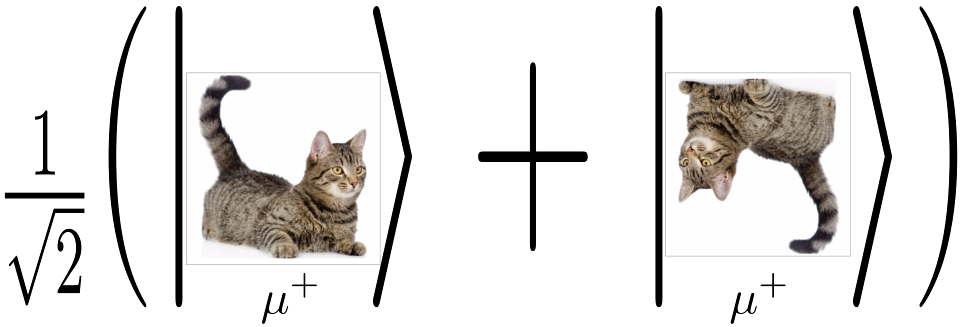
The Quantum Muon



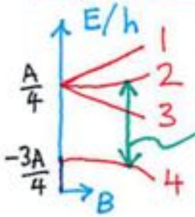
Lecture 3: More complex situations

Stephen J. Blundell
University of Oxford

Quantum mechanics explains more exotic states

- Muonium can be anisotropic
- Dipolar coupling to nuclei leads to other muon-coupled states
- Level crossings
- Fluorine states
- Muon sites

Longitudinal-field experiment   initial muon polarization // B // z



only 2 ⟷ 4 transition possible

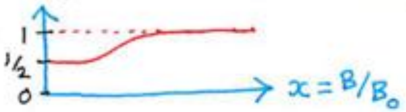
$P(t) = 1 - a_{24} + a_{24} \cos \omega_{24} t$

$\frac{1}{2} \sin^2 2\xi = \frac{1}{2} \frac{1}{\sqrt{1+x^2}}$

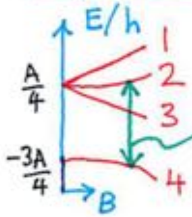
$\nu_{24} > A$ so the oscillatory term is high frequency

⇒ just observe $1 - a_{24}$

REPOLARISATION



Longitudinal-field experiment   initial muon polarization // B // z

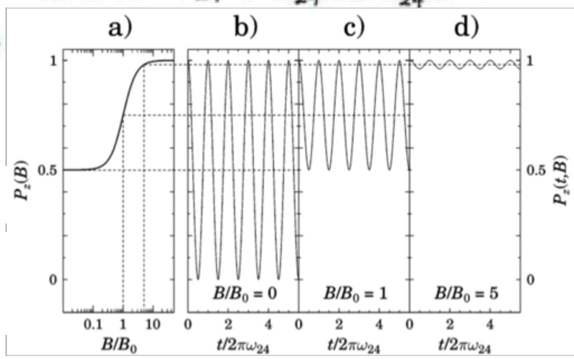


only 2 ⟷ 4 transition possible

$P(t) = 1 - a_{24} + a_{24} \cos \omega_{24} t$

⇒ just observe $1 - a_{24}$

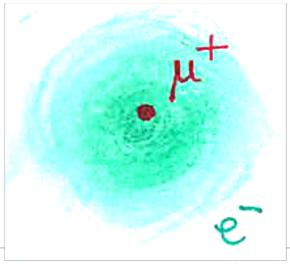
REPOLARISATION



S. J. Blundell, Chem. Rev. **104**, 5717 (2004)

Anisotropic muonium

• why? muons form bonds



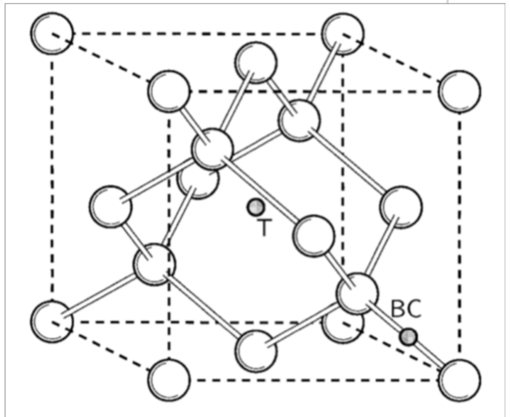
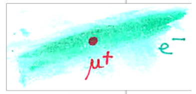


Figure 11. The crystal structure of silicon, showing the possible muonium sites (T= tetrahedal site, BC= bond-centre site).

S. J. Blundell, Contemp. Phys. **40**, 175 (1999)

Anisotropic muonium

• why? muons form bonds



$$\underline{\underline{A}} = \begin{pmatrix} A_\perp & 0 & 0 \\ 0 & A_\perp & 0 \\ 0 & 0 & A_\parallel \end{pmatrix} = A_s \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} + A_p \begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix}$$

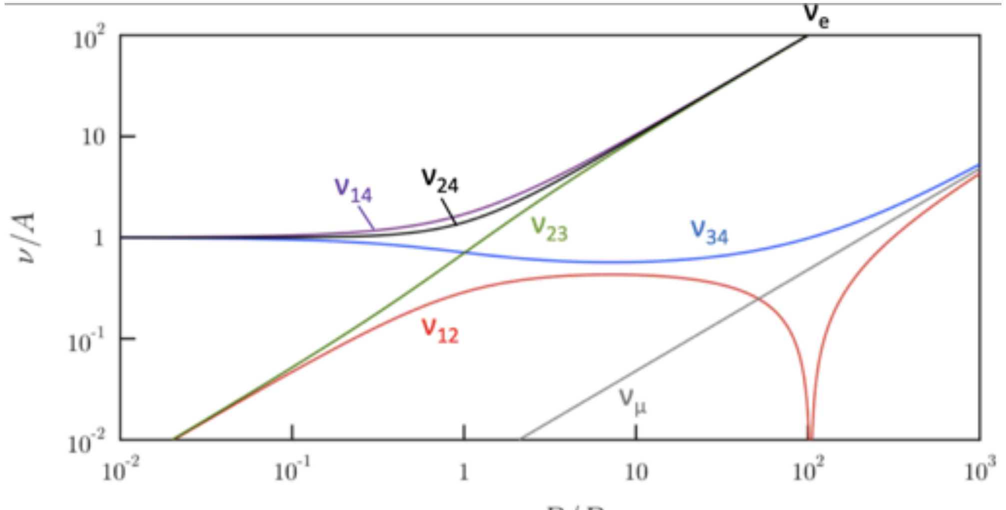
A_{iso} $\qquad$ $D_1/2$

$$= \nu_0 \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} + \nu^* \begin{pmatrix} 0 & & \\ & 0 & \\ & & 1 \end{pmatrix}$$

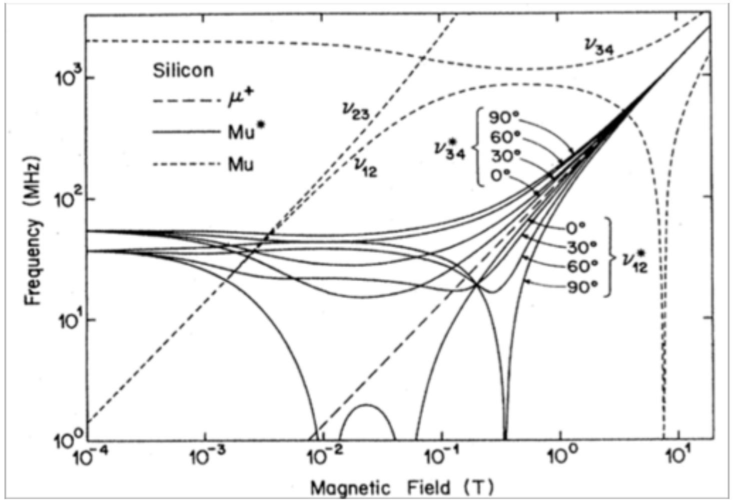
$\nu_0 = A_\perp = A_s - A_p$, $\nu^* = A_\parallel - A_\perp = 3A_p$

$= 92.6\ \mathrm{MHz}$ $\qquad$ $= -75.8\ \mathrm{MHz}$ for Si

(compare $\nu_0 = 2006\ \mathrm{MHz}$ for isotropic muonium state)



B. D. Patterson, Rev. Mod. Phys. 60 , 69 (1988)



B. D. Patterson, Rev. Mod. Phys. 60 , 69 (1988) muons don't interact with paired spins

($\because$ they are entangled $\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$)

but plenty of unpaired spins

e.g. electron in muonium, in radicals, partially filled shells (d, f band) & nuclei

interactions can be hyperfine [isotropic/anisotropic] or dipolar

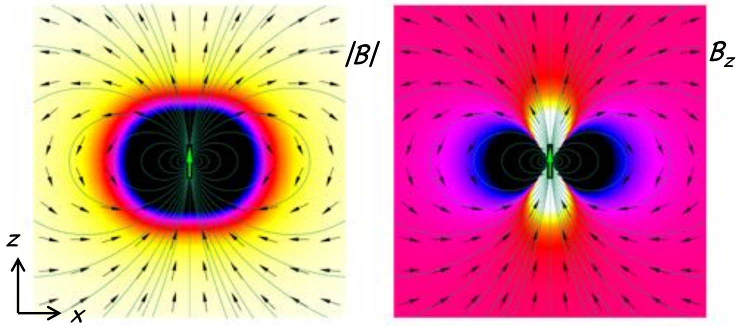
Dipole fields

$$D_i^{\alpha\beta}(\mathbf{r}_\mu) = \frac{\mu_0}{4\pi R_i^3}\left(\frac{3R_i^\alpha R_i^\beta}{R_i^2} - \delta^{\alpha\beta}\right)$$

$$B^\alpha(\mathbf{r}_\mu) = \sum_i D_i^{\alpha\beta}(\mathbf{r}_\mu)\, m_i^\beta$$

Dipole field at muon-site

i^{th} moment



Dipole fields

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Dipole field at muon-site

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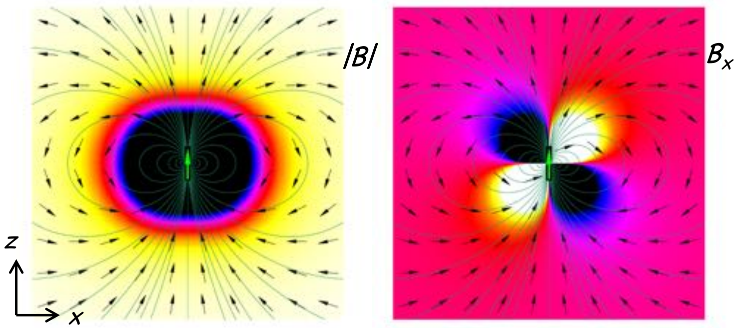


Density matrix for muon + K spins

$$N = 2\prod_{k=1}^{K}(2J^k+1)$$

e.g. muonium $K=1$: $N = 2(2\times\frac{1}{2}+1) = 4$

F-μ-F $K=2$: $N = 2(2\times\frac{1}{2}+1)^2 = 8$

$$\rho_q = \frac{1}{N}(1+\sigma_q)\otimes\prod_{k=1}^{K}\mathbb{1}^k$$

polarised

unpolarised

$$P_q(t) = \mathrm{Tr}[\sigma_q(t)\,\rho_q] = \frac{1}{N}\mathrm{Tr}[\sigma_q(t)\,\sigma_q]$$

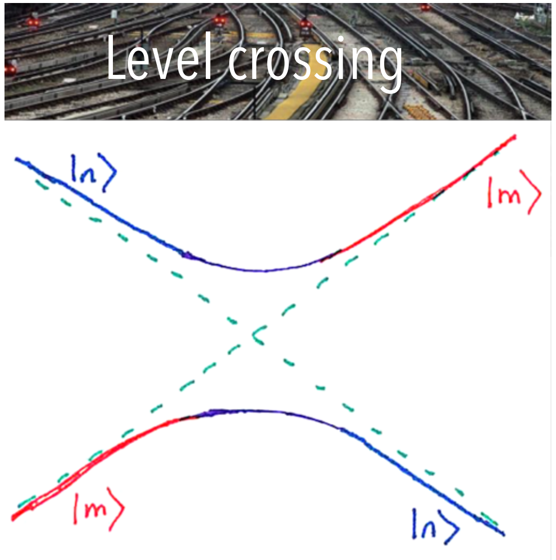
only bit that survives the trace

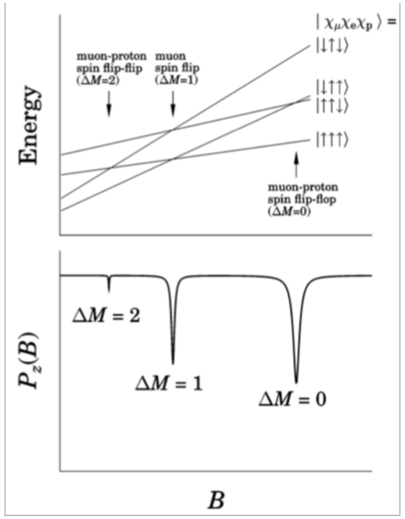
$\sigma_q(t) = e^{i\hat{H}t}\sigma_q e^{-i\hat{H}t}$

$$= \frac{1}{N}\sum_{abcd}\langle a|\sigma_q|b\rangle\underbrace{\langle b|e^{i\hat{H}t}|c\rangle}_{e^{i\omega_b t}\delta_{bc}}\langle c|\sigma_q|d\rangle\underbrace{\langle d|e^{-i\hat{H}t}|a\rangle}_{e^{-i\omega_a t}\delta_{ad}}$$

$$= \frac{1}{N}\sum_{ab}|\langle a|\sigma_q|b\rangle|^2 e^{i\omega_{ba}t}$$

3d average over q $\therefore \frac{1}{3}\sum_{\alpha=x,y,z}|\langle a|\sigma_\alpha|b\rangle|^2$





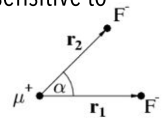
S. J. Blundell, Chem. Rev. **104**, 5717 (2004)

F-μ-F state

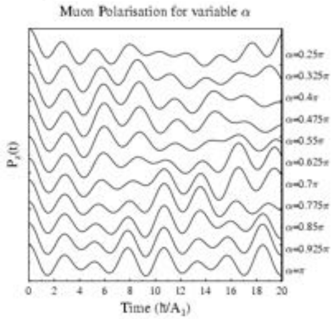
F=small, high nuclear moment, very electronegative

and very sensitive to

- r_1
- r_1/r_2
- α



Anion	Abundance	Spin	Ionic radius (pm)	Magnetic moment (μ_N)
^{19}F	100%	1/2	119	2.6
^{35}Cl	$\sim$ 75%	3/2	167	0.82
^{37}Cl	$\sim$ 25%	3/2	167	0.68
^{79}Br	$\sim$ 50%	3/2	182	2.1
^{81}Br	$\sim$ 50%	3/2	182	2.3
^{127}I	100%	5/2	206	2.8
^{17}O	0.04%	5/2	126	-1.9
^{33}S	0.76%	3/2	170	0.64
^{77}Se	7.6%	1/2	184	0.53
^{123}Te	0.89%	1/2	207	-0.73
^{125}Te	7.1%	1/2	207	-0.89



$$\hat H_{dipole} = \frac{\mu_0}{4\pi r^3}\left[\vec\mu_1\cdot\vec\mu_2 - 3(\vec\mu_1\cdot\hat r)(\vec\mu_2\cdot\hat r)\right]$$

$$= \underbrace{\frac{\mu_0\hbar^2\gamma_1\gamma_2}{4\pi r^3}}_{\hbar\omega_D}\ \frac{1}{4}\left(\vec\sigma_1\cdot\vec\sigma_2 - 3(\vec\sigma_1\cdot\hat r)(\vec\sigma_2\cdot\hat r)\right)$$

Simple μ-F with $\hat r = \hat z$

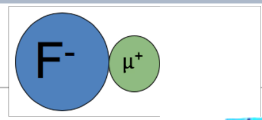
$$\hat H_{dipole} = \frac{\hbar\omega_D}{2}\underbrace{\begin{pmatrix} -1 & & & \\ & 1 & 1 & \\ & 1 & 1 & \\ & & & -1 \end{pmatrix}}_{\text{eigenvalues } -1,-1,0,2}$$

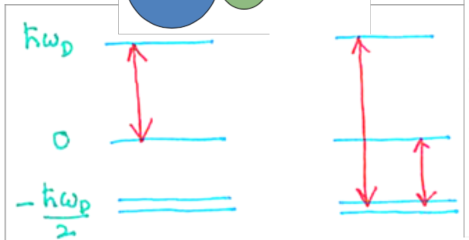
$\frac{|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle}{\sqrt2}$ —— $\hbar\omega_D$

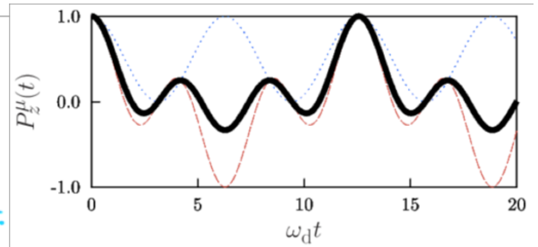
$\frac{|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle}{\sqrt2}$ —— 0

$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$ —— $-\frac{\hbar\omega_D}{2}$

The F-μ state





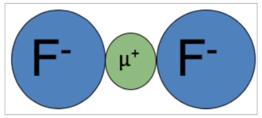


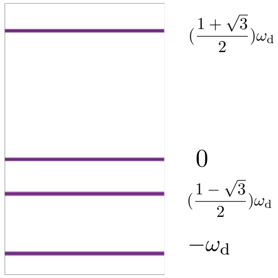
$P_z(t) = \frac{1}{2}(1+\cos\omega_D t)$ $\quad P_x(t) = \frac{1}{2}\left(\cos\frac{\omega_D t}{2} + \cos\frac{3\omega_D t}{2}\right)$

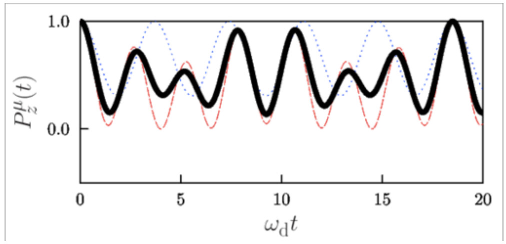
Average over all angles

$$P(t) = \frac{1}{6}(1+\cos\omega_D t) + \frac{1}{3}\left(\cos\frac{\omega_D t}{2} + \cos\frac{3\omega_D t}{2}\right)$$

The F-μ–F state







F − μ − F

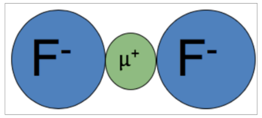
F...F interactions smaller by a factor of $\frac{\gamma_F}{\gamma_\mu} \times \frac{1}{8} = 0.037$

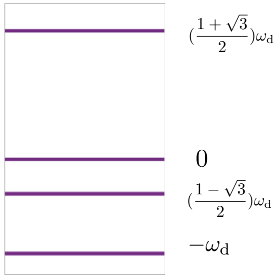
0.296

but they do make a difference, as do interactions with more distant fluorines.

$$P_z(t) = \frac{1}{6}\left(3 + \cos\sqrt{3}\omega t + \left(1 - \frac{1}{\sqrt{3}}\right)\cos\left[\frac{3-\sqrt{3}}{2}\omega t\right] + \left(1 + \frac{1}{\sqrt{3}}\right)\cos\left[\frac{3+\sqrt{3}}{2}\omega t\right]\right)$$

Simulating the F-μ-F state





Density matrix:

$$\rho_q = \frac{1}{N}(1+\sigma_q)\otimes\prod_{k=1}^{K} 1^k$$

$$N = 2\prod_{k=1}^{K}(2J^k+1)$$

Muon polarization:

$$P_q(t) = \frac{1}{N}\sum_{m,n}|\langle m|\sigma_q|n\rangle|^2 e^{i\omega_{mn}t}$$

$$\omega_{mn} \equiv \omega_m - \omega_n$$

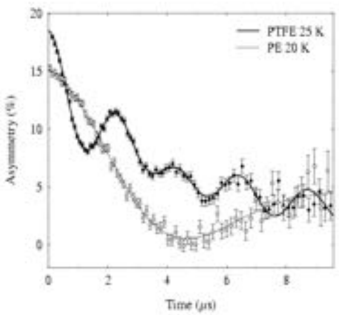
Polycrystalline average:

$$P(t) = \frac{1}{3N}\sum_{m,n}(|\sigma_x^{mn}|^2 + |\sigma_y^{mn}|^2 + |\sigma_z^{mn}|^2)e^{i\omega_{mn}t}$$

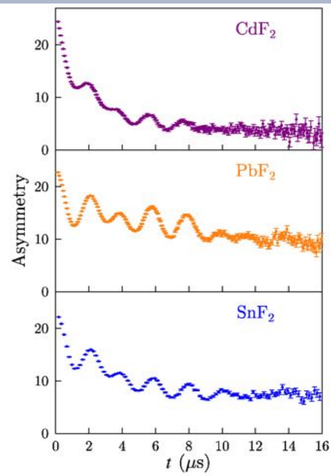
$$\sigma_q^{mn} \equiv \langle m|\sigma_q|n\rangle$$

The F-μ-F state

state found in many **ionic fluorides** [first by Brewer et al., Phys. Rev. B **33**, 7813 (1986)], and also teflon (PTFE)



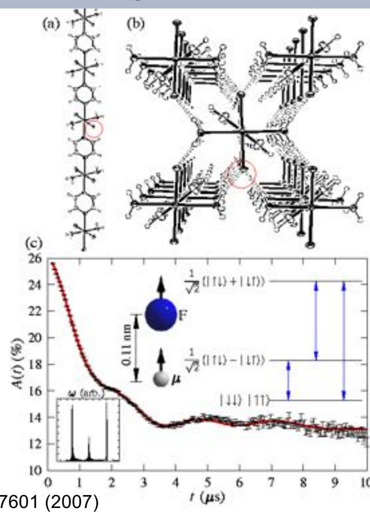
F. L. Pratt et al., Physica B **326**, 34 (2003),
See also T. Lancaster et al., JPCM 21, 346004 (2009)



S. J. Blundell in preparation

Case 1: Interaction with a single fluorine ion

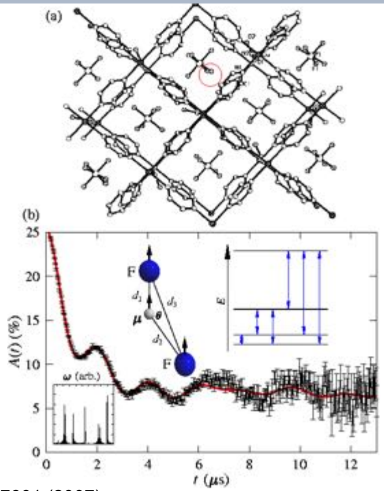
$CuF_2(H_2O)_2(pyz)$



T. Lancaster et al. Phys. Rev. Lett. **99**, 267601 (2007)

Case 2: Crooked FμF bond close to a PF_6^- ion

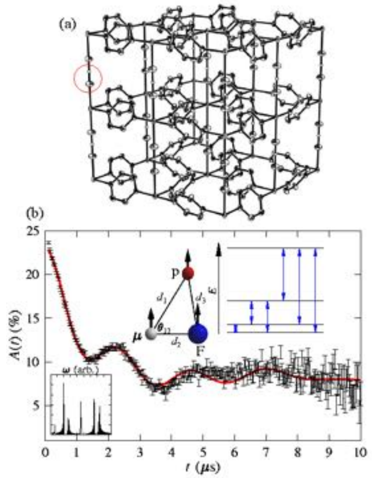
$[CuNO_3(pyz)_2]PF_6$



T. Lancaster et al. Phys. Rev. Lett. **99**, 267601 (2007)

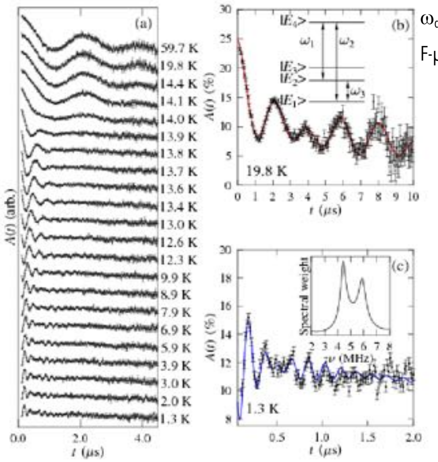
Case 3: Interaction with a HF_2^- ion

$[Cu(HF_2)(pyz)_2]X$



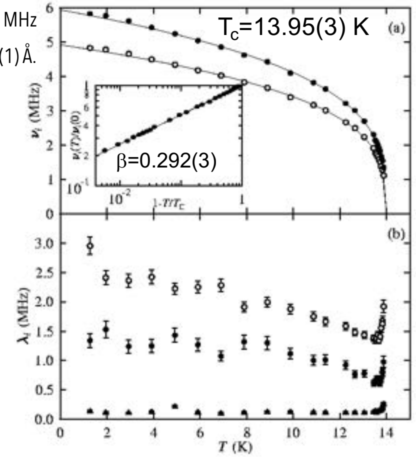
T. Lancaster et al. Phys. Rev. Lett. **99**, 267601 (2007)

Magnetism and muon sites in Cs_2AgF_4



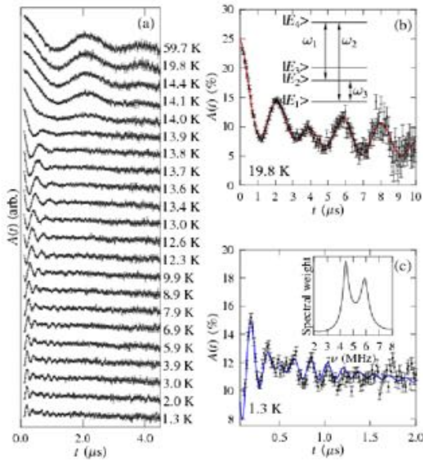
$\omega_d = 2\pi \times 0.211(1)$ MHz

F-μ separation 1.19(1) Å.



T. Lancaster et al. Phys. Rev. B **75**, R220408 (2007)

Magnetism and muon sites in Cs_2AgF_4



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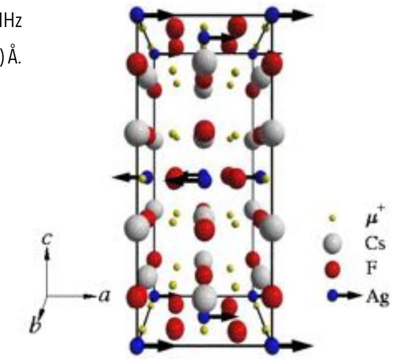
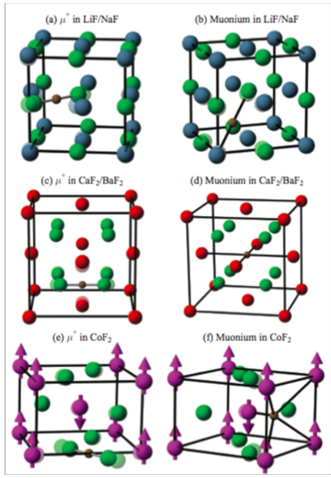


Twice as many sites in [CsF] planes as [AgF2] planes.

F-μ separation 1.19(1) Å. F ions close to Ag shift by ~0.4 Å, i.e. the muon induces a non-negligible distortion (which we can measure!)

T. Lancaster et al. Phys. Rev. B **75**, R220408 (2007)

DFT+μ



Quantum states of muons in fluorides

J. S. Möller,[1,*] D. Ceresoli,[2] T. Lancaster,[3] N. Marzari,[4] and S. J. Blundell

TABLE I. Calculated (DFT) and experimental (exp) properties of the diamagnetic F-μ-F states in solid and vacuum, and of the $(FHF)^-$ molecular ion in vacuum. r (Å) is the muon-fluoride bond length, ν is the frequency (cm^{-1}) of the symmetric stretch (SS), asymmetric stretch (AS), and bending (B) mode, and ZPE is the zero-point energy (eV). [a]Our calculation. [b]Experimental data (Ref. 19). [c]Ref. 20 reports 1377 cm^{-1}.

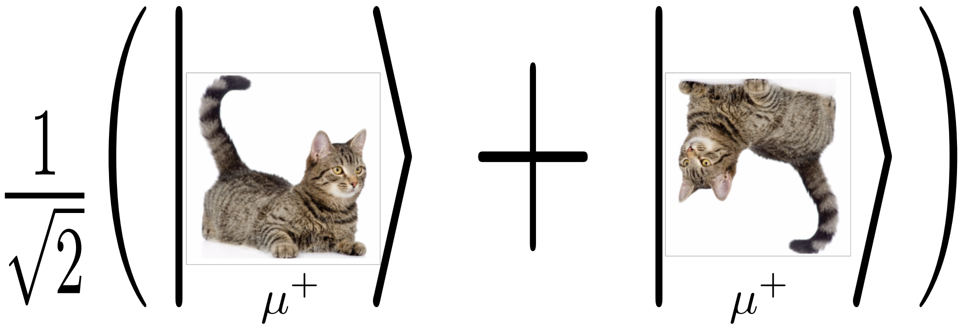
	$2r_{DFT}$	$2r_{exp}$	ν_{SS}	ν_B	ν_B	ν_{AS}	ZPE
$(FHF)^{-a}$	2.36	2.28	581	1289	1289	1611	0.30
$(FHF)^{-b}$		2.28	583	1286	1286	1331[c]	0.28
$(F\text{-}\mu\text{-}F)^-$	2.36		581	3797	3797	4748	0.80
LiF	2.34[18]	2.36(2)[12]		2825	4603	4881	0.76
NaF	2.35	2.38(1)[12]		3071	4363	4813	0.76
CaF_2	2.31	2.34(2)[12]	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

J. S. Möller et al., Phys. Rev. B **87**, 121108(R) (2013)
[see also F. Bernadini et al., ibid **87**, 115148 (2013)]

μ^+

quantum or classical?

The Quantum Muon



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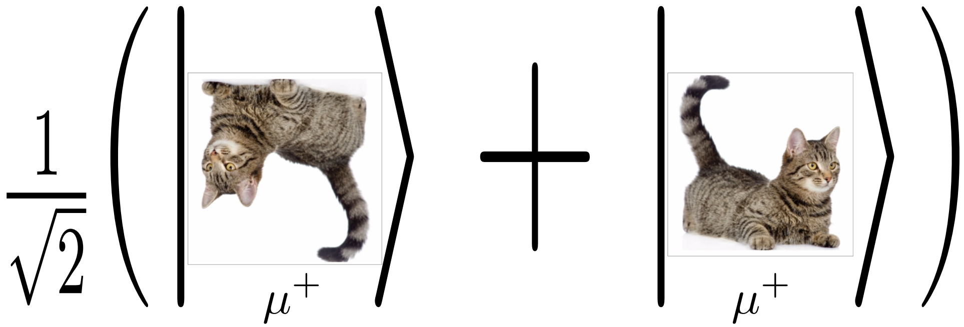
The Quantum Muon



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