# Calculations of NMR chemical shifts in solids

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NMR spectroscopy

$m_S = -1/2$

$\Delta E = E_{-1/2} - E_{+1/2}$

$m_S = +1/2$

Energy

$B_0 = 0$ $B_0 \neq 0$ Magnetic Field

$$\Delta E = -\gamma m \hbar (B_{ext} + B_{ind})$$

$E_\uparrow$

$E_\downarrow$

$B_{ext} + B_{ind}$

nucleus with
dipole moment
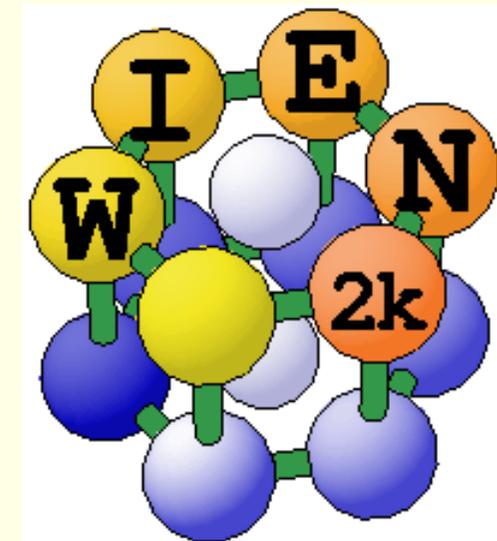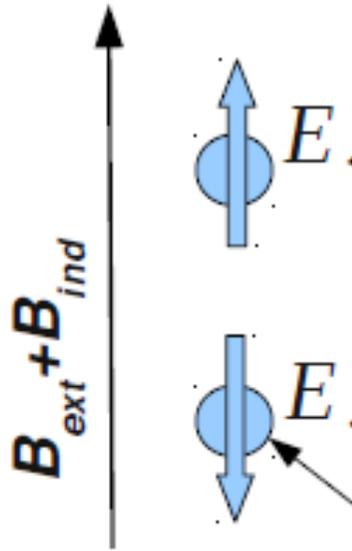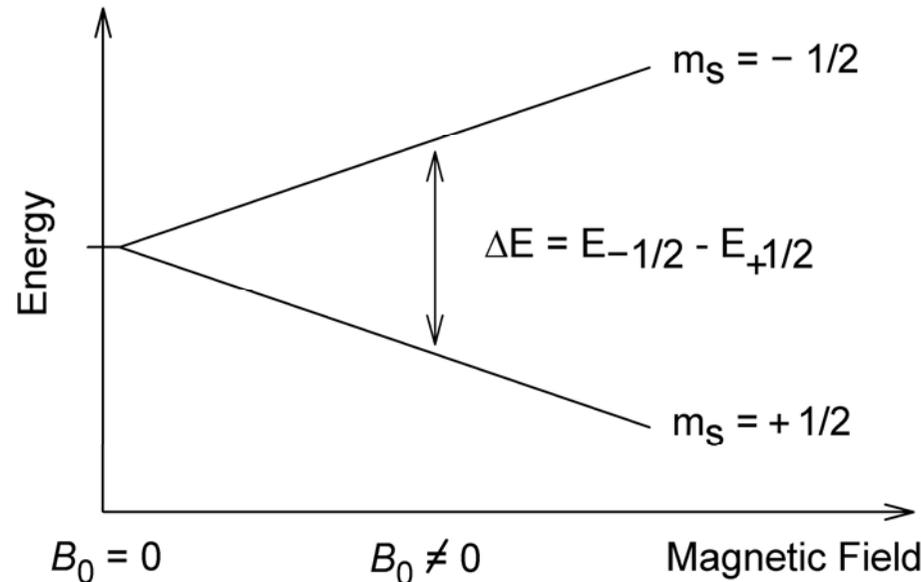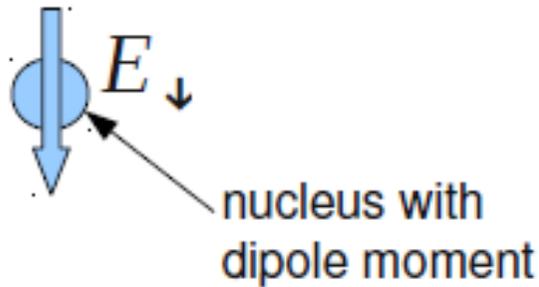
$B_{ext} + B_{ind}$ is measured at any nucleus by detecting transition
energy related to reorientation of its magnetic moment

NMR Hamiltonian

perturbation

$$H_{NMR} = H_Z + H_\sigma + H_Q + H_D + H_J + \ldots$$

electric quadrupole
interaction (EFG)

Indirect spin-
spin coupling

$$H_Z = -\mu \cdot B_{ext}$$

Zeeman Hamiltonian

direct dipolar
coupling

$$H_\sigma = -\mu \cdot B_{ind}$$

magnetic shielding

$$H_{NMR} = H_Z + H_\sigma + H_Q + H_D + H_J + \ldots$$

$$H_Z = -\mu \cdot B_{ext}$$

Zeeman Hamiltonian

$$H_Q \approx eQ\Phi / h$$

quadrupole interaction

$$H_\sigma = -\mu \cdot B_{ind}$$

magnetic shielding

NMR shielding, chemical shift:

$$B_{ext} \rightarrow j_{ind}(r) \rightarrow B_{ind}(r)$$

$$B_{ind}(R) = -\overline{\sigma}(R)\, B_{ext}$$
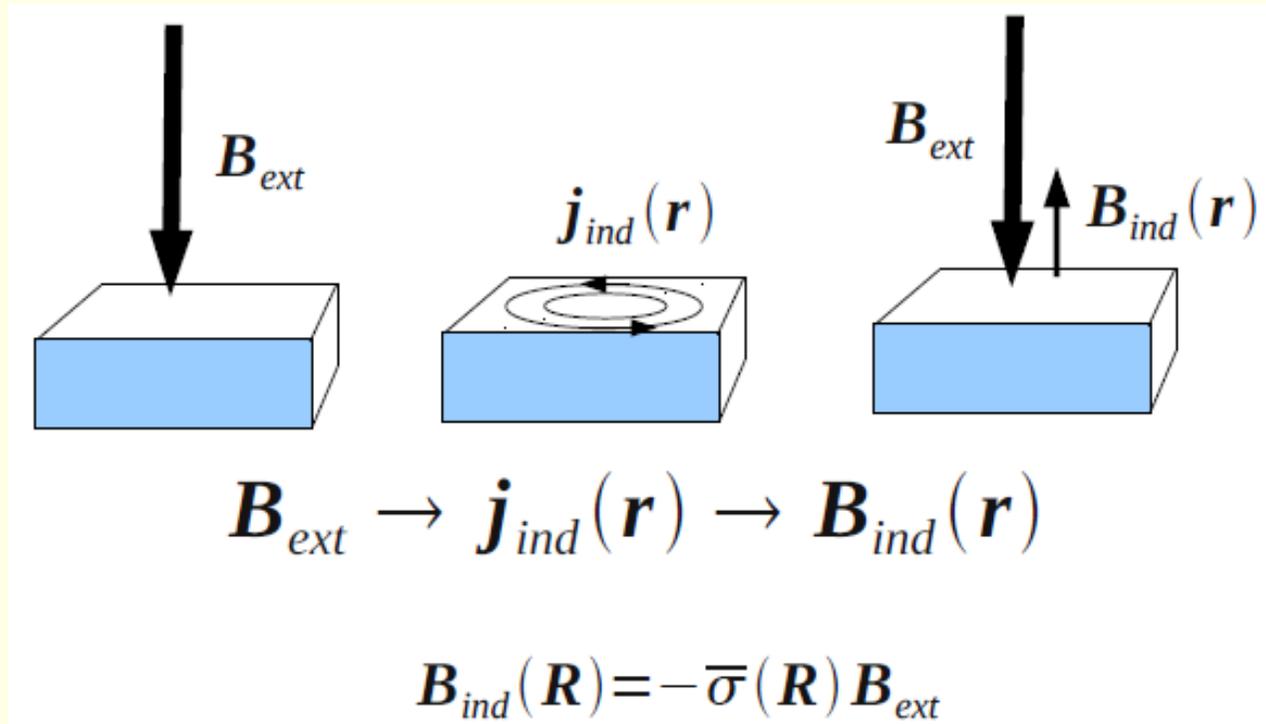
$\sigma(R)$ is the **shielding tensor** at the nucleus R

chemical shift:
$$\delta(ppm) = \frac{\sigma_{ref} - \sigma}{1 - \sigma_{ref}} \times 10^6$$

Biot - Savart law

The induced **magnetic field** (B_{ind}) is derived from the **induced current** (j_{ind}) using a standard formula:

$$B_{ind}(r) = \frac{1}{c} \int d^3 r' \, j(r') \times \frac{r - r'}{|r - r'|^3}$$

in DFT the **current density $j(r)$** will be:

$$j_{ind}(\mathbf{r'}) = \sum_o \left[\langle \Psi_o^{(1)} | \mathbf{J}^{(0)}(\mathbf{r'}) | \Psi_o^{(0)} \rangle + \langle \Psi_o^{(0)} | \mathbf{J}^{(0)}(\mathbf{r'}) | \Psi_o^{(1)} \rangle \right. \qquad \text{diamagn.}$$

$$\left. + \langle \Psi_o^{(0)} | \mathbf{J}^{(1)}(\mathbf{r'}) | \Psi_o^{(0)} \rangle \right], \qquad (4) \quad \text{paramagn.}$$

perturbed w.f. Ψ^1 is obtained from perturbation theory

$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle \Psi_e^{(0)} | H^{(1)} | \Psi_o^{(0)} \rangle}{\epsilon_o - \epsilon_e} \qquad H^{(1)} = \frac{1}{2c} \mathbf{r} \times \mathbf{p} \cdot \mathbf{B}$$

sum over all empty states   **magnetic field**

sum over **ALL** empty states:

$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle \Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon_o - \epsilon_e}$$

- standard APW basis set $u_l(r,E_l)$ only good near linearization E_l

- adding additional LOs at high energies (up to 1000 Ry !!!)

- $H^{(1)}$ contains the ∇ operator, so we need to represent the radial derivative of $u_l(r,E_l)$ at $l \pm 1$

- adding "NMR-los"

$$\xi_{l,k}(r,\tilde{\epsilon}) = \begin{cases} r\frac{d}{dr}u_{l+1}(r,\tilde{\epsilon}) + (l+2)u_{l+1}(r,\tilde{\epsilon}), & k=1 \\ r\frac{d}{dr}u_{l-1}(r,\tilde{\epsilon}) - (l-1)u_{l-1}(r,\tilde{\epsilon}), & k=2 \end{cases}$$

- x_nmr -mode in1 [-focus nmr_atom] will set that up automatically

practical calculation

- **run normal scf cycle**

- **x_nmr_lapw -mode in1 [-focus O]**
  - *view the resulting *in1c_nmr file*

- **x_nmr_lapw [-p]**
  - *creates several directories ("nmr_q0, nmr_pqx, nmr_mqx, nmr_pqy, ..) and performs lapw1/2 steps for several k-meshes (k ± q)*
  - *creates the current*
  - *integrates the current*

- **tail case.outputnmr_integ**
  - *:NMRTOT003   ATOM: O 3 NMR (total/ppm) TRACE = -366.9034   ANISO = -264.8134   ASYM = -0.9504*

- **for analysis one can calculate the shift from certain bands (energy range) only**
  - *x_nm_lapw [-p] -noinit -emin xx [-emax yy]*

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WFFIL  EF=.533144859350   (WFFIL, WFPRI, ENFIL,
   7.00       10     4 (R-MT*K-MAX; MAX L IN WF, V-NMT
   0.30   19  0     (GLOBAL E-PARAMETER WITH n OTH
   0  -0.58576    0.002 CONT 1
   0   4.80000    0.000 CONT 1
   0  36.60000    0.000 CONT 1
   0  66.66000    0.000 CONT 1
   0 104.26000    0.000 CONT 1
   0 149.26000    0.000 CONT 1
   0 201.50000    0.000 CONT 1
   ...
```

$$\mathbf{r}\cdot\hat{\mathbf{u}}_i = \lim_{q\to 0} \frac{1}{2q}\left(e^{iq\hat{\mathbf{u}}_i\cdot\mathbf{r}} - e^{-iq\hat{\mathbf{u}}_i\cdot\mathbf{r}}\right)$$
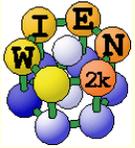
- the current **j** and chemical shielding **σ** of a **spherical atom** can be calculated "exactly" from the density **ρ(r)** (no perturbation theory) by:

$$\mathbf{j}_\rho(\mathbf{r}') = -\frac{1}{2c}\rho(\mathbf{r}')\mathbf{B} \times \mathbf{r}'$$
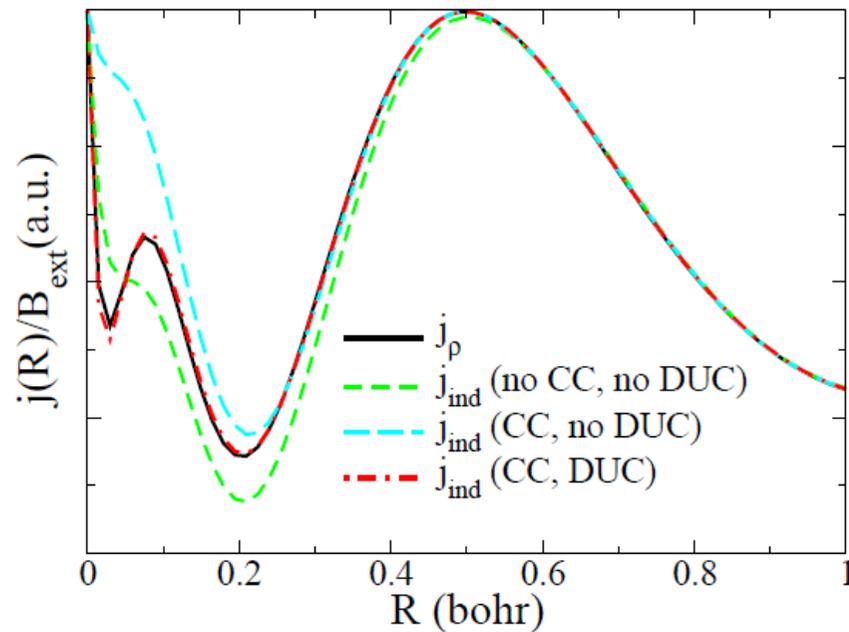
FIG. 1: Comparison of the induced current computed for an Ar atom with and without DUC and CC corrections (see text). For clarity only the valence 3s and 3p contribution is shown. $j\rho$ is the diamagnetic current calculated with the spherical charge density of 3s and 3p states using Eq.18.
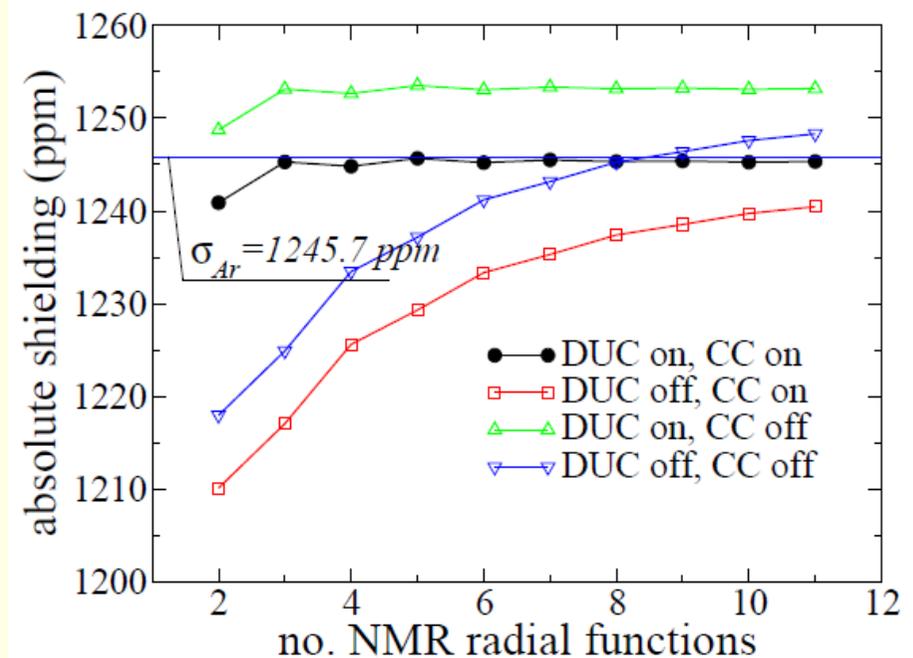
Induced current field for BaO (fcc) , $\boldsymbol{B}_{ext}$ in (001)
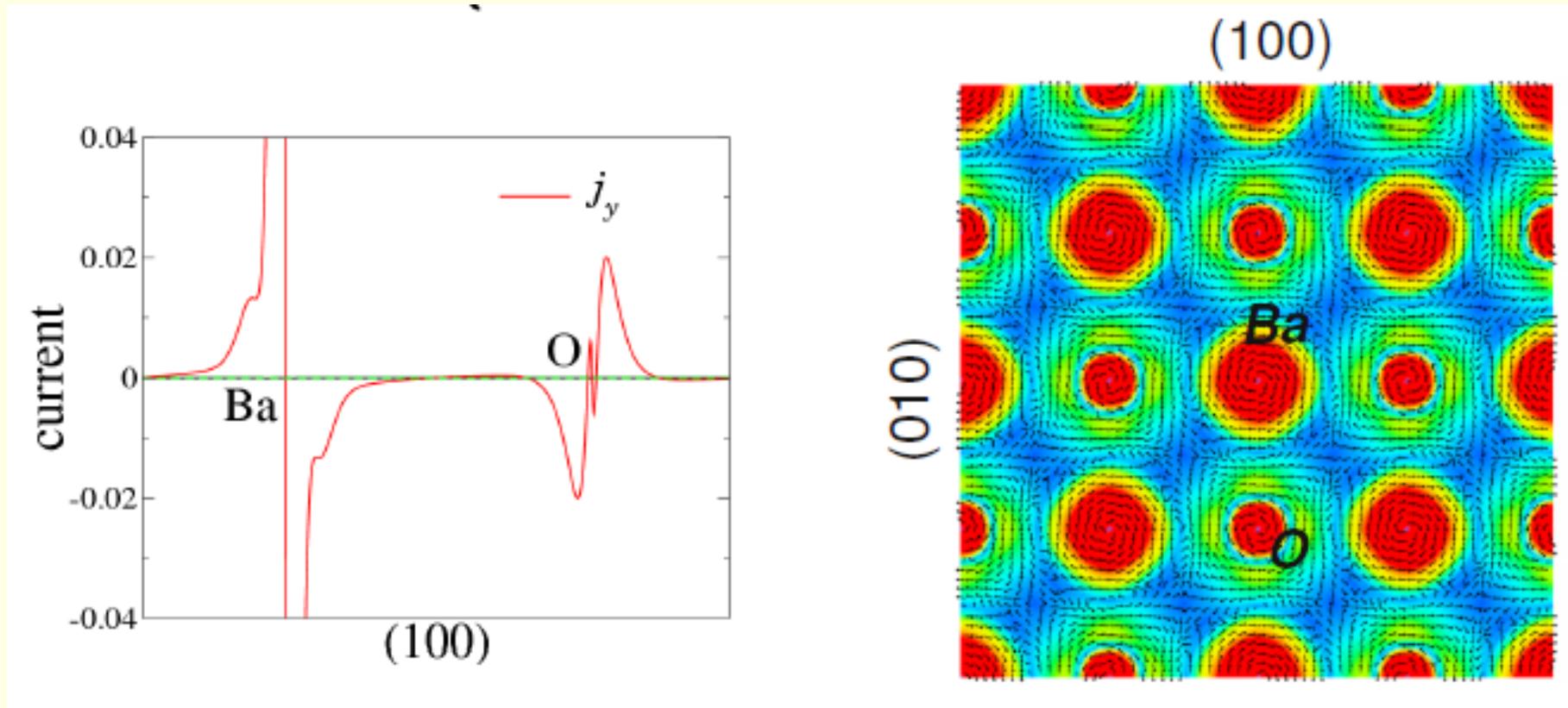
$$\mathbf{j}_{ind}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \mathbf{j}_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \mathbf{j}_{l,m}^{\alpha}(r) Y_{l,m}(\hat{r}). & \mathbf{r} \in S_{\alpha} \end{cases}$$
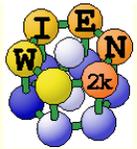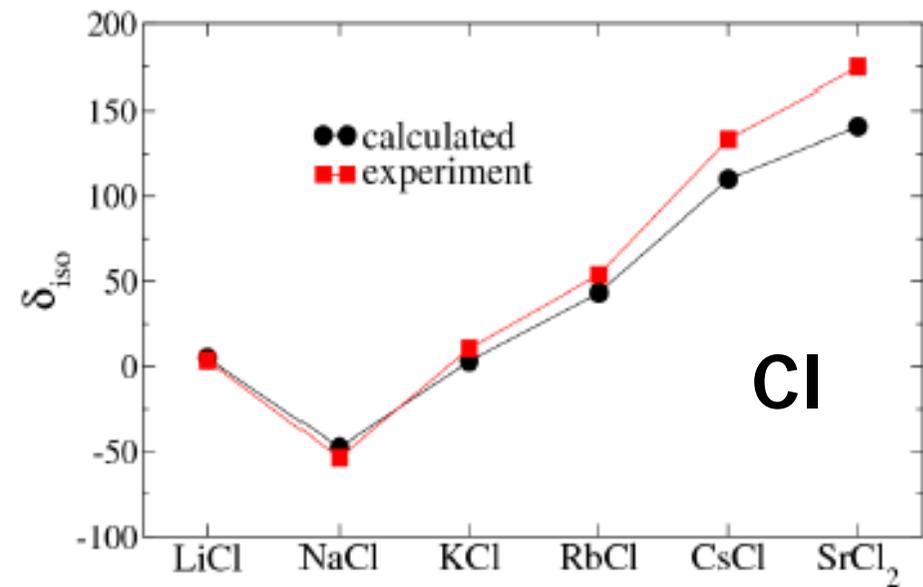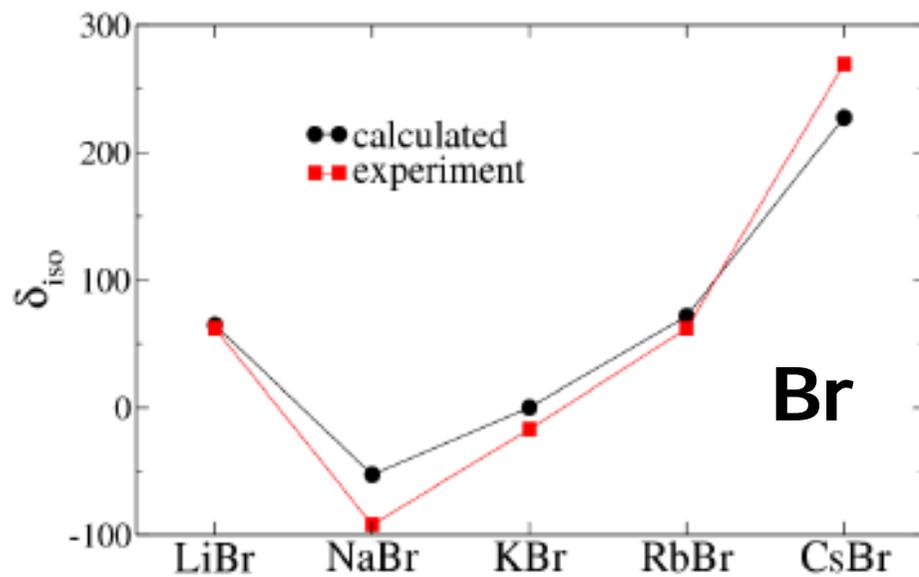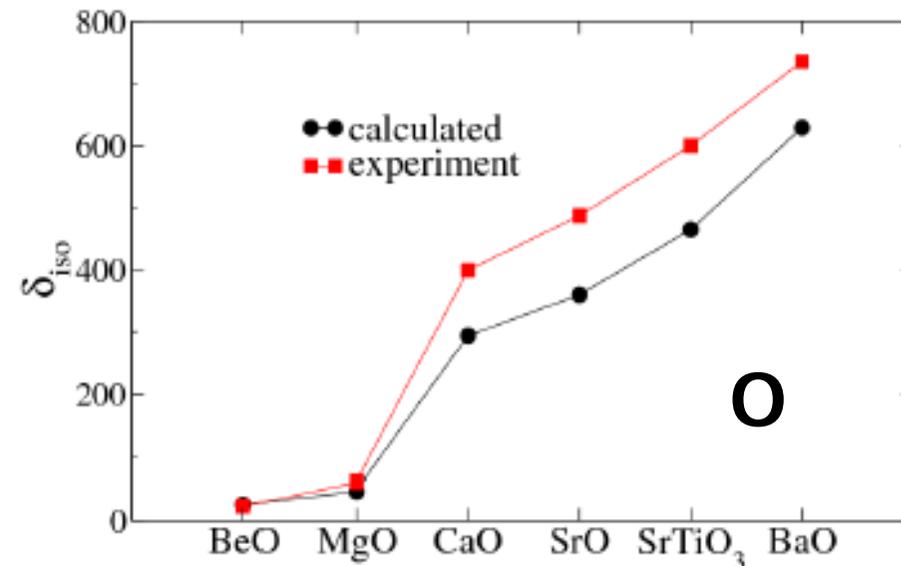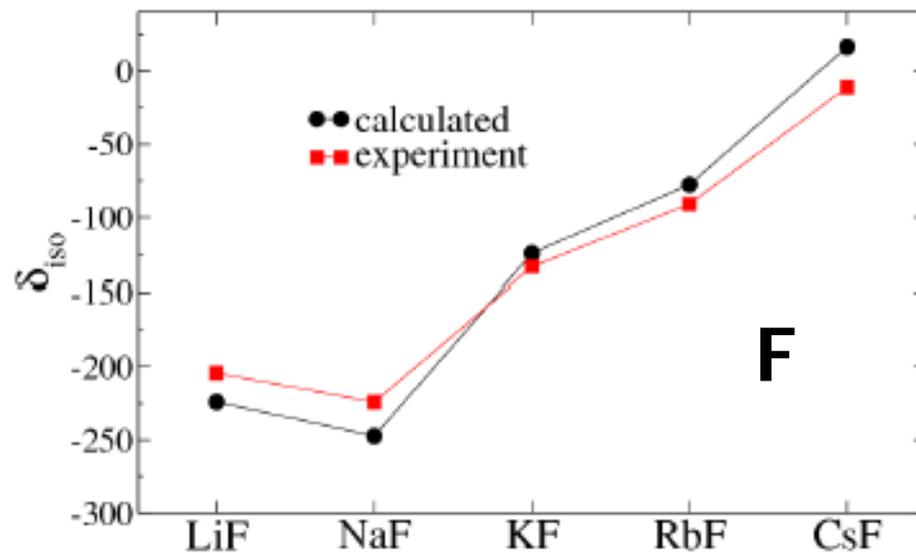
- band wise analysis

- character analysis (s,p,d) of the wave function of occupied and unoccupied states

DOS of alkali fluorides (CsF)
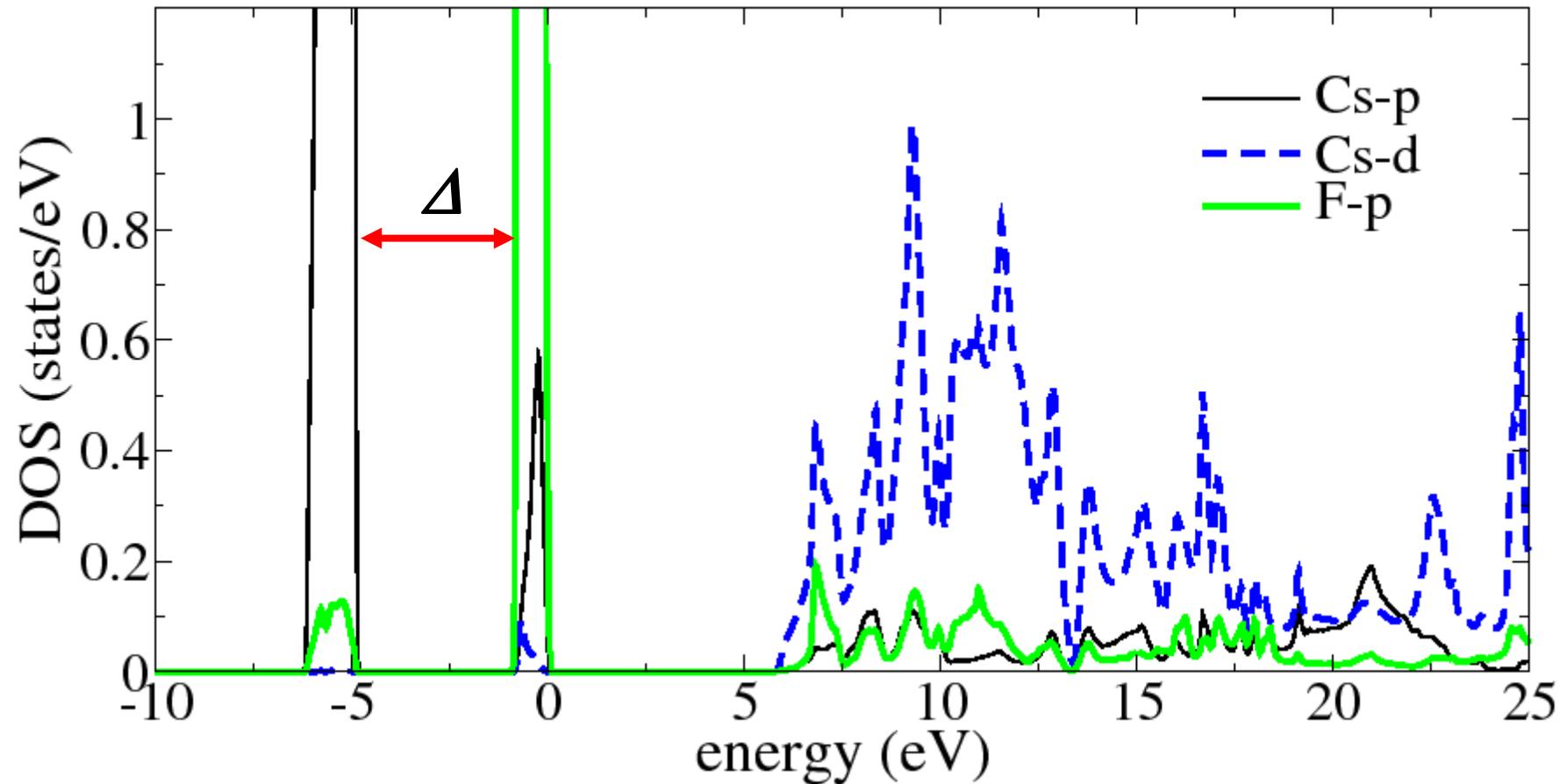
Δ varies between 5 eV for CsF to 20 eV for NaF
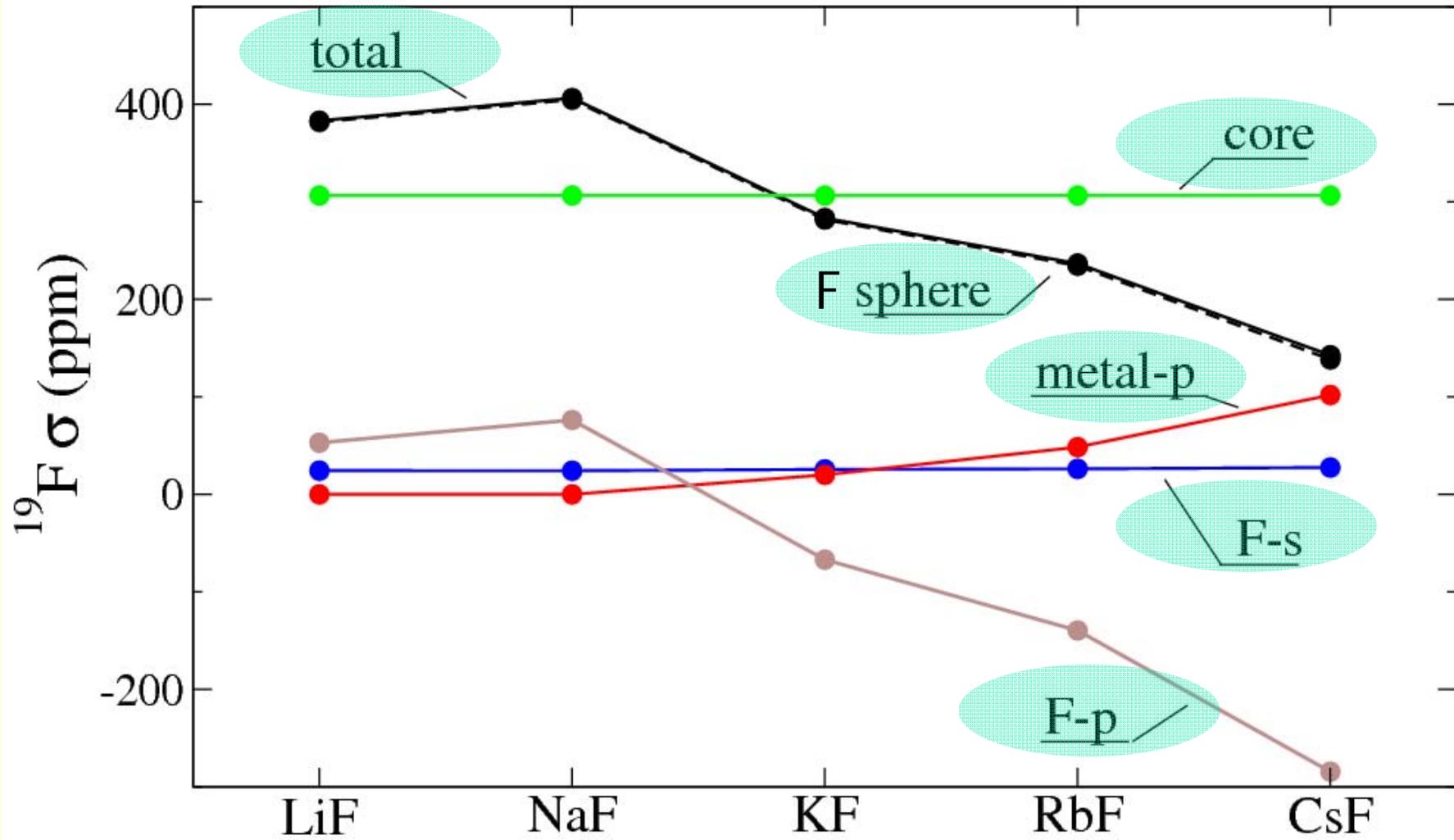
Decomposition of NMR shift

- decomposition of NMR shift according to s, p, d - character
  and   atom

$$\Psi_o = \Sigma_{at}\ \Sigma_{lm}\ R_{at,lm}\ Y_{lm}$$

- decomposition according to ground state $\Psi_o^{(0)}$
  and perturbed states $\Psi_o^{(1)}$

$$j_{ind}(r') = \frac{1}{c}\sum_o \Re\left[\langle \Psi_o^{(0)}|J^p(r')\,G(\varepsilon_o)(r-r')\times p\cdot B|\Psi_o^{(0)}\rangle\right]$$

$\Psi_o^{(1)}$

$$j_{ind}(r') = \frac{1}{c} \sum_o \Re \left[\langle \Psi_o^{(0)} | J^p(r') | \Psi_o^{(1)} \rangle \right]$$

$\Psi_o^{(0)}|_{F, l=1}$

$\Psi_o^{(1)}|_{F, l=1}$

metal-p total
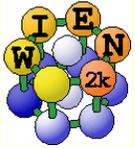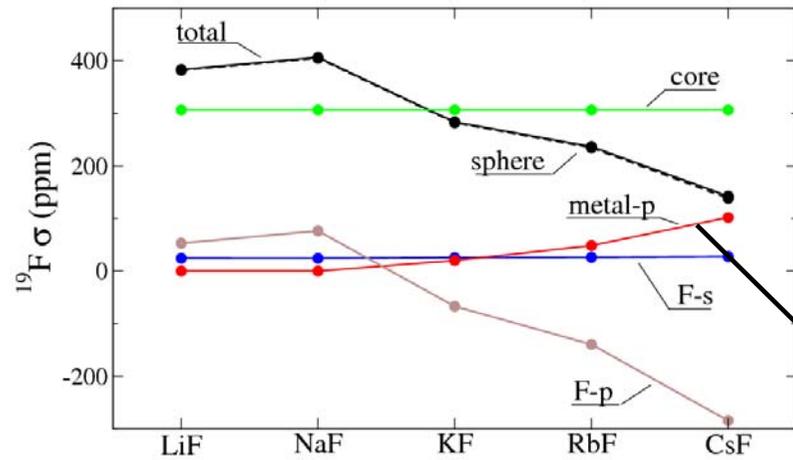
F-p band contribution

$$j_{ind}(r') = \frac{1}{c} \sum_o \Re \left[\langle \Psi_o^{(0)} | J^p(r') | \Psi_o^{(1)} \rangle \right]$$

$\Psi_o^{(1)}|_{F,\ l=2}$

$\Psi_o^{(0)}|_{F,\ l=1}$
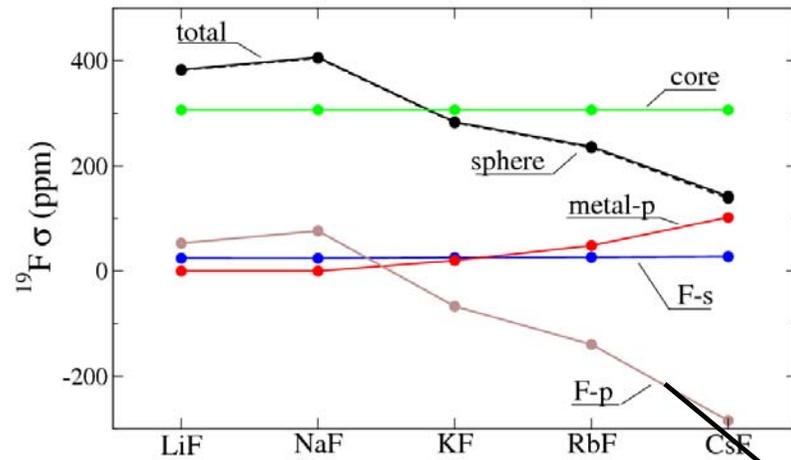
$\Psi_o^{(1)}|_{F,\ l=1}$
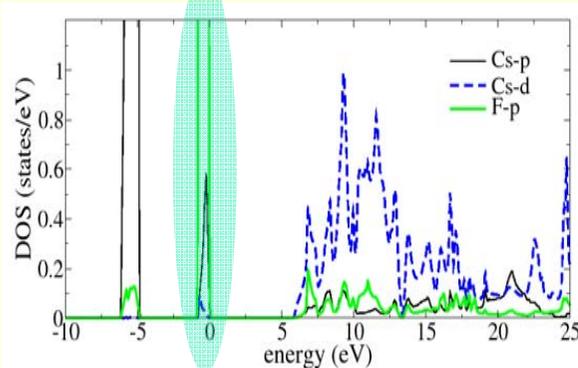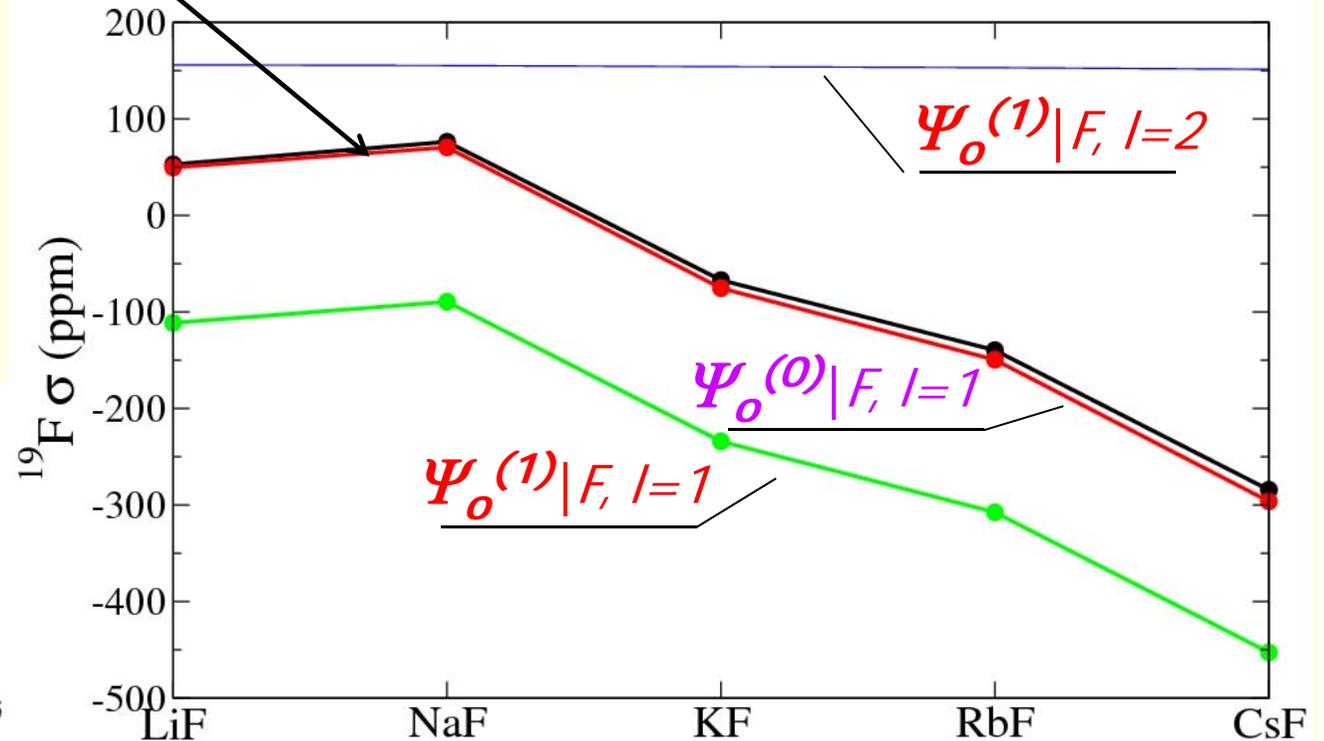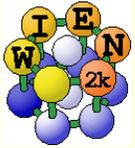
metal p band
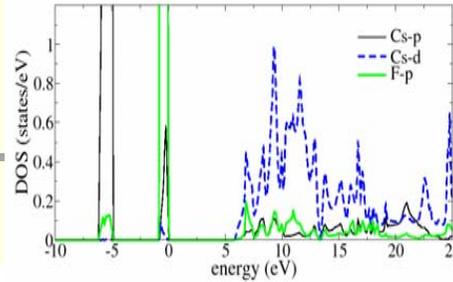
F-p band
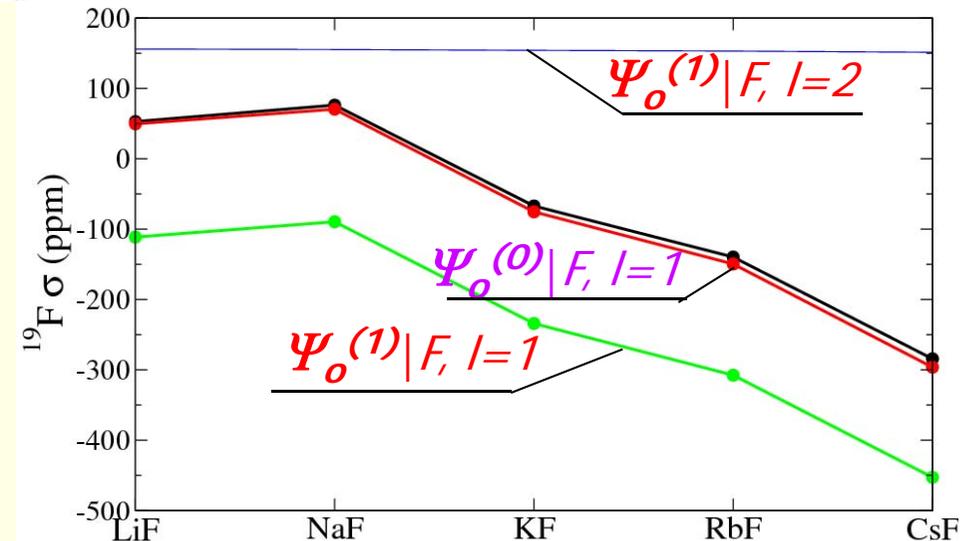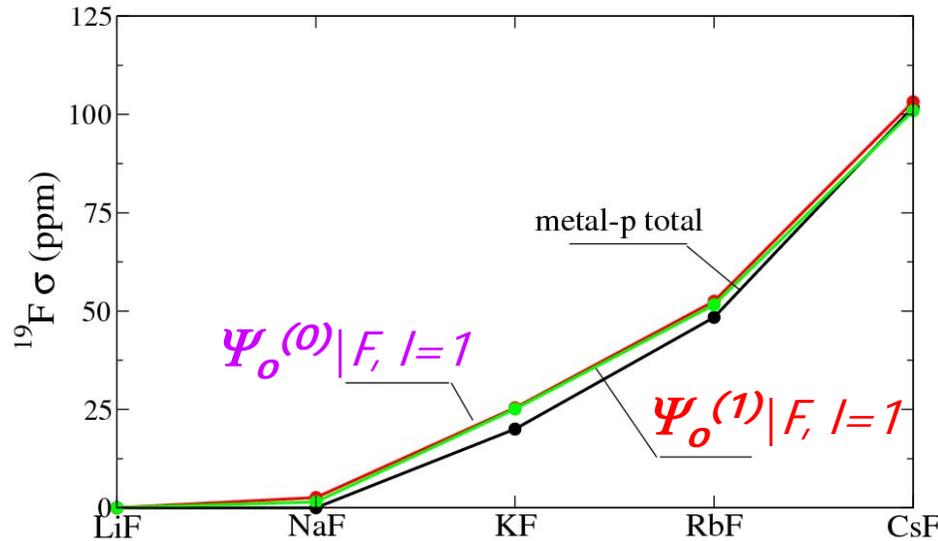
the only important ground state contribution

$\Psi_o^{(0)}|F, l=1$

the only important ground state contribution

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positive, increasing contribution within the series

$\Psi_o^{(1)}|F, l=1$

negative, decreasing contribution within the series

$\Psi_o^{(1)}|F, l=2$

constant contribution within the series

Re[Ψ] at X-point of **CsF**
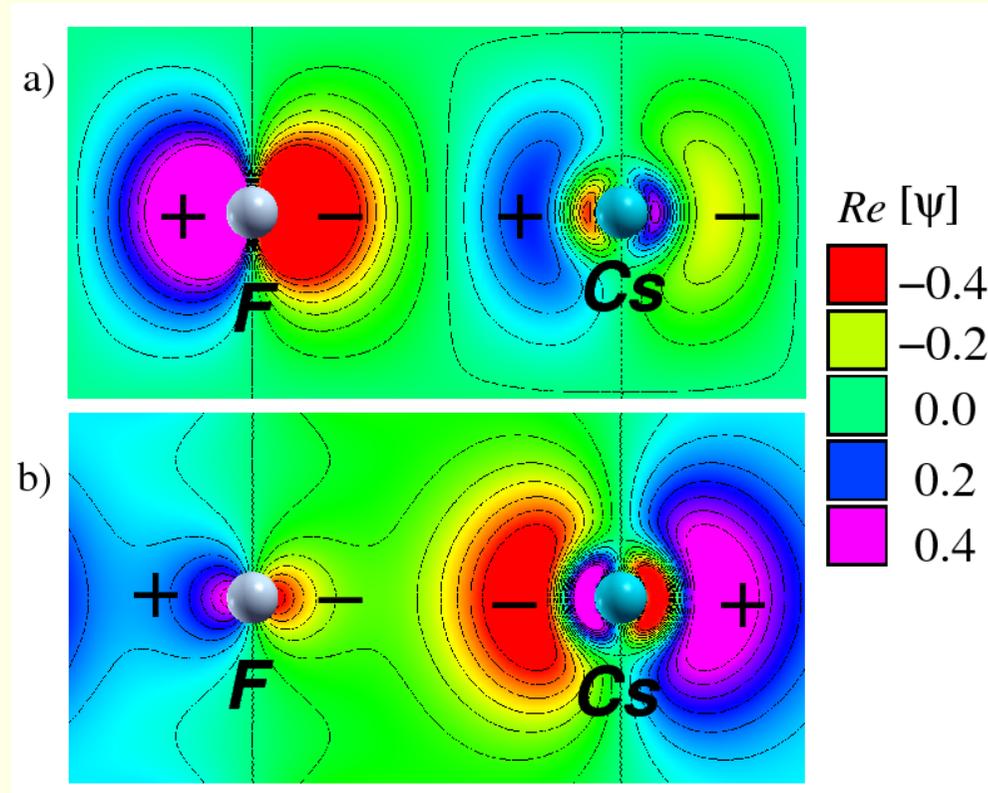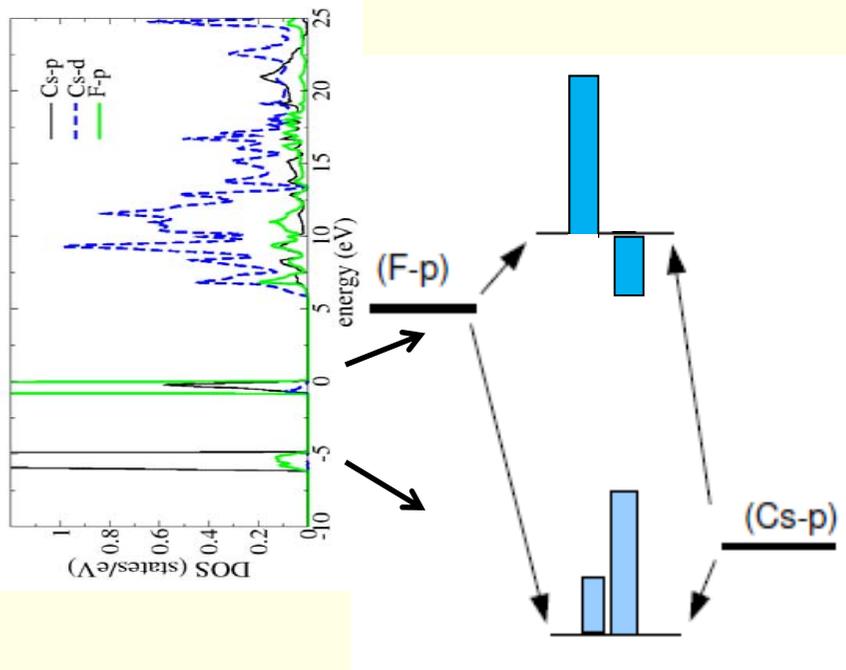

a)   F-p band, **anti-bonding** character of the Cs-p and F-p orbitals,
     negative contribution to the shielding
b)   Cs-p band, **bonding** character between Cs-p and F-p orbitals,
   **positive** contribution to the shielding.
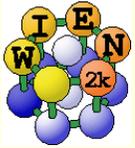
metal-p band contribution
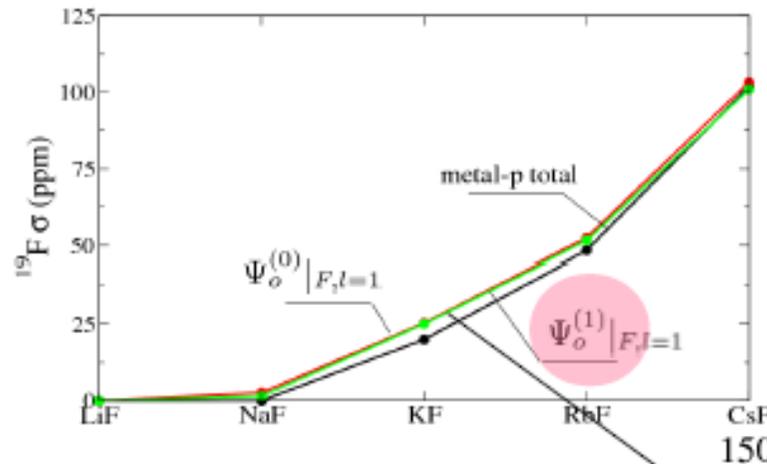
$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle \Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon - \epsilon_e}$$
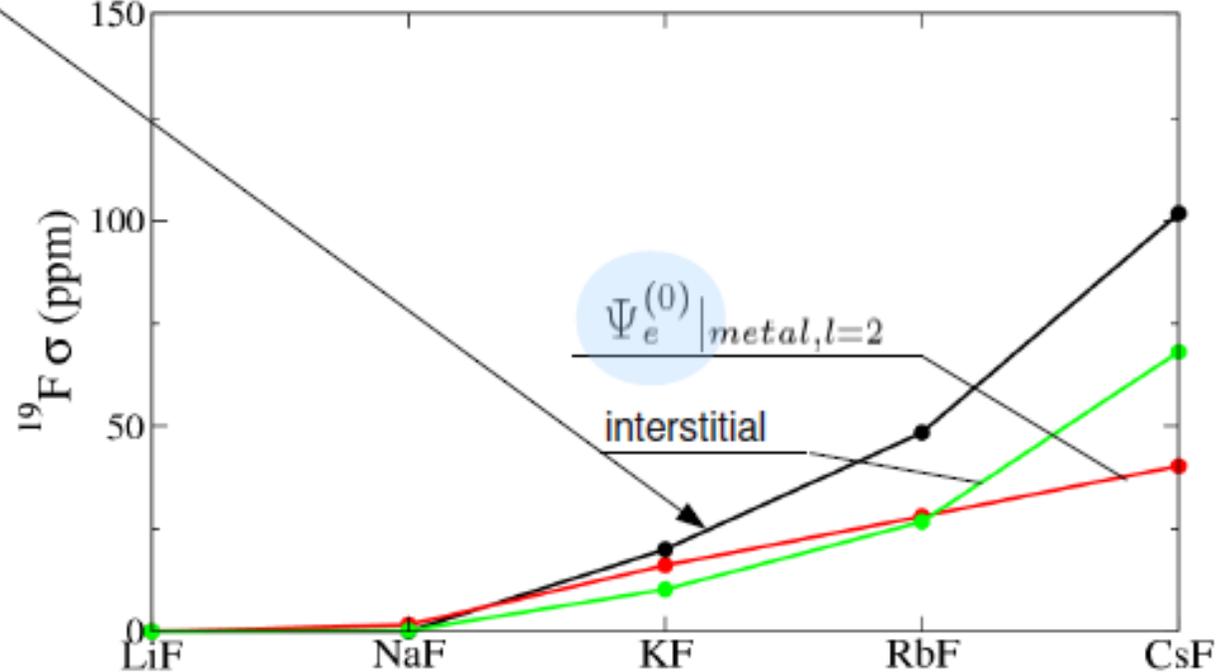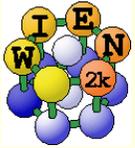
# Interactions relevant for NMR chemical shifts in alkali fluorides
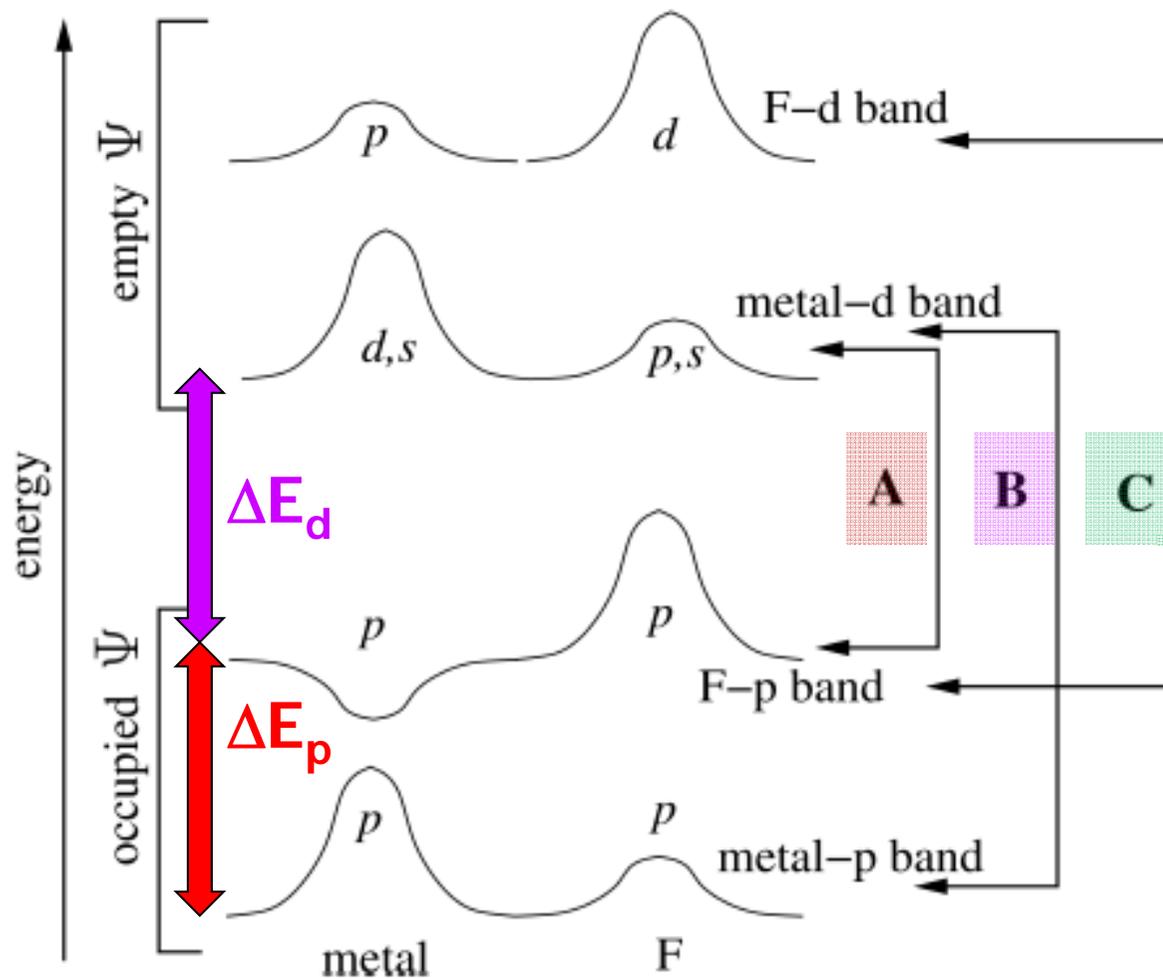
A, contributes to $\Psi_o^{(1)}\big|_{F,l=1}$ component, negative contribution to the shielding.

B, contributes to $\Psi_o^{(1)}\big|_{F,l=1}$ component, positive contribution to the shielding.

C, contributes to $\Psi_o^{(1)}\big|_{F,l=2}$ constant contribution to the shielding.
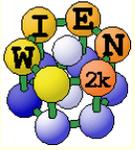
A, B interactions:

coupling to the metal-d states, due to F-p – metal-p hybridization

d-band position
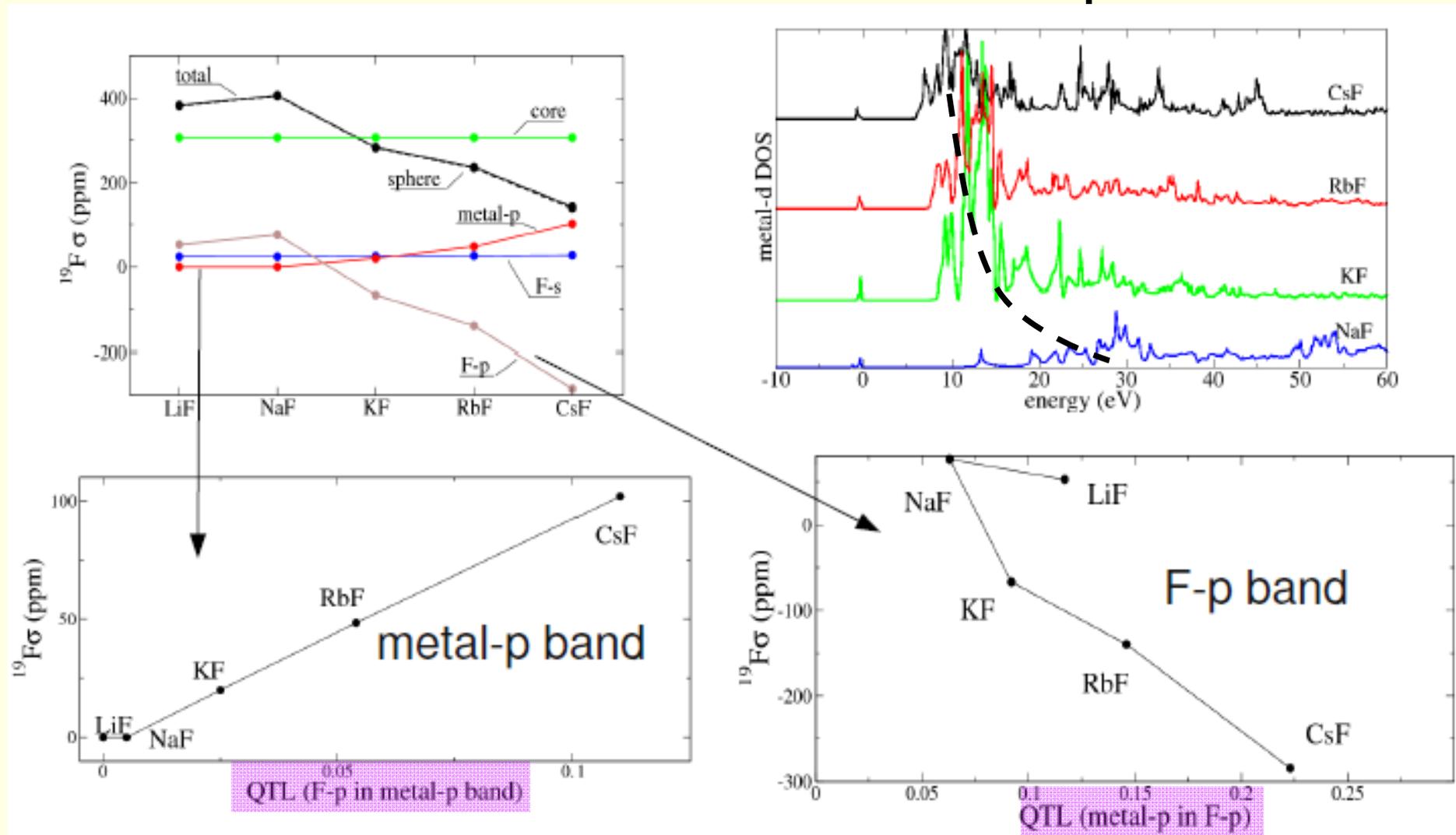
Effect of bond distance on the shielding
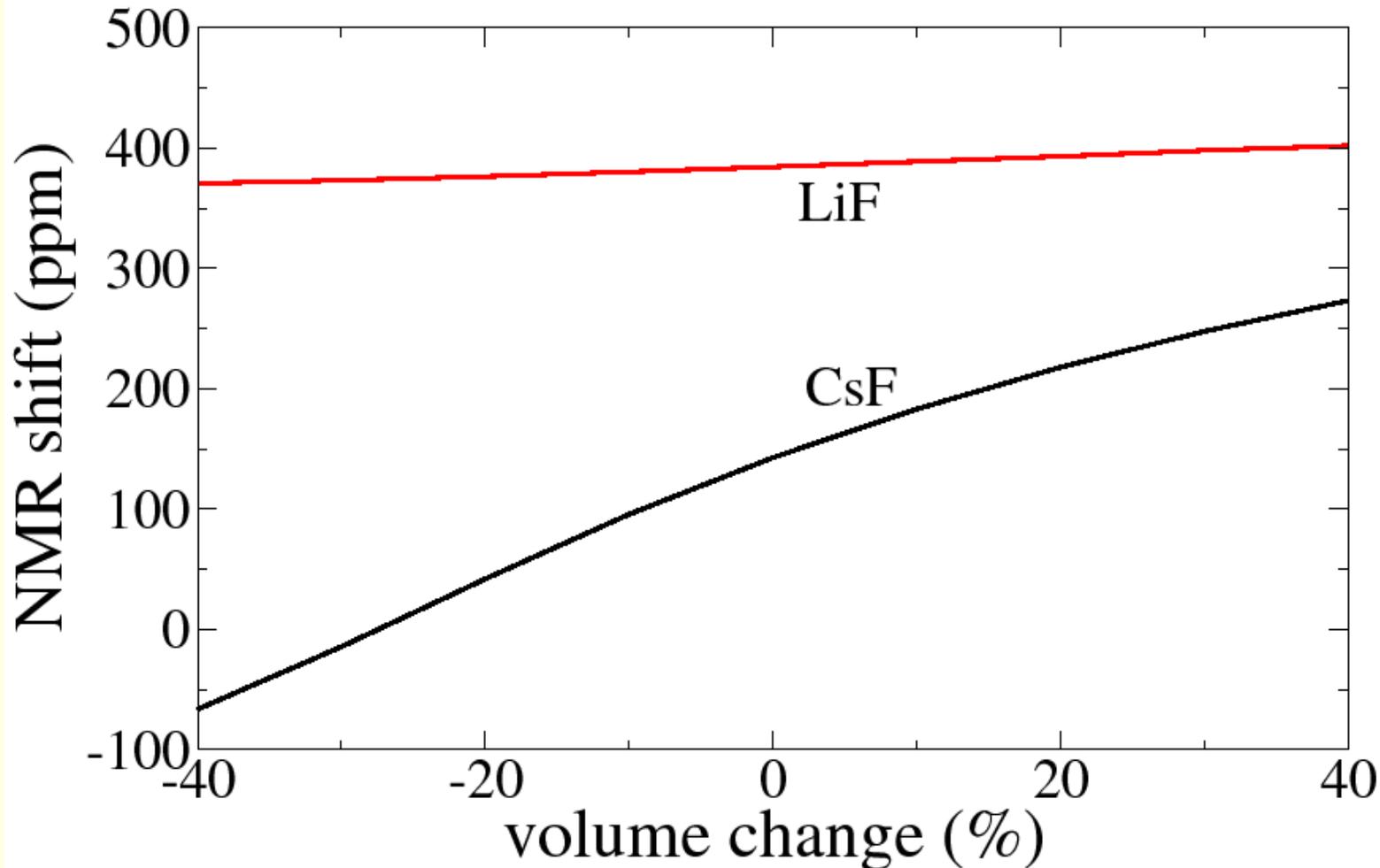
- decreasing volume leads to stronger Me-p F-p interaction and to more negative shielding (Li does not have "Li-p band")

- **LDA+U acting on Cs-d**

$$|\Psi_o^{(1)}\rangle = \sum_e |\Psi_e^{(0)}\rangle \frac{\langle\Psi_e^{(0)}|H^{(1)}|\Psi_o^{(0)}\rangle}{\epsilon - \epsilon_e}$$
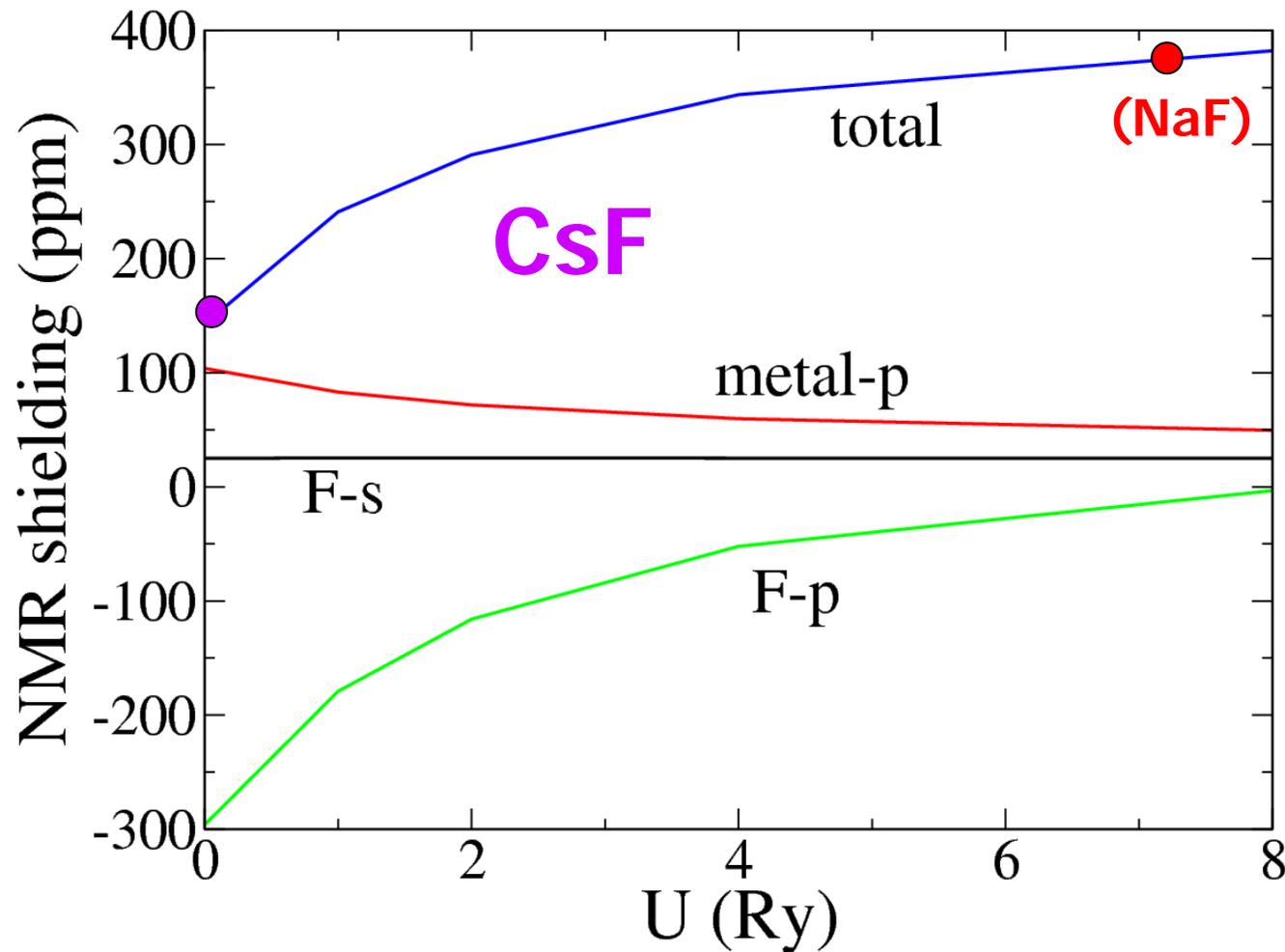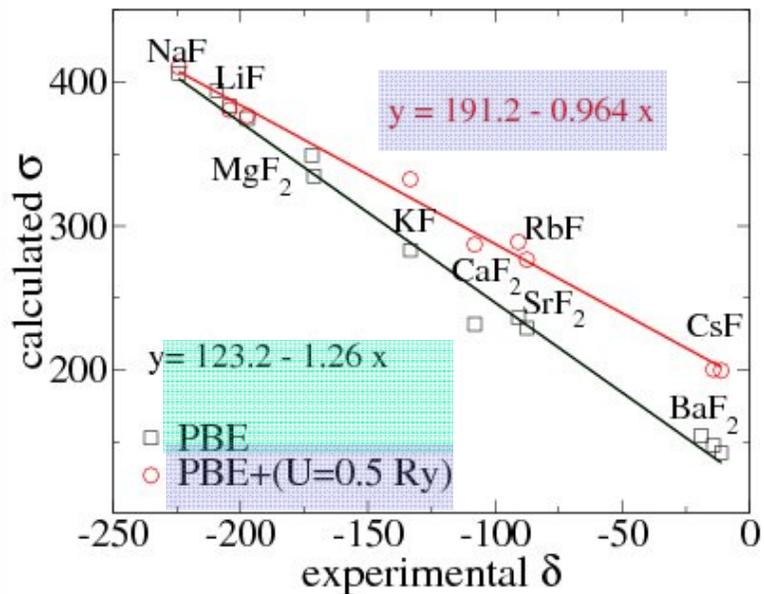
**exp.** δ **vs. theoretical** σ:
The slope must be **ONE**

PBE: slope is too **big**

PBE+U (metal d-states):
with **one** U value it is **not**
possible to fix **oxygen AND**
fluorine CS.
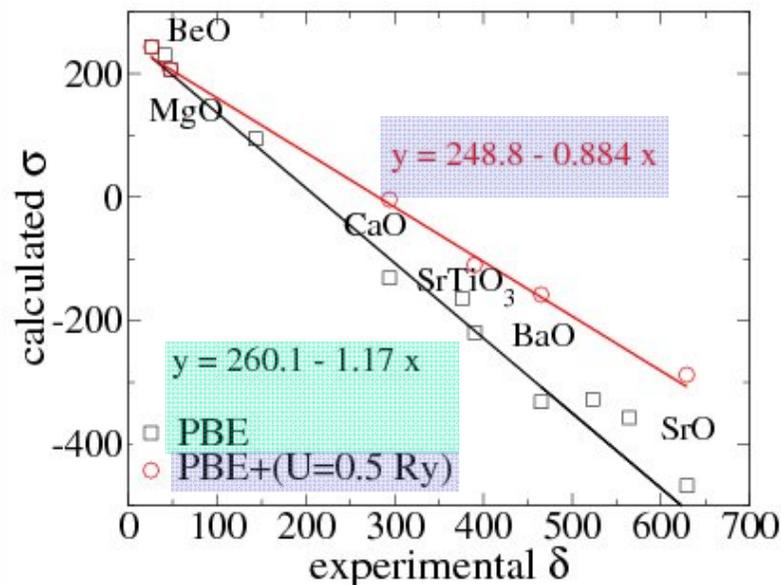
the slope - problem
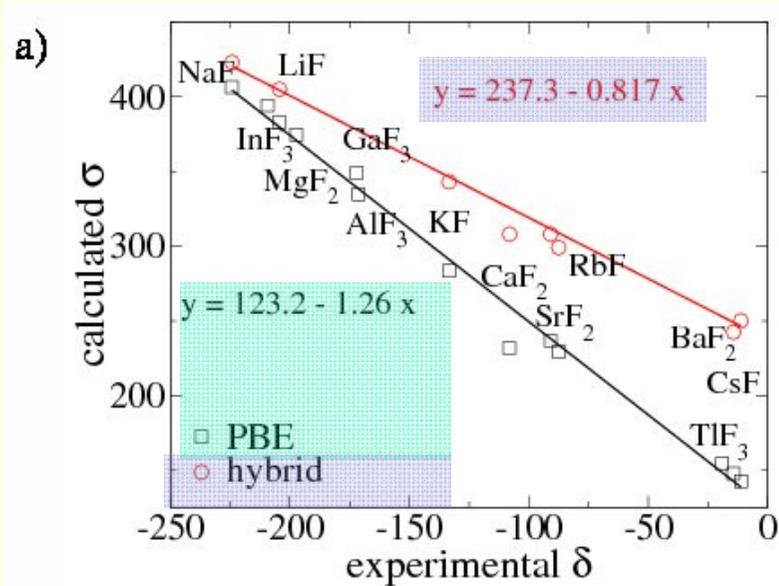
- **hybrid-DFT** is the standard method in CS calculations of **molecules** (Gaussian)

- for (ionic) **solids** YS-PBE0 (HSE) gives a much **too large** correction (smaller mixing ??)
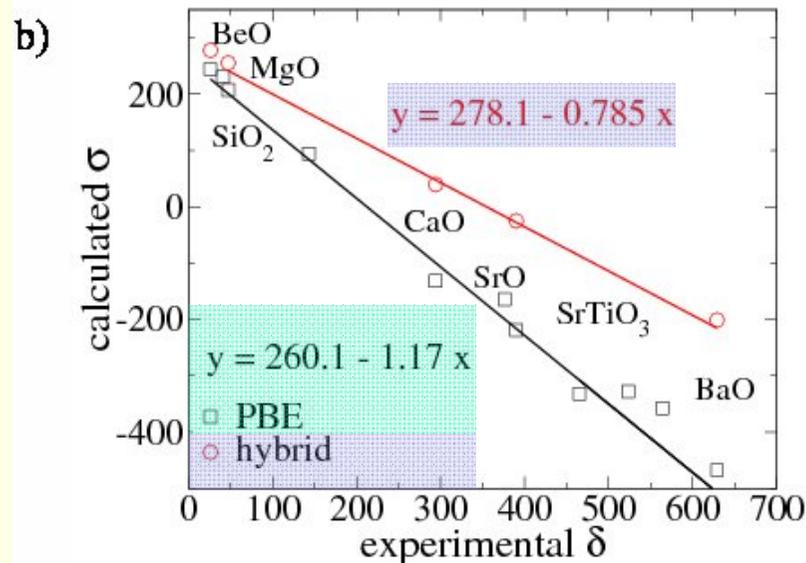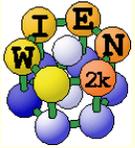
**BJ**-potential (OEP) seems quite reasonable for ionic compounds
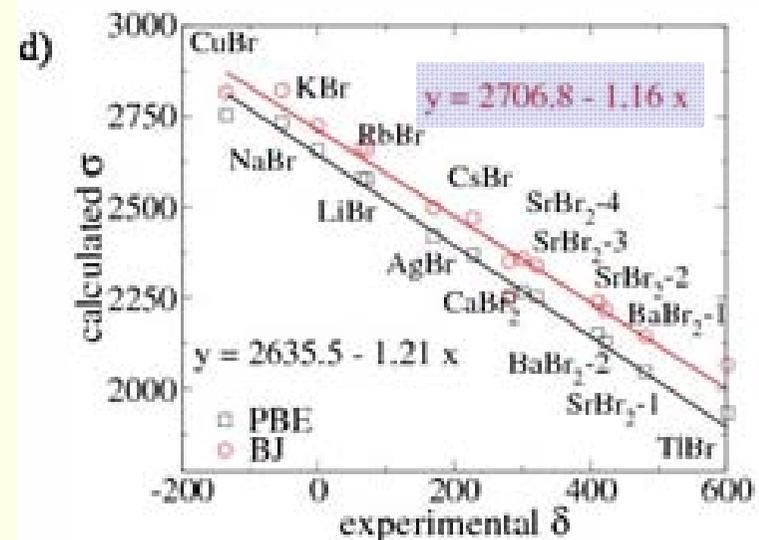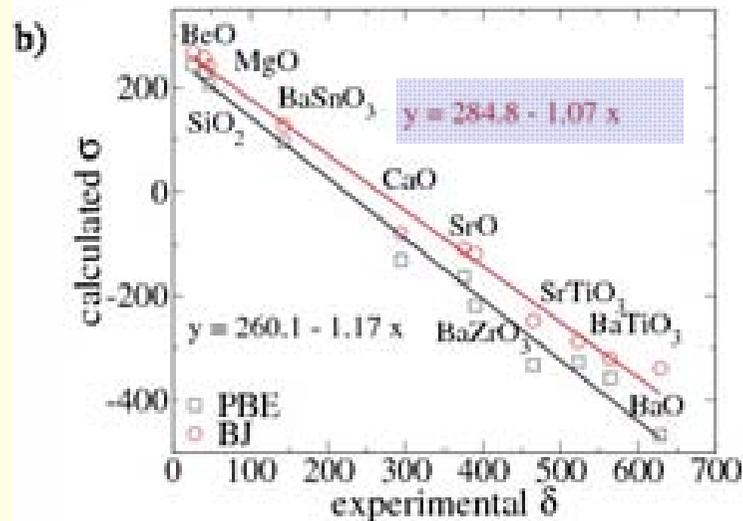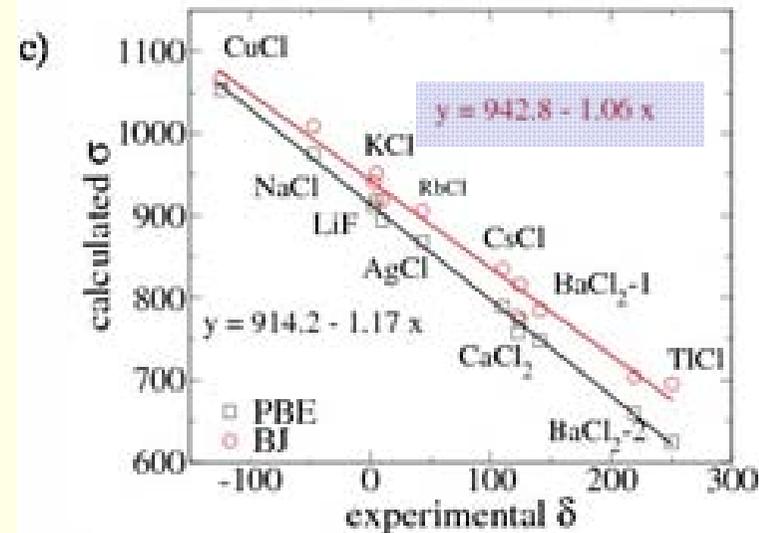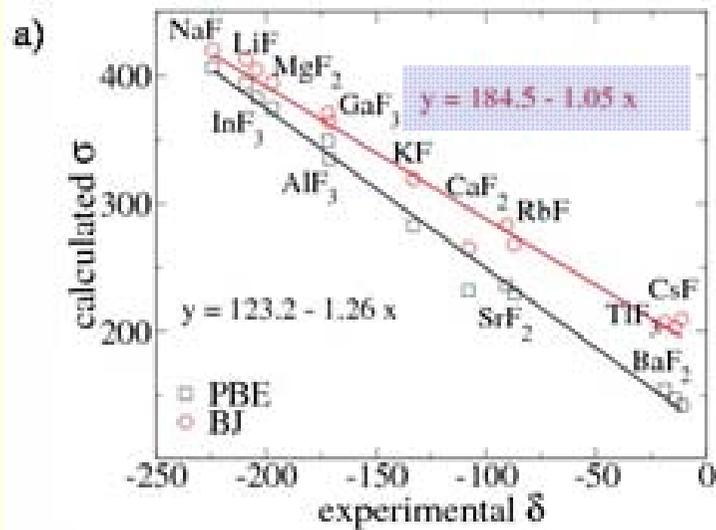
Summary:

NMR chemical shifts:

- shielding of anions in solids determined by:
  - *strength of metal-p -- F-p hybridization*
    - distance of metal-p band from anion-p band
    - bond distance, number of neighbors
  - *position of empty metal-d states*
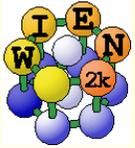
Robert Laskowski (TU Vienna)

Thank you for your attention !