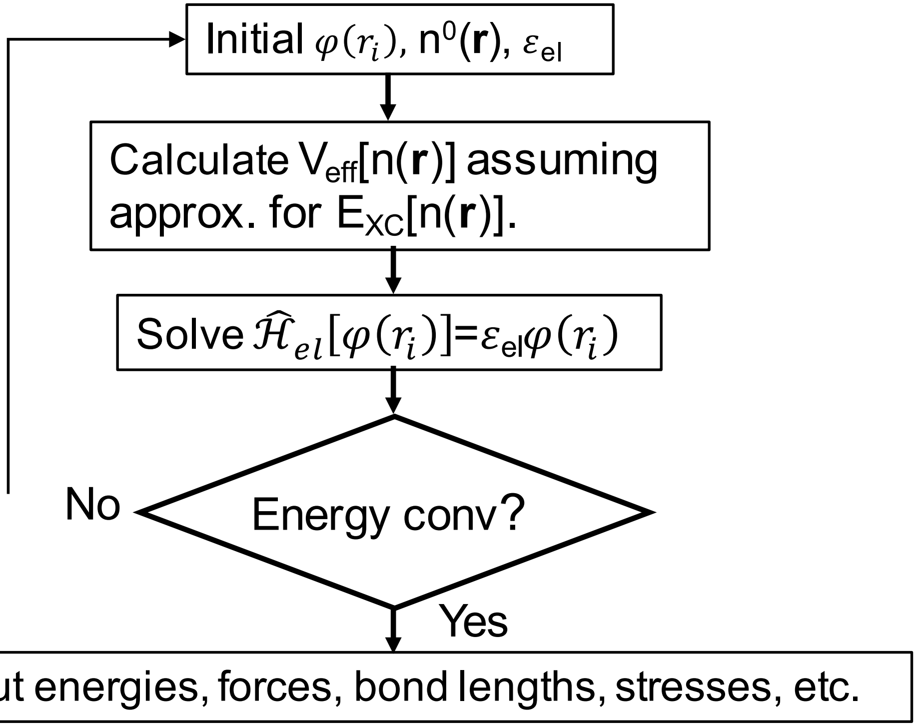
- **Problem reduced to solve the Schrödinger equation of one independent particle.** $\boldsymbol{\widehat{\mathcal{H}}_{el}[\varphi(r_i)]=\varepsilon_{\mathrm{el}}\varphi(r_i)}$

The Trick of Density Functional Theory (DFT)

Problem reduced to solve the Schrödinger equation of one independent particle.

$$\boldsymbol{\widehat{\mathcal{H}}_{el}[\varphi(r_i)]=\varepsilon_{\mathrm{el}}\varphi(r_i)}$$

$$\boldsymbol{\varphi(r_i)=\sum a_k\theta(ri)_k}$$



Initial $\varphi(r_i)$, $n^0(\mathbf{r})$, $\varepsilon_{\mathrm{el}}$

Calculate $V_{\mathrm{eff}}[n(\mathbf{r})]$ assuming approx. for $E_{XC}[n(\mathbf{r})]$.

Solve $\widehat{\mathcal{H}}_{el}[\varphi(r_i)]=\varepsilon_{\mathrm{el}}\varphi(r_i)$

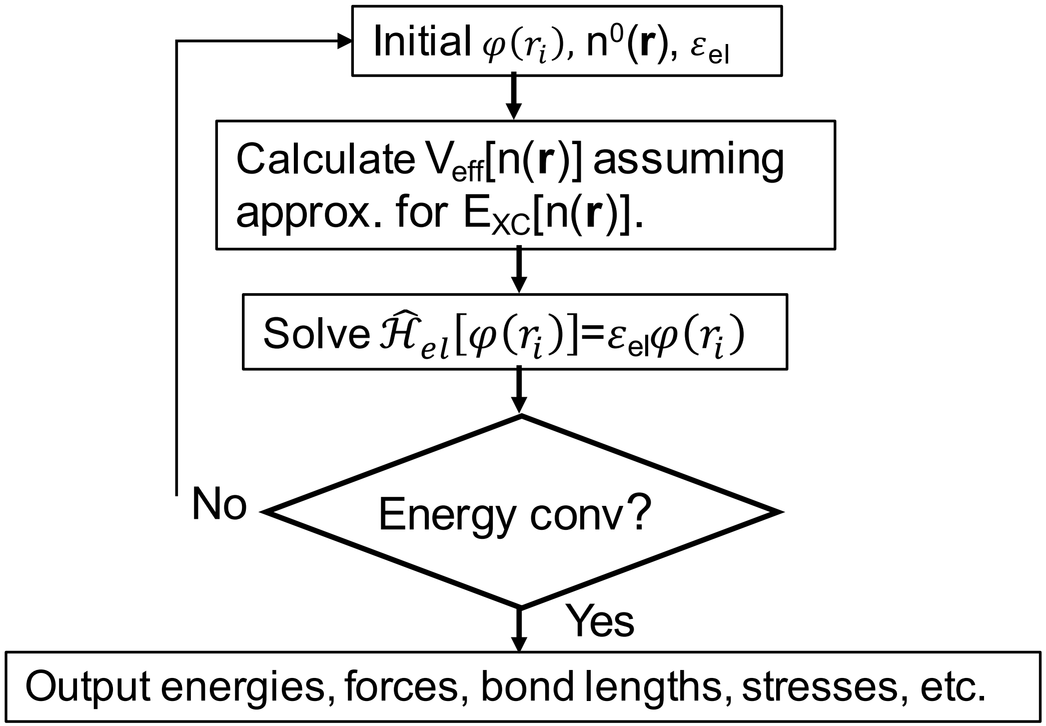
Energy conv?

No

Yes

Output energies, forces, bond lengths, stresses, etc.

The Trick of Density Functional Theory (DFT)



Initial $\varphi(r_i)$, $n^0(\mathbf{r})$, ε_{el}

Calculate $V_{eff}[n(\mathbf{r})]$ assuming approx. for $E_{XC}[n(\mathbf{r})]$.

Solve $\widehat{\mathcal{H}}_{el}[\varphi(r_i)]=\varepsilon_{el}\varphi(r_i)$

Energy conv?

No

Yes

Output energies, forces, bond lengths, stresses, etc.

- Choose Code for your problem
- Basis set for $\varphi(r_i)$: plane waves (CASTEP, VASP, ESPRESSO), localised basis set (CRYSTAL, SIESTA, GAUSSIAN).
- Approximate $E_{XC}[n(\mathbf{r})]$ (LDA, GGA, etc).
- Use pseudopotential to replace core electrons.
- Run self consistent calculation.

CASTEP

QUANTUMESPRESSO

a computational tool for solid state chemistry and physics

CRYSTAL

VASP

b-initio

ackage

imulation

ienna

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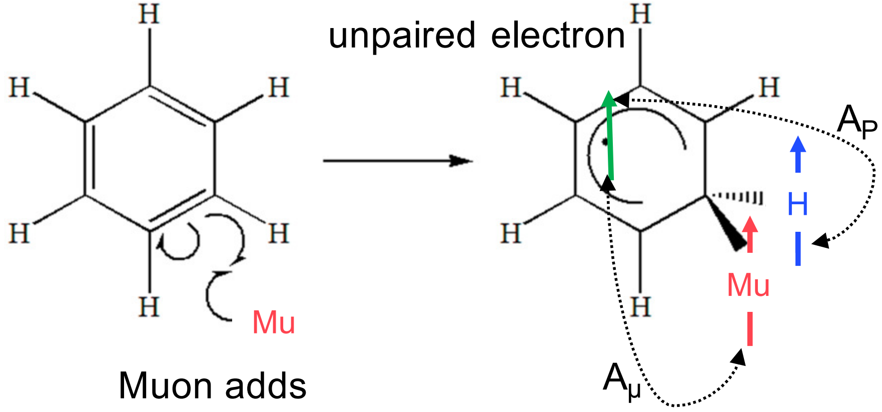
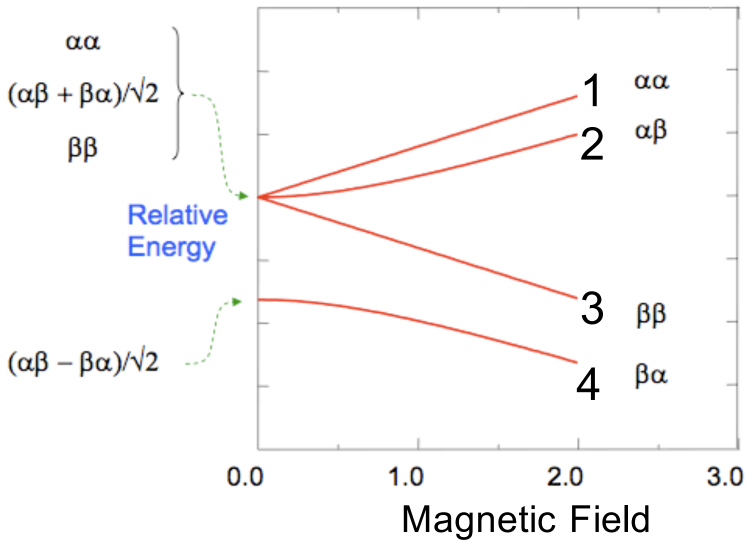
Muons in Molecular Systems

$\mu^+e^- = Mu$



Muon adds across double bond

Breit-Rabi diagram



- Hfcc in vacuum muonium organic radicals range from 0 to 600 MHz.

- In paramagnetic muon states muon and electron's spin interact.

- Gas and liquids, the hfcc is given by the isotropic hfcc:

$$A_\mu \cong A_{iso} = \frac{2\mu_0}{3}\gamma_e\gamma_n\rho(r_n)$$

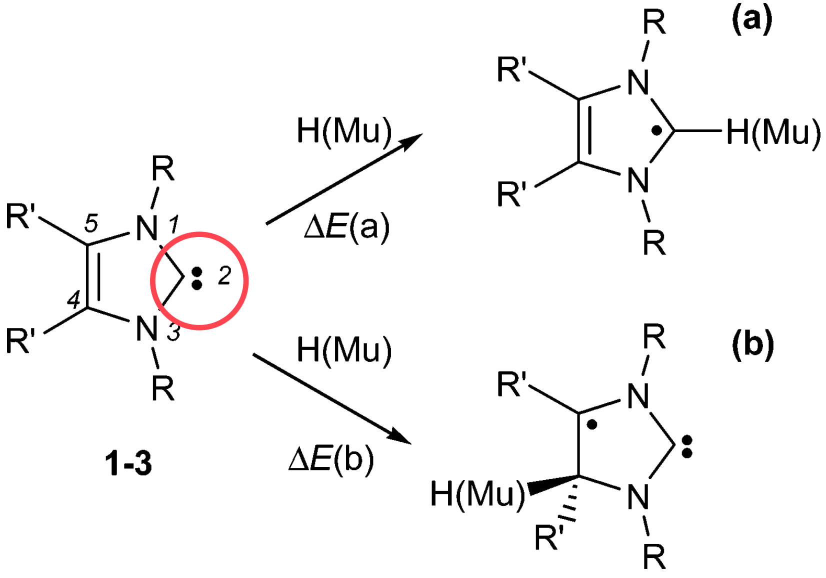
- F-µSR to calculate A_μ as:

$$A_\mu = \nu_{34} - \nu_{12}$$

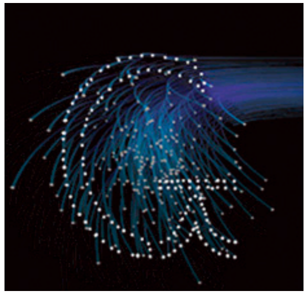
- Hfcc can indicate the spatial distribution of unpaired spin density, but do not provide the molecule's structure directly.

- Unpaired electron's spin interacts with spins of muons AND other nuclei. And you can calculate the nuclear hfcc (A_p) using ALC techniques. **Here we focus on A_μ.**

Muons in Molecular Systems: Carbenes



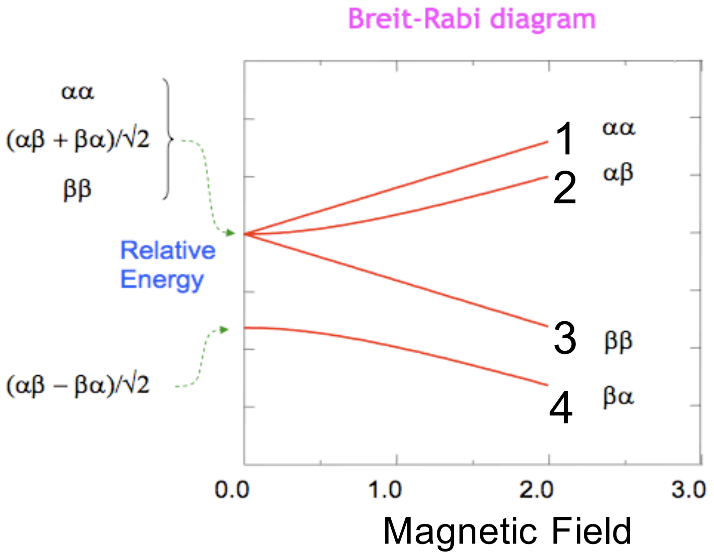
Imidazole-type Carbene



- Use basis set of local functions.
- Approximate $E_{XC}[n(\mathbf{r})]$ using B3LYP hybrid functional
- Hydrogen as Mu placed in chosen molecular sites.
- F-µSR to calculate A_μ as
$$A_\mu = \nu_{34} - \nu_{12}$$
- Used calculated reaction energies to place Mu in the molecule: (a) preferred site.
$$\Delta E(a) = E_{radical.} - (E_{carbene.} + E_H)$$
- Empirical treatment of zero point vibrational motions to determine geometry of molecule (isotope effect). C-Mu bond extended by 4.9% and fixed. Out-of-plane angle for the C-Mu bond optimized with experimental hfcc.

I. McKenzie, *et al., J. AM. CHEM. SOC.* 9 VOL. 125, NO. 38, (2003)

Muons in Molecular Systems: Carbenes, TF-μSR



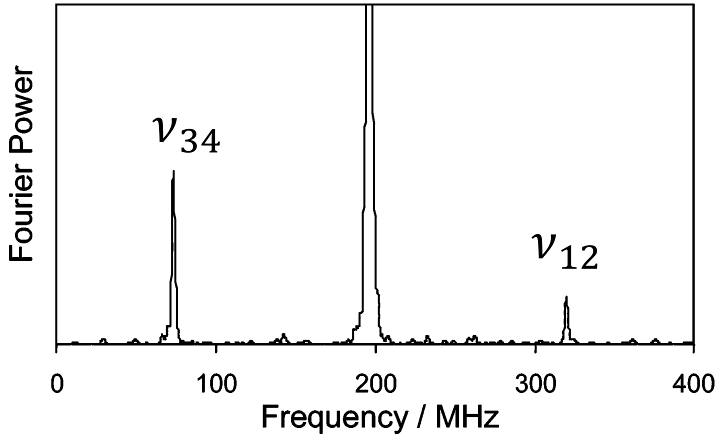
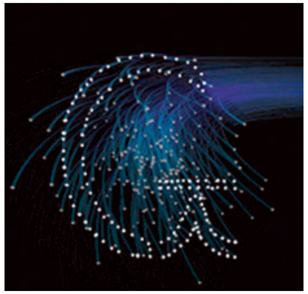


Figure 3. Transverse field μSR spectrum at 14.4 kG from **1** in THF at 298 K. The pair of peaks at ca. 73 and 320 MHz is due to a muoniated radical.



- Use basis set of local functions.
- Approximate $E_{XC}[n(\mathbf{r})]$ using B3LYP hybrid functional
- Hydrogen as Mu placed in chosen molecular sites.
- F-µSR to calculate A_μ as

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

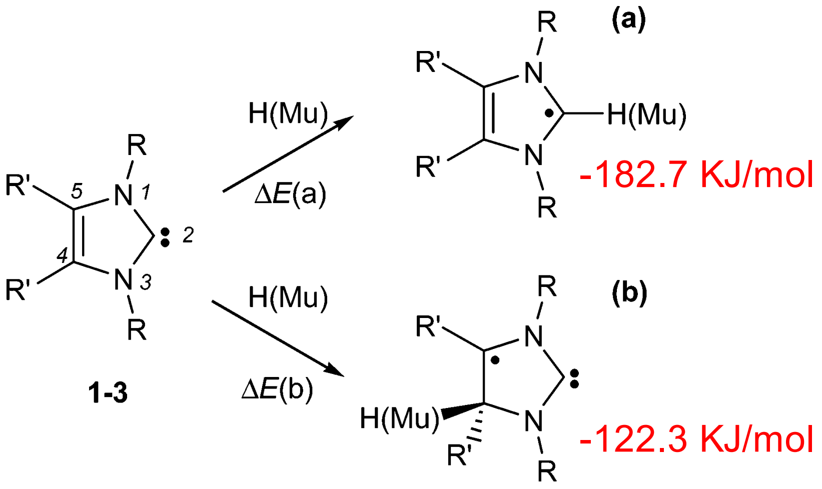
- Used calculated reaction energies to place Mu in the molecule: (a) preferred site.

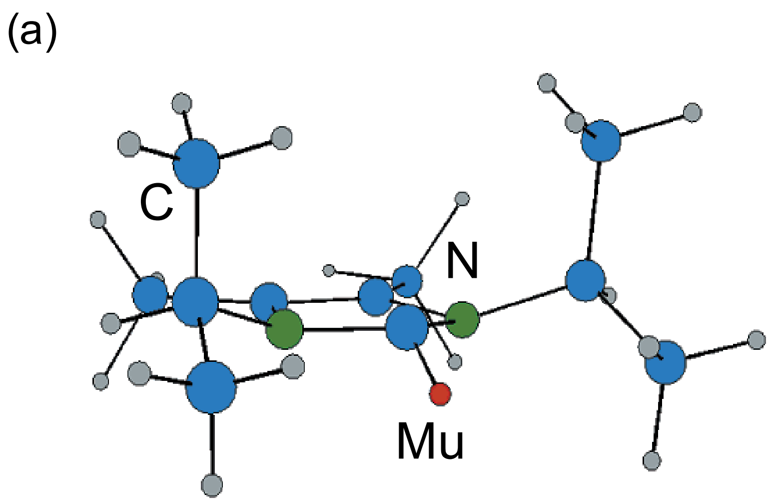
$$\Delta E(a) = E_{radical.} - (E_{carbene.} + E_H)$$

- Empirical treatment of vibrational motions to determine geometry of molecule (isotope effect). C-Mu bond extended by 4.9% and fixed. Out-of-plane angle for the C-Mu bond optimized with experimental hfcc.

I. McKenzie, *et al.*, **J. AM. CHEM. SOC.** 9 VOL. 125, NO. 38, (2003)

Muons in Molecular Systems: Carbenes and DFT





A_μ=246.4 MHz (adjusted to experiment)

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

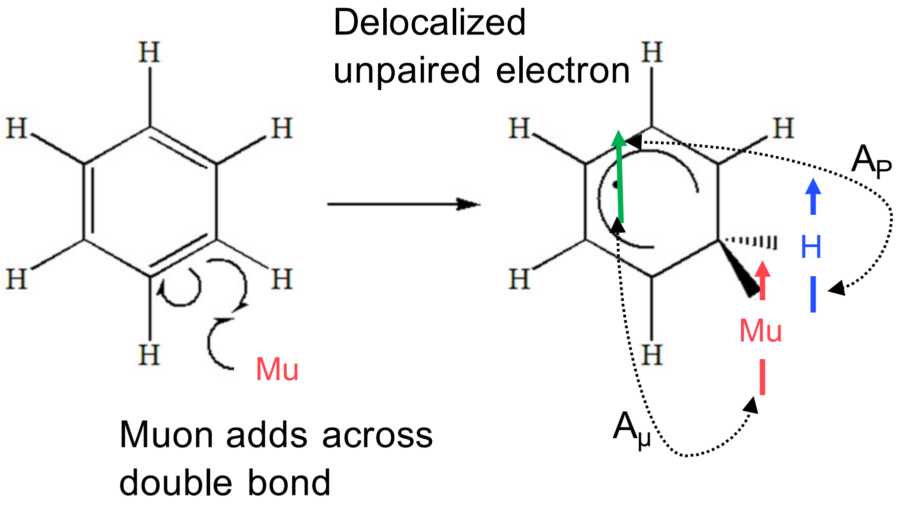
$$\Delta E(a) = E_{radical.} - (E_{carbene.} + E_H)$$

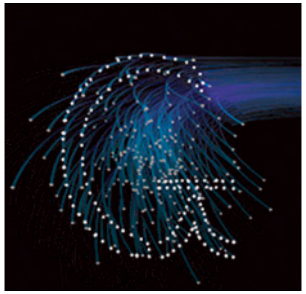
- Adjust the theoretical A_μ to agree with the experimental value.
- A_μ forms part of the Hamiltonian, it is directly related to the DFT's total energy. Need to account for ZPE and Temperature effect.
- Empirical treatment of vibrational motions to determine geometry of molecule. C-Mu bond extended by 4.9% and fixed. Out-of-plane angle for the C-Mu bond optimized with experimental hfcc.
- Model not transferable. Difficult to reproduce. Cannot predict muon stopping sites.

I. McKenzie, *et al.*, **J. AM. CHEM. SOC.** 9 VOL. 125, NO. 38, (2003)

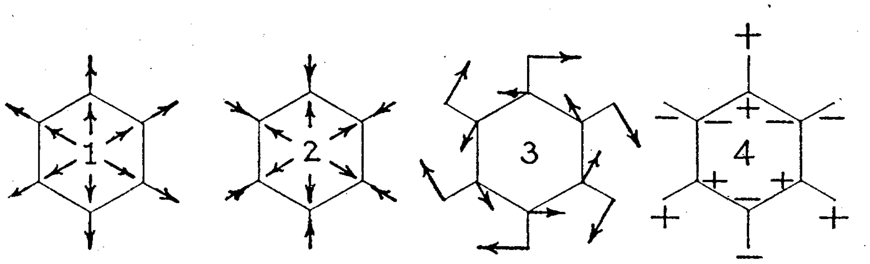
Muons in Molecular Systems: C_6H_7 and C_6H_6-Mu

$\mu^+e^- = Mu$





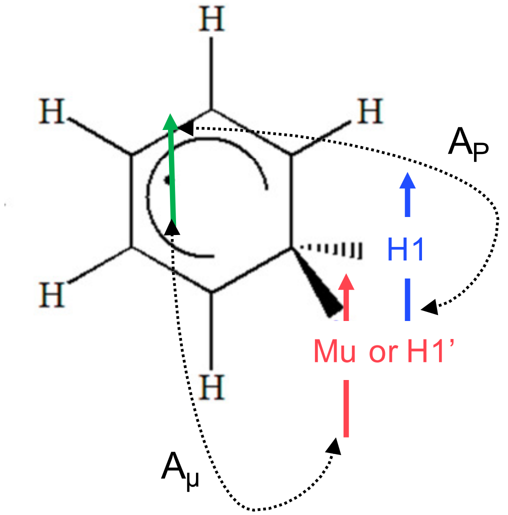
- Use basis set of local functions.
- Approximate $E_{XC}[n(\mathbf{r})]$ using B3LYP hybrid functional
- Hydrogen and Mu added to a C in C_6H_6.
- Empirical treatment of zero point vibrational motions to determine isotope effect.
- C-Mu/H bond length changed to represent vibrational stretching mode.
- Out-of-plane/ In-plane bending angle for C-Mu/H bond is changed to represent bending modes.
- Value of hyperfine constant averaged over populated zero-point level geometries.



Eg. Vibrational modes for the Benzene Molecule

- B. Hudson, *et al., Molecules*, *18*, 4906-4916 (2013)
- **Simulating hyperfine coupling constants of muoniated radicals.** J. Peck, S. Cottrell and F. Pratt.

Muons in Molecular Systems: C_6H_7 and C_6H_6-Mu



$$A \approx \frac{2\mu_0}{3}\gamma_e\gamma_n\left|\psi(r_n\ )\right|^2$$

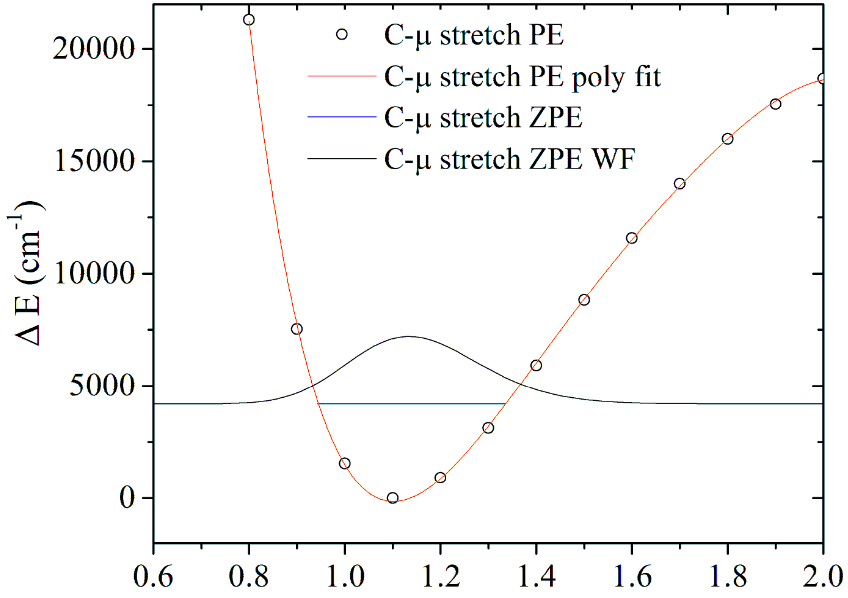
$$\langle A\rangle = \frac{\sum_{i,j}\left|\psi(r_i^j)\right|^2 A(r_i^j)}{\sum_{i,j}\left|\psi(r_i^j)\right|^2}$$

	$A_\mu(C_6H_6\text{-Mu})-A_\mu(C_6H_6\text{-H1'})$ (in Gauss)
Exp.	12.32
Calc.	11.32

Quantum Harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi(x;n)}{\partial x^2} + \frac{1}{2}m\omega^2x^2\phi(x;n) = E_n\phi(x;n)$$

n	$\frac{2E_n}{\hbar\omega}$	$\phi(x;n)e^{+\frac{x^2}{2a^2}}$
0	1	N_0
1	3	$N_1\cdot\left(\frac{2x}{a}\right)$
2	5	$N_2\cdot\left(\frac{4x^2}{a^2}-2\right)$
$\vdots$	$\vdots$	$\vdots$
n	$2n+1$	$N_n\mathcal{H}_n\left(\frac{x}{a}\right)$

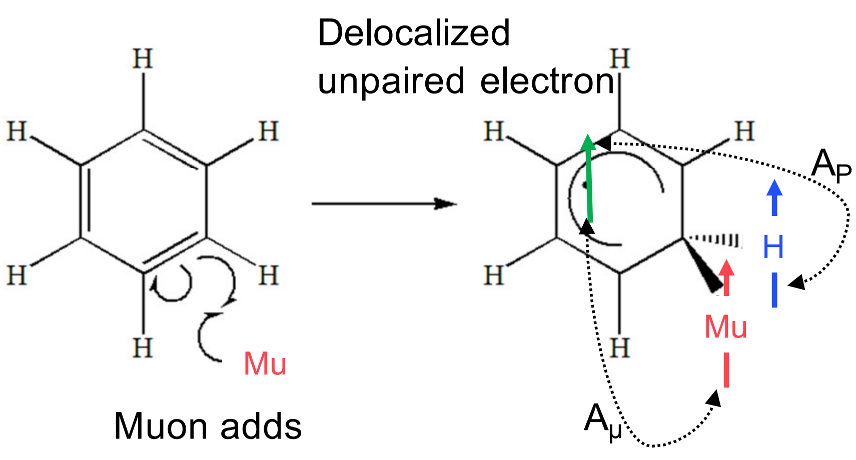


Stretching potential energy with ZPC levels and probability distributions for H and Mu and variation.

- B. Hudson, *et al.*, *Molecules*, *18*, 4906-4916 (2013)
- **Simulating hyperfine coupling constants of muoniated radicals.** J. Peck, S. Cottrell and F. Pratt.

Muons in Molecular System: Summary

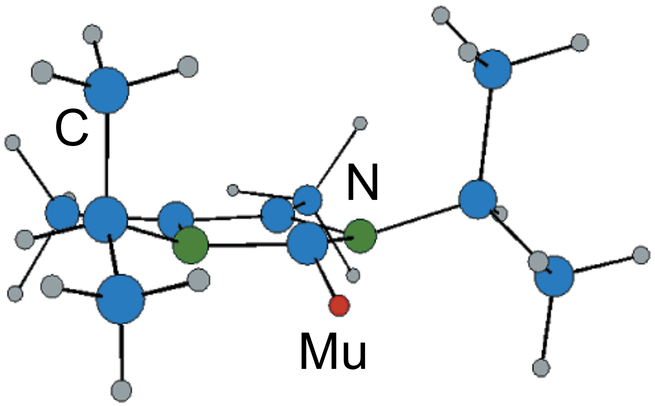
$\mu^+e^- = \mathrm{Mu}$



Delocalized unpaired electron

Muon adds across double bond

(a)



- Basis set of local functions and B3LYP hybrid functional provide sensible structures for the molecules.
- Mu placed in chosen molecular sites. Sites chosen using DFT reaction energies.
- Empirical treatment of vibrational motions to determine the isotope effect. Uses few vibrational modes and assume those to be isolated.
- Method for ZPE not necessarily transferable to more complex molecules.
- Current DFT calculations can assist the experiments.
- Needs to develop method for treatment of vibrational contributions.

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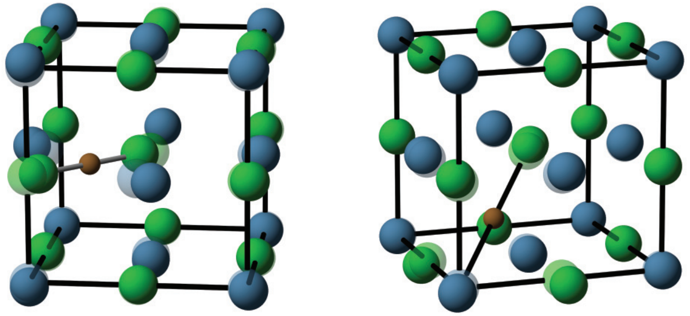
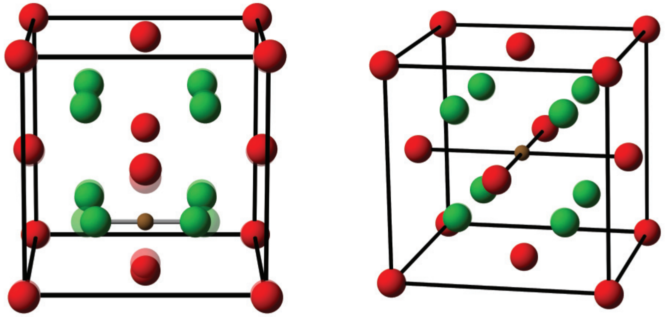
μ^+/Muonium in Fluorides



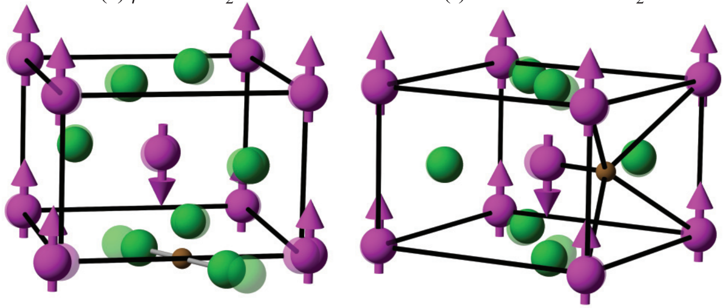
(a) μ^+ in LiF/NaF

(b) Muonium in LiF/NaF



(c) μ^+ in CaF_2/BaF_2

(d) Muonium in CaF_2/BaF_2



(e) μ^+ in CoF_2

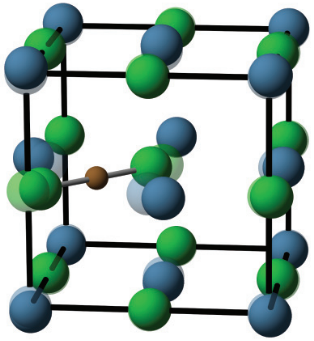
(f) Muonium in CoF_2

- Use basis set of plane waves.
- Approximate $E_{XC}[n(\mathbf{r})]$ using GGA
- Pseudopotentials used for core electrons.
- μ^+ (diamagnetic) and Muonium (paramagnetic) placed in chosen low-symmetry crystalline sites of Fluorides.
- All ions were allowed to relax until forces below threshold.
- Calculated total energies, band structures, vibrational modes at gamma, estimated magnetic moments.

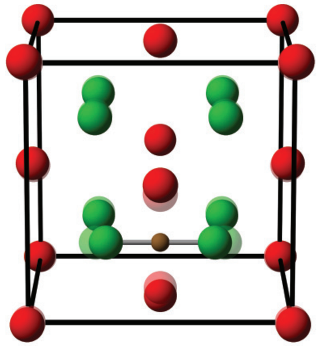
J. Moller, *et al.,* Phys. Rev. B **87**, 121108(R) (2013)

μ^+ in Fluorides: Cations Displacement and F-μ-F State

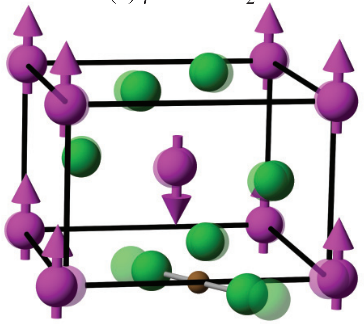
(a) μ^+ in LiF/NaF

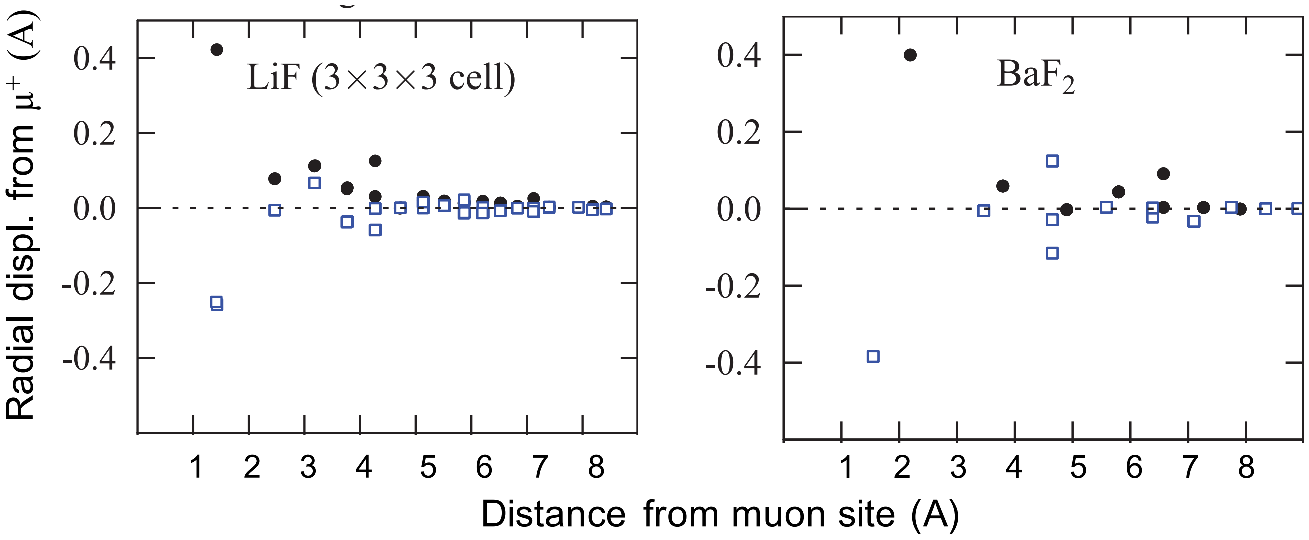


(c) μ^+ in CaF_2/BaF_2



(e) μ^+ in CoF_2





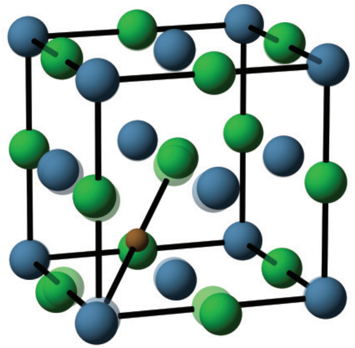
	$2r_{DFT}$	$2r_{exp}$
$(FHF)^{-a}$	2.36	2.28
$(FHF)^{-b}$		2.28
$(F\text{-}\mu\text{-}F)^{-}$	2.36	
LiF	2.34[18]	2.36(2)[12]
NaF	2.35	2.38(1)[12]
CaF_2	2.31	2.34(2)[12]
BaF_2	2.33	2.37(2)[12]
CoF_2	2.36	2.43(2)

- Equilibrium geometries predict the formation of F-μ-F in all the fluorides. In agreement with experiments for LiF, NaF, CaF_2 and BaF_2.
- No experimental evidence of any other stable diamagnetic state in these series.
- Perturbation caused by muon in host's cations is large but short ranged. Exceeds that of F^- in F-μ-F.
- No experimental evidence of F-μ-F in CoF_2. **F-μ-F state in CoF_2 predicted by calculations and confirmed by experiments.**

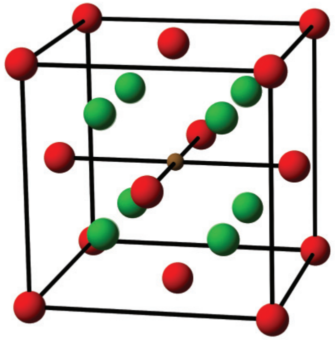
J. Moller, *et al.,* Phys. Rev. B **87**, 121108(R) (2013)

Muonium in Fluorides: Hyperfine Coupling and ZPE

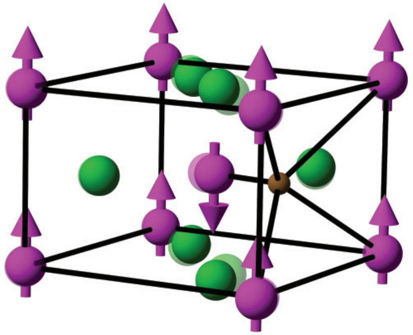
(b) Muonium in LiF/NaF

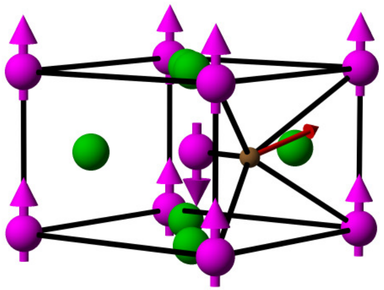


(d) Muonium in CaF$_2$/BaF$_2$



(f) Muonium in CoF$_2$



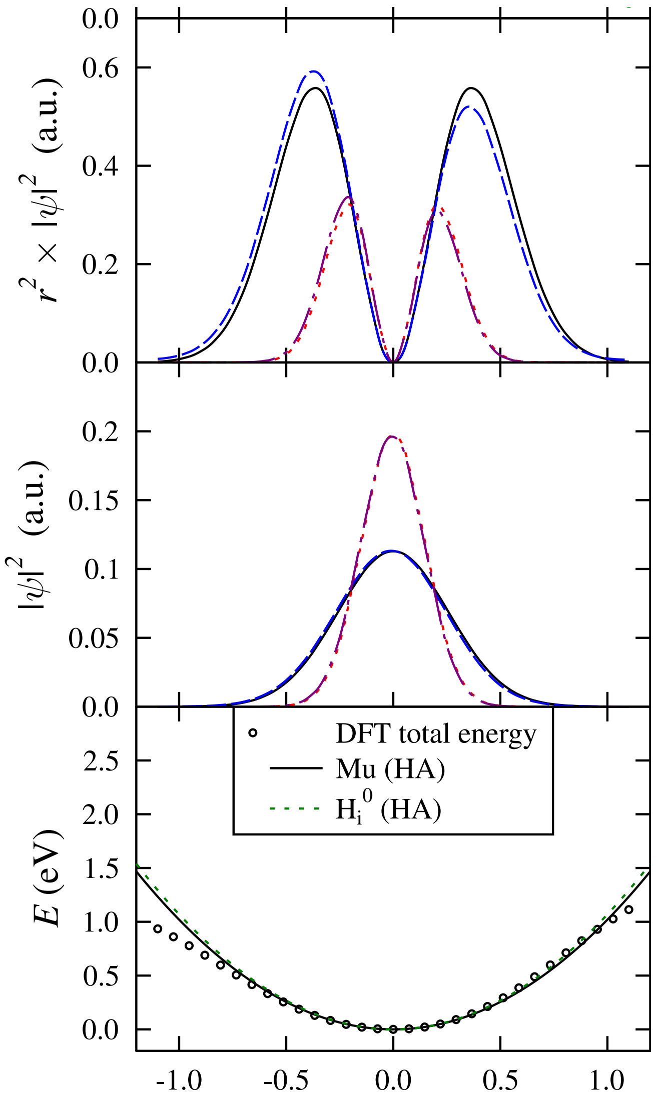


$$A = \frac{2\mu_0}{3}\gamma_e\gamma_n\rho(r_n)$$

$$\langle A\rangle = \frac{\int r^2 dr|\psi(r)|^2 A(r)}{\int r^2 dr|\psi(r)|^2}$$

Harmonic Method:
$\psi(r_i^j)$: wave-function of quantum Harmonic oscillator.

Finite Differences Method:
$\psi(r_i^j)$: wave-function obtained via constrained DFT calculation.



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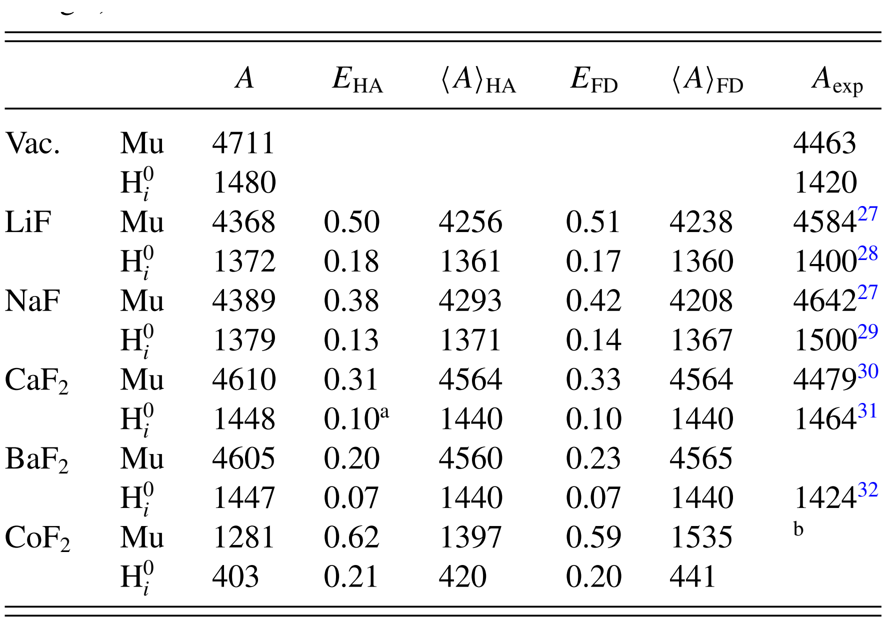
Muonium in Fluorides: Hyperfine Coupling and ZPE

$$\langle A \rangle = \frac{\sum_{i,j} (r_i^j) | \psi(r_i^j) | A(r_i^j)}{\sum_{i,j} (r_i^j) | \psi(r_i^j) |}$$

$$A = \frac{2\mu_0}{3} \gamma_e \gamma_n \rho(r_n)$$



		A	E_{HA}	$\langle A \rangle_{HA}$	E_{FD}	$\langle A \rangle_{FD}$	A_{exp}
Vac.	Mu	4711					4463
	H_i^0	1480					1420
LiF	Mu	4368	0.50	4256	0.51	4238	4584[27]
	H_i^0	1372	0.18	1361	0.17	1360	1400[28]
NaF	Mu	4389	0.38	4293	0.42	4208	4642[27]
	H_i^0	1379	0.13	1371	0.14	1367	1500[29]
CaF_2	Mu	4610	0.31	4564	0.33	4564	4479[30]
	H_i^0	1448	0.10[a]	1440	0.10	1440	1464[31]
BaF_2	Mu	4605	0.20	4560	0.23	4565	
	H_i^0	1447	0.07	1440	0.07	1440	1424[32]
CoF_2	Mu	1281	0.62	1397	0.59	1535	[b]
	H_i^0	403	0.21	420	0.20	441	

Harmonic Method:
$\psi(r_i^j)$: wave-function of quantum Harmonic oscillator.

Finite Differences Method:
$\psi(r_i^j)$: wave-function obtained via constrained DFT calculation.

- **Muonium placed in chosen low-symmetry crystalline sites.**
- In CaF_2, BaF_2 and CoF_2 Mu occupies octahedral sites.
- Contact hyperfine coupling A between muon spin and surrounding spin density calculated.
- Vibrational modes of the defect calculated.

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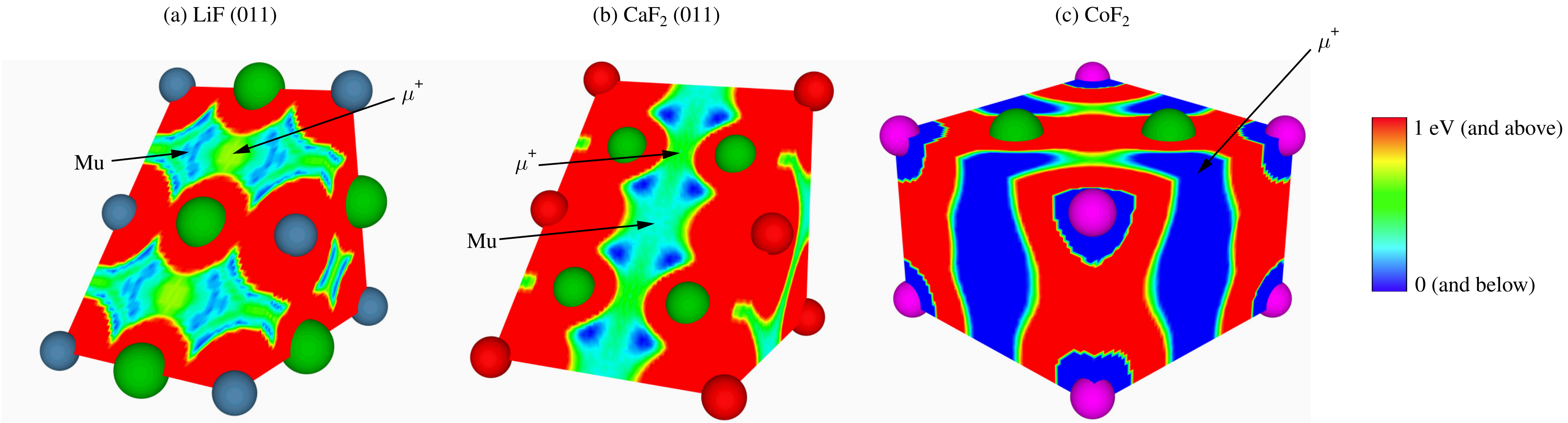
μ^+ /Muonium in Fluorides: Stopping Sites



- **μ^+/Muonium stopping sites DO NOT coincide with minimum of electrostatic potential.**
- Stopping site for μ^+ related to energy minimization of F-μ-F state.
- Muonium's electron screens μ^+, and it is not attracted to the electrostatic minimum.

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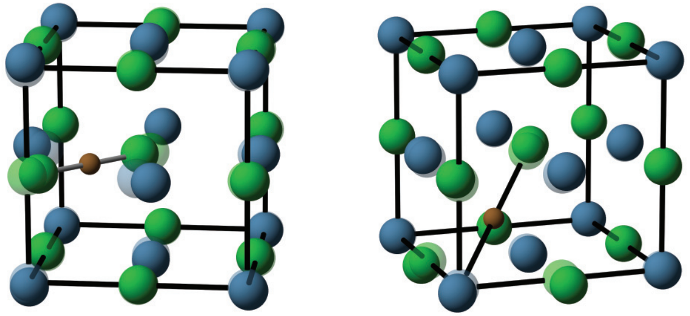
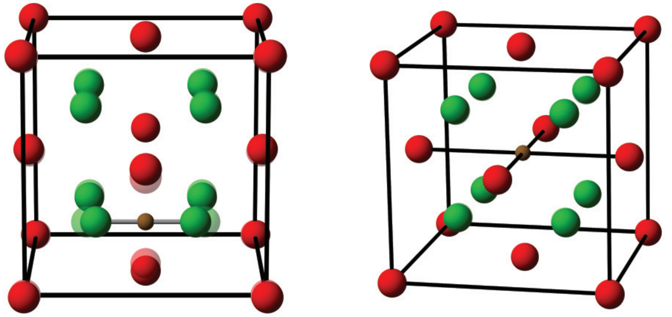
μ^+ /Muonium in Fluorides: Summary

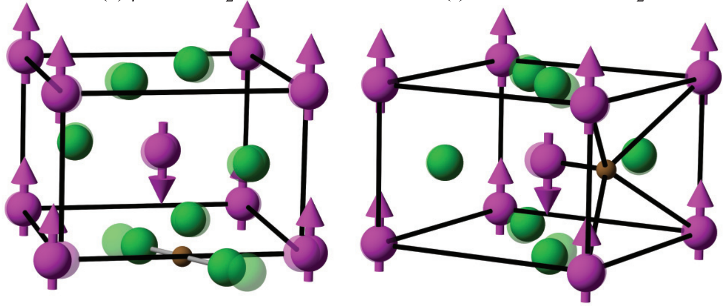
(a) μ^+ in LiF/NaF (b) Muonium in LiF/NaF



(c) μ^+ in CaF_2/BaF_2 (d) Muonium in CaF_2/BaF_2



(e) μ^+ in CoF_2 (f) Muonium in CoF_2



- **Muon/Muonium placed in chosen crystalline sites.**
- DFT calculation performed with Plane-wave code Quantum espresso. Pseudopotentials used.
- DFT predicted formation of the linear F-μ-F states in LiF, NaF, CaF_2 and BaF_2, in agreement with experiments. DFT **predicted a F-μ-F state in CoF_2**, which was then found in experiments.
- DFT **predicted the perturbation to the cation lattice** caused by the muon implantation, and its effect on dipolar field.
- **The method that estimate the contribution of the vibrational modes is, again, not necesarily transferable. And the effect of temperature is ignored.**
- DFT used to discard the use of the minima of the electrostatic potential in the unperturbed host to identify potential μ^+ /muonium stopping sites.

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Organization of the Talk

SECTION 1:

Key concepts, approximations and computer implementations of DFT.

SECTION 2:

How DFT results can be related to muon results in molecular systems: the case of Carbene, C_6H_6-Mu and C_6H_7

SECTION 3:

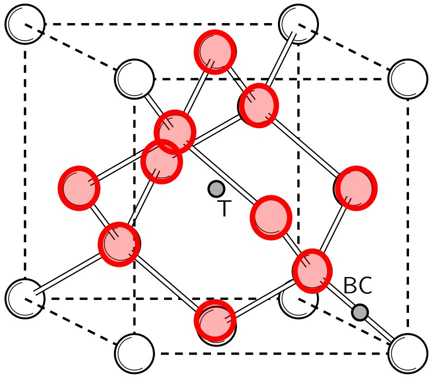
How DFT results can be related to muon results in periodic systems: the case of fluorides.

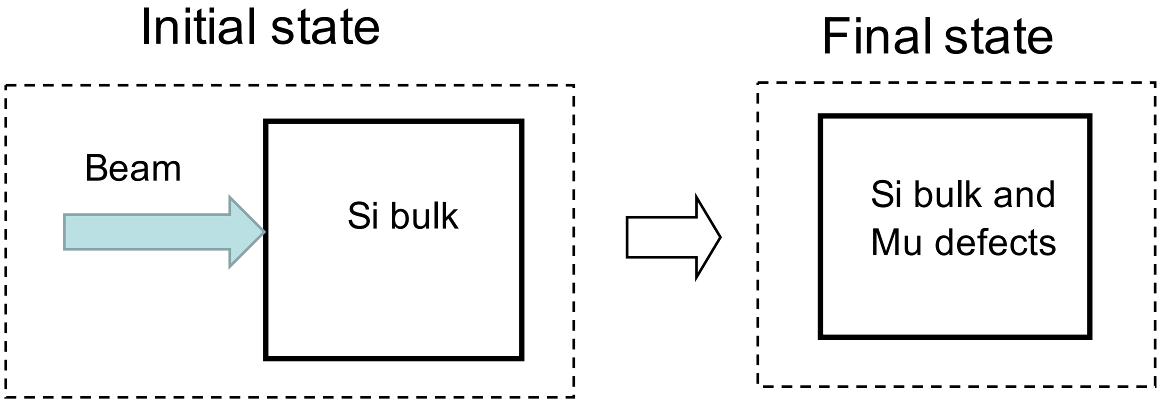
SECTION 4:

How to improve the approximations used in DFT: Treatment of the vibrational contributions and the location of the muon stopping sites.

PyAIRSS and Ab Initio Thermodynamics for Defects

Mu in Silicon




Initial state

Beam

Si bulk

Final state

Si bulk and Mu defects

$$\begin{aligned}\Delta G_f^{Def}(T,p_{O_2}) = \frac{1}{n_{TiO_2}}\Big(G^{\mathrm{sup}cell}(T,p_{O_2}) + n_O^{Def}\,\mu_O^{ref}(T,p_{O_2})\Big) - \\ - \frac{1}{n_{TiO_2}}\Big(n_{TiO_2}\,\mu_{TiO_2}^{bulk}(T,p_{O_2})\Big) \qquad (1)\end{aligned}$$

Random Structure Searching:

1)Choose region in Si cell to be disrupted.

2)Chose Si atoms whose positions will be randomised within the chosen region.

3)Placed Mu or μ^+ in the chosen region.

4)Relax using calculated DFT forces

5)Then estimate defect formation energies.

Proven to work for: solids under high pressure, defective systems in crystals , surfaces, metastable solids.

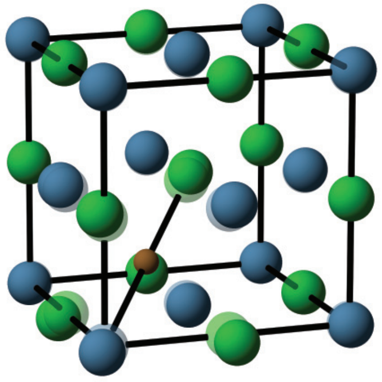
A. J. Morris, *et. al.,* Phys. Rev. B 80, 144112 (2009).
L. Liborio, *et. al.*, Phys. Rev. B 77, 104104, (2008).
C. Pickard et. al. **J. Phys.: Condens. Matter** 23 (2011) 053201

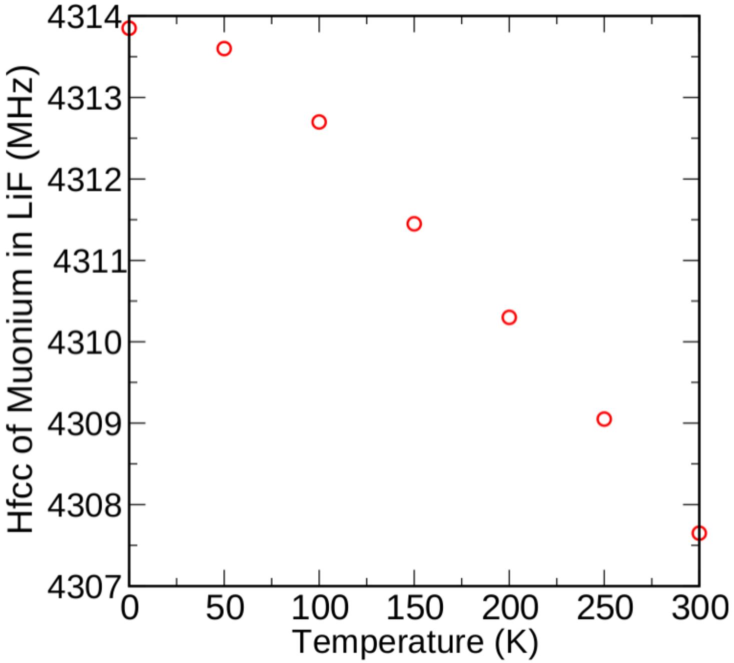
Vibrational Properties

- Unified approach to describe the effects of an-harmonicity at zero and finite temperatures.
- Define the potential energy surface (PES) for the harmonic phonon coordinates. Define $H_{vib.}$
- Explore PES at large displacements, where it becomes an-harmonic.
- Calculate the an-harmonic phonons free-energies and the associated vibrational excited states using vibrational self-consistent field (VSCF) equations.
- Use perturbation theory on the VSCF equations and correct total vibrational free energy.

$hfcc_{VSCF}$	$hfcc_{HA}$	$hfcc_{FD}$	$hfcc_{exp.}$
4308.4 (MHz)	4256 (MHz)	4238 (MHz)	**4584** (MHz)

(b) Muonium in LiF/NaF





- Bartomeu M. et. al., **PRB 87**, 144302 (2013)

Conclusions – Take Home Points

- Muon/Muonium placed in chosen crystalline/Molecular sites.

- Basis set of local functions and B3LYP hybrid functional provide sensible structures for the muonated molecules. Plane waves basis sets and GGA pseudopotential provide sensible results for muonated Crystals. Standard DFT calculations can assist experiments.
    - Location of muon in molecules.
    - Hfcc in Bencene.
    - Discard minima of electrostatic potential in crystals as stopping site.

- Choose right code and XC functional for your system.

- Methods for estimating vibrational contributions and ZPE in muonated molecules and crystals not necessarily transferable and too parametric.

- Muons stopping site cannot be determined from DFT calculations (Although DFT can help).

- AIRSS may help develop a DFT methodology to identify muon stopping sites.

- Vibrational contributions at 0K (ZPE) and at other temperatures can be estimated in a consistent way.

List of References

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- Electronic Structure Calculations for Solids and Molecules, *Jorge Kohanoff,* Cambridge University Press.
- L. M. Liborio *et. al.* **Phys. Rev. B**, 77, 104104, (2008).
- L. M. Liborio *et. al.* **J. Phys.: Condens. Matter**, 17, L223-L230, (2005).

Muons in Molecules:

- B. Hudson, *et al., Molecules*, **18**, 4906-4916 (2013)
- Simulating hyperfine coupling constants of muoniated radicals. J. Peck, S. Cottrell and F. Pratt. (Can be downloaded from here: http://nmi3.eu/about-nmi3/joint-research-activities/muons/publications.html)
- I. McKenzie, *et al.,* **J. AM. CHEM. SOC.** 9 VOL. 125, NO. 38, (2003)

Muons in Crystals:

- J. Moller, *et al.,* **Phys. Rev. B** 87, 121108(R) (2013)

Ab Initio Random Searching and Ab Initio Thermodynamics:

- C. Pickard et. al**. J. Phys.: Condens. Matter** 23 (2011) 053201
- L. M. Liborio *et. al.* **Phys. Rev. B**, 77, 104104, (2008).

Vibrational Properties

- Bartomeu M. et. al., **PRB 87**, 144302 (2013)

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Scientific Computing Department

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Muons Group, ISIS, RAL, STFC

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ISIS

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Cavendish
Laboratory

UNIVERSITY OF
CAMBRIDGE

Vibrational Properties

- Unified approach to describe the effects of an-harmonicity at zero and finite temperatures.
- Define the potential energy surface (PES) for the harmonic phonon coordinates. Define $H_{vib.}$
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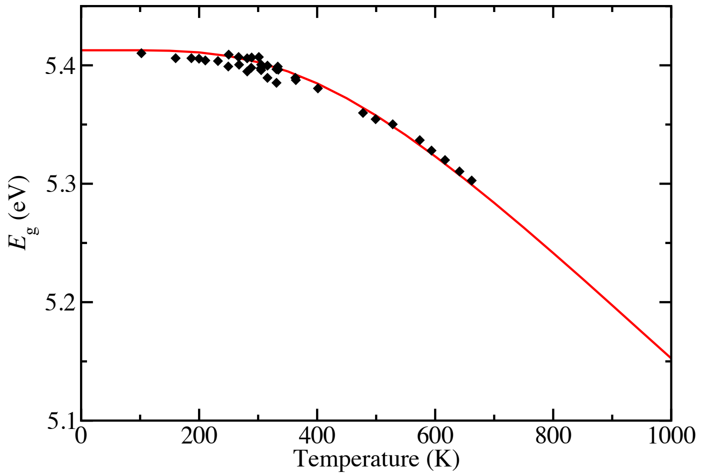


FIG. 4. (Color online) Temperature dependence of the thermal band gap E_g of diamond. The DFT result (red solid curve) is offset to match experimental data (black diamonds) at zero temperature. The experimental data are from Ref. 44.

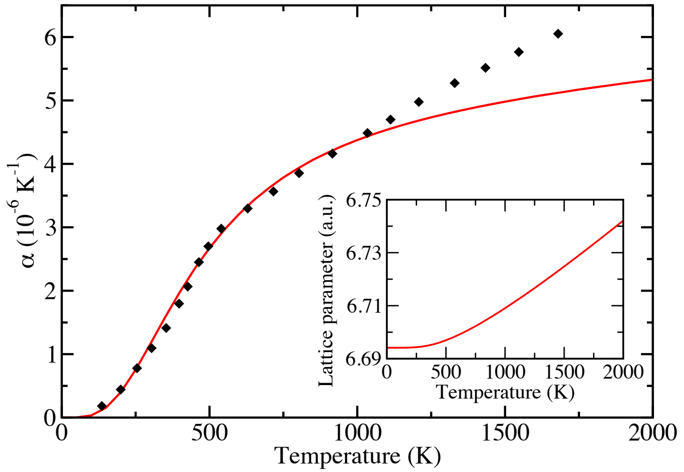
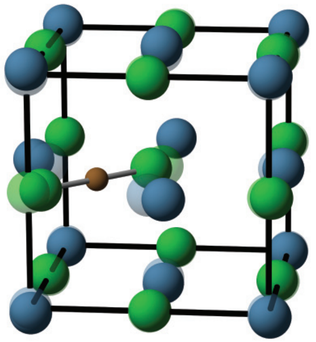


FIG. 6. (Color online) Temperature dependence of the coefficient of linear expansion α for diamond. The black diamonds are experimental results from Ref. 55. The inset shows the temperature dependence of the lattice parameter.

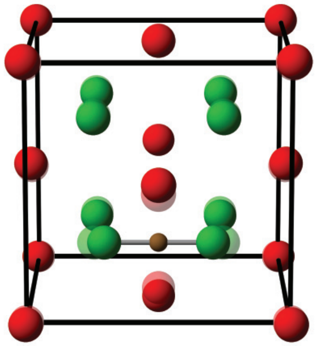
- Bartomeu M. et. al., **PRB 87**, 144302 (2013)

μ^+ in Fluorides: Dipolar Field and ZPE

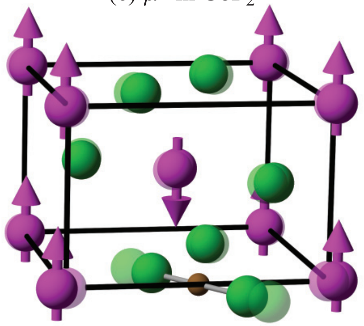
(a) μ^+ in LiF/NaF



(c) μ^+ in CaF_2/BaF_2



(e) μ^+ in CoF_2



	$2r_{\mathrm{DFT}}$	$2r_{\mathrm{exp}}$	ν_{SS}	ν_{B}	ν_{B}	ν_{AS}	ZPE
$(\mathrm{FHF})^{-a}$	2.36	2.28	581	1289	1289	1611	0.30
$(\mathrm{FHF})^{-b}$		2.28	583	1286	1286	1331[c]	0.28
$(\mathrm{F}\text{-}\mu\text{-}\mathrm{F})^{-}$	2.36		581	3797	3797	4748	0.80
LiF	2.34[18]	2.36(2)[12]		2825	4603	4881	0.76
NaF	2.35	2.38(1)[12]		3071	4363	4813	0.76
CaF_2	2.31	2.34(2)[12]	649	2737	4481	5446	0.83
BaF_2	2.33	2.37(2)[12]	613	3033	4130	4974	0.79
CoF_2	2.36	2.43(2)	585	3076	3473	4570	0.73

- Calculated spin-only moment 2.68μ_B per Co ion. Exp. Result: 2.21μ_B. The prescence of μ^+ does not affect spin-only moment in Co.
- Dipolar coupling of μ^+ with dipolar field calculated. Effect on dipolar field at muon site in agreement with experiment.
- Calculation of vibrational modes for F-μ-F: system is molecule-in-crystal.
- Consideration of quantum effects – BO does not work – via ZPE.
- ZPE of F-μ-F exceptionally large. Quantum effects important.

J. Moller, *et al.,* Phys. Rev. B **87**, 121108(R) (2013)