NMR and EPR spectroscopies with Quantum-Espresso

Davide Ceresoli – CNR-ISTM – Milan, Italy
davide.ceresoli@cnr.it

istm
istituto di scienze e
tecnologie molecolari

Outline

- **PART I:**
  - Basic principles of magnetic resonance spectroscopy
  - Introduction to experimental NMR
  - Interpretation of NMR spectra
  - Solid state NMR
- **PART II:**
  - Effective NMR spin hamiltonian
  - The GIPAW method
  - Examples
  - Brief introduction to EPR spectroscopy and EPR parameters

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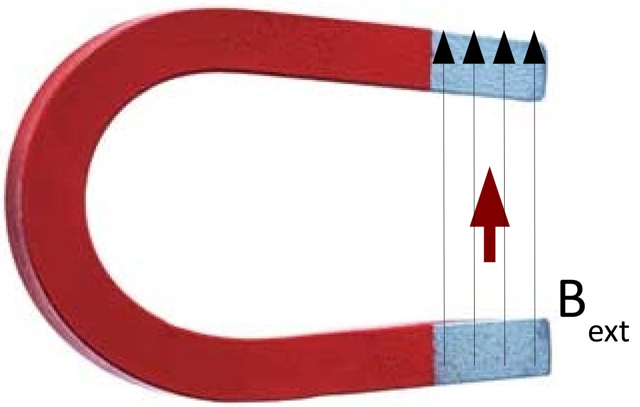
Principles of magnetic resonance

NMR = Nuclear Magnetic Resonance
EPR = Electron Paramagnetic Resonance (also ESR)



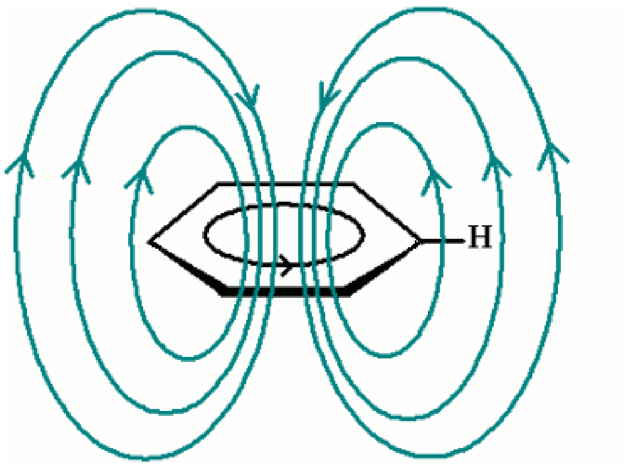
A spin (nuclear or electron),
in a magnetic field

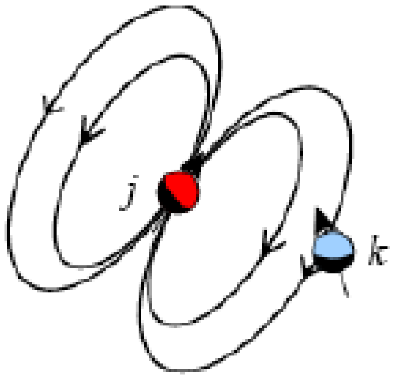
$$B_{\text{tot}} = B_{\text{ext}} + B_{\text{ind}} + B_{\text{other}}$$

External field

Induced field

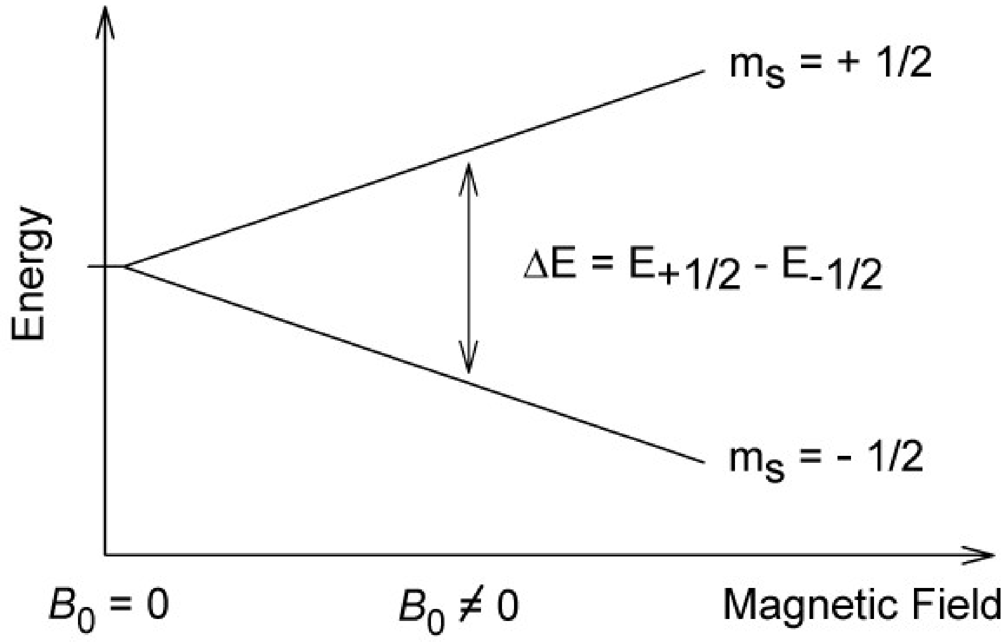
From other spins





Principles of magnetic resonance

A spin in a magnetic field will align parallel or antiparallel to the field.
The Zeeman splitting is proportional to the total magnetic field.



$$\underset{\substack{\uparrow \\ \text{Zeeman} \\ \text{splitting}}}{\Delta E} = \hbar \underset{\substack{\nwarrow \\ \text{Gyromagnetic} \\ \text{ratio}}}{\gamma} B_{\text{tot}} \Delta m_s$$

The energy splitting can be probed by an electromagnetic wave of frequency ω:

$$\Delta E = \hbar \omega$$

Some useful relations

For a nucleus

$$\gamma = \frac{Q}{2M} g = \frac{g \mu_N}{\hbar}$$

γ = gyromagnetic ratio
q = charge
m = mass
g = g-factor
μ_N = nuclear magneton

For the electron

$$\gamma_e = \frac{e}{2m_e} g_e = \frac{g_e \mu_B}{\hbar}$$

μ_B = bohr magneton (>> nuclear magneton)

For example:

$g(^1H) = 5.585694 \rightarrow \gamma(^1H) = 2.67 \cdot 10^8$ Hz/T
$g(\text{elec.}) = -2.002319 \rightarrow \gamma(\text{elec.}) = 1760 \cdot 10^8$ Hz/T

Resonance frequency is proportional to γ: **^{1}H @ 9.306 T → 400 MHz**

NMR active nuclei

Atom	Isotope	Spin	Larmor frequency (MHZ at 9.306 T)	Abundance (%)	Absolute sensitivity	Quadrupole (barn)
Hydrogen	1H	1/2	-400.00	99.98	1.00E+000	0
Deuterium	2D	1	-61.40	0.02	1.45E-006	0.00273
Lithium	6Li	1	-58.86	7.42	6.31E-004	-0.0008
Lithium	7Li	3/2	-155.45	92.58	2.70E-001	-0.045
Boron	10B	3	-42.98	19.58	3.90E-003	0.074
Boron	11B	3/2	-128.34	80.42	1.30E-001	0.0355
Carbon	13C	1/2	-100.58	1.11	1.76E-004	0
Nitrogen	14N	1	-28.90	99.63	1.01E-003	0.016
Nitrogen	15N	1/2	40.53	0.37	3.85E-006	0
Oxygen	17O	5/2	54.23	0.04	1.08E-005	-0.026
Fluorine	19F	1/2	-376.31	100.00	8.30E-001	0
Sodium	23Na	3/2	-105.80	100.00	9.25E-002	0.12
Magnesium	25Mg	5/2	24.48	10.13	2.71E-004	0.22
Aluminum	27Al	5/2	-104.23	100.00	2.10E-001	0.149
Silicon	29Si	1/2	79.46	4.70	3.69E-004	0
Phosphorus	31P	1/2	-161.92	100.00	6.63E-002	0
Sulfur	33S	3/2	-30.68	0.76	1.72E-005	-0.055
Chlorine	35Cl	3/2	-39.19	75.53	3.55E-003	-0.08
Chlorine	37Cl	3/2	-32.62	24.47	6.63E-004	-0.0632
Potassium	39K	3/2	-18.67	93.10	4.73E-004	0.055
Potassium	41K	3/2	-10.24	6.88	5.78E-006	0.067
Calcium	43Ca	7/2	26.91	0.15	9.28E-006	-0.05

NMR history

1937	**Rabi** predicts and observes nuclear magnetic resonance
1946	**Bloch, Purcell** first nuclear magnetic resonance of bulk sample
1953	**Overhauser** NOE (nuclear Overhauser effect)
1966	**Ernst, Anderson** Fourier transform NMR
1975	**Jeener, Ernst** 2D NMR
1985	**Wüthrich** first solution structure of a small protein (BPTI) from NOE derived distance restraints
1987	3D NMR + 13C, 15N isotope labeling of recombinant proteins
1990	pulsed field gradients (artifact suppression)
1996	new *long range* structural parameters: residual dipolar couplings and cross-correlated relaxation

Nobel prizes

1944	*Physics*	Rabi
1952	*Physics*	Bloch, Purcell
1991	*Chemistry*	Ernst
2002	*Chemistry*	Wüthrich
2003	*Medicine*	Lauterbur, Mansfield

First ^{1}H NMR spectra of water

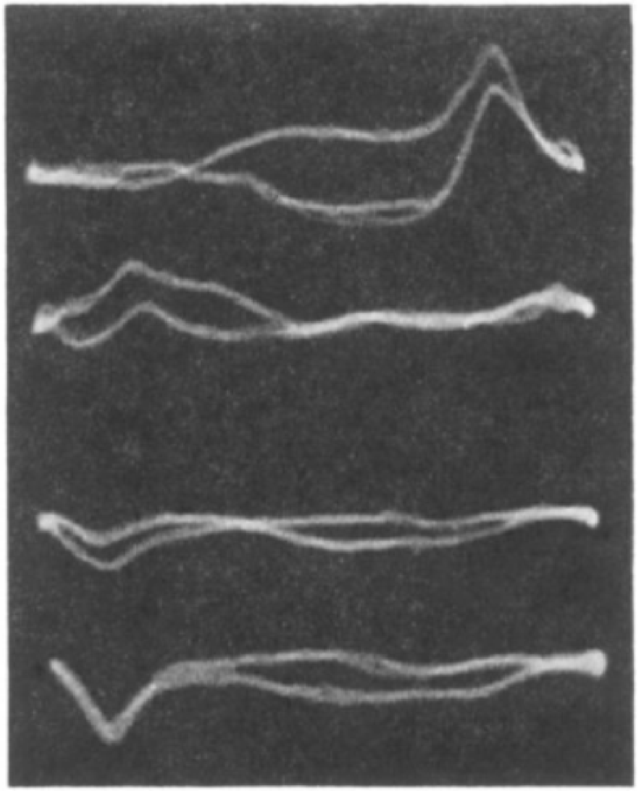
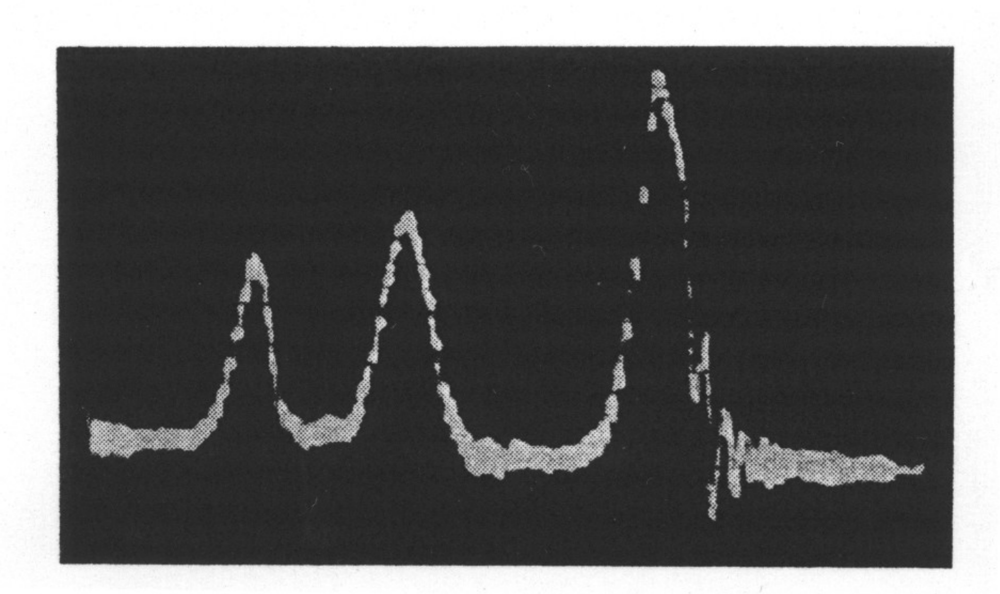


FIG. 10. Photographic record of the proton signal in water. The four traces from top to bottom correspond to the times t_1, t_2, t_3, t_4 of Fig. 9. In the text they are referred to as a, b, c, d, respectively.

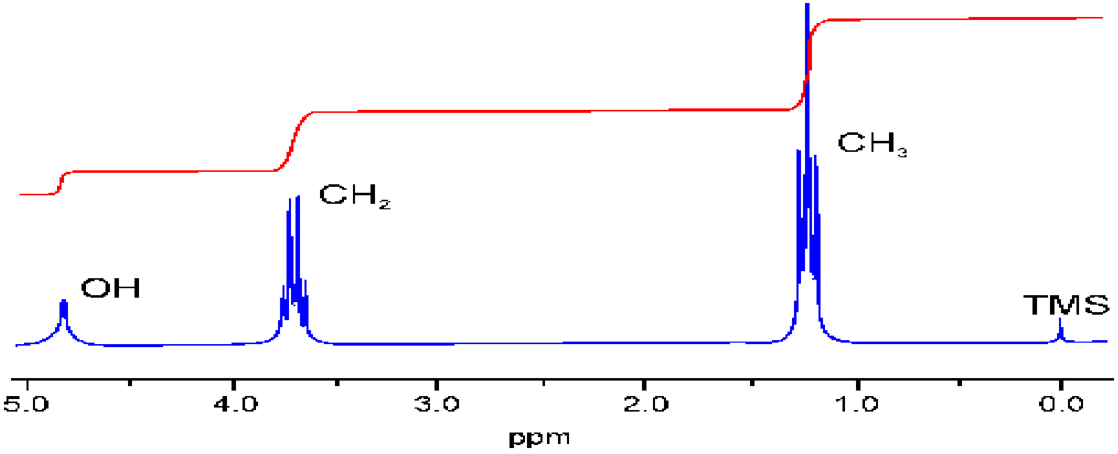
Bloch, Hansen and Packard, **The nuclear induction experiment**
Physical Review **70**, 474 (1946),

First observation of the chemical shift

^{1}H NMR spectra ethanol

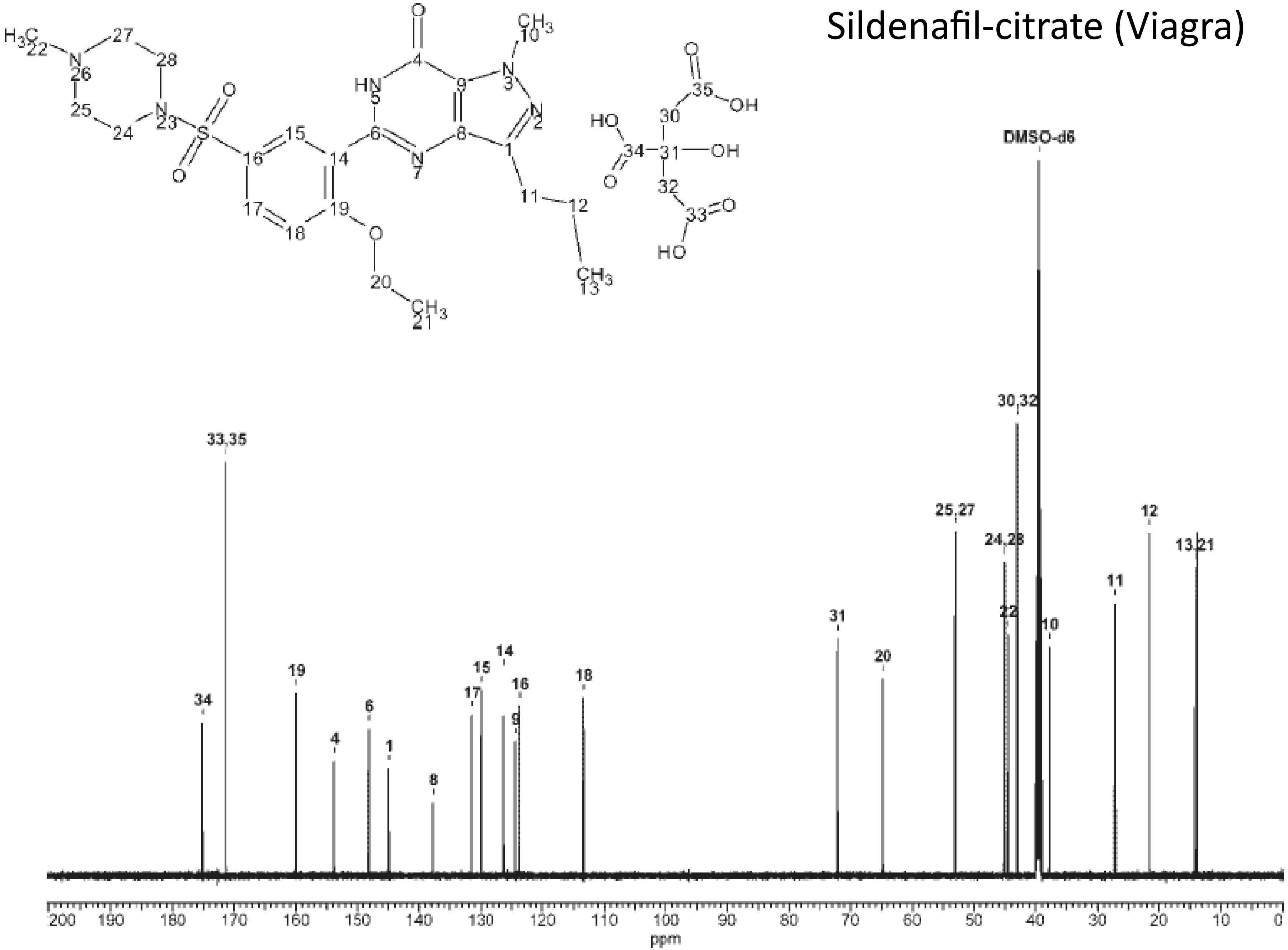


Modern ethanol spectra



Arnold, Dhamatti and Packard, J. Chem. Phys. **19,** 507 (1951)

Chemical shift as molecular fingerprint


Sildenafil-citrate (Viagra)

Typical applications of NMR

1) Structural (chemical) elucidation
- Natural product chemistry
- Synthetic organic chemistry
  - analytical tool of choice of synthetic chemists
  - used in conjunction with mass spectroscopy and IR

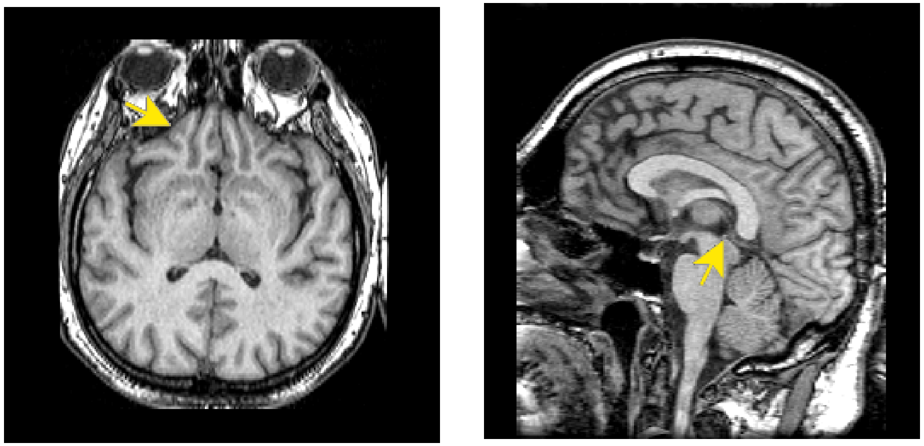
2) Study of dynamic processes
- reaction kinetics
- study of equilibrium (chemical or structural)

3) Structural (three-dimensional) studies
- Proteins, Protein-ligand complexes
- DNA, RNA, Protein/DNA complexes
- Polysaccharides

4) Drug Design

5) Medicine: MRI

MRI images of the Human Brain



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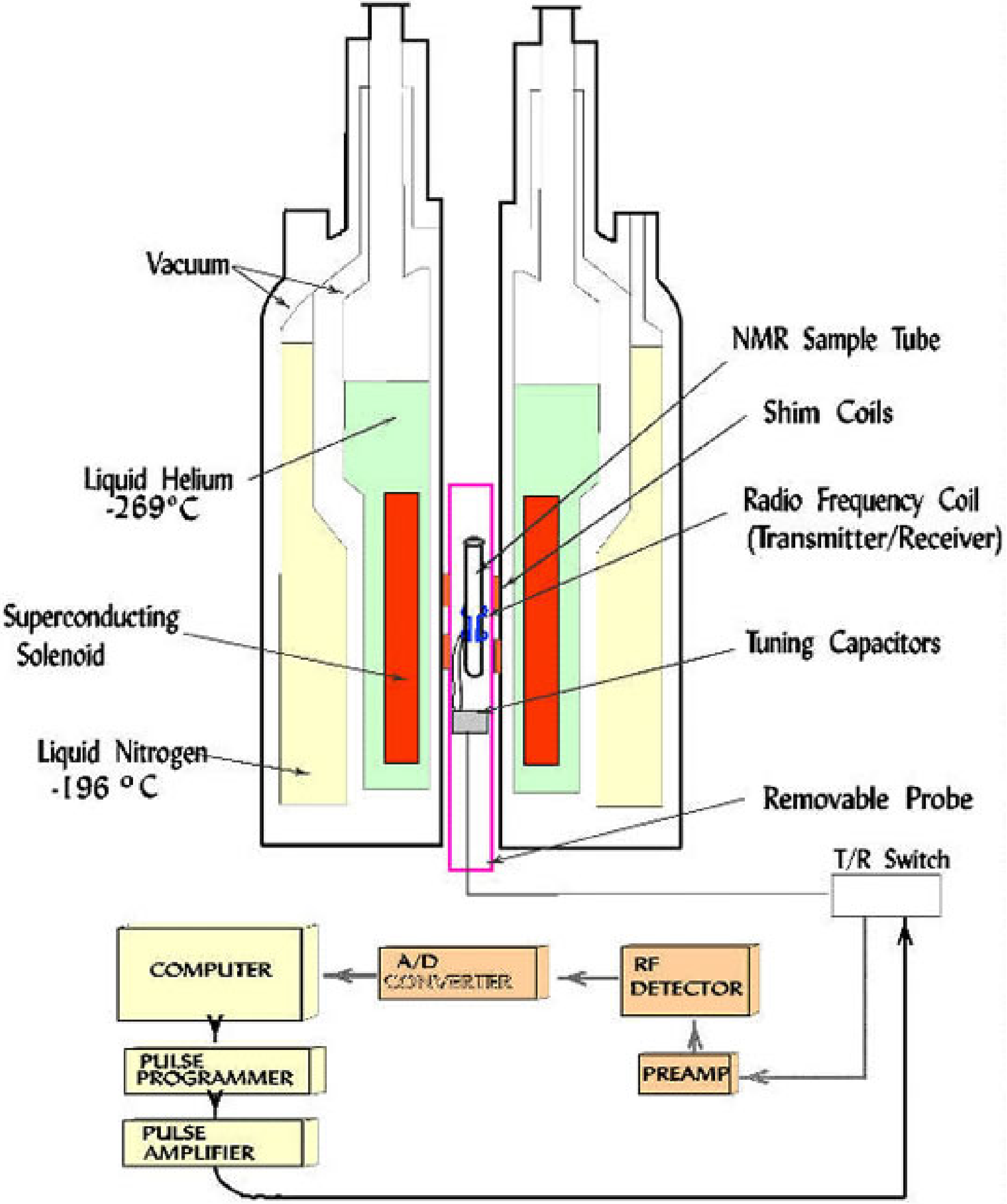
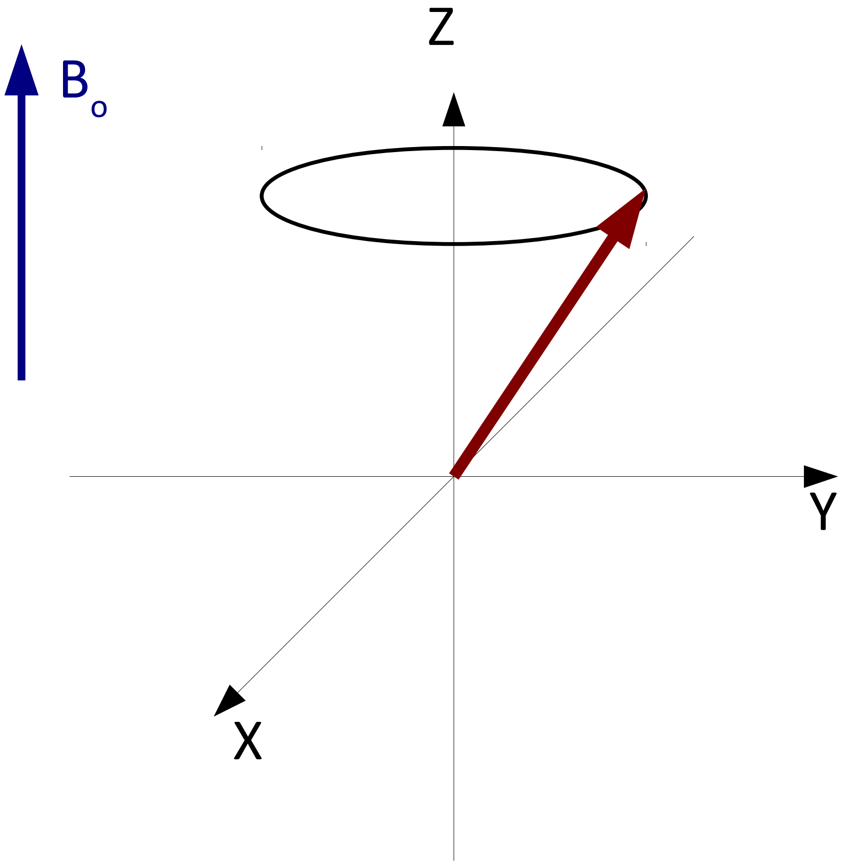
NMR spectrometer

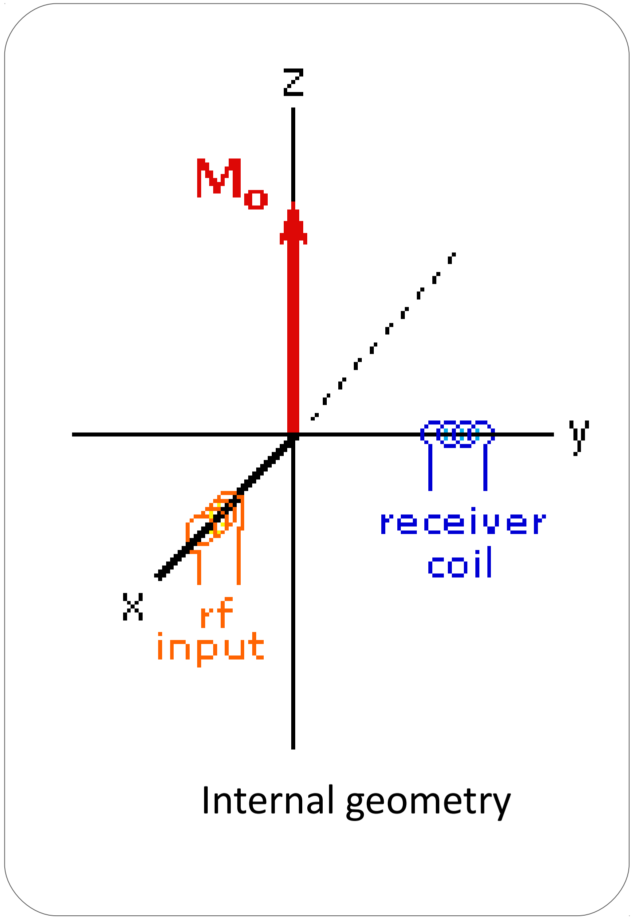
Typical fields	~14 T
Resonance	~600 MHz
Cost	~800 k$



Classical description of NMR

Spin in a magnetic field B_0 precesses forever around the magnetic field



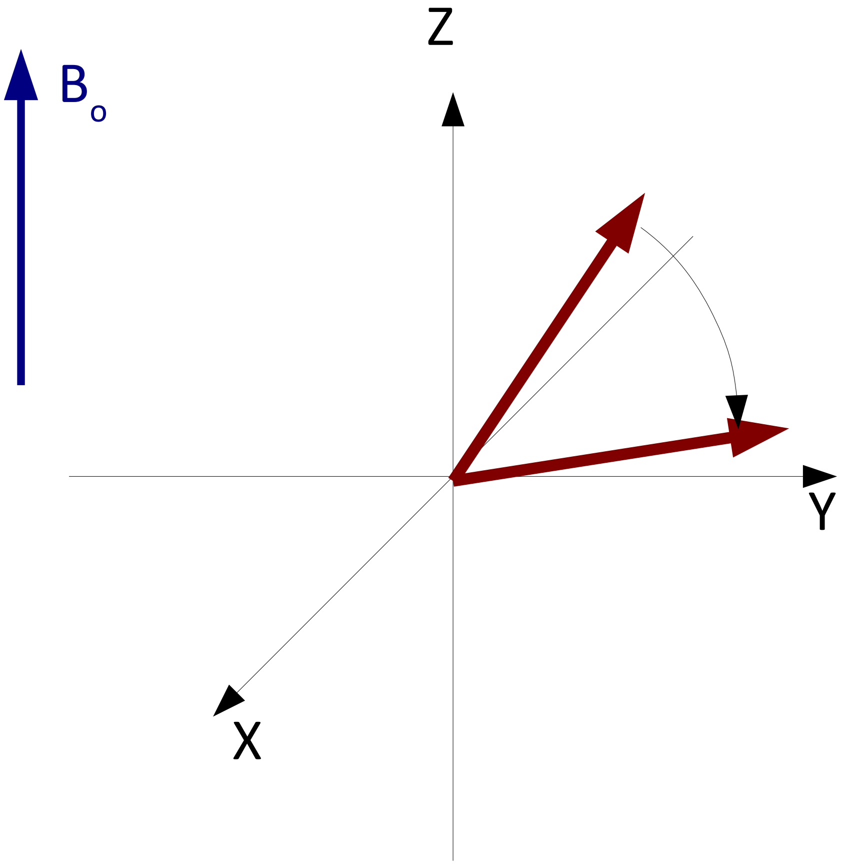


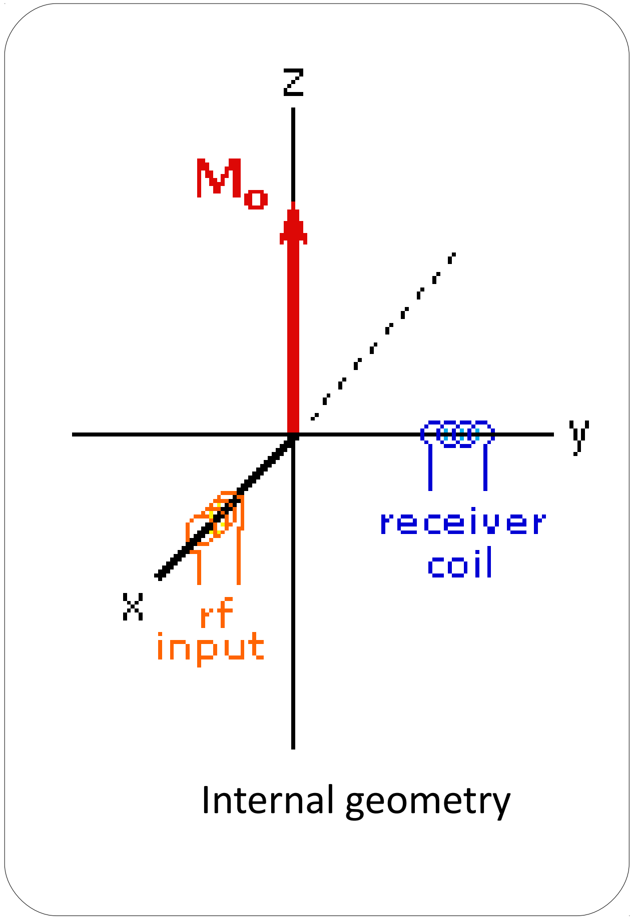
Internal geometry

On average, the magnetization lies only along the z-direction.
In order to observe NMR, we must perturb the system!

Classical description of NMR

We send a RF pulse to by 90° the precession axis ...



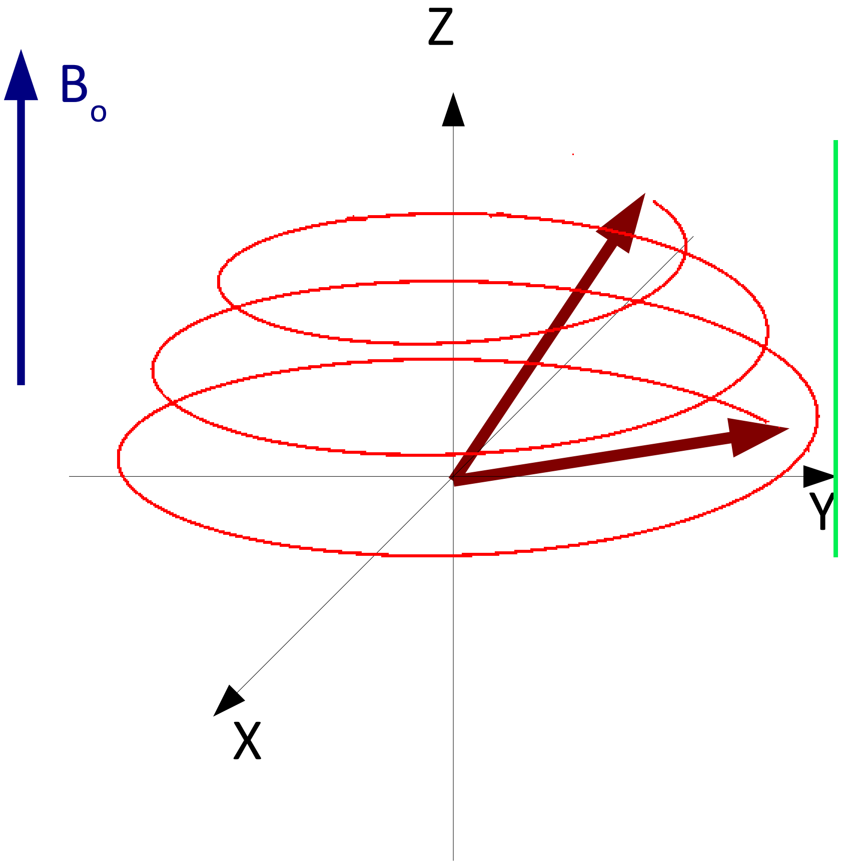


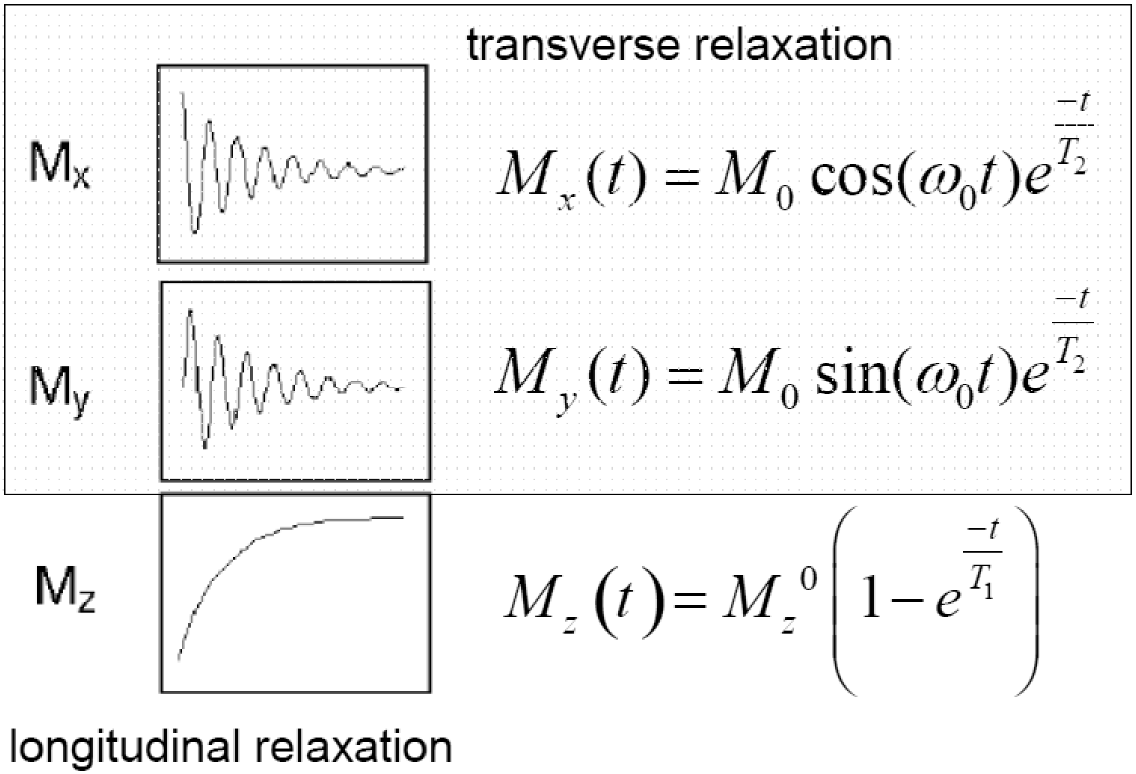
Internal geometry

... and we start recording the spin relaxing back to the initial state.

Classical description of NMR

… and we start recording the spin relaxing back to the initial state.





transverse relaxation

$$M_x(t) = M_0 \cos(\omega_0 t)e^{\frac{-t}{T_2}}$$

$$M_y(t) = M_0 \sin(\omega_0 t)e^{\frac{-t}{T_2}}$$

$$M_z(t) = M_z^0\left(1 - e^{\frac{-t}{T_1}}\right)$$

longitudinal relaxation

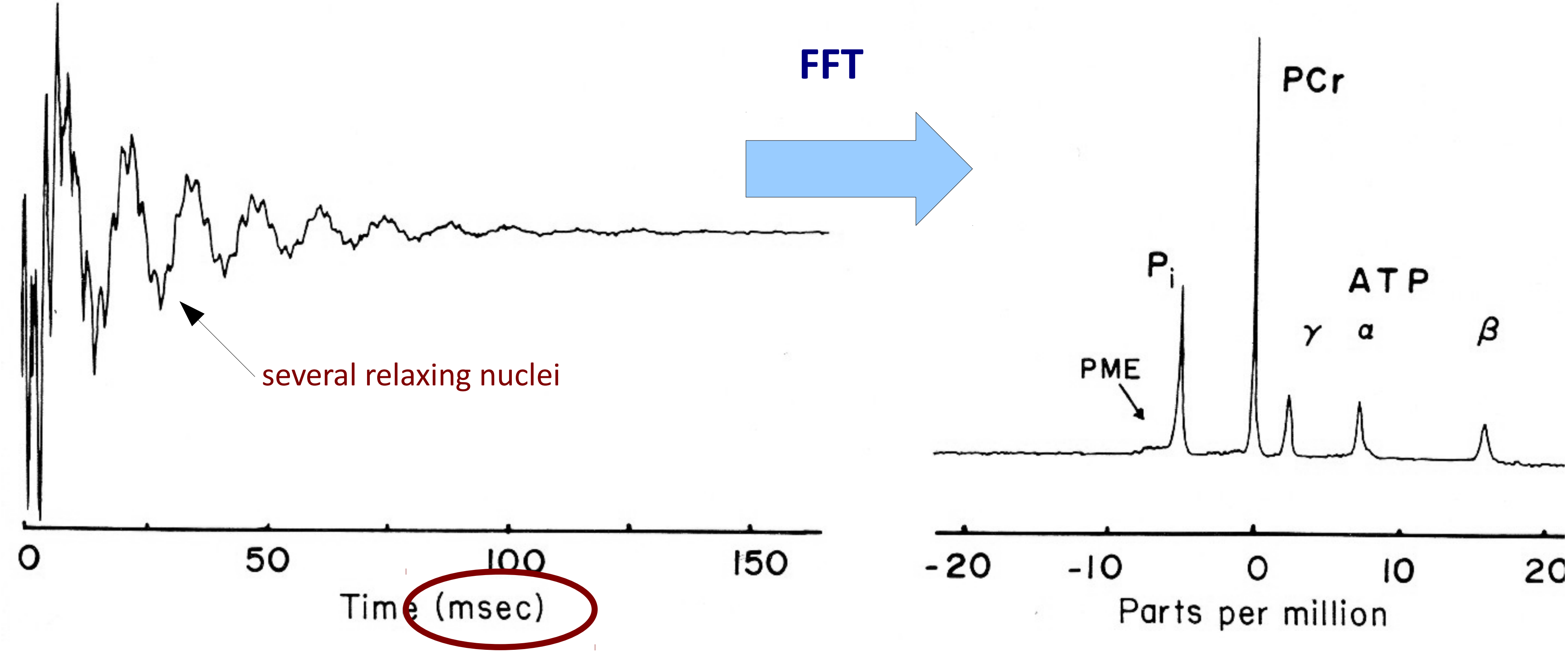
T_1 = longitudinal (spin-lattice) relaxation time

T_2 = transverse (spin-spin) relaxation time

Free Induction Decay

Signal recorded after the pulse is called Free Induction Decay (FID)

The Fourier transform of the FID yields the NMR spectrum.



several relaxing nuclei

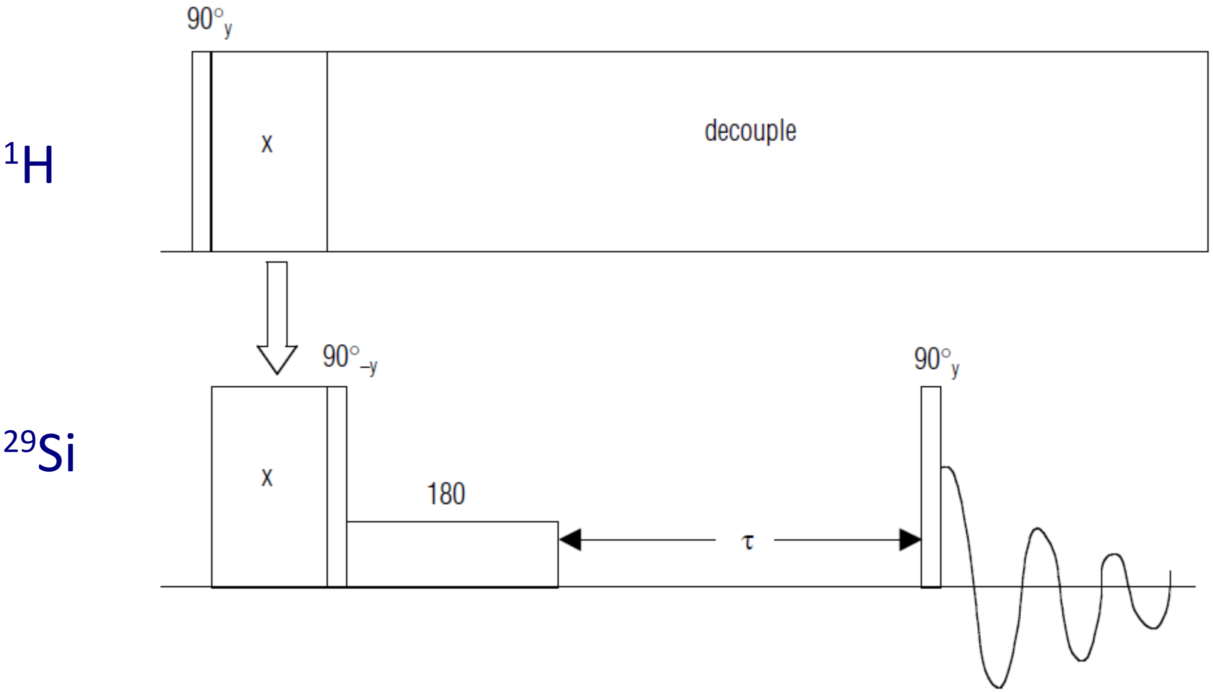
FID

NMR spectrum

Pulse sequences

The NMR spectrometer is a programmable machine!

Pulse sequences have been designed to:
- increase resolution and sensitivity, decouple spins
- find correlations between neighboring nuclei (2D and 3D NMR)



Cross-polarization (CP) pulse sequence

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Chemical shift

- Different nuclei/isotopes resonate at different Larmor frequencies.
- The resonance frequency is modified by the chemical environment.
- Every nucleus experiences a different local magnetic field.

Definition: shielding tensor σ

$$\mathbf{B}_{\text{eff}} = \mathbf{B}_{\text{ext}}(1 - \overleftrightarrow{\sigma})$$

- σ independent of magnetic field
- usually σ << 1
- measured in ppm (1 ppm = 10^{-6})

Definition: chemical shift δ

$$\delta = -(\sigma - \sigma_{\text{ref}})$$

- δ given as deviation from a reference compound
- measured in ppm (1 ppm = 10^{-6})

Reference compounds can be liquids, solutions, solids.

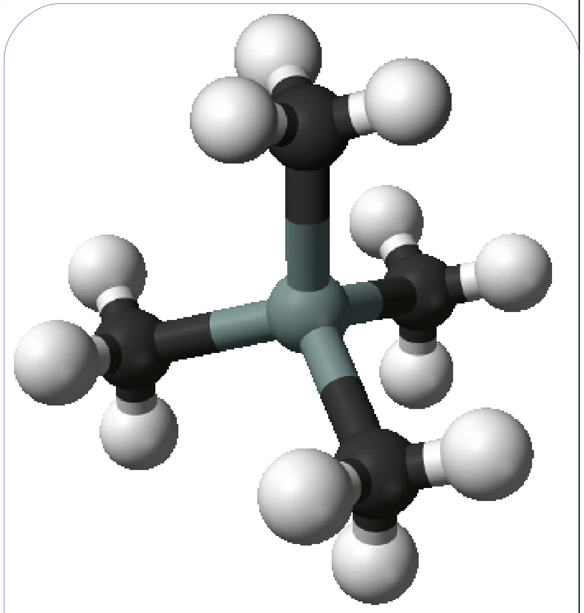
Chemical shift

In practice δ is obtained from the resonance frequencies:

$$\delta = \frac{\omega - \omega_{\mathrm{ref}}}{\omega_{\mathrm{ref}}} \cdot 10^6$$

Some reference compounds:

- ^1H, ^{13}C, ^{29}Si → tetramethylsilane (TMS)
- ^{15}N → liquid NH_3
- ^{17}O → liquid H_2O
- ^{19}F → liquid $CFCl_3$
- ^{27}Al → $AlCl_3$ in D_2O
- ^{43}Ca → $CaCl_2$(aq) 1 mol/L



TMS

It is possible to use a secondary reference if you know its chemical shift from the primary reference.

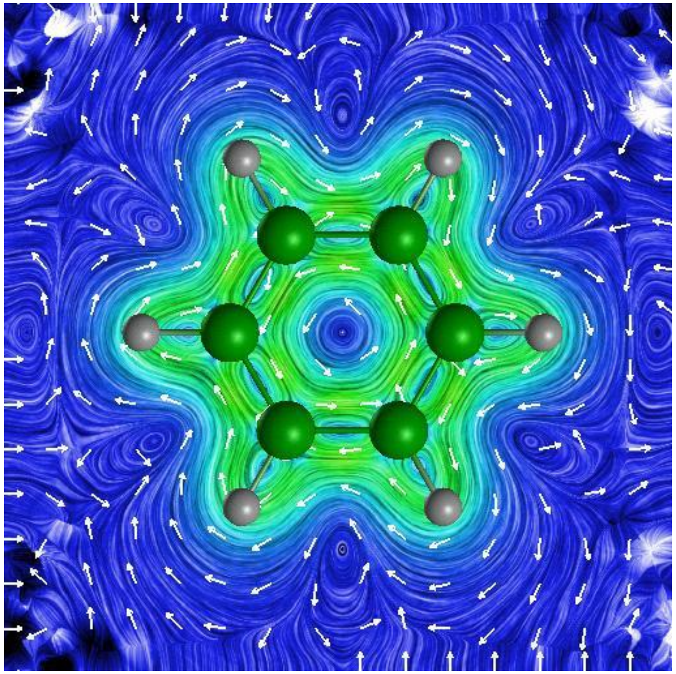
Chemical shift

The origin of the chemical shift are the orbital currents induced by the external magnetic field.

The shielding s can be decomposed into a diamagnetic ($\sigma_d > 0$) and paramagnetic ($\sigma_p < 0$) term:

σ_d depends on the density of circulating electrons
increases with electronegativity of substituents

σ_p depends on the hindering free circulation
dominates in presence of p and d orbitals, anysotropic chemical bond, positive charges, low lying electronic states, high atomic number elements

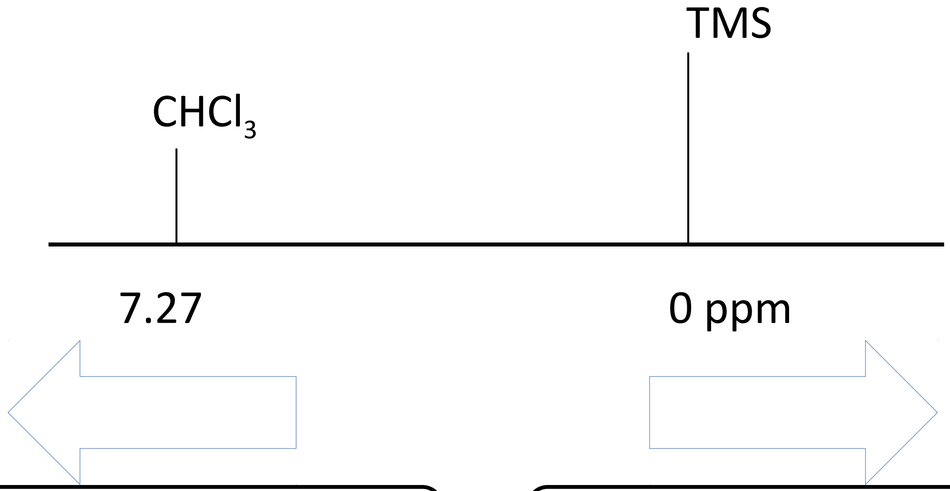


Electronic current in benzene, induced by a perpendicular magnetic field

NMR terminology

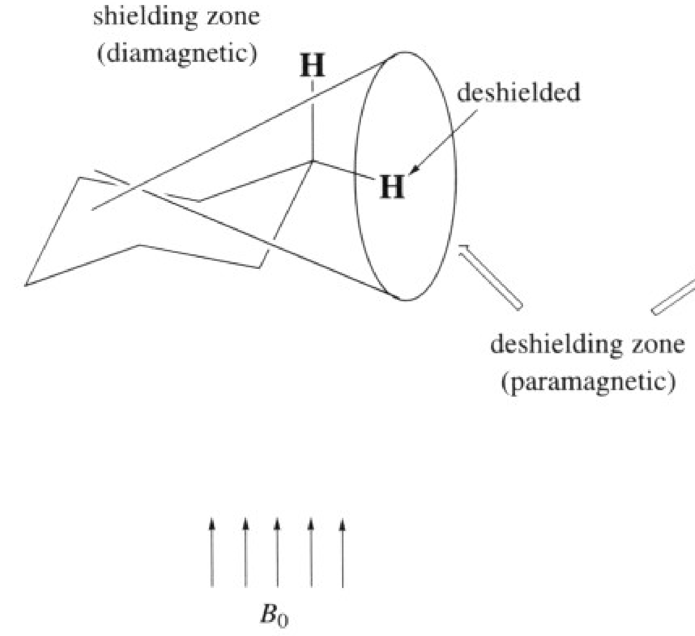
$$\mathbf{B}_{\text{eff}} = \mathbf{B}_{\text{ext}}(1 - \overleftrightarrow{\sigma})$$

$$\delta = -(\sigma - \sigma_{\text{ref}})$$

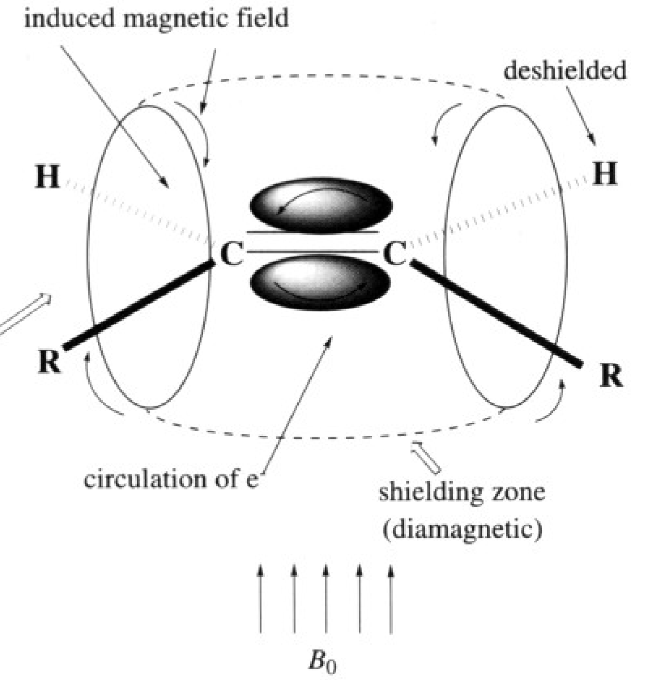


increasing δ
low field
high frequency
low shielding
paramagnetic

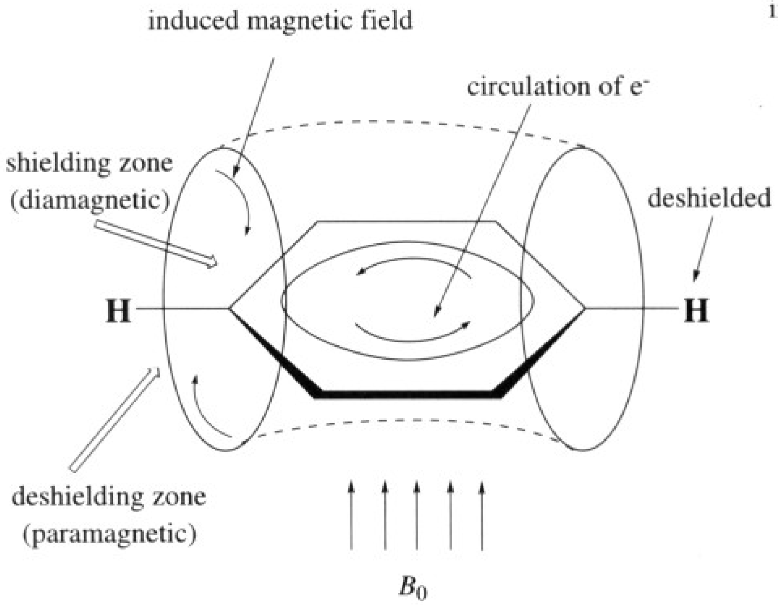
decreasing δ
high field
low frequency
high shielding
diamagnetic



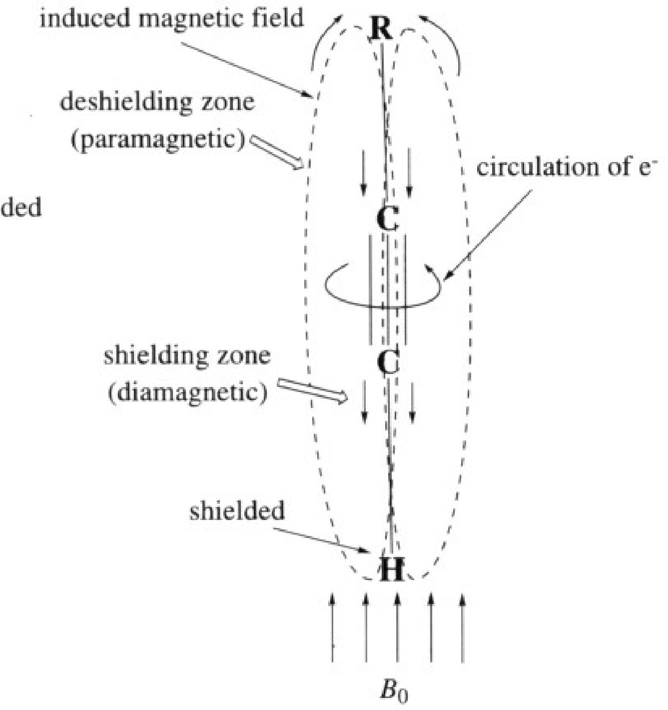
(a) Single bonds



(b) Double bonds



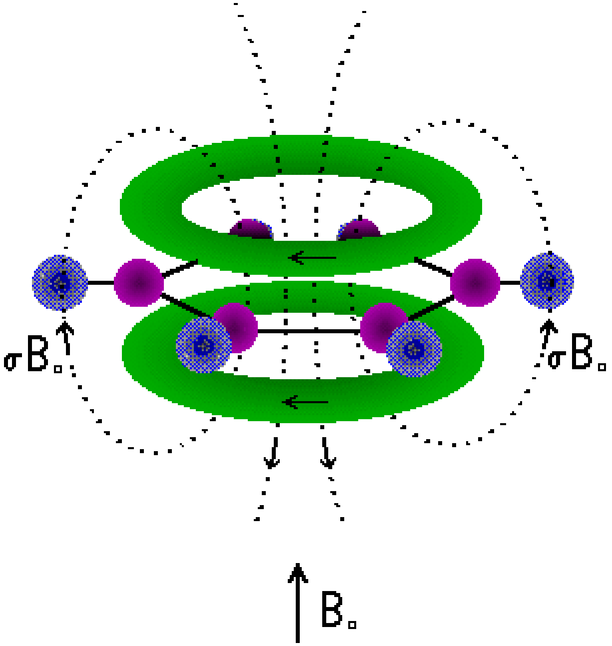
(c) Ring current at aromatic bonds



(d) Triple bonds

Ring current effect

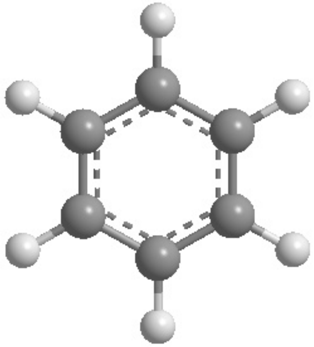
Atoms on the equatorial plane are strongly de-shielded (higher δ).



Benzene:

^{1}H : 7.16 ppm

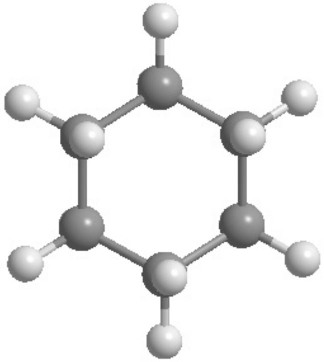
^{13}C: 128.39 ppm



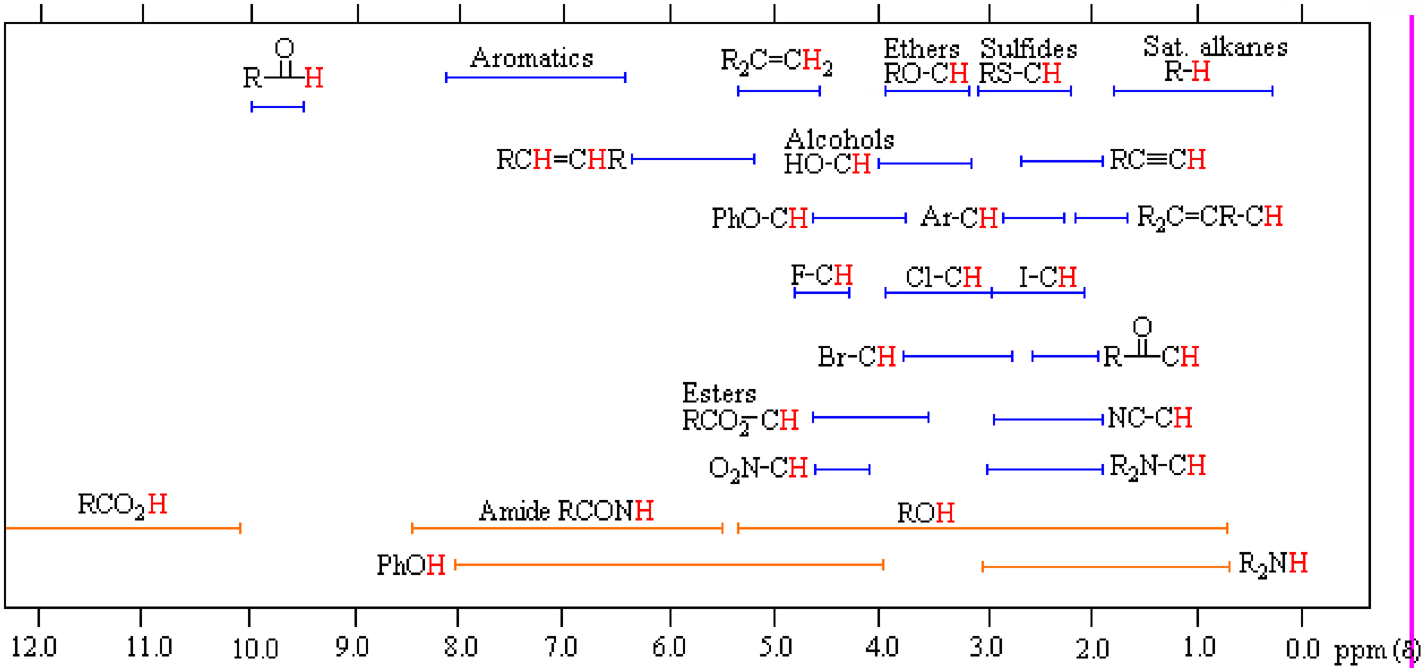
Cyclohexane:

^{1}H : 1.38 ppm

^{13}C: 26.43 ppm

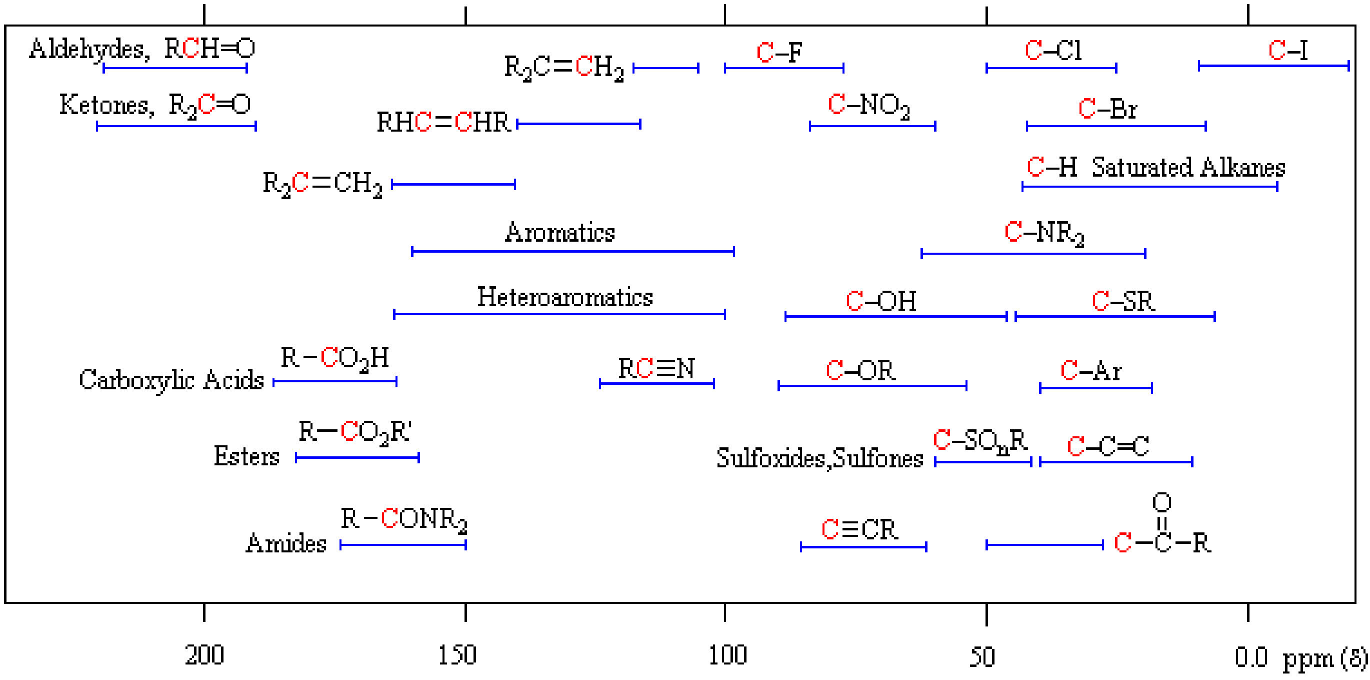


Chemical shift tables



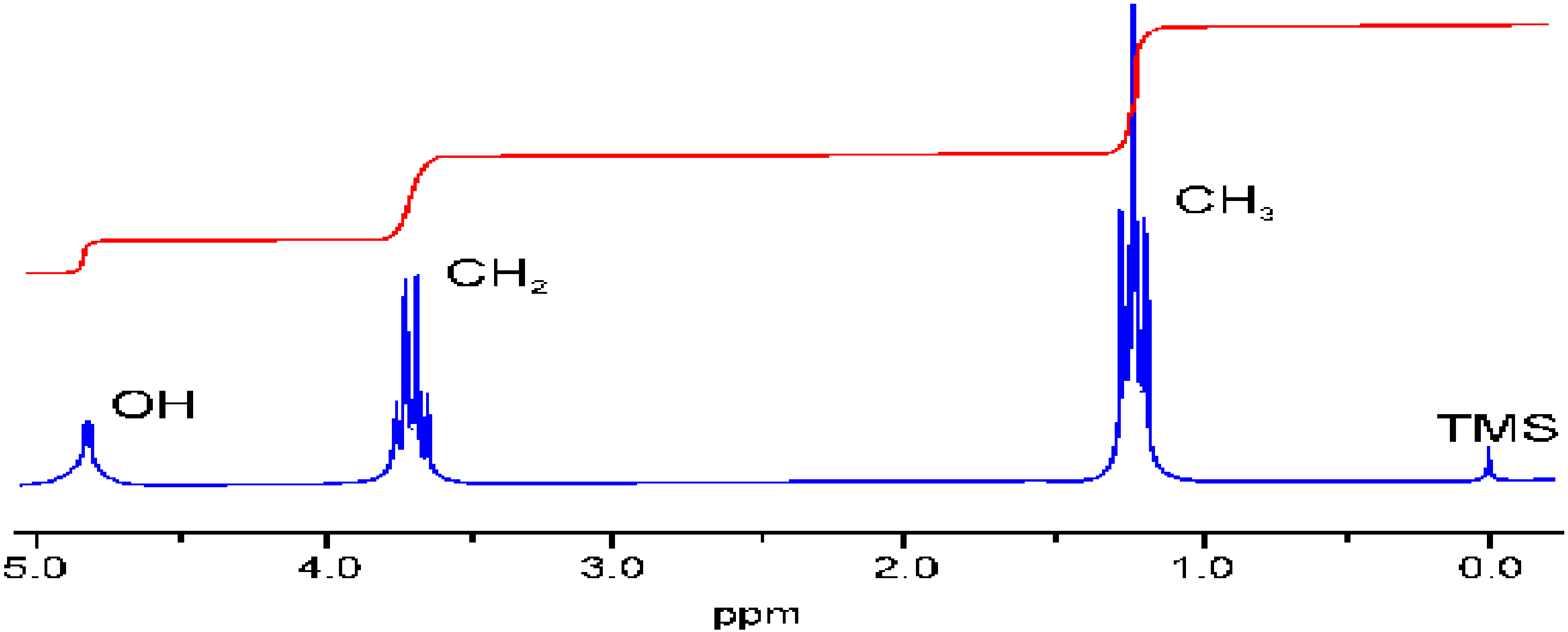
^1H

^{13}C

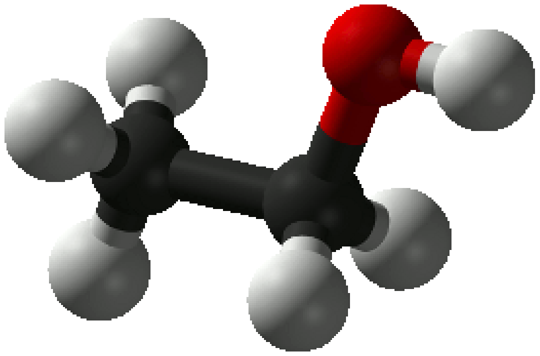


Interpretation of NMR spectra

Area of the peaks (red curve) → number of equivalent nuclei
Chemical shift table → possible chemical group
Splitting (J-coupling) → connectivity between groups

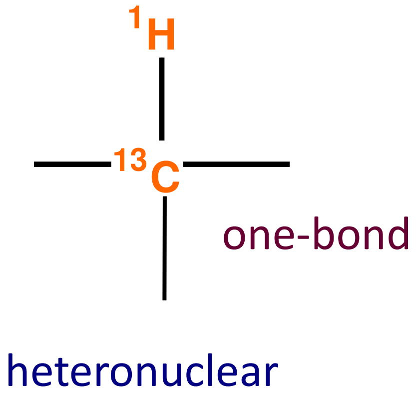


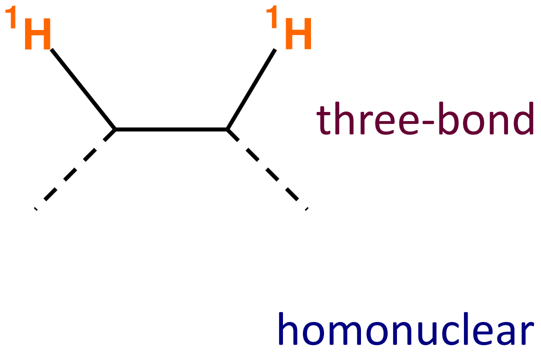
CH_3CH_2OH

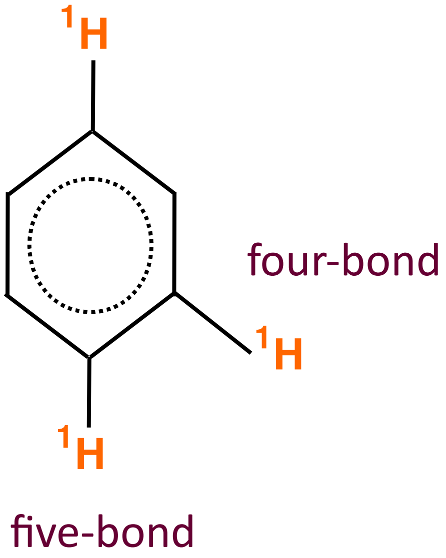


J coupling

Equivalent nuclei are coupled Heisenberg-like: $-J\, S_i \cdot S_j$
The “exchange” coupling J decays as $1/r_{ij}^{3}$
J is independent of the magnetic field (higher B → better resolution)
Coupling can be homonuclear or heteronuclear







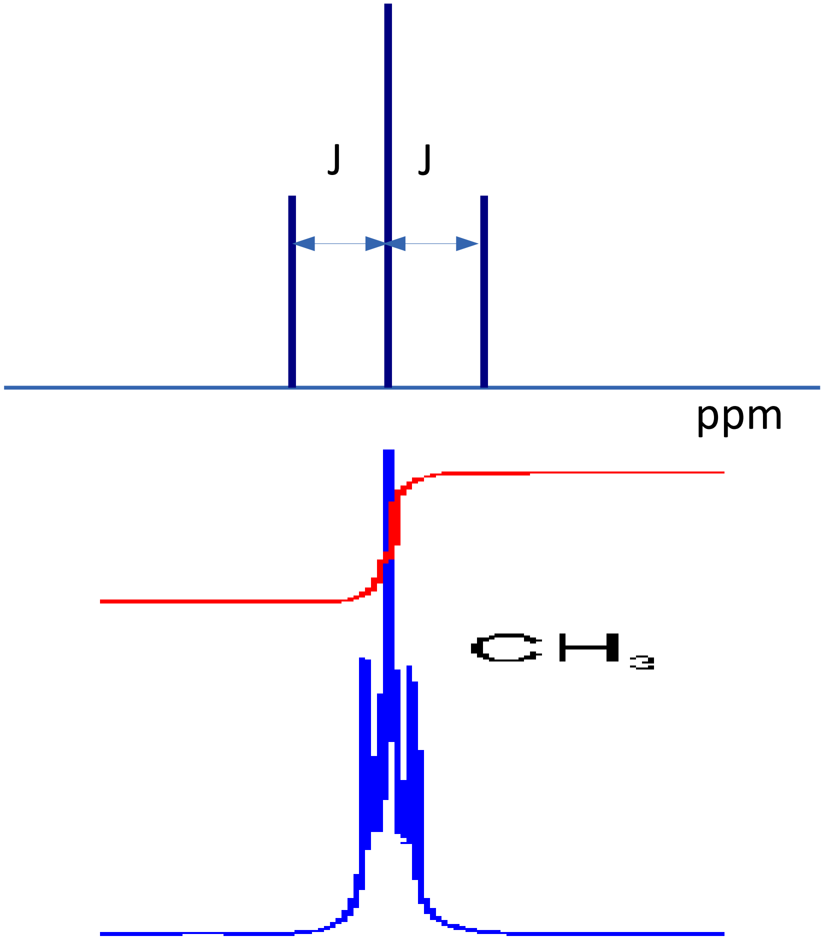
Homonuclear J coupling

Splitting intensities follow Pascal's triangle

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1

Pascal's triangle

Example: -CH_3 in ethanol
(1:2:1 triplet)



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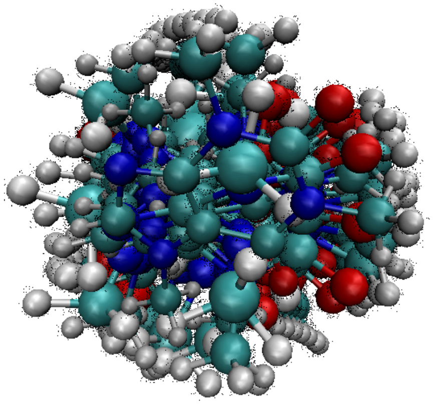
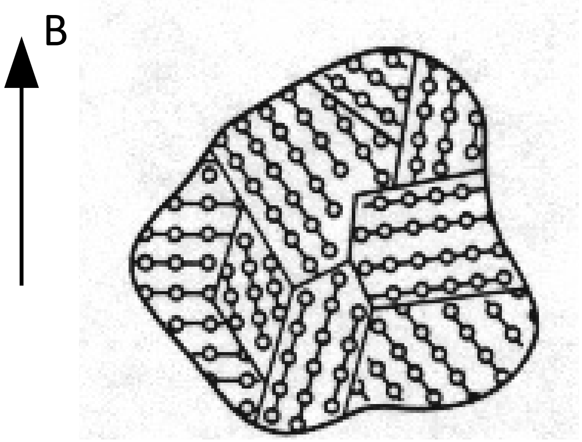
Solid-state NMR

Molecules in liquids move very fast w.r.t. NMR time, averaging over all orientations:
→ sharp NMR lines (isotropic chemical shift)

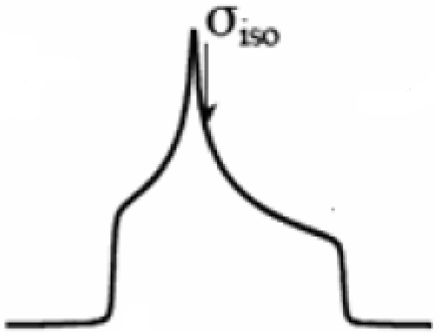
In solids nuclei are fixed in the lattice, no averaging:
→ broad NMR peaks (anysotropy)
→ interactions between spins are not averaged-out (broader lines)
→ long T_1 relaxation time (which implies longer experiments)



liquid state: rapid
molecular tumbling



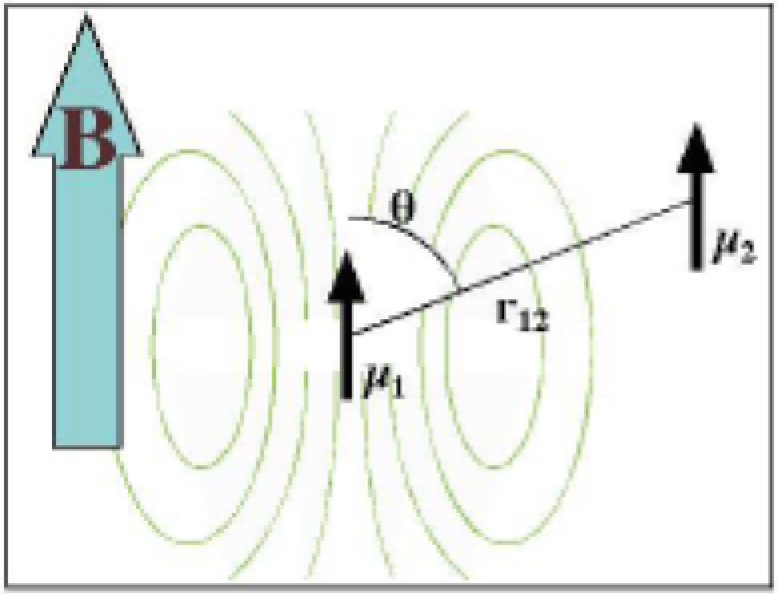
polycrystalline solid:
all possible
orientations



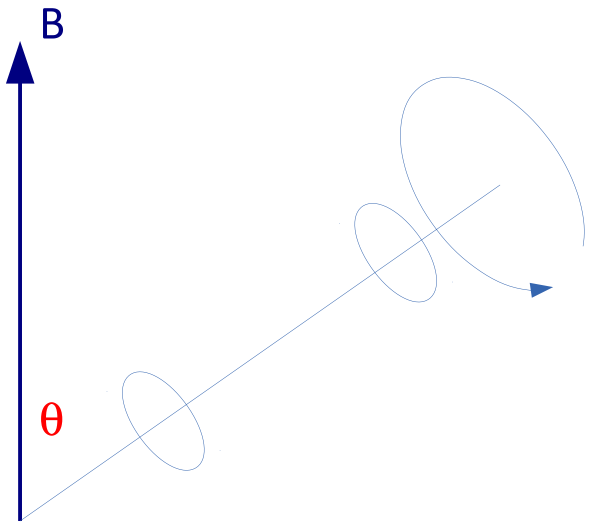
typical poly-crystalline line-shape

Magic Angle Spinning

The magnetic dipole interaction goes like ($3\cos^2\theta - 1$), where θ is the angle with the magnetic field

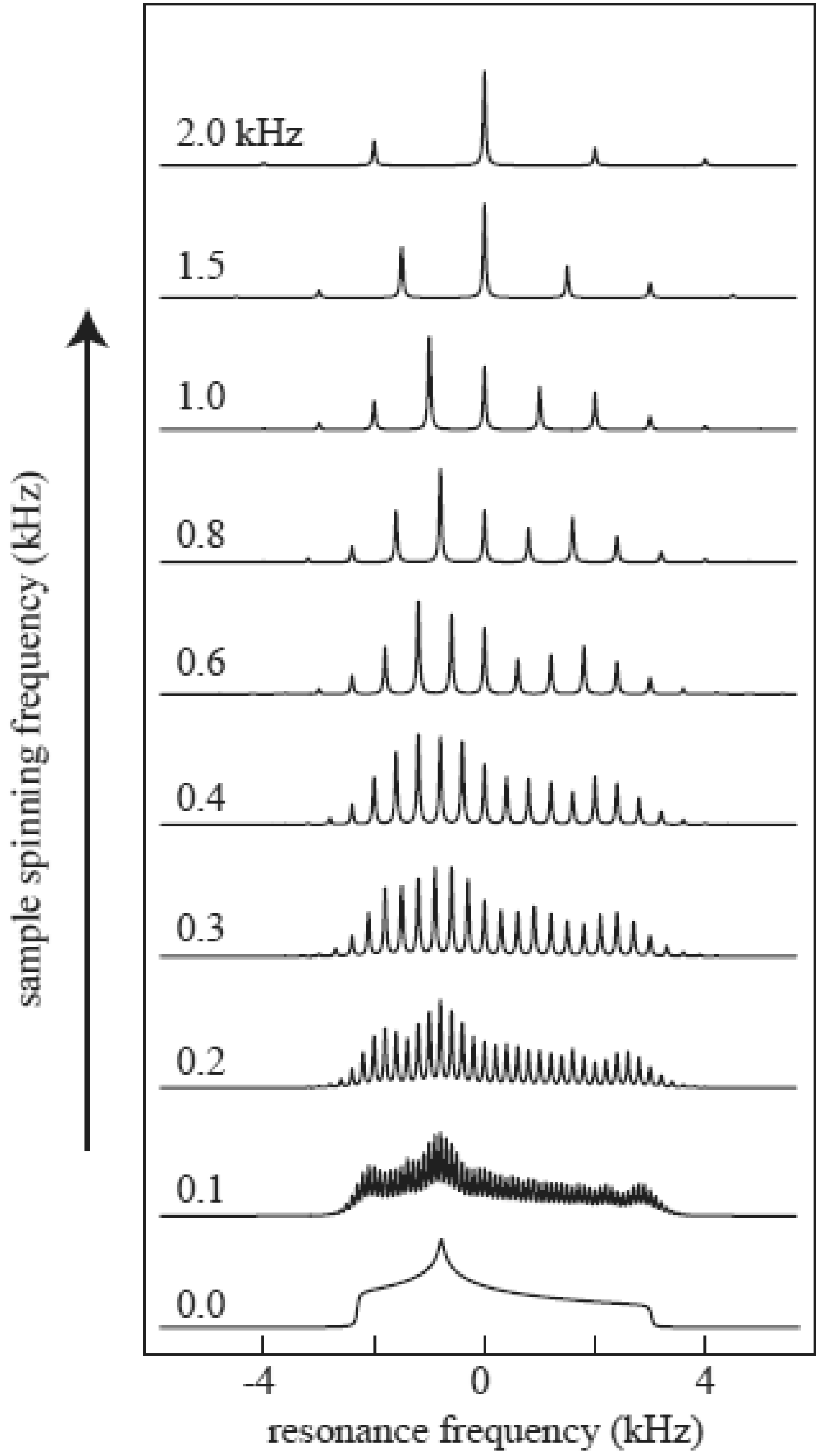


Solution: spin the sample at the magic angle θ ~ 54.74°



MAS reduces effect of chemical shift anisotropy and dipolar interactions.

Magic Angle Spinning



ss-NMR:

- sophisticated pulse sequences
- peak assignment more difficult
- need for calculations and simulations

Summary

- NMR uses radio-frequency radiation to induce transitions between different nuclear spin states of samples in a magnetic field.
- NMR can be used for quantitative measurements, but it is most useful for determining the structure of molecules.
- Different atoms in a molecule experience slightly different magnetic fields and therefore resonate at different frequencies (chemical shift).
- Splittings of the spectra lines (J-coupling) provide information about the proximity of different atoms in a molecule.

Advanced NMR topics (not covered in these notes):

- multidimensional NMR
- relaxation time, nuclear Overhauser effect

Questions?

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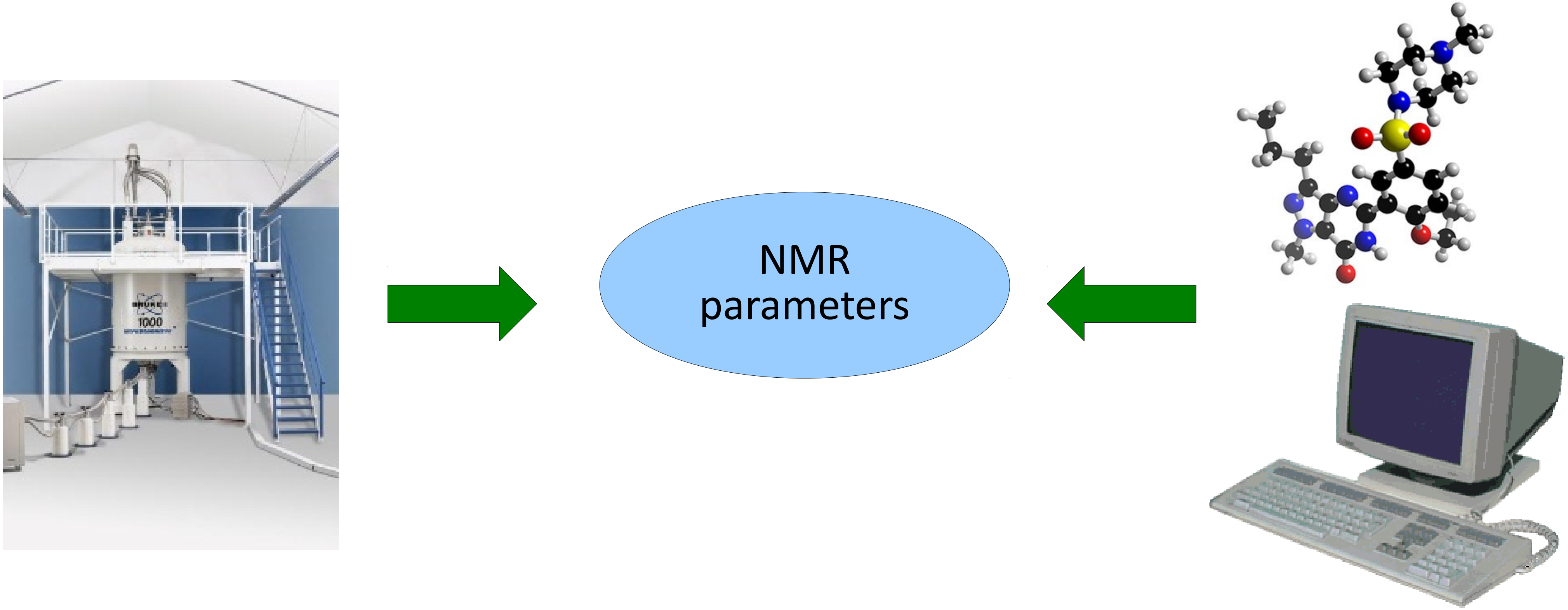
  - Brief introduction to EPR spectroscopy and EPR parameters

NMR parameters

NMR parameters are:

- → chemical shift
- → nuclear quadrupole
- → J coupling

They can be extracted by fitting the experimental spectrum or can be calculated from from first-principles, given the atomistic structure.



NMR parameters

Effective NMR Hamiltonian

$$\begin{aligned}\mathcal{H}_S(\mathrm{NMR}) \;&=\; -\hbar \sum_{I} \gamma_I \mathbf{B}_{\mathrm{ext}} \left(\bar{\bar{\mathbf{1}}} - \bar{\bar{\sigma}}\right) \mathbf{I}_I \\ &+\; \frac{1}{2}\hbar^2 \sum_{I} \sum_{J\neq I} \gamma_I \gamma_J \mathbf{I}_I \left(\bar{\bar{\mathbf{D}}}_{IJ} + \bar{\bar{\mathbf{J}}}_{IJ}\right) \mathbf{I}_J \\ &+\; \sum_{I,|\mathbf{I}_I|\geq 1} \mathbf{I}_I \bar{\bar{\mathbf{Q}}}_I \mathbf{I}_I\end{aligned}$$

chemical shift

J coupling

nuclear
quadrupole
(I>1/2)

$\mathbf{I}_I = \text{Nuclear spin};\ \mu_I = \gamma_I \hbar \mathbf{I}_I\ ;\ \sigma = \text{Nuclear chemical shielding tensor}$

$\bar{\bar{\mathbf{D}}}_{IJ} = \text{Nuclear magnetic dipolar coupling tensor}$

$\bar{\bar{\mathbf{J}}}_{IJ} = \text{Indirect nuclear spin} - \text{spin coupling tensor}$

$\bar{\bar{\mathbf{Q}}}_{II} = \text{Nuclear quarupolar coupling tensor}$

The chemical shift

From the NMR Hamiltonian the shielding tensor is defined as:

$$\mathbf{B}_{\mathrm{ind}} = -\bar{\bar{\sigma}}\mathbf{B}_{\mathrm{ext}}$$

It is the second derivative of energy w.r.t. field and nuclear moment:

$$\overset{\leftrightarrow}{\sigma}_I = \frac{\partial^2 E}{\partial \boldsymbol{\mu}_I \partial \mathbf{B}}$$

The chemical shift is then defined by:

$$\delta = -\left(\sigma - \sigma_{\mathrm{ref}}\right)$$

σ_{ref} is a reference value in a well-characterized material.

“Direct” and “converse” methods

Direct approach (traditional):

- linear response to external magnetic field
- calculate the induced current, then the induced field
- Mauri, Louie (1996); GIPAW: Pickard, Mauri (2001)

$$\boxed{\overset{\leftrightarrow}{\sigma}_I = - \left. \frac{\partial \mathbf{B}_{\mathrm{ind}}}{\partial \mathbf{B}_{\mathrm{ext}}} \right|_{r=r_I}} \qquad \mathbf{B}_{\mathrm{ind}}(\mathbf{r}) = \frac{1}{c} \int d^3\mathbf{r}' \, \frac{\mathbf{j}_{\mathrm{ind}}(\mathbf{r}') \times (\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}$$

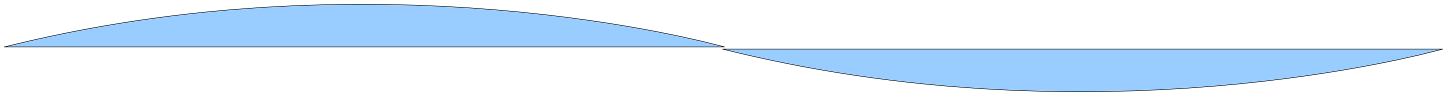
Converse approach:

- no linear response, no magnetic field, no gauge-origin problem
- calculate the change of orbital magnetization due to nuclear magnetic moment
- based on the “Modern Theory of the Orbital Magnetization”

$$\boxed{\overset{\leftrightarrow}{\sigma}_I = -\Omega \frac{\partial \mathbf{M}_{\mathrm{orb}}}{\partial \boldsymbol{\mu}_I}} \qquad \mathbf{M}_{\mathrm{orb}} = \frac{\alpha}{2} \mathrm{Im} \sum_{n\mathbf{k}} f_{n\mathbf{k}} \left\langle \partial_{\mathbf{k}} u_{n\mathbf{k}} \right| \times \left(H_{\mathbf{k}} + E_{n\mathbf{k}} - 2\mu \right) \left| \partial_{\mathbf{k}} u_{n\mathbf{k}} \right\rangle$$

Outline of linear response

Vector potential **A**(**r**)=(1/2)**B** x **r** is incompatible with crystal periodicity
Solution: apply a long-wavelength magnetic field (q << 1)



$$B(r) \propto \frac{\cos(q\,r)}{q}\hat{z} \qquad A(r) \propto \frac{\sin(q\,r)}{q}\hat{z}\times\hat{q}$$

The response to an incommensurate perturbation is obtained by Density Functional Perturbation Theory (DFPT):

$$\underset{\text{GS wfcs}}{|\phi^{(0)}_{n\sigma}\rangle} \xrightarrow{\text{DFPT to magn. field}} \underset{\text{perturbed wfcs}}{|\phi^{(1)}_{n\sigma}\rangle} \longrightarrow \underset{\text{induced current}}{\mathbf{j}^{(1)}_{\sigma}(\mathbf{r}')} \xrightarrow{\text{Biot-Savart}} \underset{\text{induced field}}{\mathbf{B}^{(1)}_{\sigma}(\mathbf{r}')}$$

EFG: electric field gradient tensor

Quadrupolar nuclei (I>1/2); non-zero only when no cubic symmetry:

$$\bar{\bar{\mathbf{Q}}}^{I}_{\alpha\beta} = \frac{eQ}{h} \langle\psi_0| \frac{\delta \mathbf{E}_\alpha}{\delta \mathbf{r}_\beta} |\psi_0\rangle = \frac{eQ}{h} \bar{\bar{\mathbf{V}}}_{\alpha\beta}$$

$$\mathbf{E} = \text{electric field} \; ; \; eQ = \text{electric quadrupole moment}$$

Principal axis system: Eigenvectors and -values of $\bar{\bar{\mathbf{V}}}_{\alpha\beta}$

Convention: $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

Observables:

- Quadrupolar coupling constant
- Asymmetry parameter

$$Cq = \frac{eQ\,V_{zz}}{h}$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

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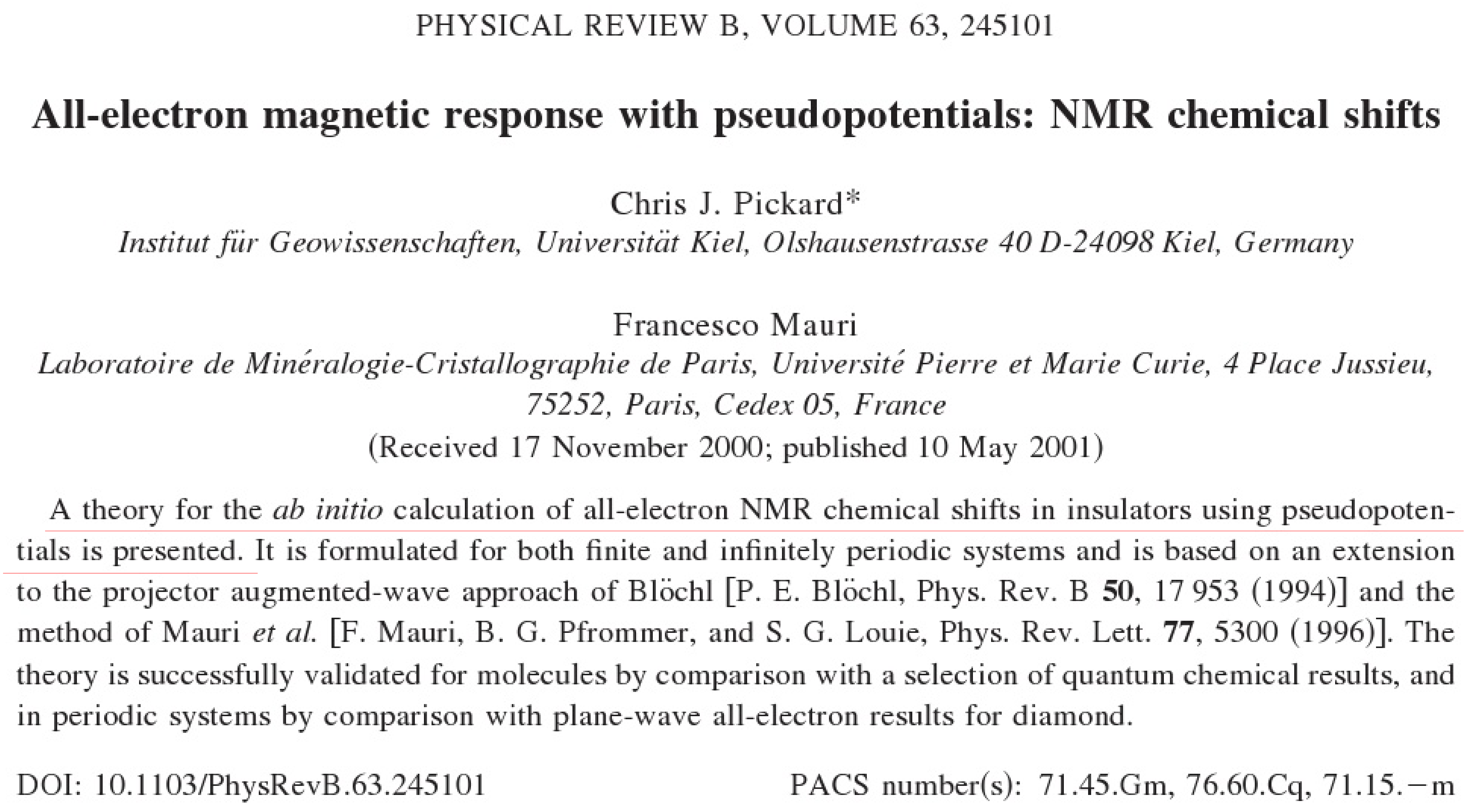
GIPAW



PHYSICAL REVIEW B, VOLUME 63, 245101

All-electron magnetic response with pseudopotentials: NMR chemical shifts

Chris J. Pickard*
Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40 D-24098 Kiel, Germany

Francesco Mauri
Laboratoire de Minéralogie-Cristallographie de Paris, Université Pierre et Marie Curie, 4 Place Jussieu, 75252, Paris, Cedex 05, France

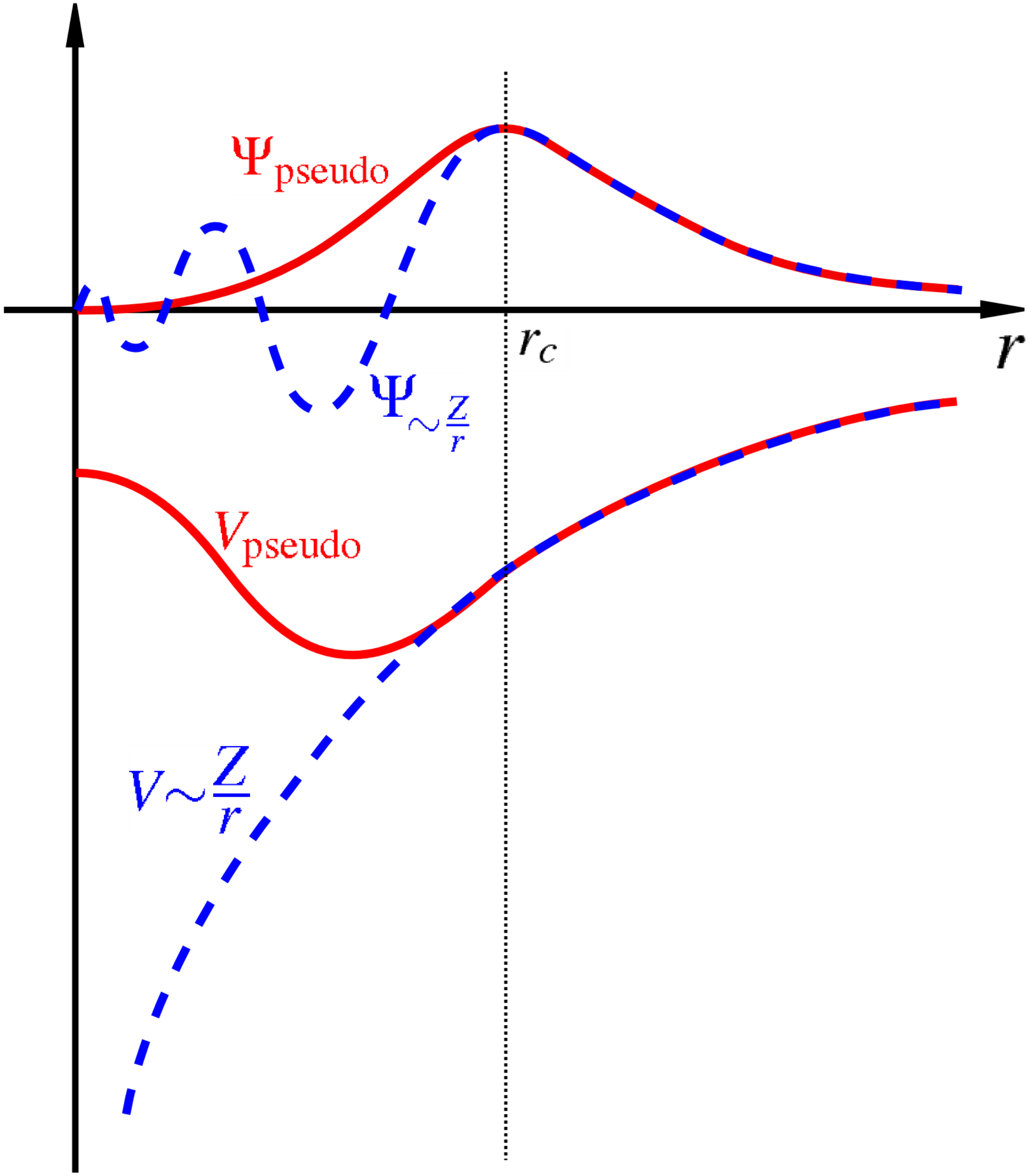
(Received 17 November 2000; published 10 May 2001)

A theory for the *ab initio* calculation of all-electron NMR chemical shifts in insulators using pseudopotentials is presented. It is formulated for both finite and infinitely periodic systems and is based on an extension to the projector augmented-wave approach of Blöchl [P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994)] and the method of Mauri *et al.* [F. Mauri, B. G. Pfrommer, and S. G. Louie, Phys. Rev. Lett. **77**, 5300 (1996)]. The theory is successfully validated for molecules by comparison with a selection of quantum chemical results, and in periodic systems by comparison with plane-wave all-electron results for diamond.

DOI: 10.1103/PhysRevB.63.245101 PACS number(s): 71.45.Gm, 76.60.Cq, 71.15.−m

Need to reconstruct the wavefunction near the nuclei!

Pseudopotential / all-electron



AE wfc (blue) oscillates rapidly near the nucleus

PS wfc (red) smooth, no nodes in the core region

PAW idea

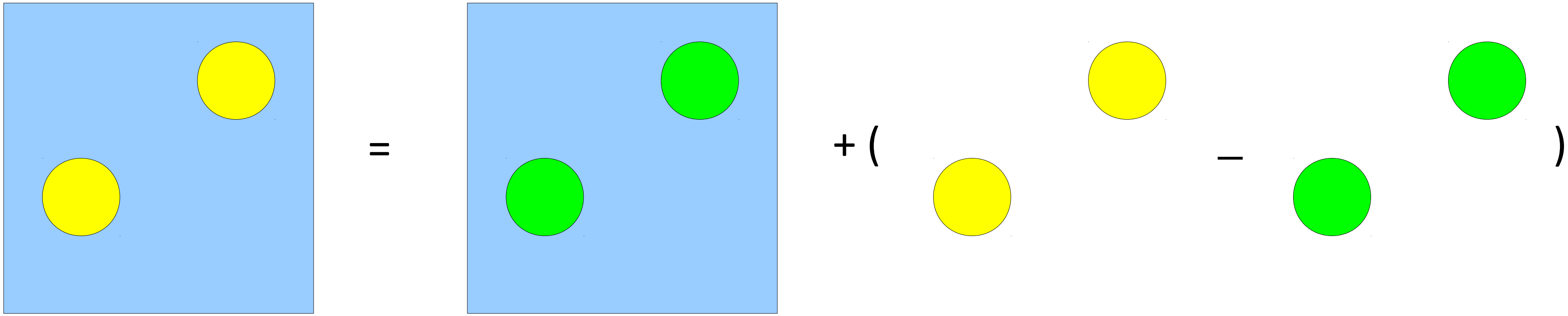
PAW (Blöchl, 1994) = projector augmented wave
Idea: “reconstruct” the AE wfc from the PS wfc

valence wfcs

$$|\psi^{\mathrm{AE}}\rangle = |\psi^{\mathrm{PS}}\rangle + \sum_{R,n} \left(|\phi^{\mathrm{AE}}_{r,n}\rangle - |\phi^{\mathrm{PS}}_{R,n}\rangle\right) \langle p_{R,n}|\psi^{\mathrm{PS}}\rangle$$

atomic partial waves

atomic projectors



Gauge Including PAW

Translation in magnetic field yields a gauge phase factor:

$$\begin{aligned} H' &= \frac{1}{2}\left[\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right]^2 + V(\mathbf{r}-\mathbf{t}) \\ \psi_i'(\mathbf{r}) &= e^{i/(2c)\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\psi_i(\mathbf{r}) \end{aligned}$$

PAW + magnetic field = GIPAW

$$\mathcal{T}_{\mathbf{B}} = \mathbf{1} + \sum_{\mathbf{R},n} e^{i/(2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\left[|\phi_{\mathbf{R},n}\rangle - \left|\tilde{\phi}_{\mathbf{R},n}\right\rangle\right]\langle\tilde{p}_{\mathbf{R},n}|\, e^{-i/(2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

Take-home message: (1) wfc reconstruction (2) gauge-invariance

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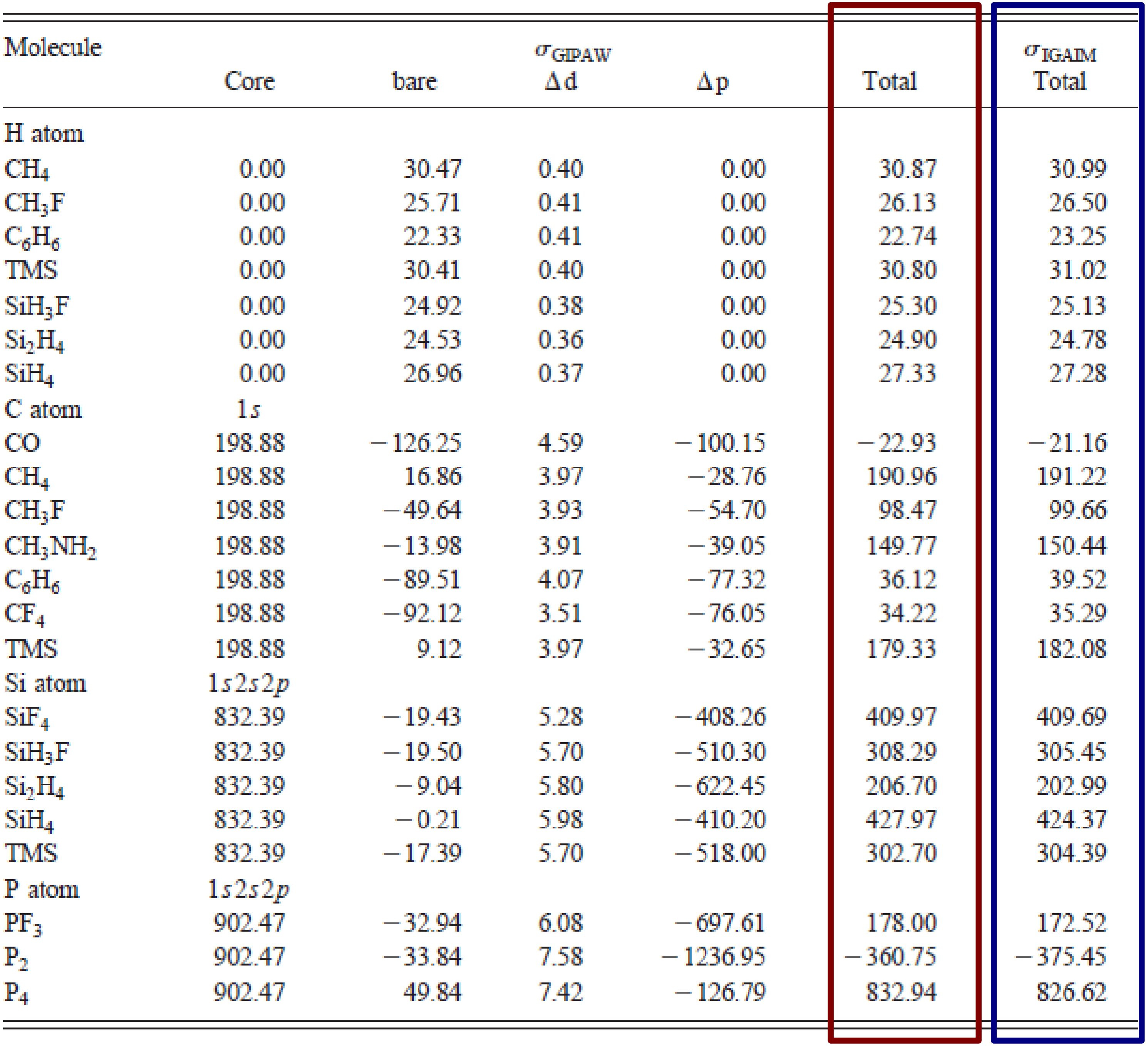
Example: molecules



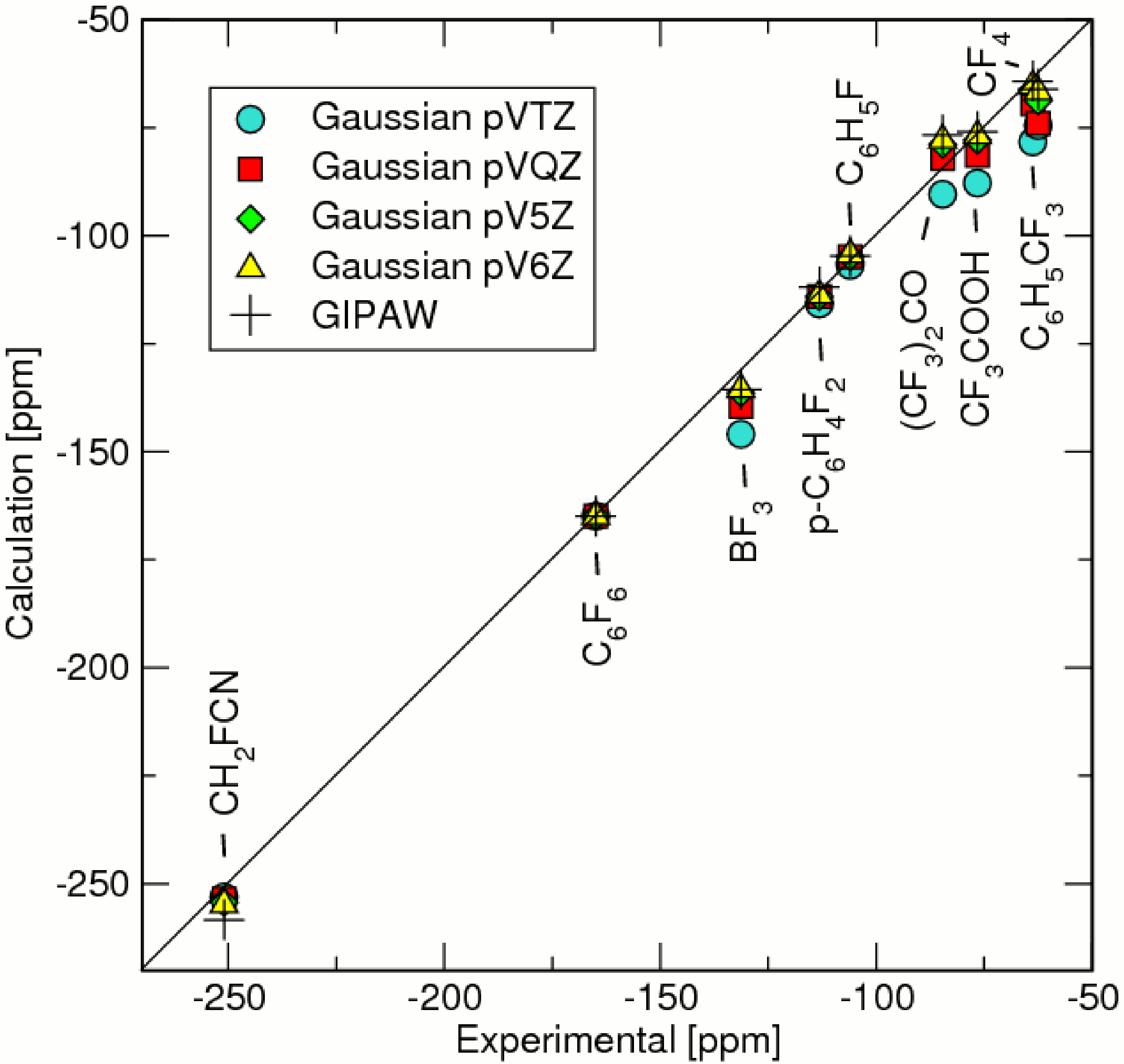
Molecule	Core	bare	σ_{GIPAW} Δd	Δp	Total	σ_{IGAIM} Total
H atom						
CH_4	0.00	30.47	0.40	0.00	30.87	30.99
CH_3F	0.00	25.71	0.41	0.00	26.13	26.50
C_6H_6	0.00	22.33	0.41	0.00	22.74	23.25
TMS	0.00	30.41	0.40	0.00	30.80	31.02
SiH_3F	0.00	24.92	0.38	0.00	25.30	25.13
Si_2H_4	0.00	24.53	0.36	0.00	24.90	24.78
SiH_4	0.00	26.96	0.37	0.00	27.33	27.28
C atom	1*s*					
CO	198.88	−126.25	4.59	−100.15	−22.93	−21.16
CH_4	198.88	16.86	3.97	−28.76	190.96	191.22
CH_3F	198.88	−49.64	3.93	−54.70	98.47	99.66
CH_3NH_2	198.88	−13.98	3.91	−39.05	149.77	150.44
C_6H_6	198.88	−89.51	4.07	−77.32	36.12	39.52
CF_4	198.88	−92.12	3.51	−76.05	34.22	35.29
TMS	198.88	9.12	3.97	−32.65	179.33	182.08
Si atom	1*s*2*s*2*p*					
SiF_4	832.39	−19.43	5.28	−408.26	409.97	409.69
SiH_3F	832.39	−19.50	5.70	−510.30	308.29	305.45
Si_2H_4	832.39	−9.04	5.80	−622.45	206.70	202.99
SiH_4	832.39	−0.21	5.98	−410.20	427.97	424.37
TMS	832.39	−17.39	5.70	−518.00	302.70	304.39
P atom	1*s*2*s*2*p*					
PF_3	902.47	−32.94	6.08	−697.61	178.00	172.52
P_2	902.47	−33.84	7.58	−1236.95	−360.75	−375.45
P_4	902.47	49.84	7.42	−126.79	832.94	826.62

red = GIPAW

blue = Gaussian™

Pickard, Mauri
PRB **63**, 245101 (2001)

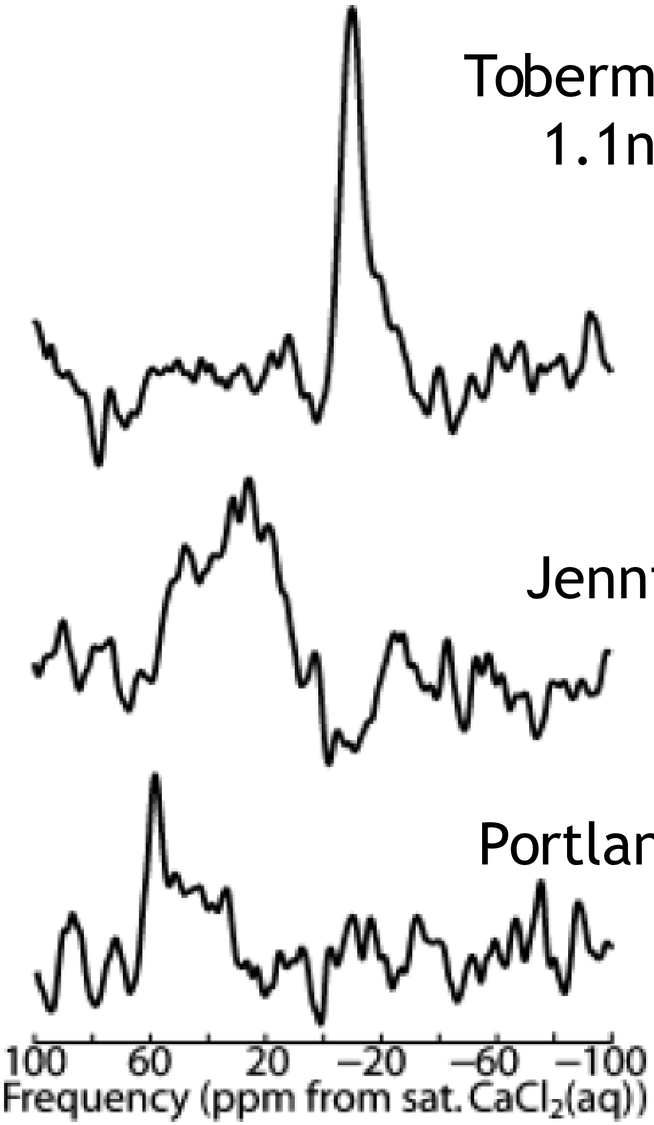
Example: ^{19}F

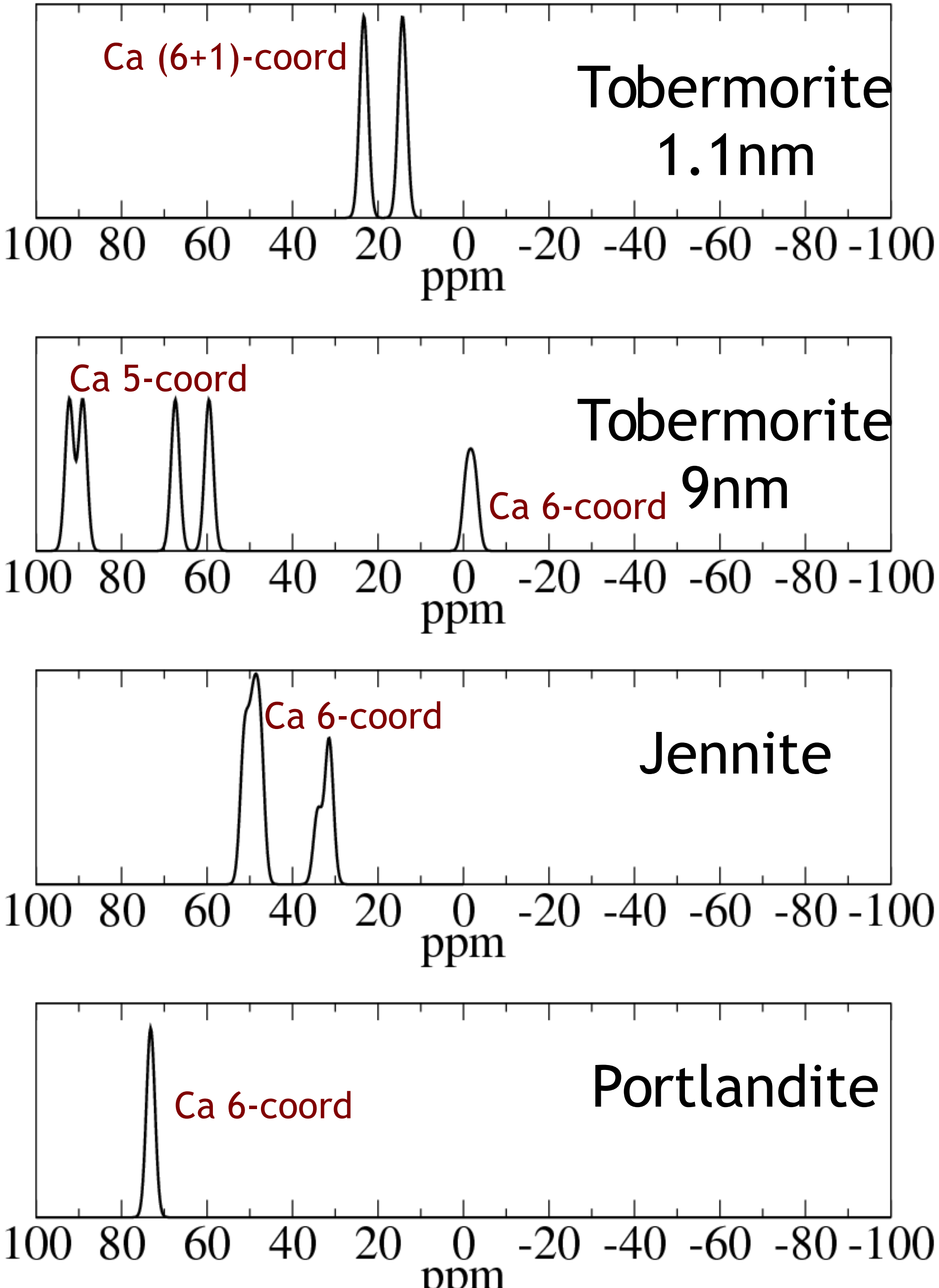


GIPAW ~ Gaussian 6Z (140 basis/atom)

Ceresoli, Marzari, Lopez, Thonhauser
PRB **81**, 184424 (2010)

Example: ^{43}Ca cement models





Bowers and Kirkpatrick, JACS 92, 545 (2009)

max(Ca-O) = 2.8 Å

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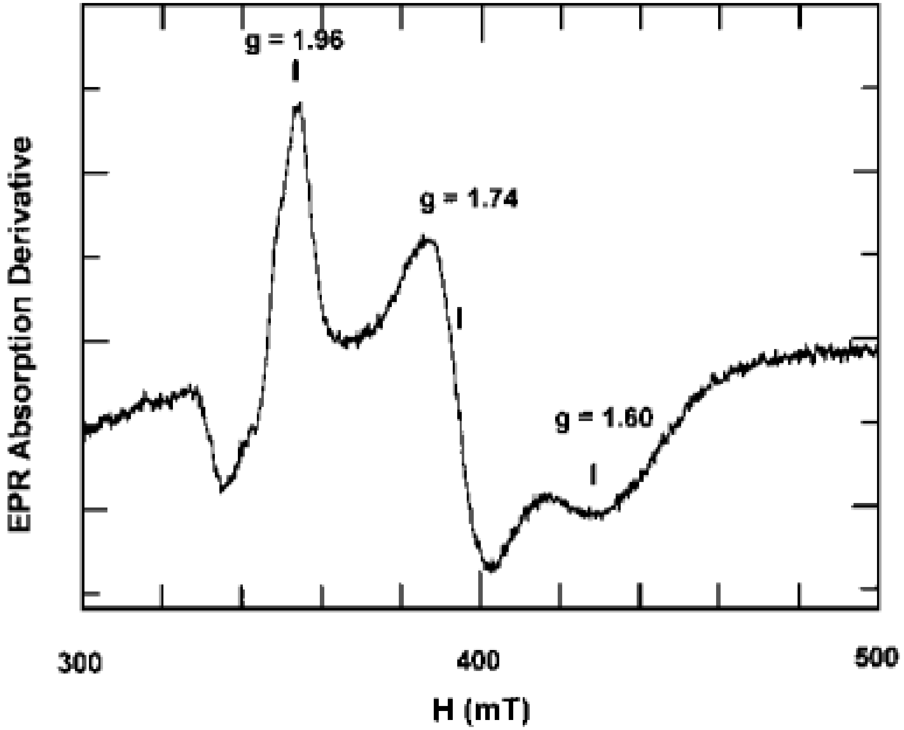
EPR/ESR spectroscopy

Electron Paramagnetic Resonance / Electron Spin Resonance



- Paramagnetic defects in solids, radicals in proteins
- Sensitive to local geometry and electronic structure (charge, hybridization)
- Non destructive, small samples, dilute spins

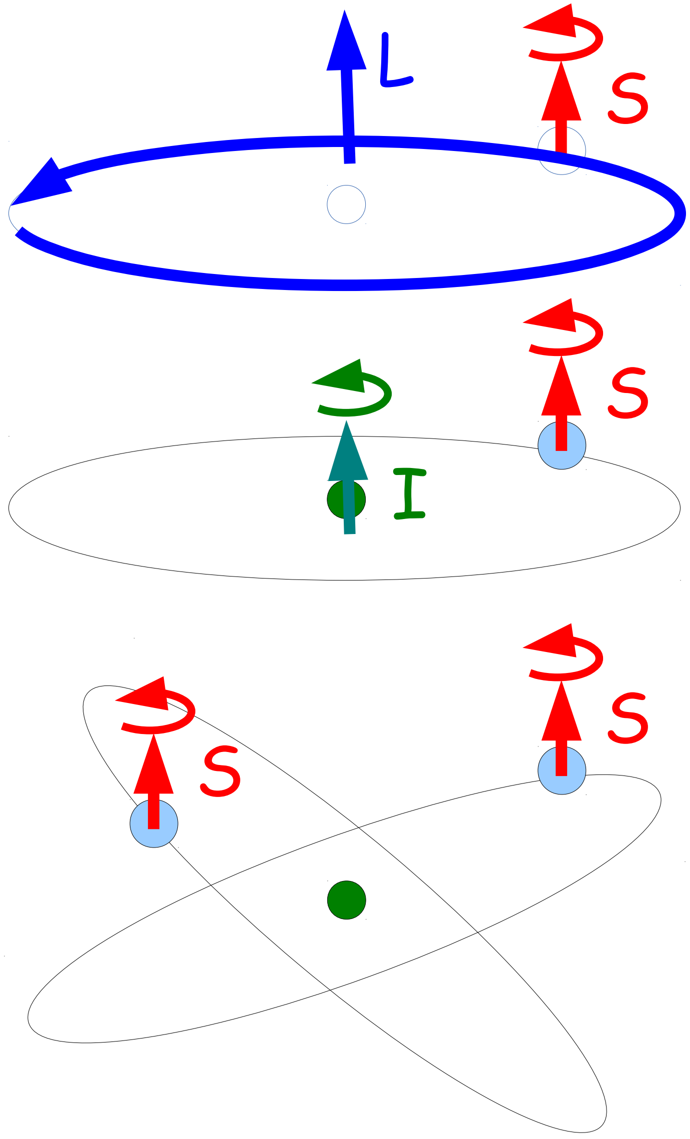
Tipical fields	~0.5 T
Resonance	~14 GHz

Interpretation of EPR spectra

$$B_{\text{tot}} = B_{\text{ext}} + B_{\text{ind}}$$

$$+ B_{\text{nucl}}$$

$$+ B_{\text{other-spin}}$$



Spin-Orbit, SOO

Hyperfine

Zero Field Splitting

Effective Spin Hamiltonian

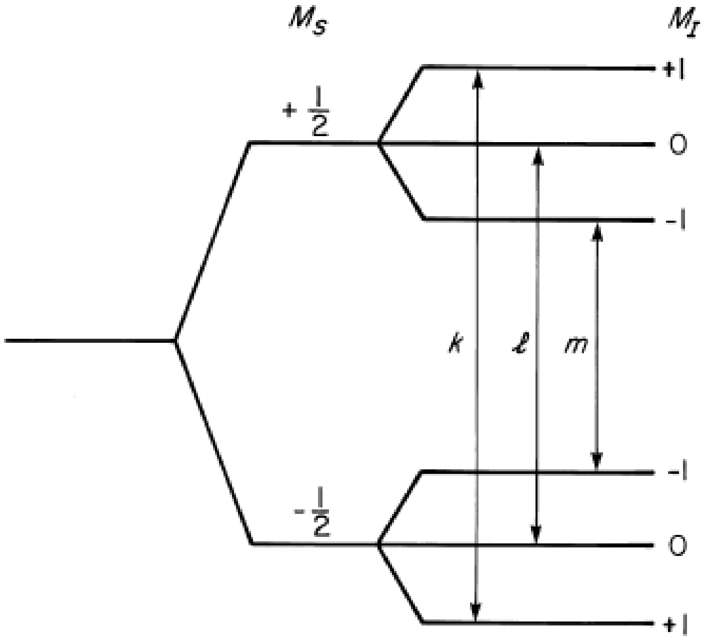
$$\mathcal{H}_{\text{eff}} = \frac{\alpha}{2}\mathbf{S}\cdot\overleftrightarrow{g}\cdot\mathbf{B} + \sum_R \mathbf{S}\cdot\overleftrightarrow{A}_R\cdot\mathbf{I}_R + \mathbf{S}\cdot\overleftrightarrow{D}\cdot\mathbf{S}$$

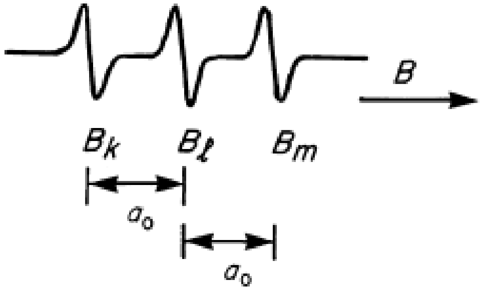
$\alpha = 1/c$

g-tensor

hyperfine

ZFS





Selection rules:

$|\Delta M_S| = 1$

$|\Delta M_I| = 0$

Theory of EPR parameters

The effective spin Hamiltonian allows to extract EPR parameters from the experiments, but in order to calculate EPR parameters, we need a "physical" Hamiltonian. The simplest non-relativistic Hamiltonian that accounts for spin is the Pauli Hamiltonian:

Mass velocity and Darwin

$$\begin{aligned}\mathcal{H}_{\mathrm{Pauli}} &= \frac{p^2}{2m} + V(\mathbf{r}) - \frac{1}{8c^2}(p^4 - \nabla^2 V) + \\ &+ \frac{g_e}{2c}\mathbf{S}\cdot\mathbf{B} - \frac{g_e}{2c^3}\frac{p^2}{2}\mathbf{S}\cdot\mathbf{B} + \\ &+ \frac{g'}{4c^2}\mathbf{S}\cdot(\nabla V \times \mathbf{p}) + \mathcal{H}_{\mathrm{SOO}} + \cdots\end{aligned}$$

Zeeman and Zeeman-KE

Spin orbit

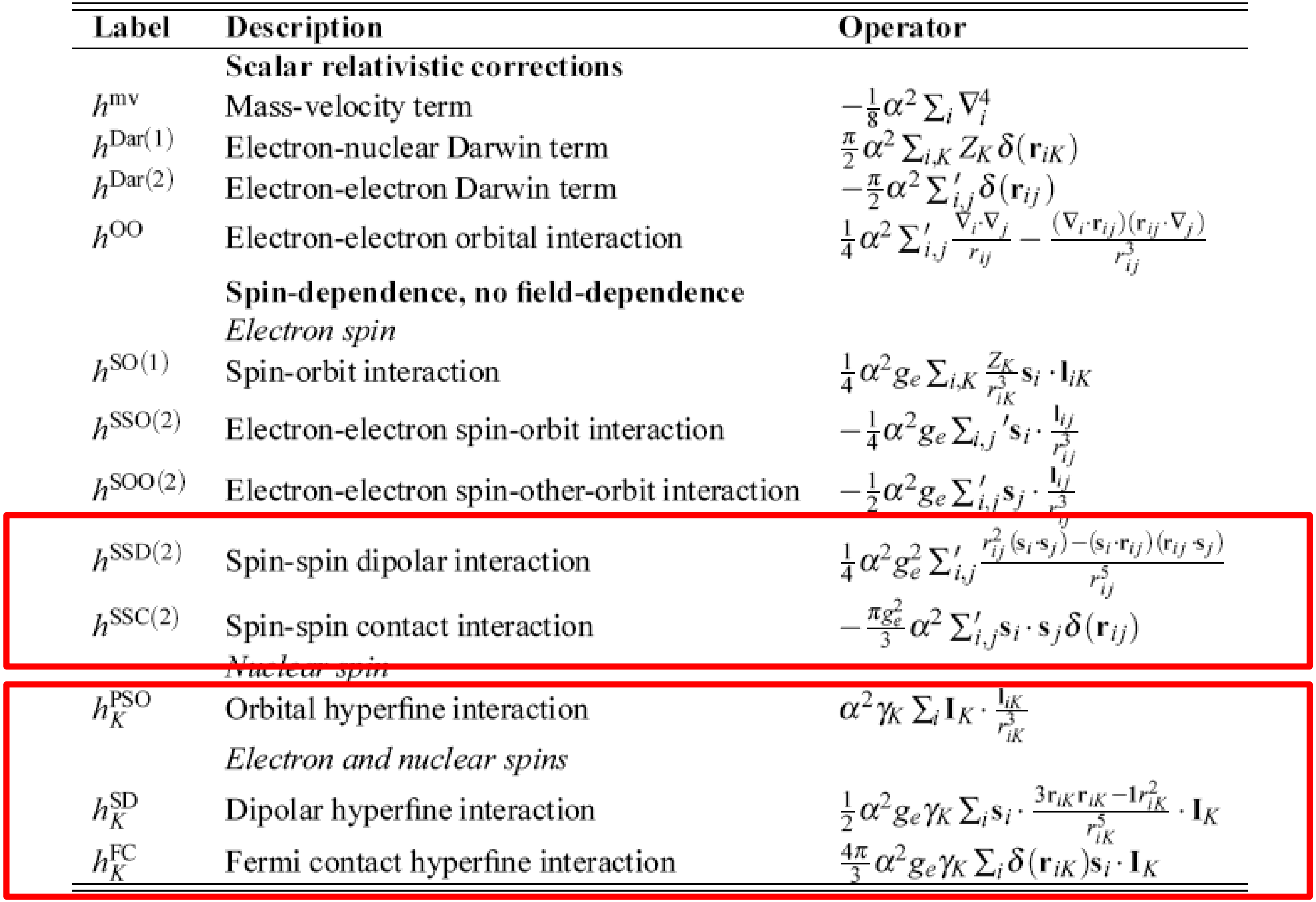
Spin other-orbit

$g_e = 2.0023192778$ $g' = 2(g_e - 1)$ $c = 1/\alpha = 137.03599$

S = (ħ/2)**σ** (**σ** = Pauli matrixes)

… plus other terms

Table 2.2. Partial listing of $\mathcal{O}(\alpha^2)$ terms of the approximate Hamiltonian.



Label	Description	Operator
	Scalar relativistic corrections	
h^{mv}	Mass-velocity term	$-\frac{1}{8}\alpha^2\sum_i \nabla_i^4$
$h^{\mathrm{Dar}(1)}$	Electron-nuclear Darwin term	$\frac{\pi}{2}\alpha^2\sum_{i,K} Z_K\,\delta(\mathbf{r}_{iK})$
$h^{\mathrm{Dar}(2)}$	Electron-electron Darwin term	$-\frac{\pi}{2}\alpha^2\sum'_{i,j}\delta(\mathbf{r}_{ij})$
h^{OO}	Electron-electron orbital interaction	$\frac{1}{4}\alpha^2\sum'_{i,j}\frac{\nabla_i\cdot\nabla_j}{r_{ij}} - \frac{(\nabla_i\cdot\mathbf{r}_{ij})(\mathbf{r}_{ij}\cdot\nabla_j)}{r_{ij}^3}$
	Spin-dependence, no field-dependence	
	Electron spin	
$h^{\mathrm{SO}(1)}$	Spin-orbit interaction	$\frac{1}{4}\alpha^2 g_e\sum_{i,K}\frac{Z_K}{r_{iK}^3}\mathbf{s}_i\cdot\mathbf{l}_{iK}$
$h^{\mathrm{SSO}(2)}$	Electron-electron spin-orbit interaction	$-\frac{1}{4}\alpha^2 g_e\sum_{i,j}{}'\mathbf{s}_i\cdot\frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SOO}(2)}$	Electron-electron spin-other-orbit interaction	$-\frac{1}{2}\alpha^2 g_e\sum'_{i,j}\mathbf{s}_j\cdot\frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SSD}(2)}$	Spin-spin dipolar interaction	$\frac{1}{4}\alpha^2 g_e^2\sum'_{i,j}\frac{r_{ij}^2(\mathbf{s}_i\cdot\mathbf{s}_j)-(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{r}_{ij}\cdot\mathbf{s}_j)}{r_{ij}^5}$
$h^{\mathrm{SSC}(2)}$	Spin-spin contact interaction	$-\frac{\pi g_e^2}{3}\alpha^2\sum'_{i,j}\mathbf{s}_i\cdot\mathbf{s}_j\,\delta(\mathbf{r}_{ij})$
	Nuclear spin	
h_K^{PSO}	Orbital hyperfine interaction	$\alpha^2\gamma_K\sum_i\mathbf{I}_K\cdot\frac{\mathbf{l}_{iK}}{r_{iK}^3}$
	Electron and nuclear spins	
h_K^{SD}	Dipolar hyperfine interaction	$\frac{1}{2}\alpha^2 g_e\gamma_K\sum_i\mathbf{s}_i\cdot\frac{3\mathbf{r}_{iK}\mathbf{r}_{iK}-1r_{iK}^2}{r_{iK}^5}\cdot\mathbf{I}_K$
h_K^{FC}	Fermi contact hyperfine interaction	$\frac{4\pi}{3}\alpha^2 g_e\gamma_K\sum_i\delta(\mathbf{r}_{iK})\mathbf{s}_i\cdot\mathbf{I}_K$

From: Pekka Manninen PhD thesis, University of Oulo, Finland (2004).

http://herkules.oulu.fi/isbn9514274318/

Zero Field Splitting

In case: S > 1/2

$$\mathcal{H}_{\mathrm{ZFS}} = \frac{g_e\,\mu_B}{r^5}\left[\left(\mathbf{s}_1\cdot\mathbf{s}_2\right)r^2 - 3\left(\mathbf{s}_1\cdot\mathbf{r}\right)\left(\mathbf{s}_2\cdot\mathbf{r}\right)\right]$$

- Two electron integrals
- Usually small (?)
- Not implemented in Espresso

$$\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$$

g-tensor: the easy part

From the effective spin Hamiltonian, the g-tensor is defined as:

$$\overleftrightarrow{g} = \frac{2}{\alpha} \frac{\partial^2 \mathcal{H}}{\partial \mathbf{S} \partial \mathbf{B}}$$

The Zeeman and Zeeman-Kinetic Energy term yield:

$$\begin{aligned} \overleftrightarrow{g}_{\mathrm{Z}} &= g_e \overleftrightarrow{1} \\ \Delta \overleftrightarrow{g}_{\mathrm{Z-KE}} &= -\frac{g_e \alpha^2}{2} \left(\sum_{S=\pm 1/2} S \, T_S \right) \overleftrightarrow{1} \end{aligned}$$

Kinetic energy of occupied orbitals

g-tensor: SO and SOO

The SO and SOO don't depend explicitly on the magnetic field, but implicitly through the wavefunctions. Their contribution can be calculated in perturbation theory:

$$\begin{tikzcd} |\phi^{(0)}_{n\sigma}\rangle \arrow[r, "\text{DFPT to magn. field}"] & |\phi^{(1)}_{n\sigma}\rangle \arrow[r] & \mathbf{j}^{(1)}_{\sigma}(\mathbf{r}') \arrow[r, "\text{Biot-Savart}"] & \mathbf{B}^{(1)}_{\sigma}(\mathbf{r}') \\ \text{GS wfcs} & \text{perturbed wfcs} & \text{induced current} & \text{induced field} \end{tikzcd}$$

Finally:

$$\Delta \overset{\leftrightarrow}{g}_{\mathrm{SO}} = \alpha^2 g' \sum_{S=\pm 1/2} S \int d^3\mathbf{r}' \, \nabla V(\mathbf{r}') \times \overset{\leftrightarrow}{j}{}^{(1)}_{S}(\mathbf{r}')$$

$$\Delta \overset{\leftrightarrow}{g}_{\mathrm{SOO}} \simeq \alpha \sum_{S=\pm 1/2} S \int d^3\mathbf{r}' \, \overset{\leftrightarrow}{B}{}^{(1)}_{S}(\mathbf{r}')\rho_S(\mathbf{r}')$$

Converse approach to the g-tensor

$$\overleftrightarrow{g} \equiv \frac{2}{\alpha}\frac{\partial^2 E}{\partial \mathbf{S}\partial \mathbf{B}} = -\frac{2}{\alpha}\frac{\partial \mathbf{M}_{\mathrm{tot}}}{\partial \mathbf{S}} = \underbrace{g_e}_{2.002319\ldots}\overleftrightarrow{1} - \underbrace{\frac{2}{\alpha}\frac{\partial \mathbf{M}_{\mathrm{orb}}}{\partial \mathbf{S}}}_{\Delta g_{SO}}$$

- “Converse” method: $\partial M_{orb}/\partial S \approx 1/(2S)\,[M_{orb}(S=\uparrow) - M_{orb}(S=\downarrow)]$
- Modern Theory of the Orbital Magnetization
- GS calc. including Spin-Orbit; no magnetic field, no linear response
- Implemented in an experimental version of Espresso (ask me)

EPR of diatomic radicals

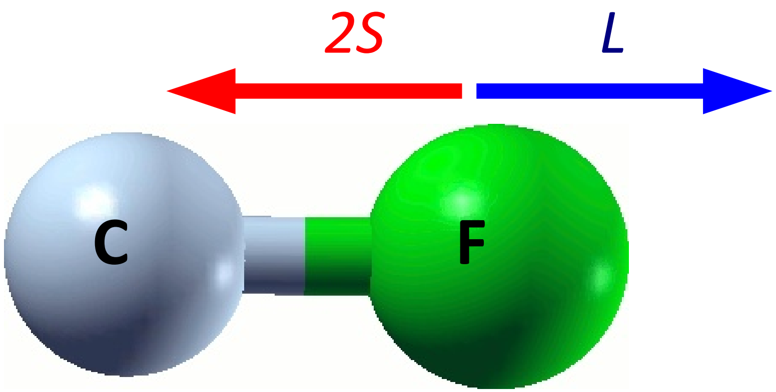
Molecule		Expt.	LR	This work
CN·	$g_{\parallel}$	2.0023	2.0022	2.0022
	$g_{\perp}$	2.0003	2.0002	2.0002
CF·	$g_{\parallel}$	0.0000	N/A	0.0002
	$g_{\perp}$	2.0002	2.0003	2.0003

L = 0

L = 1

LR = linear response

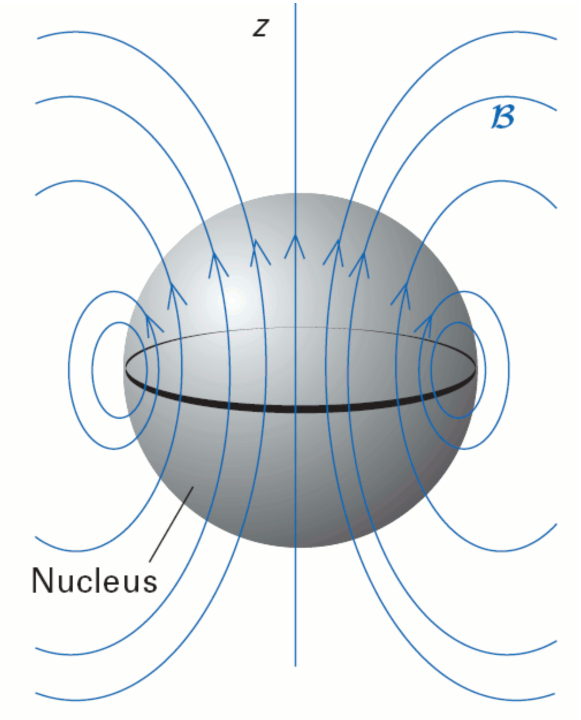
This work = converse method



Important when *g* very different from 2 (i.e. transition metals impurities)!

Hyperfine coupling

$$\overset{\leftrightarrow}{A}_R = \left\langle \frac{\partial^2 \mathcal{H}}{\partial \mathbf{S}\, \partial \boldsymbol{I}_R} \right\rangle = A_{\mathrm{iso,R}} \overset{\leftrightarrow}{1} + \overset{\leftrightarrow}{A}_{\mathrm{dip,R}}$$



Isotropic (Fermi-contact)

$$A_{\mathrm{iso}} = \frac{4\pi}{3} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \underline{\delta(\mathbf{r})}$$

$$\mathbf{r} \equiv \mathbf{r} - \mathbf{R}$$

Dipolar (traceless)

$$A^{\alpha\beta}_{\mathrm{dip}} = \frac{1}{2} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \frac{3r_\alpha r_\beta - \delta_{\alpha\beta} r^2}{r^5}$$

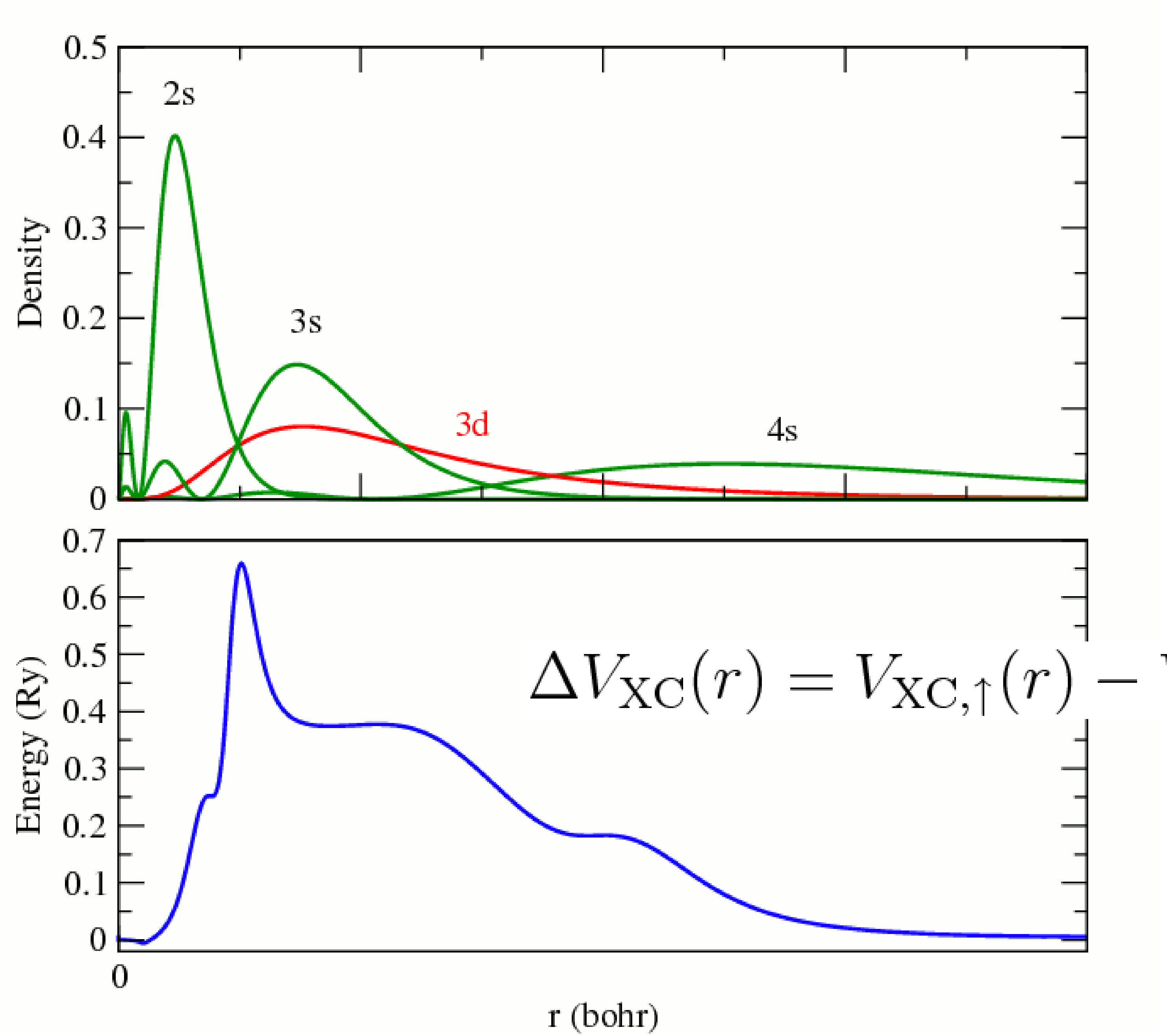
Spin density: $n_s(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$

Spin densities of isolated atoms

Atom	Configuration	1s	2s	3s	4s	Total
Li	2s(1↑,0↓)	0.003	0.219			0.222
C	$2s^2$ 2p(2↑,0↓)	-0.199	0.178			-0.021
N	$2s^2$ 2p(3↑,0↓)	-0.440	0.429			-0.011
O	$2s^2$ 2p(3↑,1↓)	-0.417	0.437			0.019
Na	3s(1↑,0↓)	0.019	-0.030	0.810		0.799
Si	$3s^2$ 3p(2↑,0↓)	-0.094	0.056	-0.193		-0.232
Mn	$4s^2$ 3d(5↑,0↓)	-0.008	-2.203	0.913	1.384	0.086
Mn^{+}	$4s^1$ 3d(5↑,0↓)	0.040	-2.215	0.833	7.194	5.852
Mn^{2+}	$4s^0$ 3d(5↑,0↓)	-0.018	-2.294	0.888	0.000	-1.424
Mn^{3+}	$4s^0$ 3d(4↑,0↓)	-0.018	-2.103	0.942	0.000	-1.179
Mn^{4+}	$4s^0$ 3d(3↑,0↓)	-0.017	-1.793	0.904	0.000	-0.907

- Calculated with *ld1.x*, extrapolated at the nucleus
- Spin-polarized LDA
- values in elec./bohr^3

Mn orbitals and ΔV_{xc}



$$\Delta V_{\mathrm{XC}}(r) = V_{\mathrm{XC},\uparrow}(r) - V_{\mathrm{XC},\downarrow}(r)$$

Core relaxation

- Project valence density around atoms and add GIPAW reconstruction

$$n_\sigma(r) = n_{\mathrm{val},\sigma}(r) + n_{\mathrm{rec},\sigma}(r), \qquad r < R_c$$

- Calculate ΔV_{XC} from projected spherical density

$$\Delta V_{\mathrm{XC}} = -\frac{2}{\pi} \frac{n_\uparrow - n_\downarrow}{(n_\uparrow + n_\downarrow)^{2/3}}$$

- Core spin density from Incomplete Perturbation Theory

$$n_{\mathrm{s,core}}(r) = 4 \sum_{u \in \mathrm{core}} \sum_{v \neq u} \frac{\langle \phi_{us} | \Delta V_{\mathrm{XC}} | \phi_{vs} \rangle}{\epsilon_{us} - \epsilon_{vs}} \phi_{us}(r) \phi_{vs}(r)$$

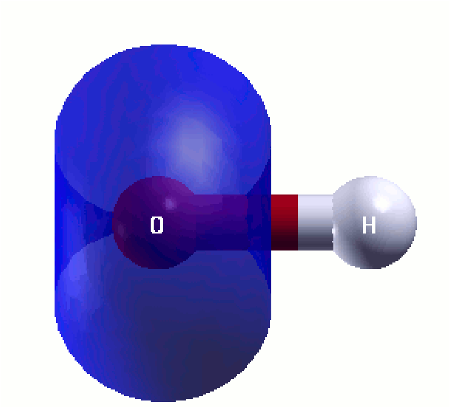
Available since GIPAW 5.4. Highly experimental!

Hyperfine couplings of 2nd row radicals

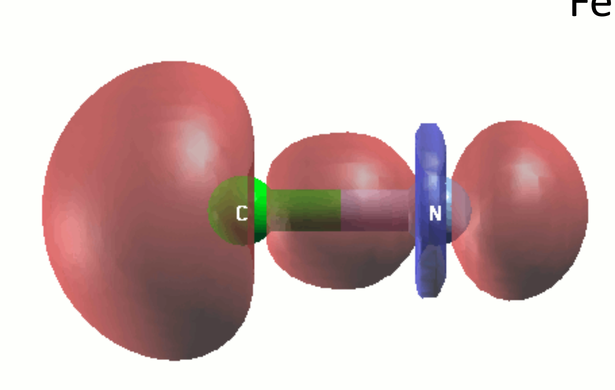
Molecule	Atom	no core relax	core relax	experiment
CH•	C	204	90	47
	H	-50	-50	-58
OH•	O	-142	-61	-45
	H	-56	-56	-73
CH_3•	C	210	122	107
	H	-69	-69	-70
CN•	C	636	581	588
	N	-7	-18	-13
H_2CN•	C	-73	-67	-81
	N	70	34	26
	H	230	230	234

Fermi contact (A_{iso}), values in MHz

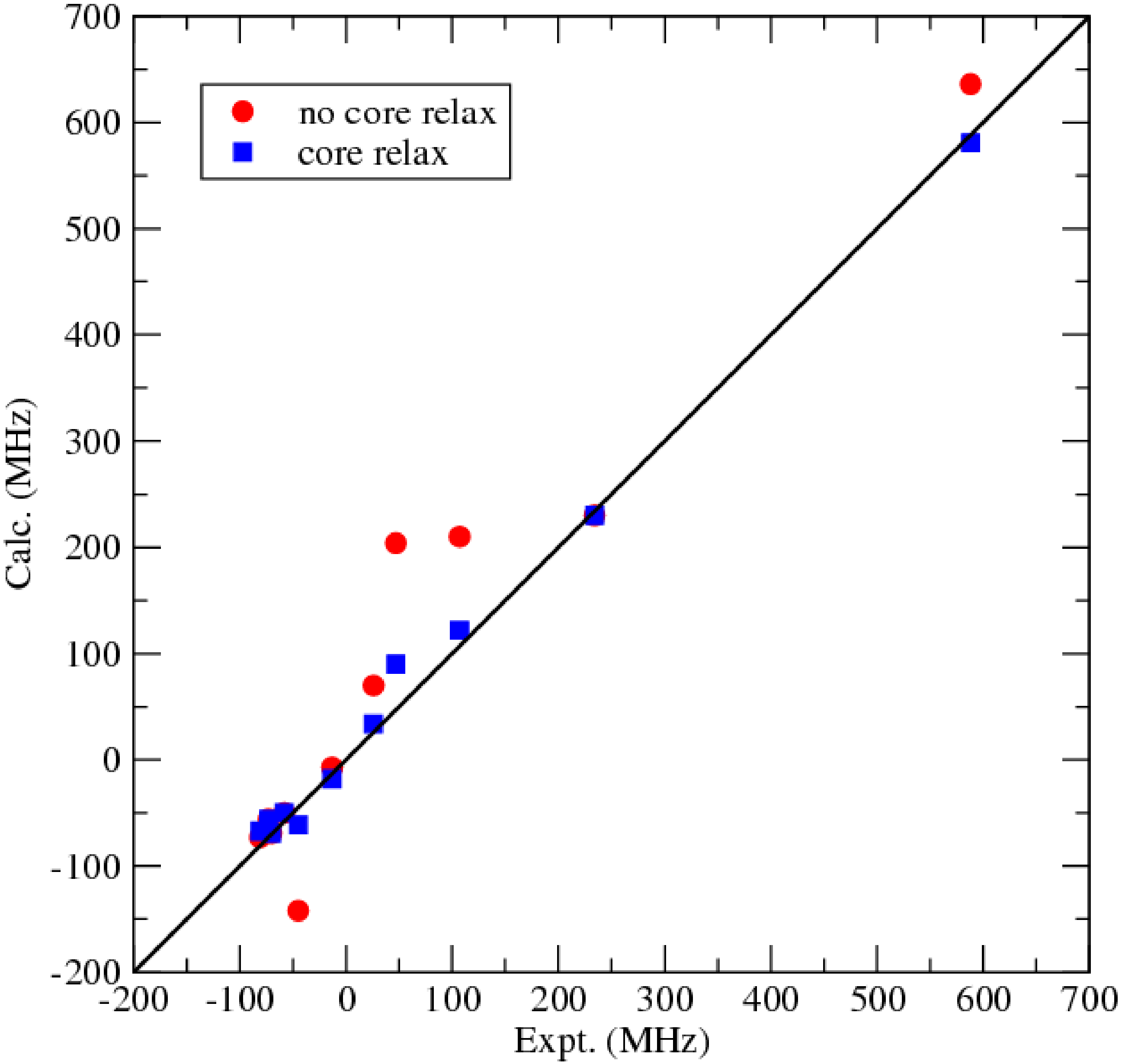
OH●



CN●

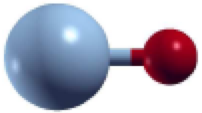


Hyperfine couplings of 2nd row radicals



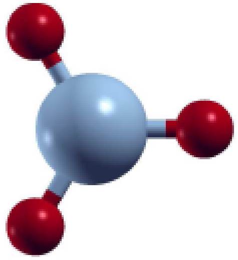
“Converse” EPR: DFT+U on MnO_x (x=1..3)

- Using experimental geometry (if unavailable, CCSD(T) geometry)
- Comparison only to available experimental data



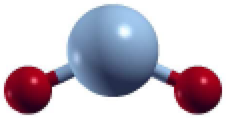
☺

MnO (S=5/2)	Aiso(Mn)	Aiso(O)
PBE	578	-8
PBE+Uscf	461	5
Expt. (MHz)	480	-8



☹

MnO_3 (S=1/2)	Aiso(Mn)	Aiso(O)
PBE	2058	197
PBE+Uscf	899	364
Expt. (MHz)	1613	81



☺

MnO_2 (S=3/2)	Aiso(Mn)	Adip(Mn)
PBE	836	-129
PBE+Uscf	665	-97
Expt. (MHz)	603	-126

Bibliography and references

Books

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- G. S. Rule and T. K. Hitchens, *Fundamentals of Protein NMR Spectroscopy*, Springer
- N. Jacobsen, *NMR spectroscopy explained*, Wiley
- M. Duer, *Solid state NMR spectroscopy*, Blackwell
- J. A. Weil and J. R. Bolton, *Electron Paramagnetic Resonance*, Wiley
- M. Knaupp, M. Bühl and V. G. Malkin, *Calculation of NMR and EPR Parameters*, Viley-VCH

Hamiltonians

The simplest Hamiltonian describing all the physics of NMR and EPR is the Dirac-Breit Hamiltonian. The DB Hamiltonian is fully relativistic (four-component) and difficult to solve. In order to make it numerically tractable, it must be reduced to a two-component non-relativistic Hamiltonian by some transformations and approximations.

Physicists apply the Foldy-Wouthuysen transformation to obtain the Pauli Hamiltonian. Chemists prefer the Douglas-Kroll-Hess transformation. Another popular approximation is the ZORA (zeroth-order regular approximation). These transformation lead to different expressions for the Hamiltonian terms, that are numerically very close.

- Pekka Manninen PhD thesis, University of Oulo, Finland (2004). http://herkules.oulu.fi/isbn9514274318/

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- S. Patchkovskii, R. T. Strong, C. J. Pickard and S. Un, J. Chem. Phys. **122**, 214101 (2005)

GIPAW and core-relaxation

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- M. S. Barhamy, M. H. F. Sluiter and Y. Kawazoe, Phys. Rev. B **76**, 035124 (2007)

Converse approach

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- T. Thonhauser, D. Ceresoli, A. A. Mostofi, N. Marzari, R. Resta and D. Vanderbilt, *A converse approach to the calculation of NMR shielding tensors*, JCP **131**, 101101 (2009)
- D. Ceresoli, N. Marzari, M. G. Lopez and T. Thonhauser, *Ab-initio converse NMR for pseudopotentials*, PRB **81**, 184424 (2010).

Modern Theory of the Orbital Magnetization

- T. Thonhauser, D. Ceresoli, D. Vanderbilt and R. Resta, *Orbital magnetization in periodic insulators*, Phys. Rev. Lett. **95**, 137205 (2005)
- D. Ceresoli, T. Thonhauser, D. Vanderbilt and R. Resta, *Orbital magnetization in crystalline solids: multi-band insulators, Chern insulators, and metals*, Phys. Rev. B **74**, 024408 (2006)
- I. Souza and D. Vanderbilt, *Dichroic f-sum rule and the orbital magnetization of crystals*, Phys. Rev. B **77**, 054438 (2008)

Online resources: blogs, codes, lectures

- NMR Wiki: http://nmrwiki.org
- Software: http://edunmrsoft.blogsome.com
- NMR periodic table:
  http://www.bruker-nmr.de/guide/eNMR/chem/NMRnuclei.html
- Solid state NMR literature blog: http://ssnmr.blogspot.com
- Other blogs:
  http://nmr-software.blogspot.com
  http://u-of-o-nmr-facility.blogspot.com
  http://scienceblogs.com/scientificactivist/2006/11/nmr_blogs.php

… and of course:
www.quantum-espresso.org
www.gipaw.net
http://qe-forge.org/projects/qe-gipaw

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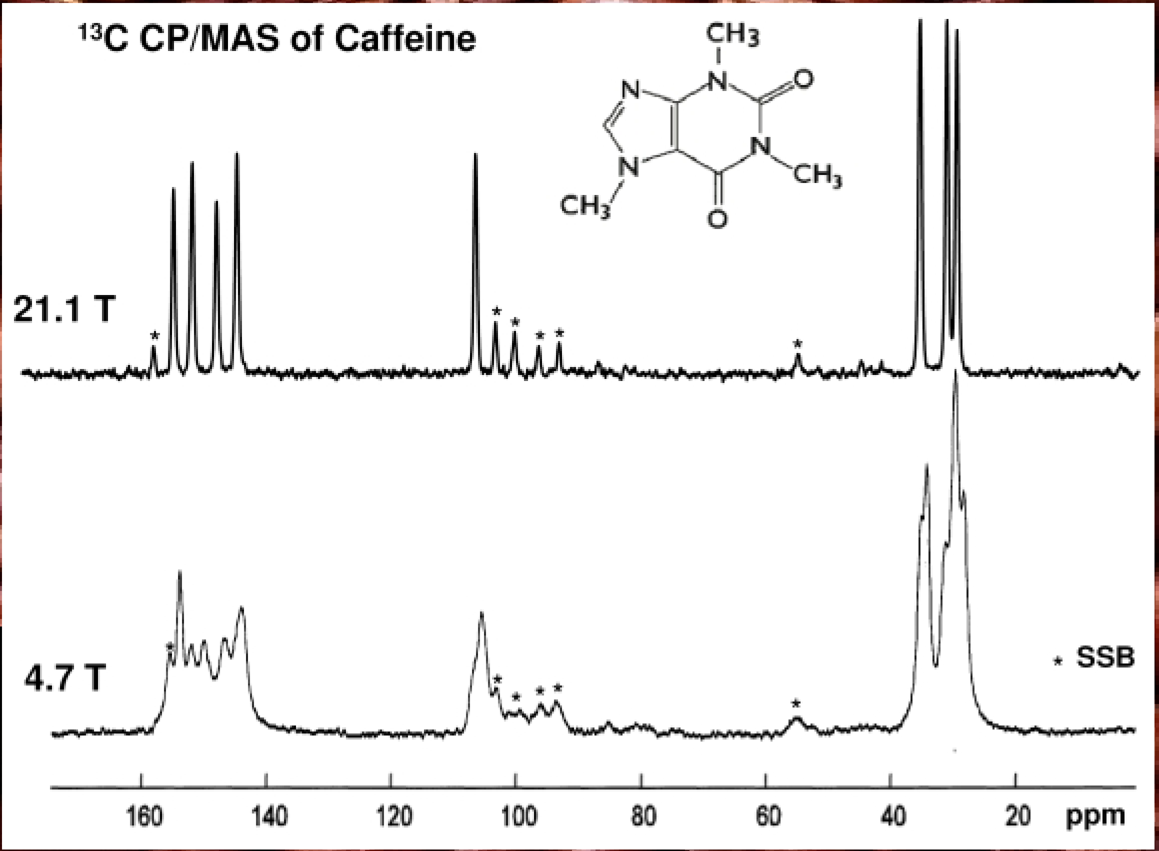
Thibault Charpentier
Carlo Nervi, Pietro Bonfà, Derek Middlemiss
GIPAW papers (Pickard, Yates, D'Avezac)
QE developers and supporters



^{13}C CP/MAS of Caffeine
CH$_3$
N
O
N
CH$_3$
N
N
CH$_3$
O
21.1 T
4.7 T
* SSB
160
140
120
100
80
60
40
20
ppm

illy
White Sugar

Extra slides

Five practical steps to NMR parameters

0 - Download and compile the code

1 - Write the input file

2 - Choose the proper pseudopotentials

3 - Get the ground state structure with PW

4 - Calculate NMR/EPR parameters with GIPAW

(5 - Simulate NMR/EPR spectra)

(6 - Publish on Science, win Nobel prize)

Step 0 – Download and compile

QE-GIPAW depends on PW code. To compile PW, you first need to configure QE, then to compile.
You need at least a UNIX-like environment (Linux, Mac OSX, Cygwin) and a working F90/F95 compiler.

Example:

```
cd espresso
```

(serial code, no blas/lapack installed)

```
./configure --disable-parallel --with-internal-blas --with-internal-lapack CC=gcc FC=gfortran \
F77=gfortran
```

(using Intel compiler, FFTW3 library path specified explicitely)

```
./configure CC=icc FC=ifort F77=ifort LIBDIRS=”/opt/fftw3/lib”
```

(assuming you have a working MPI library, compile MPI+OpenMP version with Scalapack)

```
./configure --enable-parallel --with-scalapack --enable-openmp
```

Optionally you might want to modify **make.sys** for fine tuning, and after that:

```
make pw pp
```

or

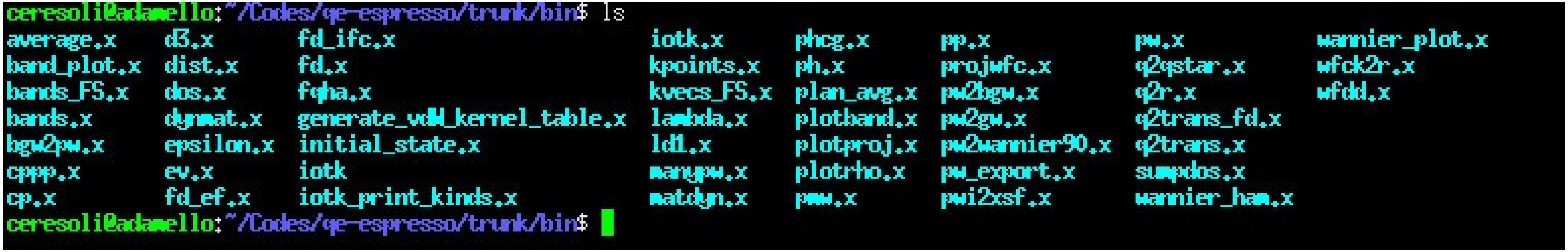
```
make all
```

Step 0 - Download and compile

If the previous compilation went well, now change into QE-GIPAW directory and:

cd GIPAW
./configure --with-qe-source=absolute_path_to_make.sys
make

The executables have the '.x' suffix and they will be placed into bin/ and GIPAW/bin/ directories



```
ceresoli@adamello:~/Codes/qe-espresso/trunk/bin$ ls
average.x    d3.x       fd_ifc.x                     iotk.x      phcg.x      pp.x            pw.x           wannier_plot.x
band_plot.x  dist.x     fd.x                         kpoints.x   ph.x        projwfc.x       q2qstar.x      wfck2r.x
bands_FS.x   dos.x      fqha.x                       kvecs_FS.x  plan_avg.x  pw2bgw.x        q2r.x          wfdd.x
bands.x      dynmat.x   generate_vdW_kernel_table.x  lambda.x    plotband.x  pw2gw.x         q2trans_fd.x
bgw2pw.x     epsilon.x  initial_state.x              ld1.x       plotproj.x  pw2wannier90.x  q2trans.x
cppp.x       ev.x       iotk                         manypw.x    plotrho.x   pw_export.x     sumpdos.x
cp.x         fd_ef.x    iotk_print_kinds.x           matdyn.x    pmw.x       pwi2xsf.x       wannier_ham.x
ceresoli@adamello:~/Codes/qe-espresso/trunk/bin$ 
```

```
ceresoli@adamello:~/Codes/qe-gipaw/trunk/bin$ ls
gipaw.x
ceresoli@adamello:~/Codes/qe-gipaw/trunk/bin$ 
```

1 - Write the input file

PW input file is composed of Fortran “namelists” followed by “cards”:

```
&control
    calculation = 'scf'                          !type of calculation: 'scf', 'relax',
                                                 !'vc-relax, 'nscf', 'bands'
    restart_mode = 'from_scratch'                !'from_scracth' or 'restart'
    prefix = 'betacrist'                         !basename for all binary files
    pseudo_dir = './pseudo/'                     !directory containing pseudopotentials
    outdir = './scratch/'                        !scratch directory for large binary files
    tstress = .true.                             !if .true., print stress tensor
    tprnfor = .true.                             !if .true., print forces
/
&system
    ibrav = 2                                    !see manual, ibrav=2 means fcc
    a = 7.1315                                   !conventional lattice spacing in Å
    nat = 6                                      !number of atoms
    ntyp = 2                                     !number of different atomic speciec
    ecutwfc = 35                                 !plane wave cutoff in Ry
    ecutrho = 350                                !density cutoff in Ry
    spline_ps = .true.                           !useful for NMR
/
&electrons
    diagonalization = 'david'                    !'davidson' (faster, more memory) or 'cg'
    diago_thr_init = 1e-4                        !eigenvalue accuracy at first diagonalization
    mixing_mode = 'plain'
    mixing_beta = 0.7                            !0.3-0.7 in insulators, <0.1 in metals
    conv_thr = 1e-10                             !SCF accuracy
/
```

continued on the next slide...

1 - Write the input file

continuing from the previous slide...

```
ATOMIC_SPECIES
Si   28.086   Si.pbe-tm-new-gipaw-dc.UPF            !atom mass pseudopotential
O    15.999   O.pbe-rrkjus-gipaw-dc.UPF

K_POINTS automatic
4 4 4 0 0 0                                         !4x4x4 not-shifted Monkhorst-Pack mesh

ATOMIC_POSITIONS alat                               !alat=cartesian in units of 'a'
Si       0.000000000  0.000000000  0.000000000      !other possibilities: crystal (=fractional)
Si       0.250000000  0.250000000  0.250000000      !or angstrom (=cartesian, in Å)
O        0.075458128  0.174541872  0.125000000
O        0.424541872  0.325458128  0.125000000
O        0.174541872  0.424541872  0.375000000
O        0.325458128  0.075458128  0.375000000
```

1 - Write the input file

- One of the most common source of misunderstanding is how to enter the crystal cell parameters
- Two possibilities: choose a Bravais lattice or enter cell vectors manually

Bravais lattices supported by QE (ibrav != 0):

ibrav=1	simple cubic
ibrav=2	cubic F (fcc)
ibrav=3	cubic I (bcc)
ibrav=4	hexagonal or trigonal P
ibrav=-5,5	trigonal R (two settings)
ibrav=6	tetragonal P
ibrav=7	tetragonal I (bct)
ibrav=8	orthorhombic (P)
ibrav=-9,9	base-centered orthorhombic (two settings)
ibrav=10	face-centered orthorhombic
ibrav=11	body-centered orthorhombic
ibrav=-12,12	monoclinic P (two settings)
ibrav=13	base-centered monoclinic
ibrav=14	tricilinic

Please, check the settings (axis) and cell vectors in **PW/Doc/INPUT_PW.def**

1 - Write the input file

If there is a Bravais lattice suitable for your input, then enter the lattice parameters in the namelist &system:

Using Bohr atomic units:
celldm(1) = a
celldm(2) = b/a
celldm(3) = c/a
celldm(4) = cos(see INPUT_PW.def)
celldm(5) = cos(see INPUT_PW.def)
celldm(6) = cos(see INPUT_PW.def)

Using Angstrom units:
a = a
b = b
c = c
cosAB = cos(*gamma*)
cosAC = cos(*beta*)
cosBC = cos(*alpha*)

Otherwise, if there is no default lattice matching your crystal structure, set **ibrav=0** and add the following card:

```
CELL_PARAMETERS [angstrom|bohr]
a_x  a_y  a_z
b_x  b_y  b_z
c_x  c_y  c_z
```

1 - Write the input file

Finally, enter the atomic coordinates in the ATOMIC_POSITIONS card:

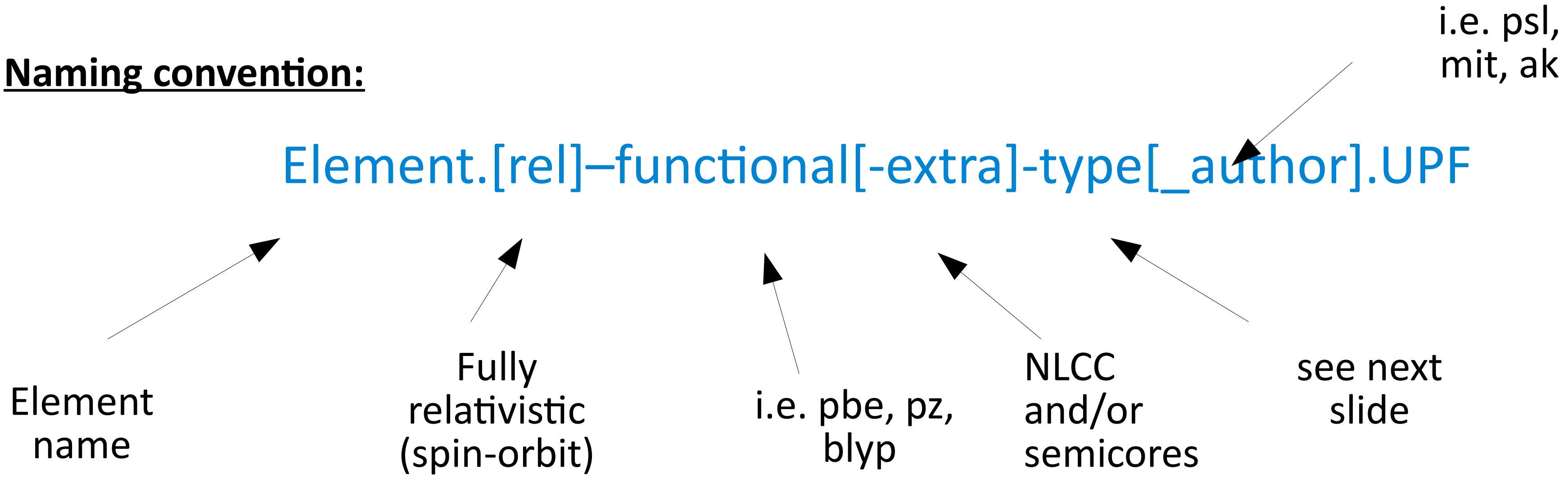
```
ATOMIC_POSITION [bohr|angstrom|alat|crystal]
atom  coord coord coord
…
…
```

- The keywords **bohr**, **angstrom** and **alat** mean that the coordinates are cartesian and in units of, respectively bohr, angstrom, a (the length of the first lattice parameter).
- Otherwise, the **crystal** keyword allows you to enter fractional coordinates (i.e. from a CIF file)
- There is no automatic symmetry generation, you must enter all atoms in the unit and not just the asymmetric unit

2 – Choose pseudopotentials

- For GIPAW calculations you need GIPAW or PAW pseudopotentials
- For sake of clarity, I will illustrate all kinds of pseudopotentials you can find
- The recommended format is UPF (v1 or v2), which is text based. Other formats are deprecated (and probably unsupported)

Naming convention:



Element.[rel]–functional[-extra]-type[_author].UPF

i.e. psl, mit, ak

Element name

Fully relativistic (spin-orbit)

i.e. pbe, pz, blyp

NLCC and/or semicores

see next slide

For example:
Fe.pw91-sp-van_ak.UPF
Fe.rel-pbe-spn-kjpaw_psl.0.2.1.UPF

2 – Choose pseudopotential

Three PP types are supported in QE, and can be mixed:

- Norm conserving (NCPP)

tm = Troullier-Martins	many elements, well tested
rrkj = Rappe-Rabe-Kaxiras-Johannopulos	few elements
vbc = Van Barth-Car	few elements
hgh = Hartwigsen-Goedecker-Hütter	most elements, high cutoff
fhi = converted from FHI table of pseudopotentials	most elements, well tested?

- Ultrasoft (USPP)

van = Vanderbilt	well tested, _ak with problems?
rrkjus = Rappe-Rabe-Kaxiras-Johannopulos ultrasoft	well tested, low cutoff

- PAW

kjpaw = Kresse-Joubert	I don't have much experience

  - there is no official naming for pseudos generated by atompaw (N. Holzwarth)

2 – Choose pseudopotential

- Slightly different naming convention for GIPAW pseudos, sorry!

Element.functional-type[-semi]-gipaw[-new]-author.UPF

semicore states

“old” are similar to
Paratec pseudos

- PAW-GIPAW pseudos generated by atompaw, are marked by '-nh' as author

<u>For example:</u>
O.pbe-tm-gipaw-new-dc.UPF
C.pbe-rrkjus-gipaw-dc.UPF
K.pbe-tm-semi-gipaw-xy.UPF
Fe.pbe-paw-gipaw-nh.UPF

<u>Beware:</u>
gipaw pseudopotentials found on www.quantum-espresso.org are for XANES core-hole calculations, not for NMR/EPR!

2 – Choose pseudopotential

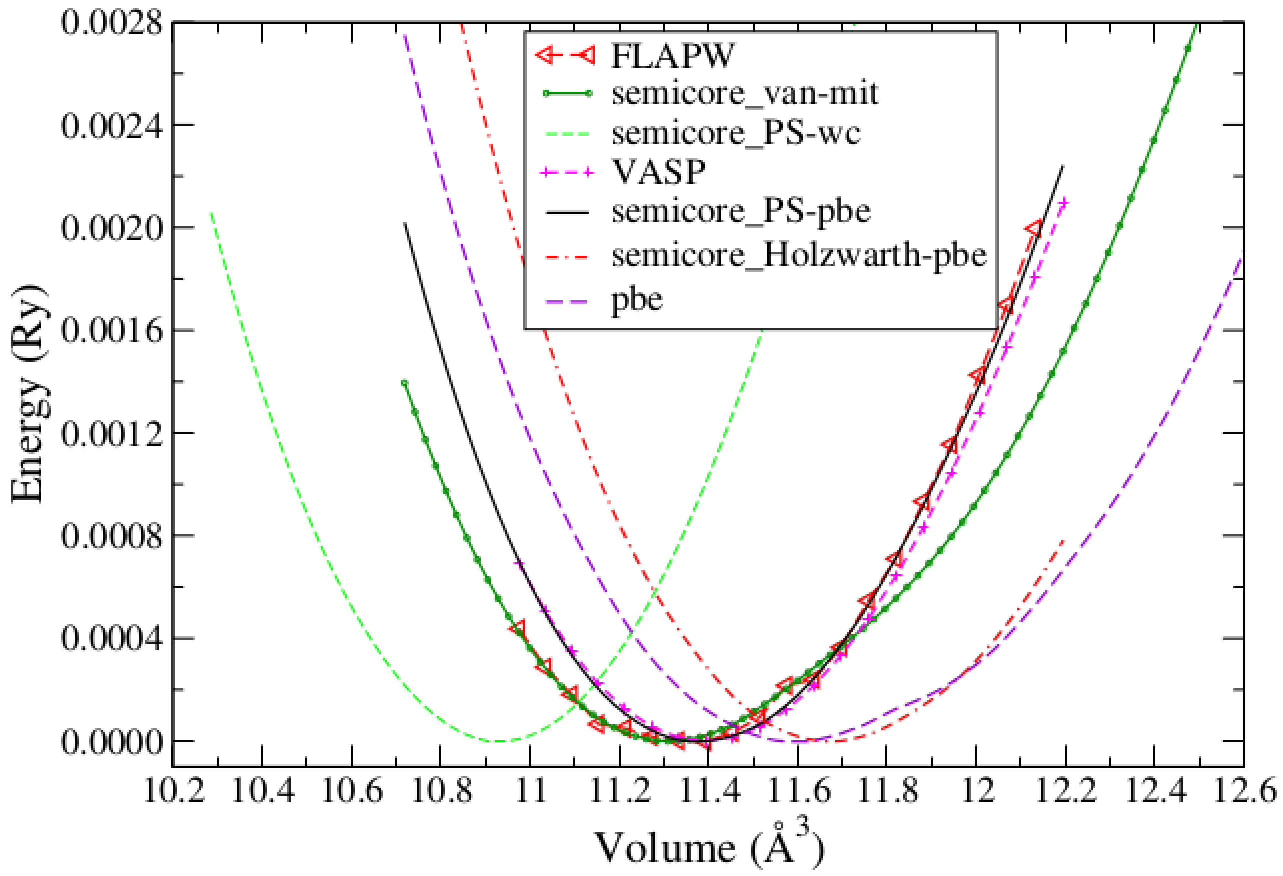
Pseudopotential sources (incomplete):

- www.quantum-espresso.org/pseudopotentials (QE official pseudos)
- sites.google.com/site/dceresoli/pseudopotentials (D. Ceresoli)
- www.impmc.jussieu.fr/~software/gipaw/pseudopotentials.html (A. Seitsonen)
- qe-forge.org/gf/project/pslibrary (A. Dal Corso)
- users.wfu.edu/natalie/papers/pwpaw/newperiodictable (N. Holzwarth)
- www.physics.rutgers.edu/gbrv (for high-trhoughput calculations)
- www.nnin.org/research-support/computation/nnin-computation-nanotechnology-resources/virtual-vaults (searchable database, many formats, many codes)
- did I miss someone?

2 - Choose pseudopotential

Fe bcc ferromagnetic, equation of state, courtesy of D. Dragoni (EPFL)

semicore_PS is from pslibrary, however cutoff is 100 Ry

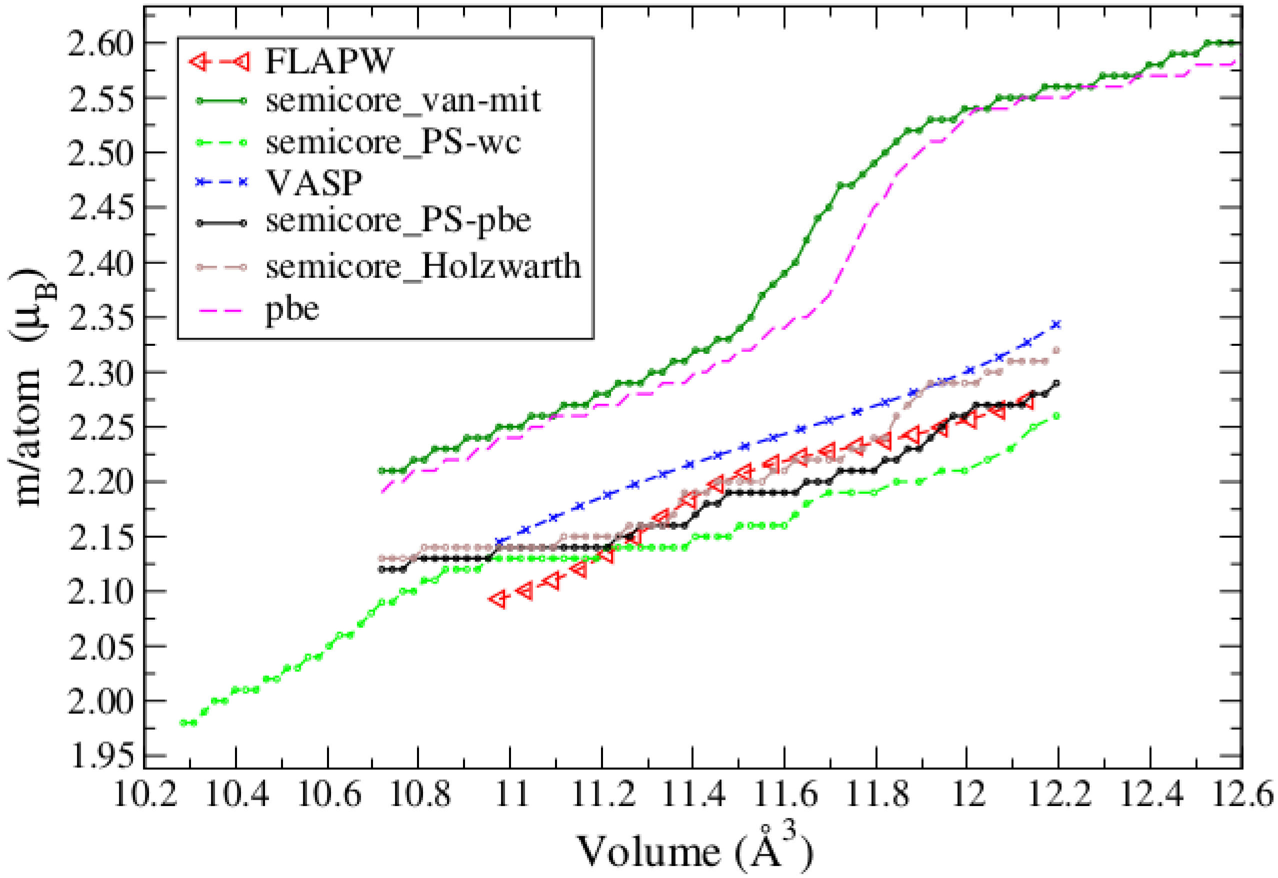


pbe is the “old” Fe.pbe-nd-rrkjus.UPF: not convex

Figure 9: E vs. V comparison of QE ($24\times24\times24$, smearing of 0.001 Ry), VASP and all-electron calculations. Different QE pseudopotentials are used while for VASP there is a single one. The ewfc cutoff varies according to the pseudopotential considered (60 Ry for the standard pbe and the semicore_van-mit while 100 Ry for the others.)

2 - Chose pseudopotential

semicore_PS is from pslibrary, however cutoff is 100 Ry



pbe is the “old” Fe.pbe-nd-rrkjus.UPF: jump in magnetization

Figure 10: M vs. V comparison of QE ($24\times24\times24$, smearing of 0.001 Ry), VASP and all-electron calculations. Details as in Fig. 9)

3 - Ground state and relaxation

- Now you are ready to obtain the ground state wavefunctions and/or relax the structure with PW
- You can relax positions and cell parameters simultaneously
- You can constrain atom positions, bonds, angles, cell shape, …
- More details during the afternoon lab

Running PW:

(in serial)

```
/path/to/pw.x <betacrist-scf.in >betacrist-scf.out &
```

(in paralllel, maybe in a job script)

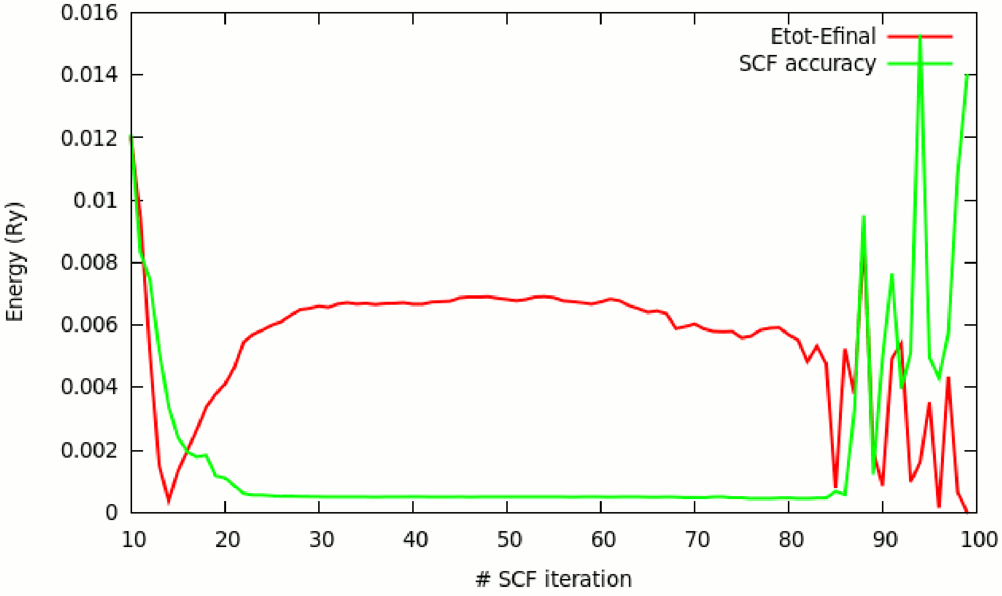
```
mpirun -np 8 /path/to/pw.x -npool 4 -ndiag 1 <betacrist-scf.in >betacrist-scf.out
```

(the most crazy line I've used, on Fermi)

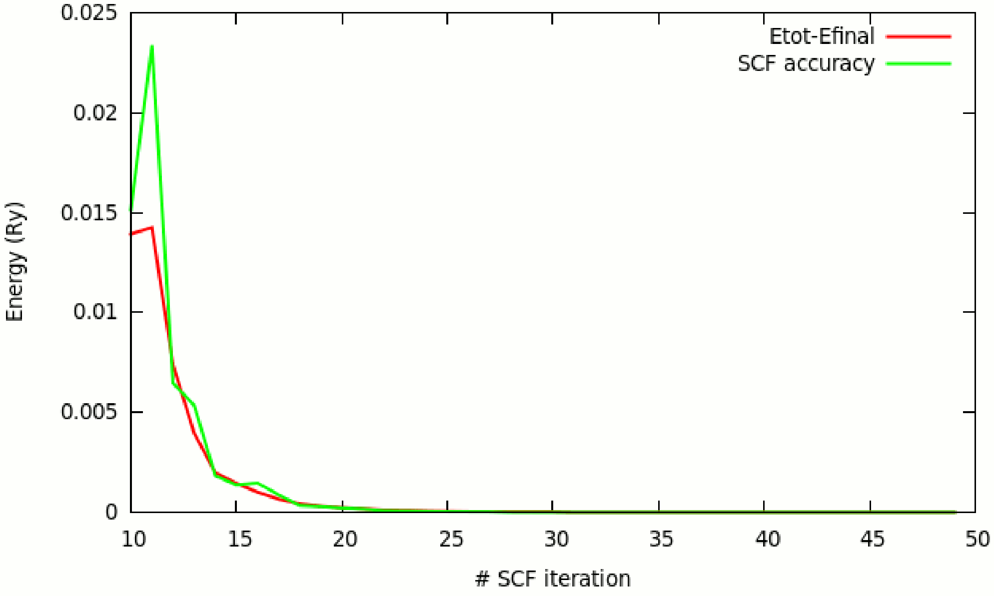
```
runjob --ranks-per-node 8 --np 2048 --envs OMP_NUM_THREADS=4 : pw.x -ndiag 16 -npool 4
-ntg 8  <Al-Al2O3-slab300atom-run09-vcmd.in >Al-Al2O3-slab300atom-run09-vcmd.out
```

3 - Ground state and relaxation

Provided that planewave cutoff and k-point mesh are sufficiently converged, the most important quantities to monitor during SCF or relaxation are: **total energy** and **SCF accuracy**



problematic convergence



fast, good convergence

In SCF convergence is problematic, maybe the system is a metal, or has a small bang gap. In that case, set: **occupations='smearing'**, **degauss=0.01** (in Ry), and reduce **mixing_beta** to 0.1 or smaller

4 - Calculate NMR/EPR parameters

- After having obtained the ground state, you can run GIPAW
- GIPAW input is much shorter and keywords have reasonable default values
- Here is an example to compute **NMR shielding tensors**

```
&inputgipaw
    job = 'nmr'                         ! for NMR shielding
    prefix = 'betacrist'                ! same as in PW input
    tmp_dir = './scratch/'              ! same as in PW input
    isolve = 0                          ! diagonalization, 0 or 1
    iverbosity = 1                      ! increase for more details
    q_gipaw = 0.01                      ! the small “q”
    spline_ps = .true.                  ! same as in PW input
    use_nmr_macroscopic_shape = .true.  ! consider sample macroscopic shape
/
```

Finally, you can run GIPAW in a similar fashion to PW:

(serial)
/path/to/gipaw.x <betacrist-nmr.in >betacrist-nmr.out

(parallel)
mpirun -np 8 /path/to/gipaw.x -ndiag 1 -npool 4 <betacrist-nmr.in >betacrist-nmr.out

4 - Calculate NMR/EPR parameters

The most important quantities in output are: f-sum rule, susceptibility and total sigmas:

```
     f-sum rule (should be   -30.7178):
           -30.7050         -0.0000          0.0000
             0.0000        -30.7050          0.0000
             0.0000         -0.0000        -30.7048
```

very important: to be fulfilled as much as possible!

```
     chi_bare pGv (HH) in 10^{-6} cm^3/mol:
           -44.2541          0.0000          0.0000
             0.0000        -44.2541          0.0000
             0.0000          0.0000        -44.5654

     chi_bare vGv (VV) in 10^{-6} cm^3/mol:
           -42.8223         -0.0000          0.0000
             0.0000        -42.8223          0.0000
            -0.0000          0.0000        -43.0973
```

the true magnetic susceptibility is in this range

```
     Total NMR chemical shifts in ppm: ---------------------------------------
     (adopting the Simpson convention for anisotropy and asymmetry)-----------

...

    Atom  3  O   pos: (  0.075458  0.174542  0.125000)  Total sigma:         225.13
```

isotropic in ppm

```
           223.7763         26.8036         31.1766
            26.8036        223.7763         31.1766
            32.1875         32.1875        227.8282
```

shielding tensor

```
     O    3    anisotropy:     90.46    eta:   -0.0663
```

Simpson convention

```
     O    3    sigma_11=  196.9727    axis=(  0.707107 -0.707107  0.000000)
     O    3    sigma_22=  192.9773    axis=(  0.434141  0.434141 -0.789331)
     O    3    sigma_33=  285.4309    axis=(  0.558142  0.558142  0.613967)
```

principal axes

4 - Calculate NMR/EPR parameters

To calculate electric field gradient (**EFG**), you must provide the nuclear quadrupole in **10^{-30} m^2**:

```
&inputgipaw
    job = 'efg'
    prefix = 'tobermorite11'
    tmp_dir = './scratch/'
    iverbosity = 1
    spline_ps = .true.
    Q_efg(1) = -4.44      ! 43Ca
    Q_efg(2) = 1.0        ! fake for Si
    Q_efg(3) = -2.55      ! 17O
    Q_efg(4) = 1.0        ! fake for H
/
```

In the output, you can find Cq, eta and principal axes:

```
     NQR/NMR SPECTROSCOPIC PARAMETERS:
     Ca   1    Vxx=   -0.0229    axis=(  0.788473  0.612926  0.051306)
     Ca   1    Vyy=   -0.1861    axis=( -0.609218  0.789729 -0.071989)
     Ca   1    Vzz=    0.2090    axis=( -0.084641  0.025505  0.996085)
     Ca   1    Q=-4.44 1e-30 m^2    Cq=  -2.1806 MHz    eta= 0.78044
```

4 - Calculate NMR/EPR parameters

To calculate the **EPR g-tensor**, your system must be spin polarized. The input file is similar to that for NMR shieldings:

```
&inputgipaw
        job = 'g_tensor'
        prefix = 'h2cn'
        tmp_dir = './scratch/'
        isolve = 0
        iverbosity = 1
        q_gipaw = 0.01
        spline_ps = .true.
        use_nmr_macroscopic_shape = .false.
/
```

In output, the deviation **Δg** in ppm from 2.002319... is (there are two different ways to compute the spin-other-orbit contributions):

```
     Delta_g total (SOO a la Paratec): ---------------------------------------
          3104.68          0.00          0.00
             0.00        -82.23          0.00
             0.00          0.00      -1925.19

     Delta_g total (SOO as in Eq.(7)): ---------------------------------------
          3195.44          0.00          0.00
             0.00        -66.90          0.00
             0.00          0.00      -1935.92
```

4 - Calculate NMR/EPR parameters

Likewise, to compute EPR **hyperfine couplings** you must provide the **nuclear g-factor** for each atomic specie:

```
&inputgipaw
        job = 'hyperfine'
        prefix = 'h2cn'
        tmp_dir = './scratch/'
        spline_ps = .true.
        iverbosity = 11
        hfi_output_unit = 'MHz'                ! 'MHz' or 'G'
        hfi_nuclear_g_factor(1) = 1.404844     ! 13C
        hfi_nuclear_g_factor(2) = 0.40376087   ! 15N
        hfi_nuclear_g_factor(3) = 5.585694     ! 1H
/
```

In output you can find the dipolar and Femi contact in the chosen units:

```
     ----- total dipolar (symmetrized) -----
     C    1      -18.889103       0.000000      -0.000001
     C    1        0.000000       2.676450       0.000001
     C    1       -0.000001       0.000001      16.212653
…

     ISOTROPIC (FERMI-CONTACT) COUPLINGS WITHOUT ZORA:
     Warning: core-relaxation is an experimental feature
                bare              GIPAW              core-relax        total
     C    1       -1.471958      -71.844171         -0.494637        -73.810766
     N    2        1.158516       68.877881        -33.425295         36.611101
     H    3      133.194574       96.213231          0.000000        229.407804
     H    4      133.194577       96.213234          0.000000        229.407811
```

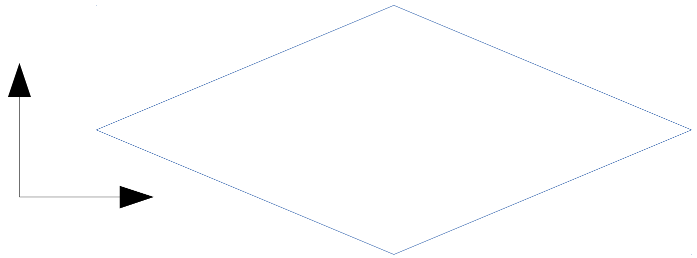
Troubleshooting

E: Error reading pseudopotential

S: open the UPF files with a text editor, locate the PP_PAW_VERSION and PP_PAW_GIPAW_VERSION sections, and change the number therein (0.1 or 1.0) to 1

E: Very strange NMR shielding or EPR g-tensor, not respecting crystal symmetry, especially for hexagonal systems

S: GIPAW is incompatible with symmetry operation that do not map cartesian axes into cartesian axes. Orient the hexagonal cell like this, or disable symmetry in SCF (nosym=.true. in &system)



E: Cell parameters relaxation stops with error: non orthogonal operation

S: The symmetry of you system is changing, disable it (nosym=.true.)

E: Difficult SCF convergence, crazy results, atoms too close

S: Check the crystal structure with Xcrysden: xcrysden --pwi betacrist-scf.in

Troubleshooting

E: Error computing Cholesky...
S: Did you compile with SCALAPACK? if not the default CAVAPACK(*) routines are very sensitive to numerical noise. Re-configure espresso with: --with-scalapack
Still not working? some versions of MKL are reported to be broken. Disable parallel diagonalization with '-ndiag 1' on the command line

E: compute_u_kq, some eigenvectors not converged
S: try to change isolve (from 0 to 1 or viceversa) in GIPAW

E: error in davcio, if you use a different number of CPUs between PW and GIPAW
S: add wf_collect=.true. in PW &control namelist

E: task groups not supported
S: this will be fixed in the next GIPAW release

E: GIPAW says: cgsolve_all: root not converged
S: maybe your system is metallic, or with a small band gap. Metallic systems, including the Knight shift term will be supported in the next GIPAW release

(*) parallel linear algebra routines by C. Cavazzoni