International Conference on Advanced Materials Modelling
ICAMM 2016
& VASP training school

NMR Calculations

F. Boucher
Institut des Matériaux Jean Rouxel (IMN)
Université de Nantes, CNRS, 44322 NANTES Cedex, FRANCE

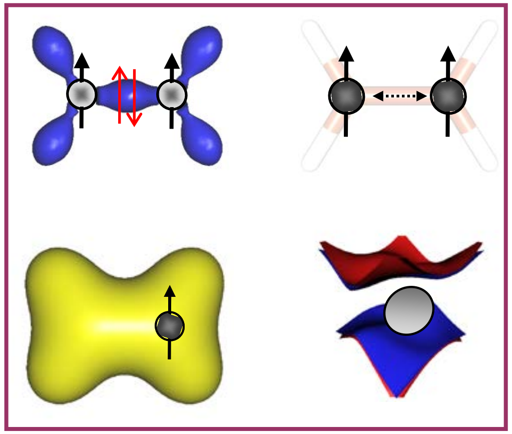
Outline

- **NMR experiments: a short introduction**
- **Quadrupolar interaction**
  - **- Calculation of EFG parameters**
  - **- Discussion on structural accuracy: some examples**
- **Chemical shift interaction**
  - **- Calculation of shielding parameters**
  - **- From shielding to chemical shift: *the slope problem***
  - **- *PP* versus *AE* calculations**

NMR experiments: a short introduction

MAS NMR: **a high precision tool to study the local environment of various nuclei in complex material**

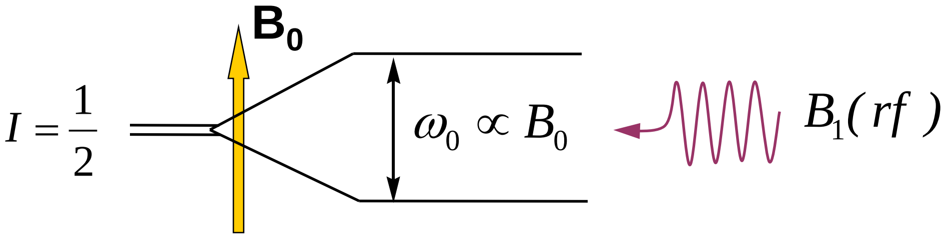
$$\hat{H}_I = \hat{H}_{int} + \hat{H}_{ext}$$



NMR experiments: a short introduction

$$\hat{H}_I = \hat{H}_{ext}$$

Zeeman effect: interaction between nuclear spin and magnetic field



ω_0 : Larmor frequency

$$\hat{H}_{ext} = -\gamma\hbar B_0 \hat{I}_z + \gamma\hbar B_1 \times \left\{ cos(\omega_{ref} t + \phi)\hat{I}_x + sin(\omega_{ref} t + \phi)\hat{I}_y \right\}$$

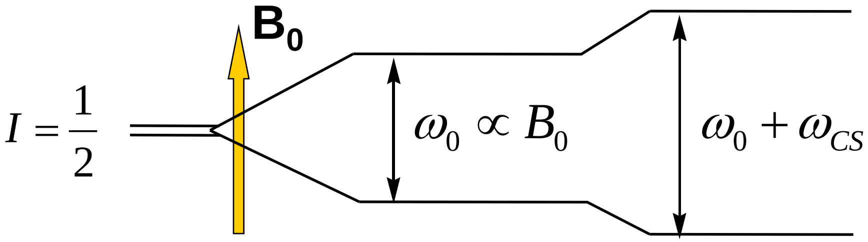
Isotope	Spin	Abund. (%)	ω_0 (7T) in MHz	ω_0 (11T) in MHz
^{1}H	1/2	99.98	300	500
^{19}F	1/2	100	282.23	470.38
^{51}V	7/2	99.76	78.86	131.44

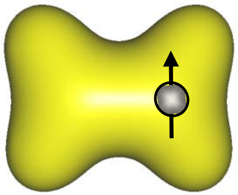
NMR experiments: a short introduction

$$\hat{H}_I = \hat{H}_{ext} + \hat{H}_{int}$$

Zeeman effect

Chemical shift interaction (*magnetic shielding*)





$$\hat{H}_{CS} = c_{CS}\vec{I} \cdot \overleftrightarrow{\sigma} \cdot \vec{B}_0$$

« chemical shift » = CS

The electronic motions induce internal magnetic fields which “shield” every nucleus from H_{ext}

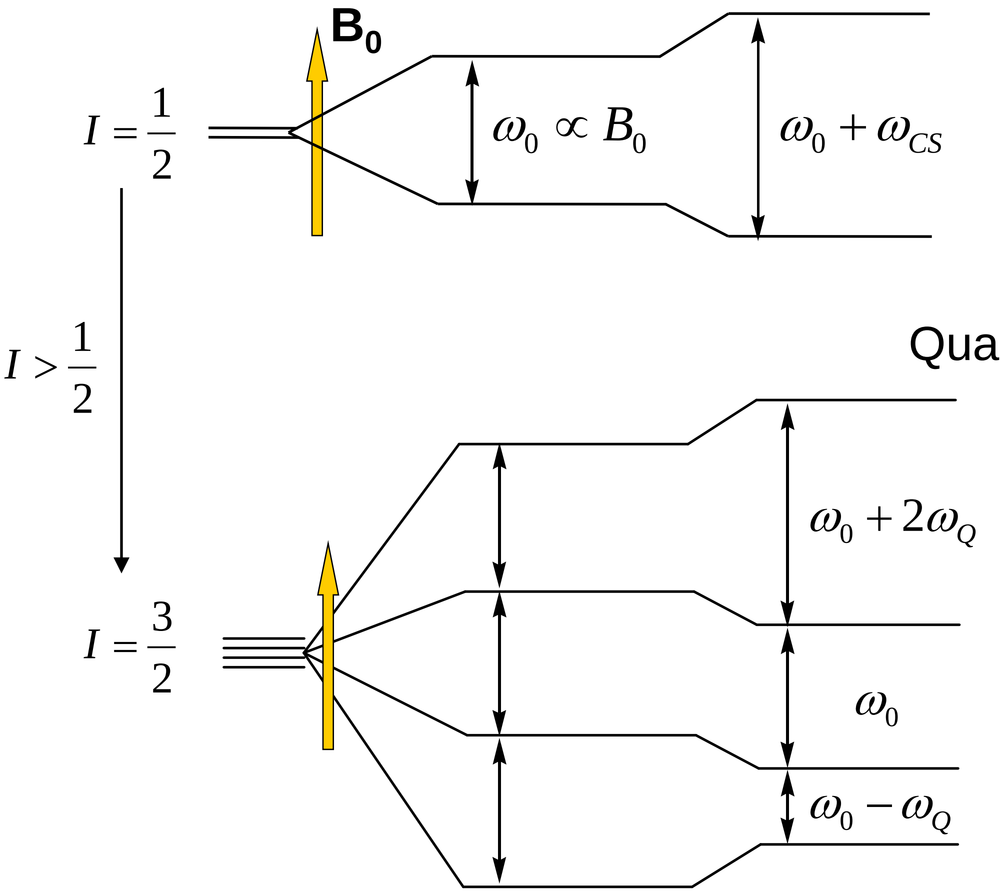
Isotope	Spin	Abund. (%)	ω_0 (7T) in MHz	ω_0 (11T) in MHz
^{1}H	1/2	99.98	300	500
^{19}F	1/2	100	282.23	470.38
^{51}V	7/2	99.76	78.86	131.44

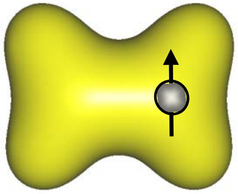
NMR experiments: a short introduction

$$\hat{H}_I = \hat{H}_{ext} + \hat{H}_{int}$$

Zeeman effect

Chemical shift interaction (*magnetic shielding*)



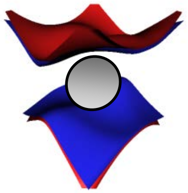


$$\hat{H}_{CS} = c_{CS}\vec{I}\cdot\overleftrightarrow{\sigma}\cdot\vec{B}_0$$

« chemical shift » = CS

Quadrupolar interaction (*electric coupling)*

Nuclei with I > 1/2 have an asymmetric distribution of nucleons (non spherical distribution of positive electric charge)



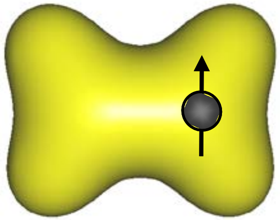
$$\hat{H}_Q = c_Q\vec{I}\cdot\overleftrightarrow{V}\cdot\vec{I}$$

Isotope	Spin
^{1}H	1/2
^{19}F	1/2
^{51}V	7/2

VASP training school - August 31st to September 3rd, 2016 - Rennes

NMR experiments: a short introduction

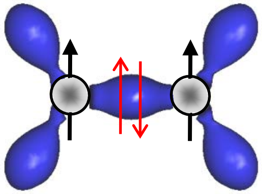
$$\hat{H}_{int} = \sum_{\lambda} \hat{H}_{\lambda} = c_{\lambda} \vec{I} \cdot \overleftrightarrow{R}^{\lambda} \cdot \vec{K}$$



$$\hat{H}_{CS} = c_{CS} \vec{I} \cdot \overleftrightarrow{\sigma} \cdot \vec{B}_0$$

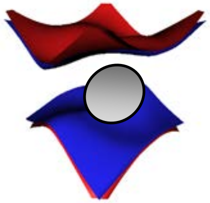
Chemical shift interaction

Magnetic shielding



$$\hat{H}_J = c_J \vec{I}_1 \cdot \overleftrightarrow{J} \cdot \vec{I}_2$$

J Coupling or scalar interaction

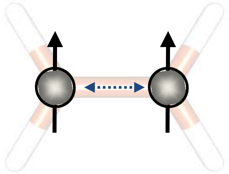


$$\hat{H}_Q = c_Q \vec{I} \cdot \overleftrightarrow{V} \cdot \vec{I}$$

…pour I > 1/2

Quadrupolar interaction

Electric coupling



$$\hat{H}_D = c_D \vec{I}_1 \cdot \overleftrightarrow{D} \cdot \vec{I}_2$$

Dipolar interaction

NMR experiments: a short introduction

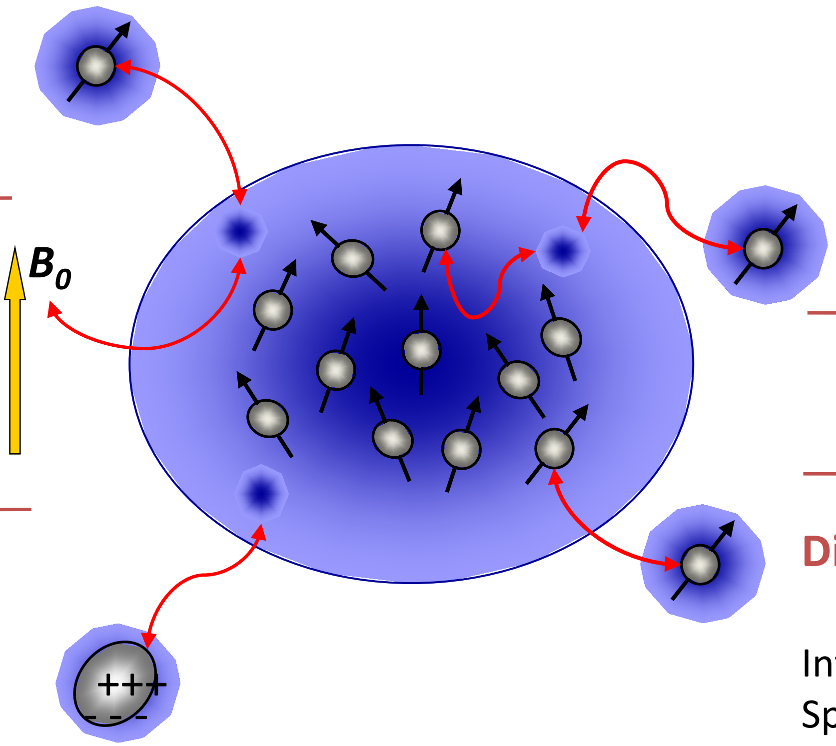
Chemical shift interaction (H_{CS})
coordination,
kind of neighbors
$\propto$ 10 kHz

(like B_0)

Zeeman Effect
~ 100 MHz

Quadrupolar interaction (H_Q)
geometry
$\propto$ MHz

(1^{st} order independent of B_0)



Scalar interaction (H_J)

Chemical bond,
connectivity
$\propto$ 100 Hz

(independent of B_0)

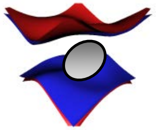
Dipolar interaction (H_D)

Interatomic distances
Spatial information
$\propto$ 10 kHz

(in $1/r^3$ and independent of B_0)

VASP training school - August 31st to September 3rd, 2016 - Rennes

Quadrupolar interaction: an electric coupling



Electric Field Gradient Tensor (EFG)

$$V_{ij}(\vec{r}) = \frac{\partial E_i(\vec{r})}{\partial r_j} - \frac{1}{3}\delta_{ij}\sum_k \frac{\partial E_k(\vec{r})}{\partial r_k}$$

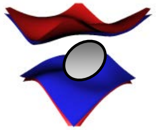
… electric field

$$E_i(\vec{r}) = \int d\vec{r}\, \frac{\rho_0(\vec{r})}{|\vec{r}-\vec{r}'|}(r_i - r_i')$$

A ground state property ! One only needs E_0 and Ψ_0

H. M. Petrilli, P. E. Blöchl, P. Blaha, K. Schwarz, *Phys. Rev. B* **57**, 14690 (1998)
M. Profeta, F. Mauri, C. J. Pickard, *J. Am. Chem. Soc*. **125**, 541 (2001)

Quadrupolar interaction: an electric coupling



Electric Field Gradient Tensor (EFG) $$V_{ij}(\vec{r}) = \frac{\partial E_i(\vec{r})}{\partial r_j} - \frac{1}{3}\delta_{ij}\sum_k \frac{\partial E_k(\vec{r})}{\partial r_k}$$

… electric field $$E_i(\vec{r}) = \int d\vec{r}\, \frac{\rho_0(\vec{r})}{|\vec{r}-\vec{r}'|}(r_i - r_i')$$

A ground state property ! One only needs E_0 and Ψ_0

H. M. Petrilli, P. E. Blöchl, P. Blaha, K. Schwarz, *Phys. Rev. B* **57**, 14690 (1998)
M. Profeta, F. Mauri, C. J. Pickard, *J. Am. Chem. Soc*. **125**, 541 (2001)

$$\overleftrightarrow{V} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \Rightarrow \begin{bmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{bmatrix}$$ with $$\begin{cases} V_{xx} + V_{yy} + V_{zz} = 0 \\ |V_{yy}| \le |V_{xx}| \le |V_{zz}| \end{cases}$$

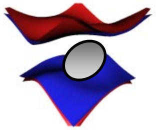
Experimentaly caracterized by:

$$C_q = \frac{eQV_{zz}}{h}$$ and $$\eta_q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

C_q : quadrupolar coupling constant

η_q : quadrupolar asymmetry parameter

Quadrupolar interaction: an electric coupling



Electric Field Gradient Tensor (EFG) $V_{ij}(\vec{r}) = \frac{\partial E_i(\vec{r})}{\partial r_j} - \frac{1}{3}\delta_{ij}\sum_k \frac{\partial E_k(\vec{r})}{\partial r_k}$

… electric field $E_i(\vec{r}) = \int d\vec{r}\, \frac{\rho_0(\vec{r})}{|\vec{r} - \vec{r}'|}(r_i - r_i')$

A ground state property ! One only needs E_0 and Ψ_0

$$C_q = \frac{eQV_{zz}}{h} \quad \text{and} \quad \eta_q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

C_q : quadrupolar coupling constant

η_q : quadrupolar asymmetry parameter

EFG calculation with VASP

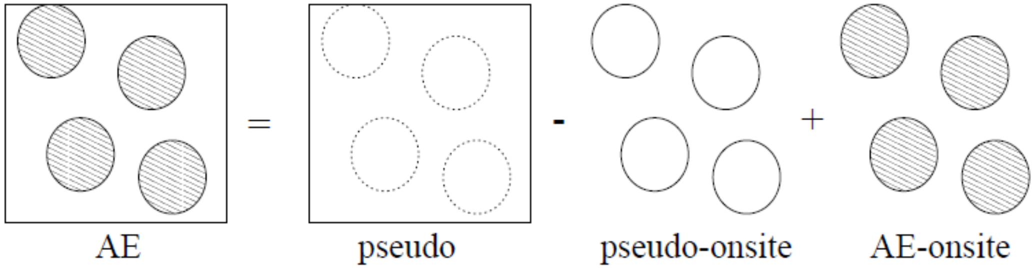
LEFG = .TRUE.

QUAD_EFG = 146.6 (^{27}Al) **25.5** (^{17}O)

Q : electric quadrupole moment
Q : in milibarn (1 mb = 10^{-31} m^2)
P. Pyykkö, Mol. Phys. 106, 1965-1974 (2008)

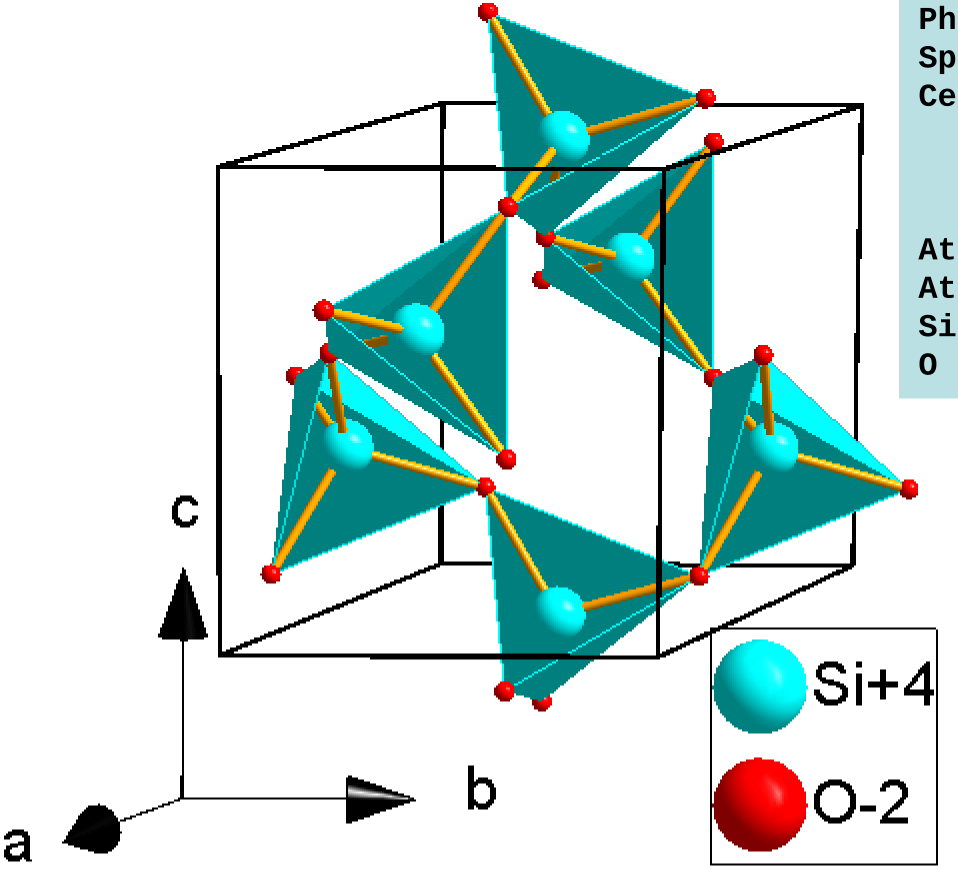
PAW formalism

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle - \sum |\tilde{\phi}_{lm\varepsilon}\rangle c_{lm\varepsilon} + \sum |\phi_{lm\varepsilon}\rangle c_{lm\varepsilon}$$



P. Blöchl *PRB* 50, pp 17953-17978 (1994)

Quadrupolar interaction: α-SiO_2 example



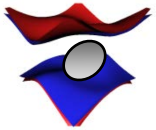
```
Phase data
Space-group P 31 2 1 (152) – trigonal
Cell       a=4.604(1) Å c=5.207(1) Å
           c/a=1.1310
           V=95.58(5) Å³
           Z=3
Atomic parameters
Atom  Ox. Wyck x/a          y/b       z/c
Si    4   3a   0.4458(2)    0         1/3
O     -2  6c   0.3951(4) 0.3031(4)  0.2412(2)
```

^{29}Si : I = 1/2
^{17}O : I = 5/2

```
EFG Calculation
LEFG = .TRUE.
QUAD_EFG = 0.0 25.5
```

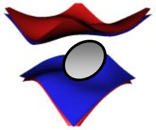
VASP training school - August 31st to September 3rd, 2016 - Rennes

Quadrupolar interaction: α-SiO_2 example



```
           NMR quadrupolar parameters

 Cq : quadrupolar parameter    Cq=e*Q*V_zz/h
 eta: asymmetry parameters     (V_yy - V_xx)/ V_zz
 Q  : nuclear electric quadrupole moment in mb (millibarn)
----------------------------------------------------------
 ion       Cq(MHz)       eta       Q (mb)
----------------------------------------------------------
   1       0.000       0.550       0.000
   2       0.000       0.549       0.000
   3       0.000       0.549       0.000
   4       4.623       0.485      25.500
   5       4.623       0.485      25.500
   6       4.623       0.485      25.500
   7       4.623       0.485      25.500
   8       4.624       0.485      25.500
   9       4.623       0.485      25.500
----------------------------------------------------------
```

Quadrupolar interaction: α-SiO$_2$ example

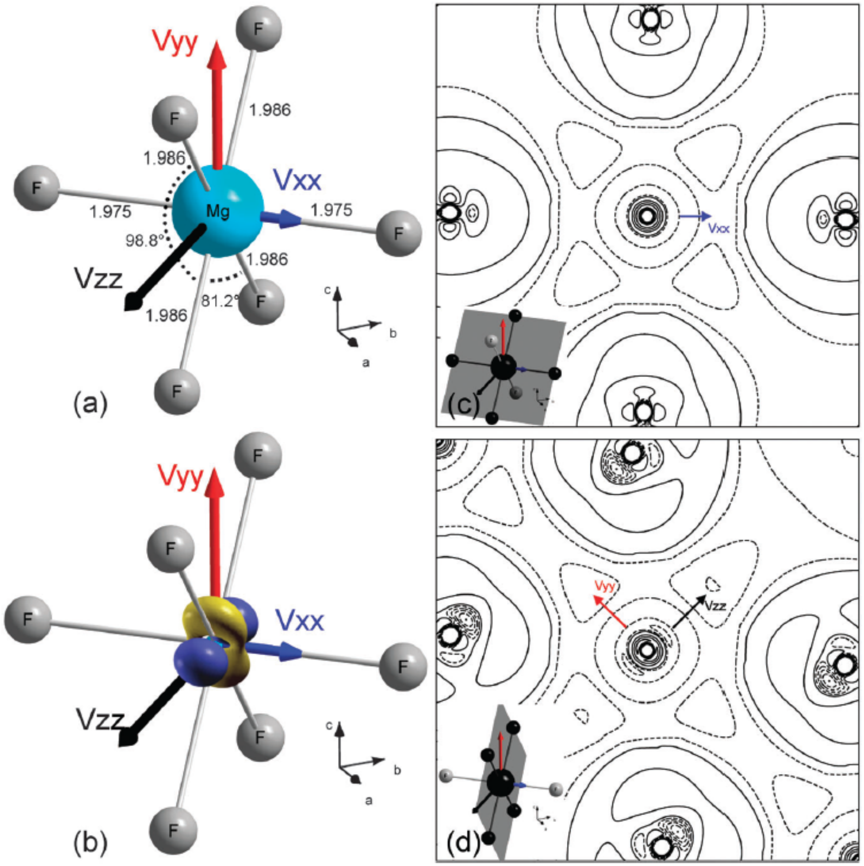


```
Electric field gradients (V/A^2)
---------------------------------------------------------------------
 ion       V_xx      V_yy      V_zz      V_xy      V_xz      V_yz
---------------------------------------------------------------------
   1       2.121    -0.126    -1.995    -0.005    -0.000     8.310
   2       0.436     1.560    -1.995    -0.974    -7.194    -4.154
   3       0.442     1.559    -2.000     0.977     7.196    -4.155
   4     -19.572    18.456     1.116   -28.070     4.999   -58.074
   5     -15.380    14.236     1.144    30.506    47.792    33.362
   6      33.249   -34.390     1.141    -2.422   -52.795    24.705
   7      33.261   -34.375     1.114     2.432    52.794    24.707
   8     -19.586    18.441     1.145    28.078    -5.003   -58.077
   9     -15.384    14.241     1.143   -30.503   -47.795    33.363
---------------------------------------------------------------------

 Electric field gradients after diagonalization (V/A^2)
 (convention: |V_zz| > |V_xx| > |V_yy|)
----------------------------------------------------------------------
 ion       V_xx      V_yy      V_zz     asymmetry (V_yy - V_xx)/ V_zz
----------------------------------------------------------------------
   1       7.302     2.121    -9.423       0.550
   2       7.299     2.122    -9.421       0.549
   3       7.299     2.125    -9.425       0.549
   4     -55.690   -19.293    74.983       0.485
   5     -55.689   -19.294    74.983       0.485
   6     -55.691   -19.294    74.985       0.485
   7     -55.690   -19.294    74.984       0.485
   8     -55.692   -19.300    74.992       0.485
   9     -55.694   -19.290    74.984       0.485
----------------------------------------------------------------------
```

Quadrupolar interaction: accuracy

Electric Field Gradient Tensor (EFG)

		V_{zz}/ 10^{21} V m^{-2}	V_{yy}/ 10^{21} V m^{-2}	V_{xx}/ 10^{21} V m^{-2}	C_Q/MHz	η_Q
MgF_2						
Exp		0.728(6)	−0.480(8)	−0.248(8)	3.51(3)	0.32(2)
IS	CASTEP	0.631	−0.434	−0.196	3.04	0.38
	WIEN2K	0.637	−0.498	−0.139	3.06	0.56
APO	CASTEP	0.655	−0.364	−0.291	3.16	0.11
	WIEN2K	0.658	−0.431	−0.228	3.17	0.31



Drawing of the charge density deformation coming from |L|=2

Blue is accumulation (Vzz > 0)
Green is depletion (Vzz < 0)

NMR parameters in alkali, alkaline earth and rare earth fluorides from first principle calculations
From Sadoc *et al. Phys. Chem. Chem. Phys.*, **2011**, 13, 18539–185

Quadrupolar interaction: accuracy

Convergence of EFG has to be checked

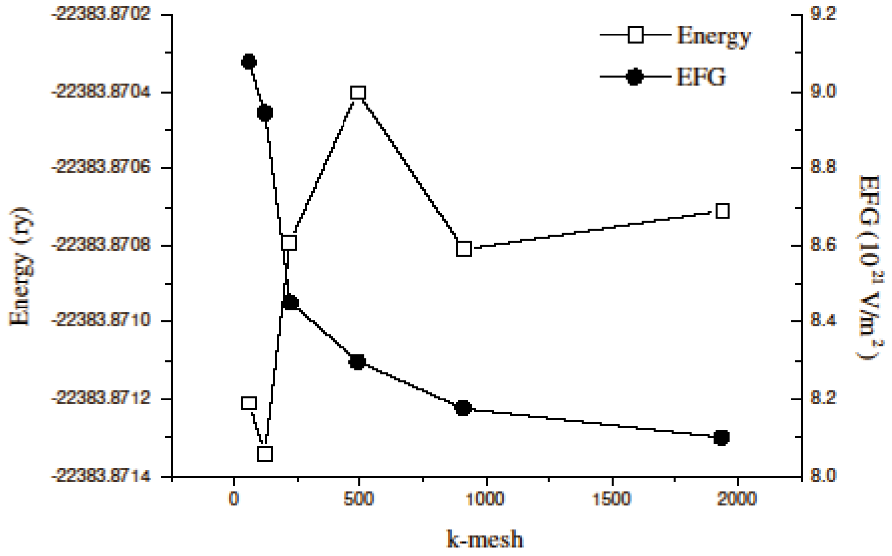
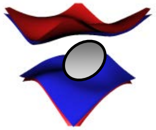


Figure 6.2: *Total energy and electric-field gradient as a function of k-mesh size for hcp-Cd* ($R_{mt}K_{max} = 7.0$).

Quadrupolar interaction: accuracy

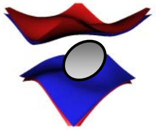


Electric Field Gradient can be really useful!

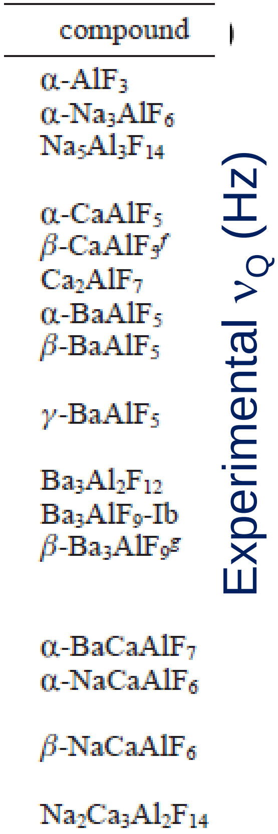
When available EFG *vs* Cq correlation has to be used

- EFG very sensitive to really small deformation
- EFG is a ground state property, cheap to calculate
- EFG can be calculated with AE or PP codes
  - good way to test/validate your PP
  - EFG can be calculated even for I=1/2
- EFG tensor orientation can be useful:
  - for interpreting the deformation
  - for getting the Eulerian angles for fitting NMR parameters

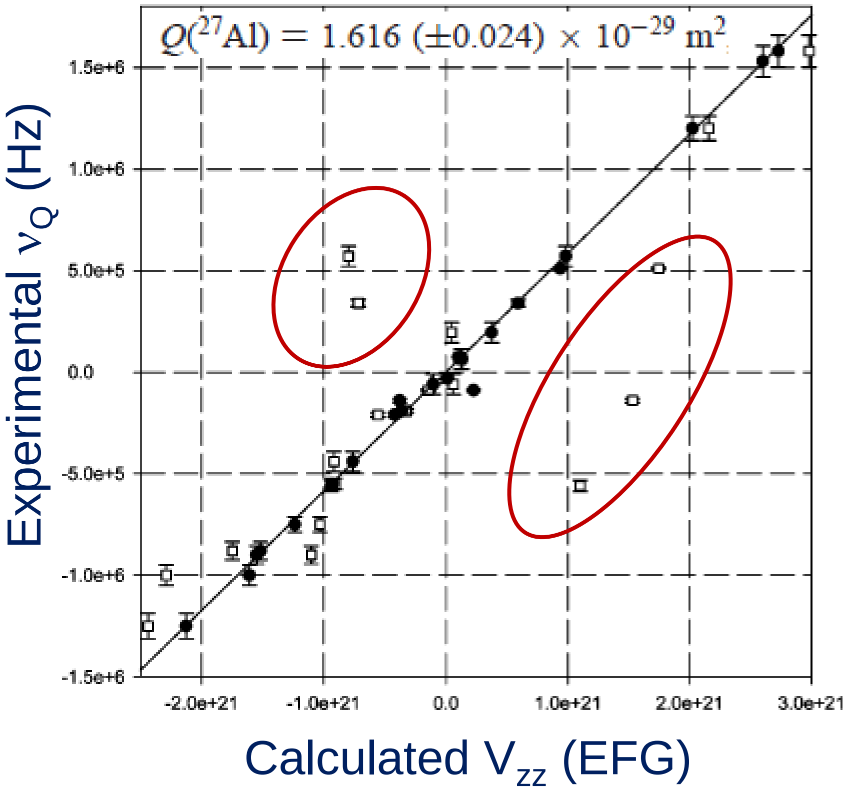
Quadrupolar interaction: accuracy



EFG ^{27}Al



compound
α-AlF_3
α-Na_3AlF_6
$Na_5Al_3F_{14}$
α-$CaAlF_5$
β-$CaAlF_5$^{f}
Ca_2AlF_7
α-$BaAlF_5$
β-$BaAlF_5$
γ-$BaAlF_5$
$Ba_3Al_2F_{12}$
Ba_3AlF_9-Ib
β-Ba_3AlF_9^{g}
α-$BaCaAlF_7$
α-$NaCaAlF_6$
β-$NaCaAlF_6$
$Na_2Ca_3Al_2F_{14}$

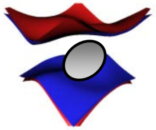


Poor accuracy for data coming from powder diffraction (X-Ray or Neutron)

Advances in Structural Analysis of Fluoroaluminates Using DFT Calculations of ^{27}Al Electric Field Gradients (WIEN2k)

From Body *et al. J. Phys. Chem. A* **2007**, 111, 11873-11884

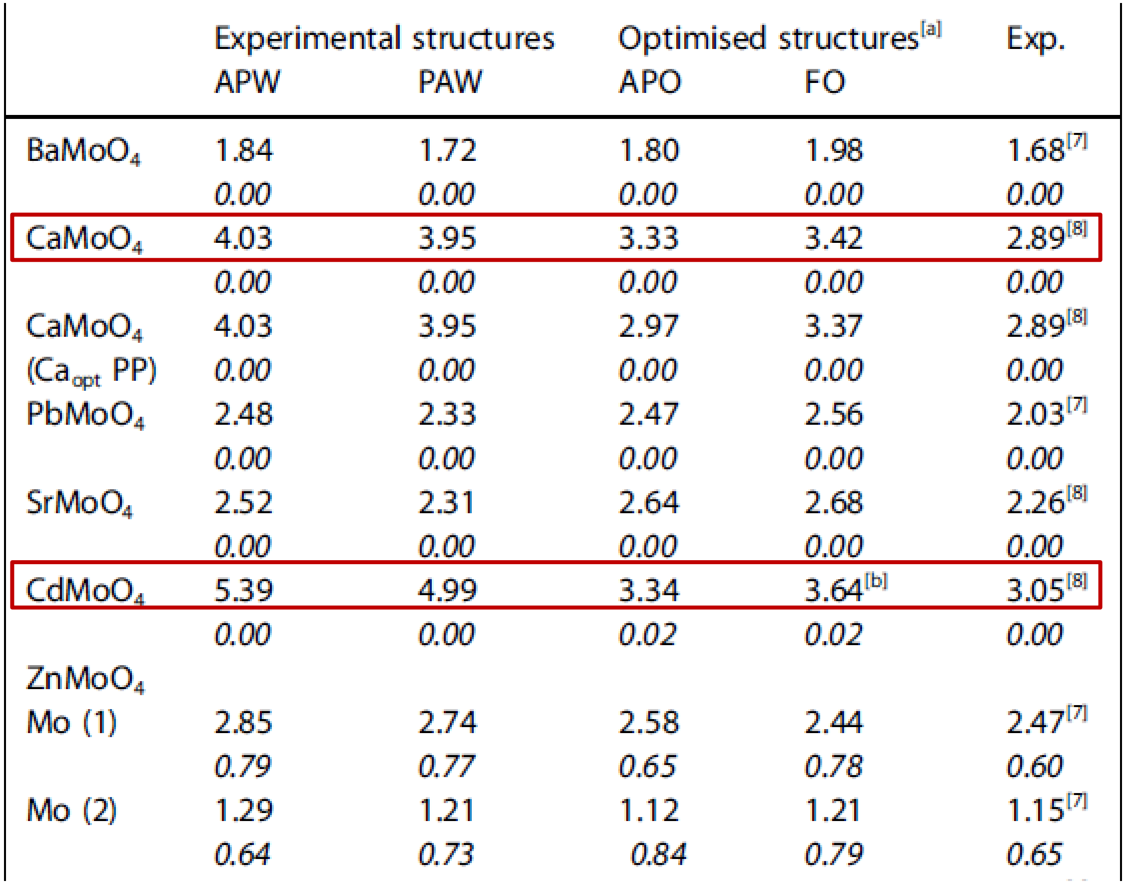
Quadrupolar interaction: accuracy



Density Functional Theory Calculations of ^{95}Mo NMR Parameters in Solid-State Compounds

From Cuny *et al. ChemPhysChem* ***2009****, 10, 3320 – 3329*

^{95}Mo Cq (MHz) experimental versus calculated



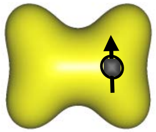
	Experimental structures		Optimised structures[a]		Exp.
	APW	PAW	APO	FO	
$BaMoO_4$	1.84	1.72	1.80	1.98	1.68[7]
	0.00	*0.00*	*0.00*	*0.00*	*0.00*
$CaMoO_4$	4.03	3.95	3.33	3.42	2.89[8]
	0.00	*0.00*	*0.00*	*0.00*	*0.00*
$CaMoO_4$	4.03	3.95	2.97	3.37	2.89[8]
(Ca_{opt} PP)	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
$PbMoO_4$	2.48	2.33	2.47	2.56	2.03[7]
	0.00	*0.00*	*0.00*	*0.00*	*0.00*
$SrMoO_4$	2.52	2.31	2.64	2.68	2.26[8]
	0.00	*0.00*	*0.00*	*0.00*	*0.00*
$CdMoO_4$	5.39	4.99	3.34	3.64[b]	3.05[8]
	0.00	*0.00*	*0.02*	*0.02*	*0.00*
$ZnMoO_4$					
Mo (1)	2.85	2.74	2.58	2.44	2.47[7]
	0.79	*0.77*	*0.65*	*0.78*	*0.60*
Mo (2)	1.29	1.21	1.12	1.21	1.15[7]
	0.64	*0.73*	*0.84*	*0.79*	*0.65*

Validation of ^{95}Mo PP
(LAPW as a reference can
be done also for I=1/2)

Effect of geometry
optimization (APO, FO)

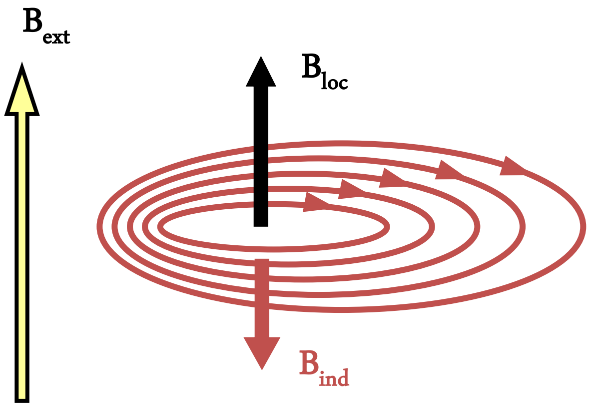
Powder diffraction !

Chemical shift interaction: a magnetic shielding



Response to an applied external magnetic field (B^{ext})

Electronic cloud generates a weak magnetic field B^{ind} opposite to B^{ext}



$$\mathbf{B}(\mathbf{r}) = \mathbf{B}^{ext} + \mathbf{B}^{ind}(\mathbf{r})$$

The nucleus is shielded from B^{ext} by

$$\mathbf{B}(\mathbf{r}) = \mathbf{B}^{ext}(1-\sigma)$$

Shielding tensor σ

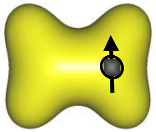
$$\mathbf{B}_s^{ind} = \overset{\leftrightarrow}{\sigma}_s \cdot \mathbf{B}^{ext}$$

Indice s = quantity at position $\mathbf{r}_s$ (site of nucleus s)

Chemical shift interaction: a magnetic shielding

Yates, J. R. and Pickard, C. J. **Computations of Magnetic Resonance Parameters for Crystalline Systems**:

Encyclopedia of Magnetic Resonance, 2008, 1-9



$$\sigma_{s,\alpha\beta} = \frac{\partial B^{ind}_{s,\alpha}}{\partial B^{ext}_{\beta}}$$

Biot-Savart law: induced magnetic field obtained from the induced current

$$\mathbf{B}^{ind}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \mathbf{j}(\mathbf{r'}) \times \frac{\mathbf{r} - \mathbf{r'}}{|\mathbf{r} - \mathbf{r'}|^3}$$

DFPT = Density functional perturbation theory

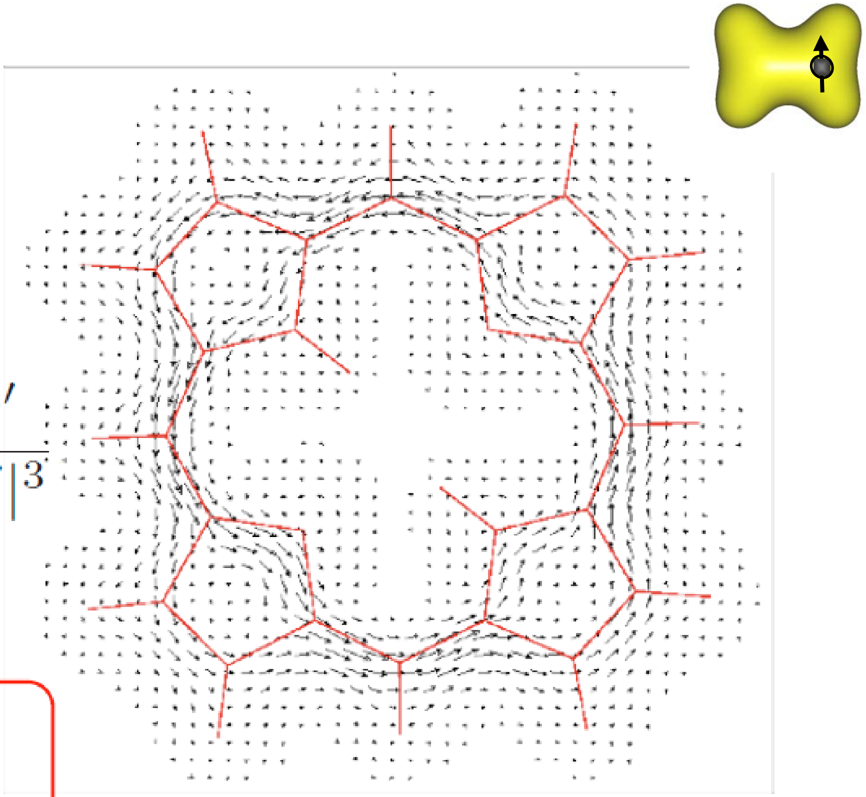
$$\mathbf{j}^{(1)}(\mathbf{r'}) = 2\sum_{o} \left[\langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r'}) | \Psi_o^{(1)} \rangle + \langle \Psi_o^{(1)} | \mathbf{J}^p(\mathbf{r'}) | \Psi_o^{(0)} \rangle \right]$$
$$+2\sum_{o} \langle \Psi_o^{(0)} | \mathbf{J}^d(\mathbf{r'}) | \Psi_o^{(0)} \rangle$$

Chemical shift interaction: a magnetic shielding

To compute the chemical shifts we just need to calculate the current induced by the external magnetic field

Biot-Savart

$$\mathbf{B}_{\mathrm{in}}(\mathbf{r}) = \frac{1}{c}\int d^3r'\,\mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}$$



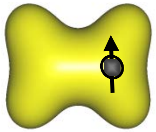
Obtain current within perturbation theory (linear response)

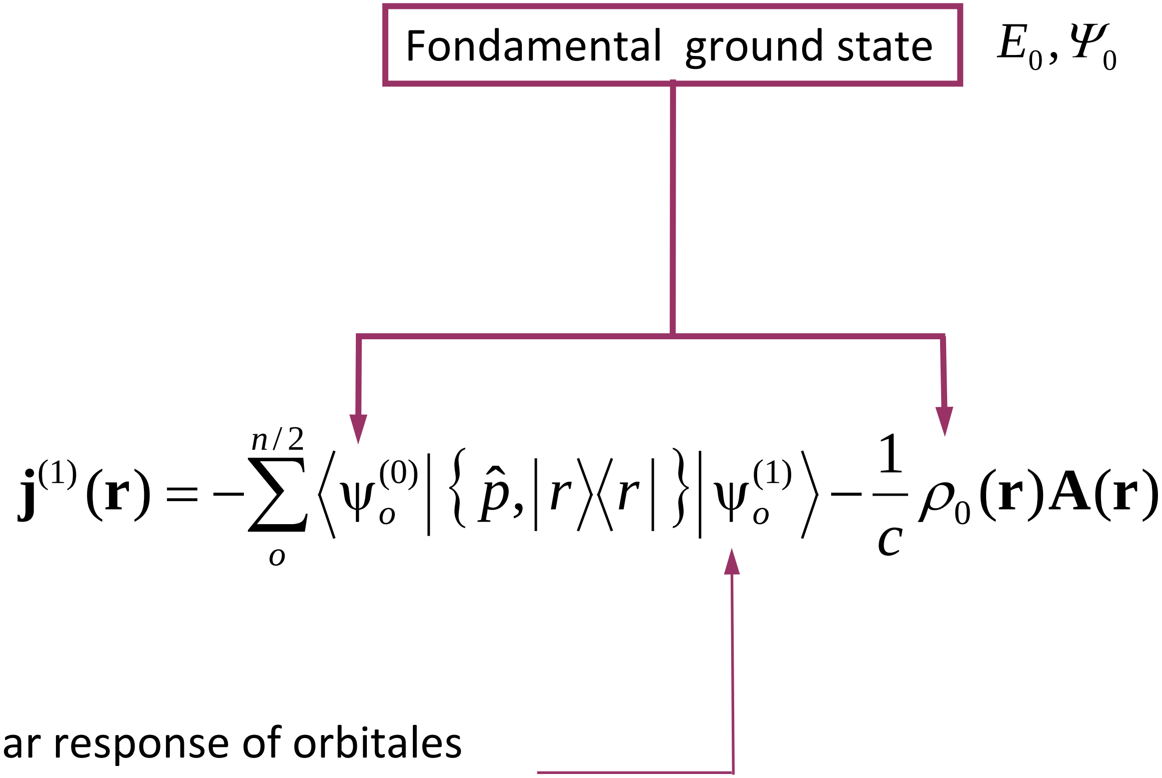
$$O = O^{(0)} + O^{(1)} + \mathcal{O}(\mathbf{B}^2)$$

$$B_{\mathrm{in}} = -\sigma B_0$$

note: σ is a rank 2 tensor

Chemical shift interaction: a magnetic shielding





Fondamental ground state

E_0, Ψ_0

$$\mathbf{j}^{(1)}(\mathbf{r}) = -\sum_{o}^{n/2} \left\langle \psi_o^{(0)} \right| \left\{ \hat{p}, |r\rangle\langle r| \right\} \left| \psi_o^{(1)} \right\rangle - \frac{1}{c}\rho_0(\mathbf{r})\mathbf{A}(\mathbf{r})$$

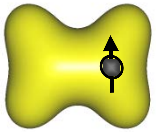
Linear response of orbitales

to the perturbation of **B**

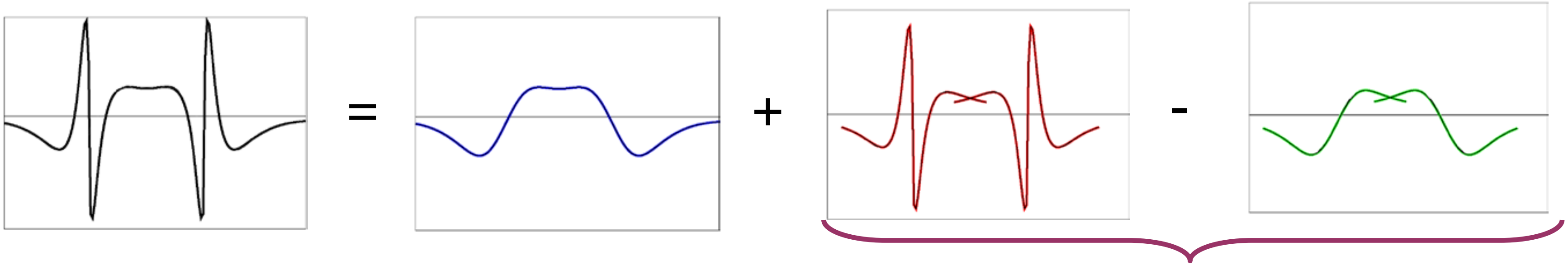
Chemical shift interaction: a magnetic shielding

Gauge Included Projector Augmented Wave (GIPAW)

C. J. Pickard, F. Mauri, *Phys. Rev. B*, **63**, 245101 (2001)

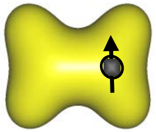


$$\mathbf{j}^{(1)}(\mathbf{r}) = \underbrace{-\sum_{o}^{n/2}\left\langle \tilde{\psi}_o^{(0)} \middle| \left\{ \hat{p}, |r\rangle\langle r| \right\} \middle| \tilde{\psi}_o^{(1)} \right\rangle - \frac{1}{c}\tilde{\rho}_0(\mathbf{r})\mathbf{A}(\mathbf{r})}_{\text{Induced current from pseudo wave functions}} + \overbrace{\mathbf{j}'^{(1)}_{\Delta\mathrm{d}}(\mathbf{r}) + \mathbf{j}'^{(1)}_{\Delta\mathrm{p}}(\mathbf{r})}^{\text{Paramagnetic and diamagnetic corrections due to GIPAW reconstruction}} + \underbrace{\mathbf{j}'^{(1)}_{\mathrm{core}}(\mathbf{r})}_{\text{Frozen core approximation}}\ !$$



$$\overleftrightarrow{\sigma}_{\mathrm{GIPAW}} = \overleftrightarrow{\sigma}_{\mathrm{ps}} + \overleftrightarrow{\sigma}_{\Delta\mathrm{d}} + \overleftrightarrow{\sigma}_{\Delta\mathrm{p}} + \overleftrightarrow{\sigma}_{\mathrm{core}}$$

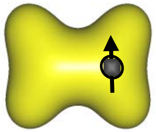
Chemical shift interaction: α-SiO$_2$ example



Linear response chemical shift tensor in VASP

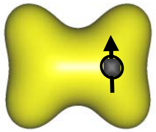
```
PREC = A                          # nice
ENCUT = 600.0                     # typically higher cutoffs than usual are needed
ISMEAR = 0; SIGMA= 0.1            # no fancy smearings, SIGMA sufficiently small
EDIFF = 1E-10                     # you'd need much smaller EDIFFs.
NBANDS = ???                      # to safe memory, ??? = NELECT/2

LCHIMAG = .TRUE.                  # to switch on linear response for chemical shifts
DQ = 0.001                        # often the default is sufficient
ICHIBARE = 1                      # often the default is sufficient
LNMR_SYM_RED = .TRUE.             # be on the safe side
NSLPLINE = .TRUE.                 # only needed if LREAL is NOT set. LREAL = A
                                  # helps for speed for large systems, not needed
```

Chemical shift interaction: α-SiO_2 example



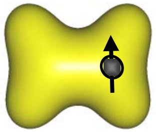
```
FIRST STANDARD SCF
 N        E                     dE             d eps       ncg     rms          rms(c
DAV:   1    -0.669222998366E+02   -0.66922E+02   -0.41316E+02   408   0.883E+01    0.
DAV:   2    -0.704321174703E+02   -0.35098E+01   -0.35491E+01   480   0.264E+01    0.898E+00

DAV:  16    -0.704128711670E+02   -0.19218E-08   -0.52524E-10   328   0.154E-04    0.195E-03
DAV:  17    -0.704128711673E+02   -0.24193E-09   -0.51088E-11   304   0.469E-05
   1 F= -.70412871E+02 E0= -.70412871E+02  d E =-.237236E-10

Linear response by applying B and looking for DQ derivative
Calculate the DQ derivative applying +/- DQ in each cartesian direction
EXTERNAL FIELD APPLIED IN DIRECTION            1
RMM:  10    -0.162591029970E+03   -0.12611E-09   -0.15888E-10   414   0.592E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RMM:  10    -0.162588558523E+03   -0.12272E-09   -0.15456E-10   413   0.589E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RMM:  10    -0.162585056650E+03   -0.11977E-09   -0.15086E-10   414   0.589E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RMM:  10    -0.162611477371E+03   -0.14026E-09   -0.16817E-10   417   0.628E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RMM:  10    -0.162612646509E+03   -0.13992E-09   -0.16762E-10   414   0.632E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RMM:  10    -0.162612794520E+03   -0.13975E-09   -0.16748E-10   417   0.632E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
RLQ:   8    -0.196497939884E+01   -0.65299E-09   -0.85862E-10   461   0.840E-05
------------------------ aborting loop because EDIFF is reached ----------------------------
```

Chemical shift interaction: α-SiO_2 example



```
---------------------------------------------------------------------------------
 CSA tensor (J. Mason, Solid State Nucl. Magn. Reson. 2, 285 (1993))
---------------------------------------------------------------------------------
            EXCLUDING G=0 CONTRIBUTION             INCLUDING G=0 CONTRIBUTION
        -----------------------------------   -----------------------------------
 ATOM    ISO_SHIFT        SPAN        SKEW     ISO_SHIFT        SPAN        SKEW
---------------------------------------------------------------------------------
 (absolute, valence only)
    1     422.3094     14.9400     -0.3663      413.0871     14.7512     -0.3570
    2     422.3062     14.9367     -0.3669      413.0839     14.7426     -0.3578
    3     422.3062     14.9367     -0.3669      413.0839     14.7426     -0.3578
    4      85.9453     59.7776      0.3883       76.7230     59.8349      0.3846
    5      85.9463     59.7793      0.3882       76.7239     59.8283      0.3842
    6      85.9475     59.7714      0.3883       76.7251     59.8215      0.3846
    7      85.9475     59.7714      0.3883       76.7251     59.8215      0.3846
    8      85.9453     59.7776      0.3883       76.7230     59.8349      0.3846
    9      85.9463     59.7793      0.3882       76.7239     59.8283      0.3842
---------------------------------------------------------------------------------
 (absolute, valence and core)
    1    -415.5747     14.9400     -0.3663     -425.9027     14.7512     -0.3570
    2    -415.5779     14.9367     -0.3669     -425.9059     14.7426     -0.3578
    3    -415.5779     14.9367     -0.3669     -425.9059     14.7426     -0.3578
    4    -185.1314     59.7776      0.3883     -195.4594     59.8349      0.3846
    5    -185.1304     59.7793      0.3882     -195.4585     59.8283      0.3842
    6    -185.1292     59.7714      0.3883     -195.4573     59.8215      0.3846
    7    -185.1292     59.7714      0.3883     -195.4573     59.8215      0.3846
    8    -185.1314     59.7776      0.3883     -195.4594     59.8349      0.3846
    9    -185.1304     59.7793      0.3882     -195.4585     59.8283      0.3842
---------------------------------------------------------------------------------
```

Chemical shift interaction: the slope problem



- Simulation: Isotropic chemical shielding σ_{iso}

$$\sigma_{iso} = \frac{1}{3} Tr\{\boldsymbol{\sigma}\}$$

- Experiment: Isotropic chemical shift δ_{iso} is defined from a reference

$$\delta_{iso} = -[\sigma_{iso} - \sigma_{ref}]$$

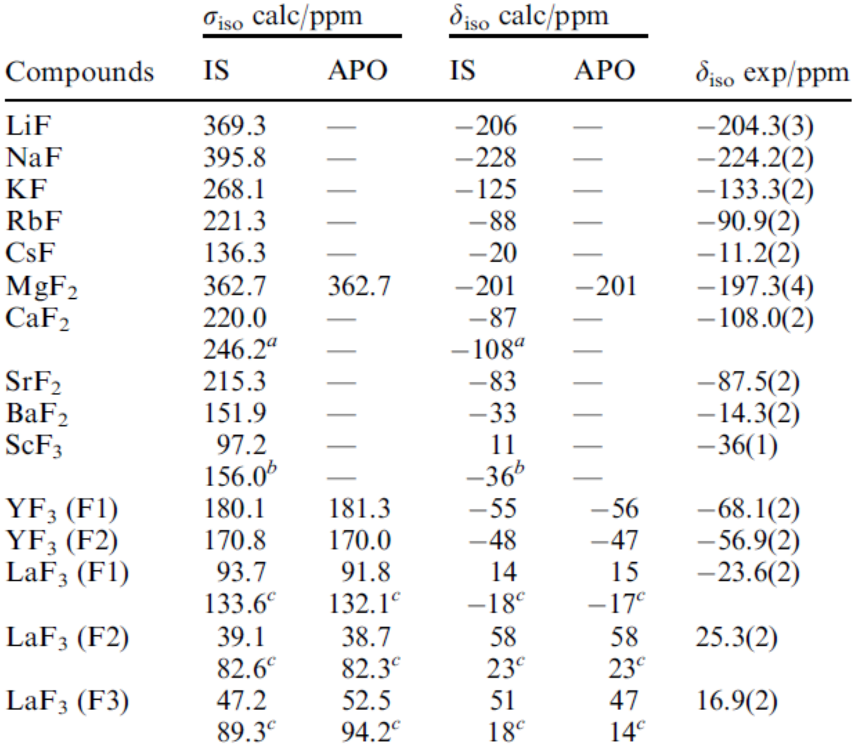
^{19}F NMR - Ref: CFCl$_3$
GIPAW σ_{ref} = 113.2 ppm

Chemical shift interaction: the slope problem

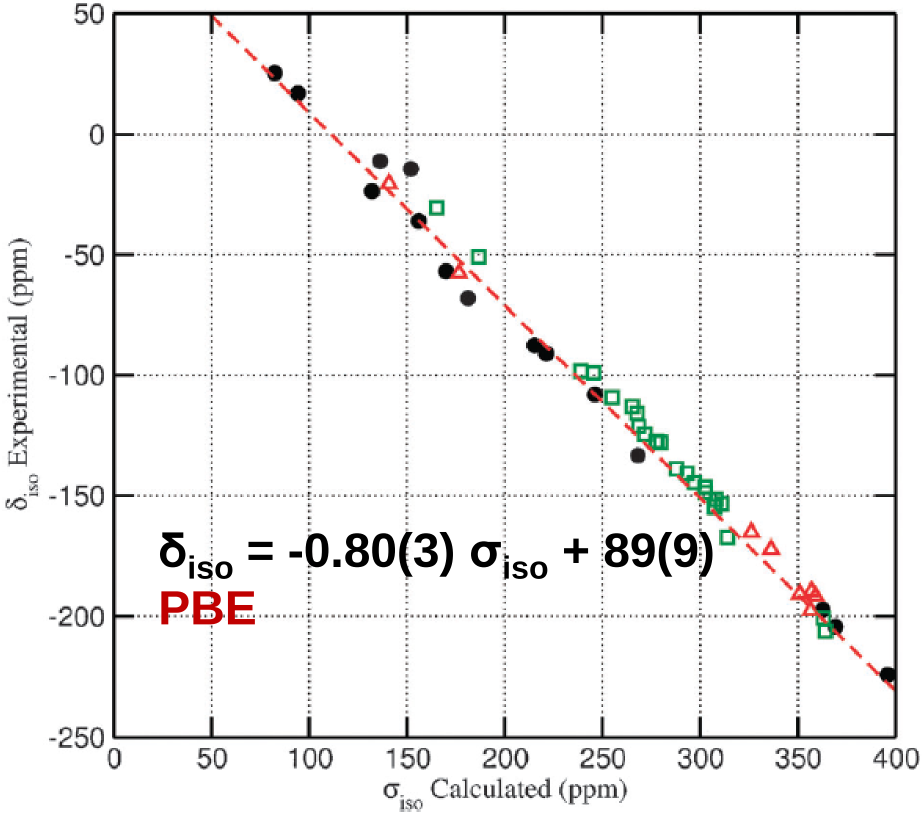
Experimental chemical shift *vs* shielding calculations

^{19}F NMR shielding calculations: RMN3MPL results

From Sadoc et al. Phys. Chem. Chem. Phys., **2011**, 13, 18539–185



	σ_{iso} calc/ppm		δ_{iso} calc/ppm		
Compounds	IS	APO	IS	APO	δ_{iso} exp/ppm
LiF	369.3	—	−206	—	−204.3(3)
NaF	395.8	—	−228	—	−224.2(2)
KF	268.1	—	−125	—	−133.3(2)
RbF	221.3	—	−88	—	−90.9(2)
CsF	136.3	—	−20	—	−11.2(2)
MgF_2	362.7	362.7	−201	−201	−197.3(4)
CaF_2	220.0	—	−87	—	−108.0(2)
	246.2^a	—	-108^a	—	
SrF_2	215.3	—	−83	—	−87.5(2)
BaF_2	151.9	—	−33	—	−14.3(2)
ScF_3	97.2	—	11	—	−36(1)
	156.0^b	—	-36^b	—	
YF_3 (F1)	180.1	181.3	−55	−56	−68.1(2)
YF_3 (F2)	170.8	170.0	−48	−47	−56.9(2)
LaF_3 (F1)	93.7	91.8	14	15	−23.6(2)
	133.6^c	132.1^c	-18^c	-17^c	
LaF_3 (F2)	39.1	38.7	58	58	25.3(2)
	82.6^c	82.3^c	23^c	23^c	
LaF_3 (F3)	47.2	52.5	51	47	16.9(2)
	89.3^c	94.2^c	18^c	14^c	



$\delta_{iso} = -0.80(3)\ \sigma_{iso} + 89(9)$

PBE

VASP training school - August 31st to September 3rd, 2016 - Rennes

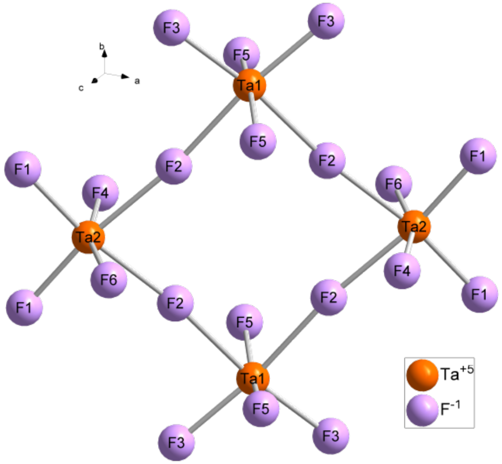
Chemical shift interaction: the slope problem

Experimental chemical shift *vs* shielding calculations

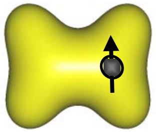
Unambiguous attribution for the fluorine signals in TaF_5

From Biswal et al. J. Solid State Chem., **2013**, 207, 208–217

NMR experiment			**NMR simulation**		
δ_{iso} (ppm)	**Multi-plicity**	**Assignement**	**σ_{iso} (ppm)**	**δ_{iso} (ppm)**	**Assign.**
-70.1	4	F2	210.7	-75.4	F2
106.4	2	F4, F6	10.0	90.1	F4
121.9	4	F1, F3, F5	-31.7	124.5	F5
136.3	2	F4, F6	-43.4	134.2	F6
168.6	4	F1, F3, F5	-86.1	169.4	F1
175.9	4	F1, F3, F5	-89.4	172.1	F3

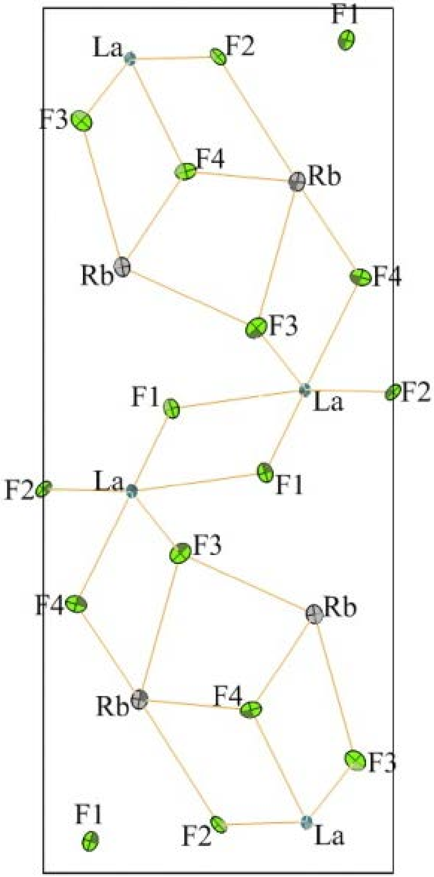


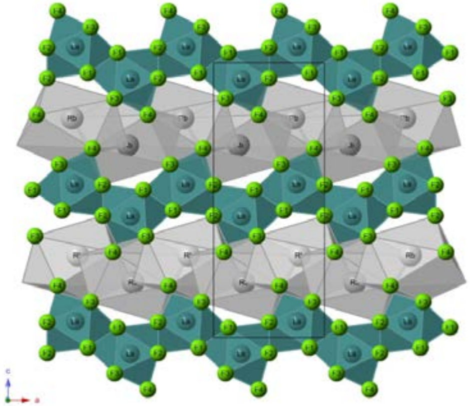
Chemical shift interaction: the slope problem

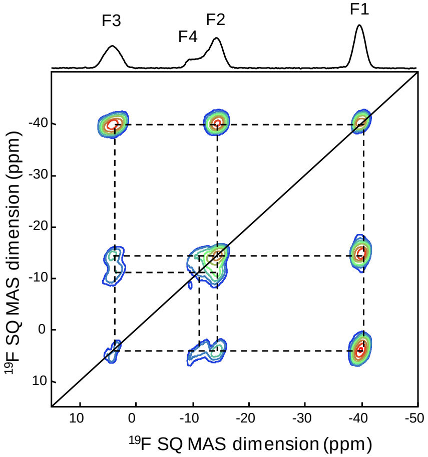


^{19}F NMR attribution in $RbLaF_4$ using the La(4f) shift

From Rollet et al. Inorg Chem, **2012**, 51, 2272-2282



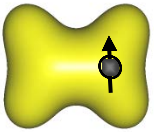




$$\boxed{\delta_{iso}/CFCl_3 = -\,0.80(3)\,\sigma_{iso} + 89(9)}$$

Site	$\sigma_{iso\ calc.}$ (ppm)		**$\delta_{iso\ calc.}$ (ppm)**		**$\delta_{iso\ exp.}$ (ppm)**
	ES	APO	**ES**	APO	
F1	160.1	157.7	**-39.1**	-37.2	**-39.8(2)**
F2	133.1	132.1	**-17.5**	-16.6	**-14.3(2)**
F3	108.4	105.5	**2.3**	4.6	**4.3(3)**
F4	128.8	127.9	**-14.0**	-13.3	**-10.8(2)**

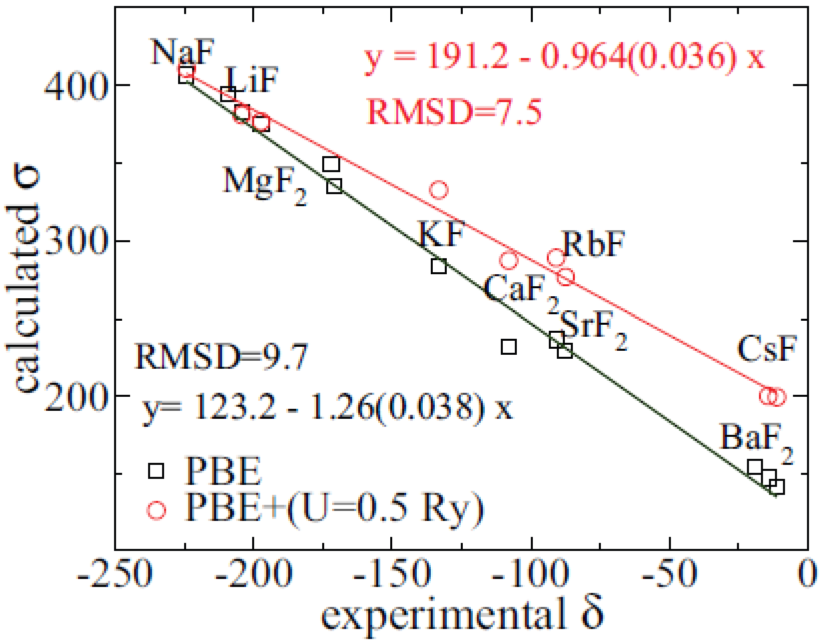
Chemical shift interaction: the slope problem



Experimental chemical shift *vs* shielding calculations

^{19}F NMR shielding calculations: recent WIEN2k results

Assessment of DFT functionals with NMR chemical shifts
From Laskowski et al. Phys. Rev. B, **2013**, 87, 195130



δ_{iso} = -0.80(3) σ_{iso} + 89(9)
RMN3MPL (PBE)

δ_{iso} = -0.794 σ_{iso} + 98
WIEN2k (PBE)

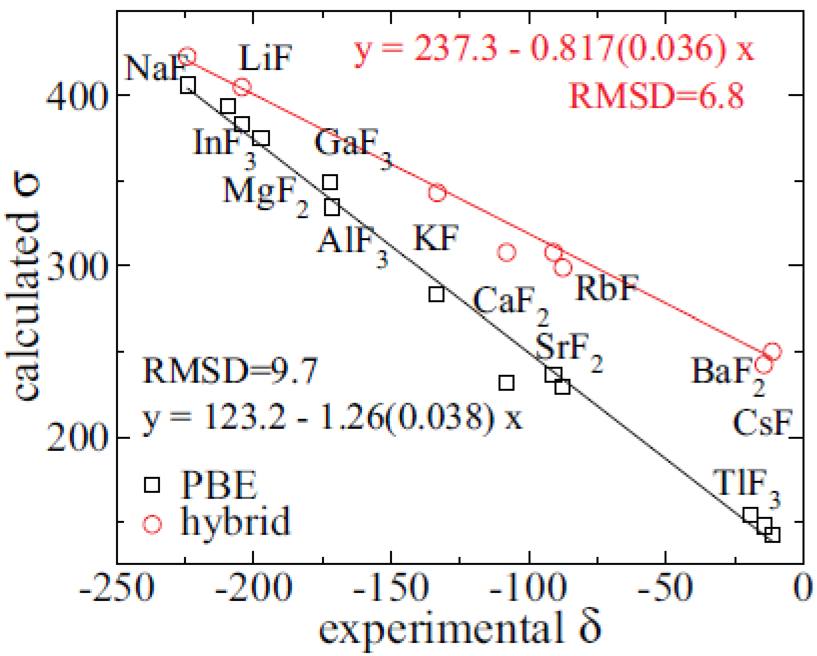
δ_{iso} = -1.037 σ_{iso} + 198
WIEN2k (PBE+U)

Chemical shift interaction: the slope problem

Experimental chemical shift *vs* shielding calculations

^{19}F NMR shielding calculations: recent WIEN2k results

Assessment of DFT functionals with NMR chemical shifts
From Laskowski et al. Phys. Rev. B, **2013**, 87, 195130



δ_{iso} = -0.80(3) σ_{iso} + 89(9)
RMN3MPL (PBE)

δ_{iso} = -0.794 σ_{iso} + 98
WIEN2k (PBE)

δ_{iso} = -1.037 σ_{iso} + 198
WIEN2k (PBE+U)

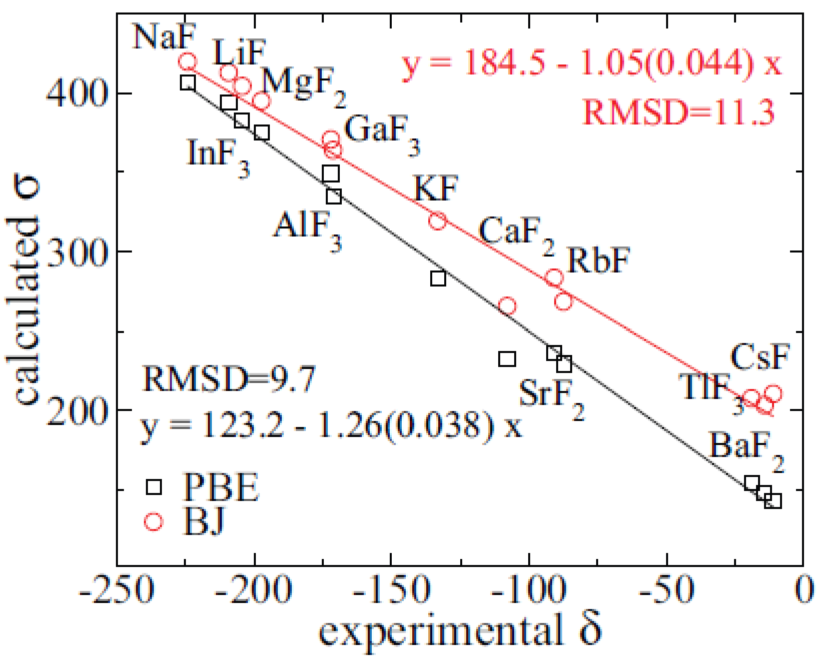
δ_{iso} = -1.224 σ_{iso} + 290
WIEN2k (Hybrid)

Chemical shift interaction: the slope problem

Experimental chemical shift *vs* shielding calculations

^{19}F NMR shielding calculations: recent WIEN2k results

Assessment of DFT functionals with NMR chemical shifts
From Laskowski et al. Phys. Rev. B, **2013**, 87, 195130



δ_{iso} = -0.80(3) σ_{iso} + 89(9)
RMN3MPL (PBE)

δ_{iso} = -0.794 σ_{iso} + 98
WIEN2k (PBE)

δ_{iso} = -1.037 σ_{iso} + 198
WIEN2k (PBE+U)

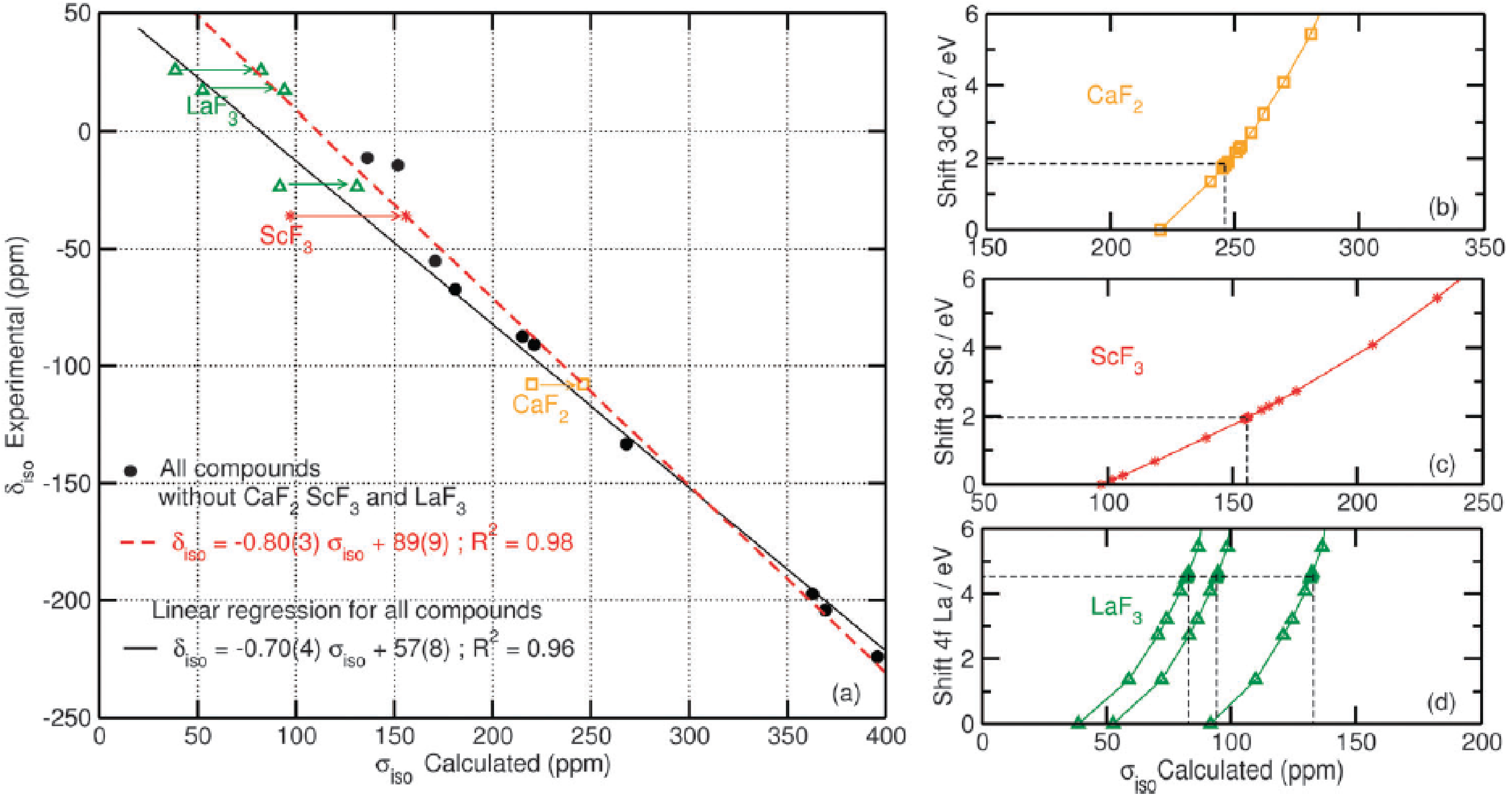
δ_{iso} = -1.224 σ_{iso} + 290
WIEN2k (Hybrid)

δ_{iso} = -0.952 σ_{iso} + 175
WIEN2k (BJ)

Chemical shift interaction: XC problem

^{19}F NMR shielding calculations: problem with 3d and 4f

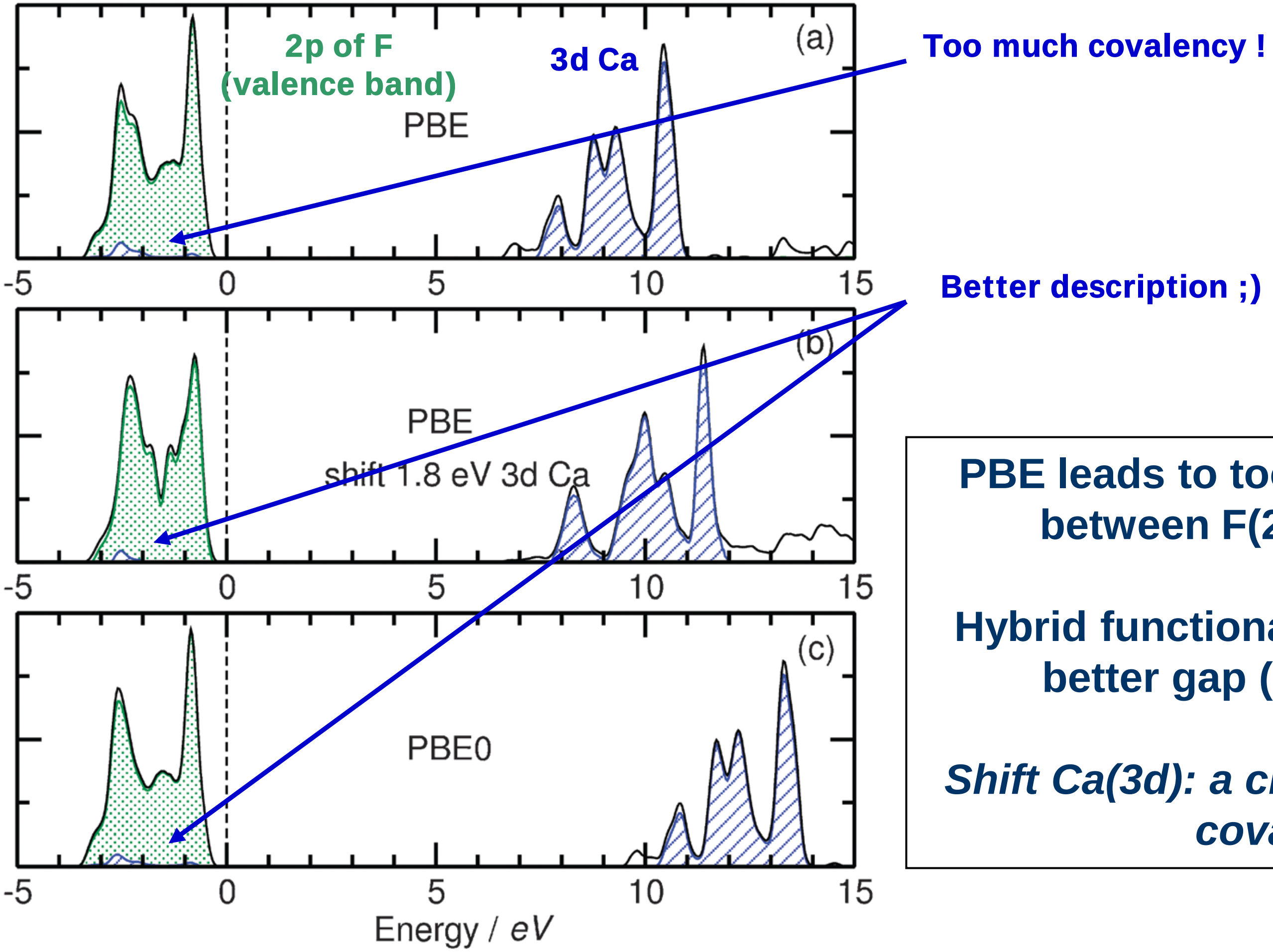
From Sadoc et al. Phys. Chem. Chem. Phys., **2011**, 13, 18539–185
Shift 3d idea form Profeta *et al. J. Am. Chem. Soc*., **2004**, 126, 12628–12635
(^{17}O on CaO and Ca Aluminosilicates)



Chemical shift interaction: XC problem

^{19}F NMR shielding calculations: problem with 3d and 4f

From Sadoc et al. Phys. Chem. Chem. Phys., **2011**, 13, 18539–185



Too much covalency !

Better description ;)

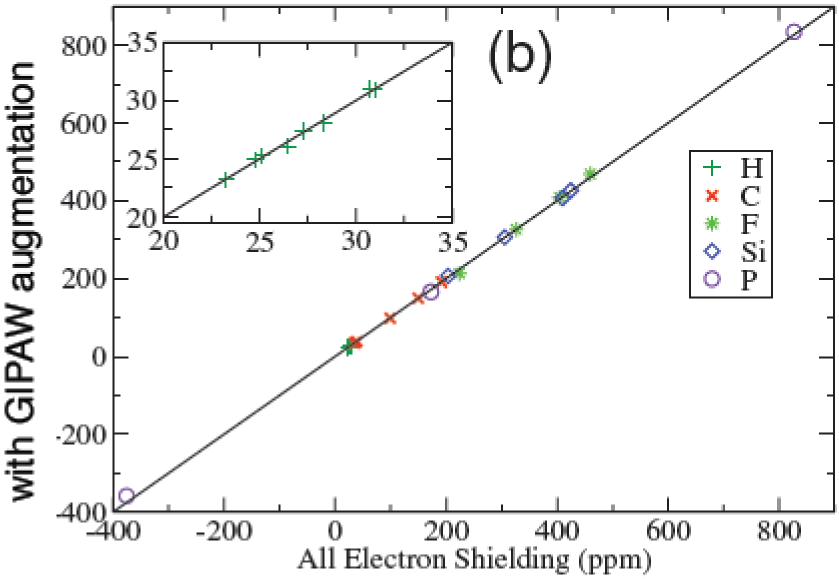
PBE leads to too much covalency between F(2p) and Ca(3d)

Hybrid functional predicts a much better gap (exp = 11.8 eV)

Shift Ca(3d): a cheap way to reduce covalency

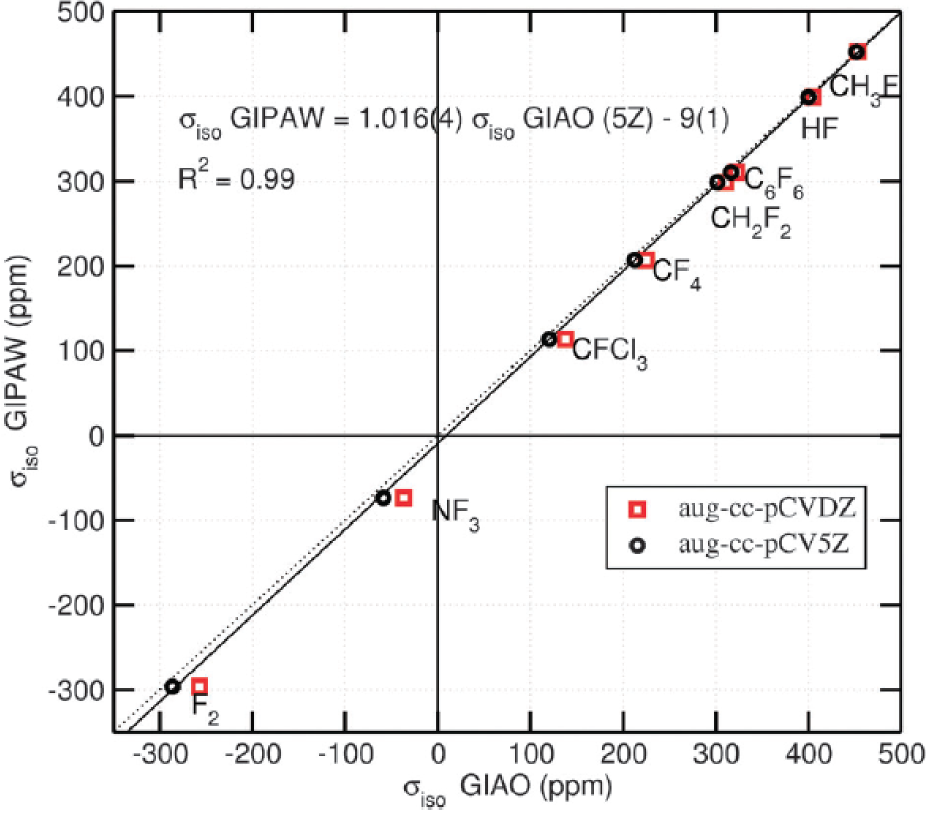
Chemical shift interaction: PP *vs* AE

From Yates et al. Phys. Rev. B, **2007***,* 76, 024401



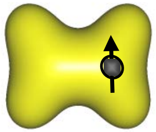
Gaussian/Molecular

From Sadoc et al. Phys. Chem. Chem. Phys., **2011**, 13, 18539–185

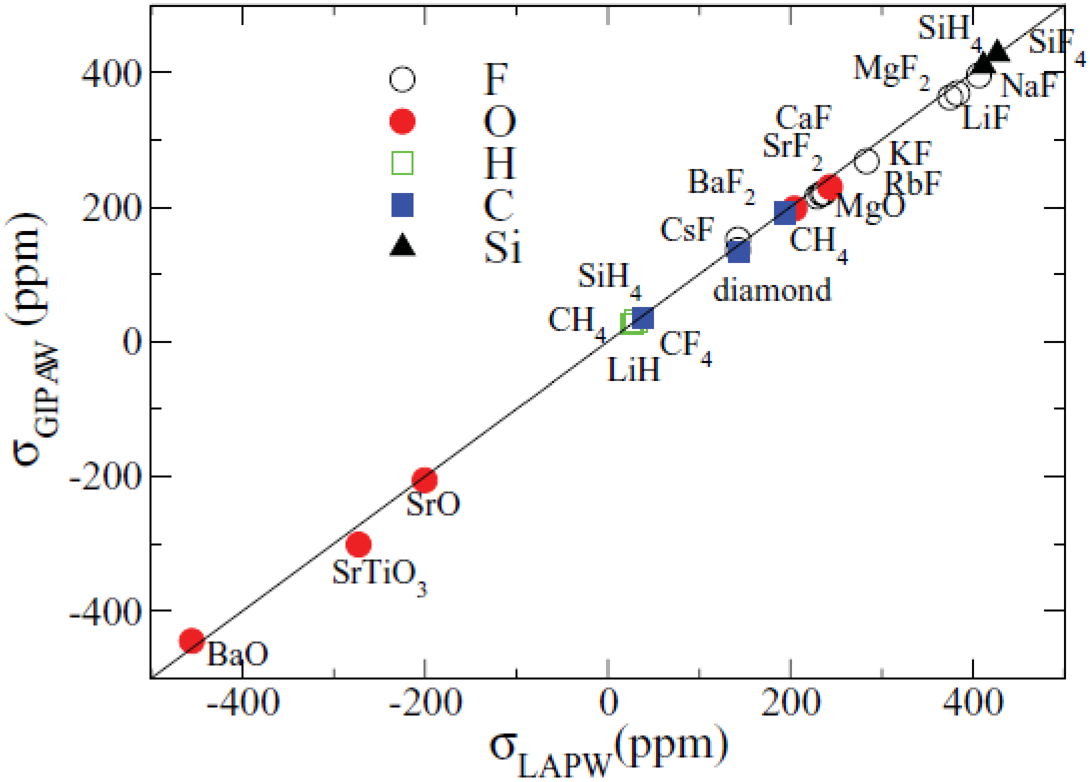


Gaussian/Molecular

Chemical shift interaction: PP *vs* AE



From Laskowski et al. Phys. Rev. B, **2012**, 85, 035102



Acknowledgments

Christophe Legein
Monique Body
Mamata Biswal (PhD)

IRIM2F
FR CNRS n° 2575

Université du Maine

RMN3MPL

Franck Fayon

Cemhti

UNIVERSITE D'ORLEANS

Région
PAYS DE LA LOIRE

Michel Ménétrier
Dany Carlier
Aurore Castets (PhD)

icmcb

UNIVERSITÉ BORDEAUX 1
Sciences Technologies

ANR
LoCharATMO

Yuesheng Zhang (Post Doc)
Aymeric Sadoc (Post Doc)
Xavier Rocquefelte
Lionel Truflandier
Christophe Payen
Michael Paris

IMN INSTITUT DES MATÉRIAUX JEAN ROUXEL

cnrs
dépasser les frontières

UNIVERSITÉ DE NANTES