

Analyzing nuclear magnetic shielding, nuclear spin-spin coupling, and EFG tensors

Jochen Autschbach

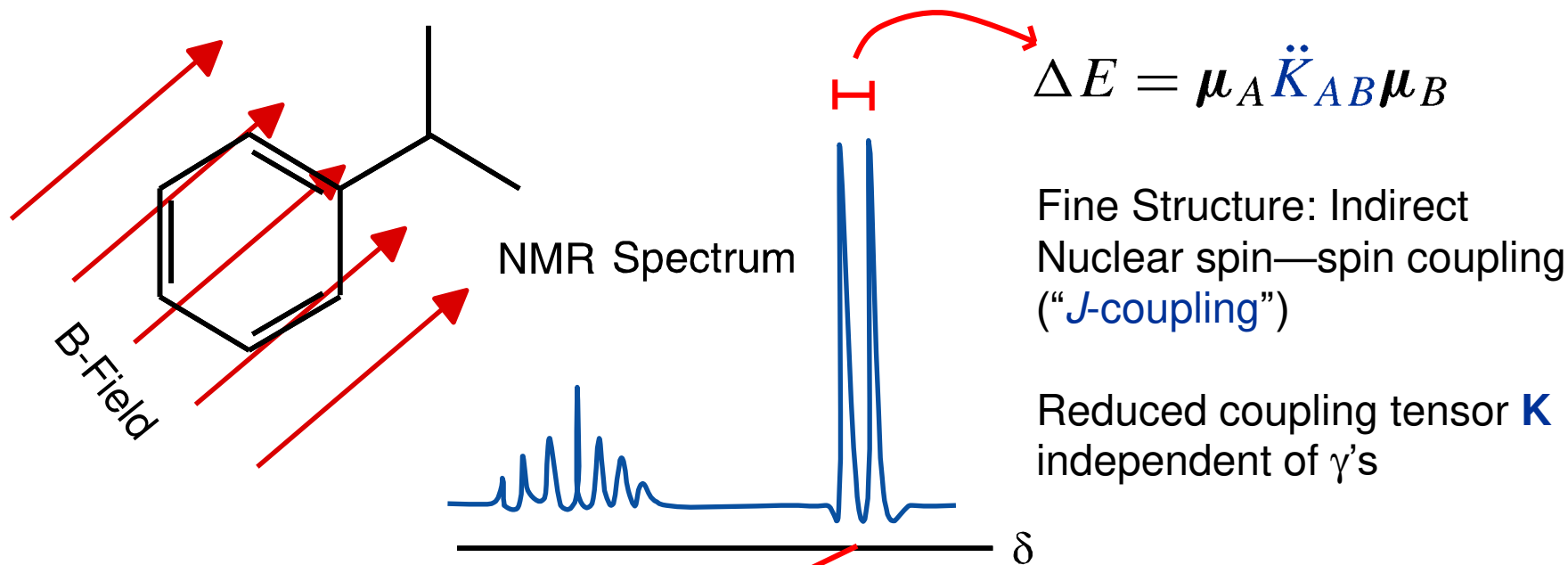
University at Buffalo, State University of New York

jochena@buffalo.edu

Webinar hosted by SCM, June 2023

- NBO / NLMO analysis of NMR shielding & J-coupling
- NBO analysis of EFG tensors

- NBO / NLMO analysis of NMR shielding & J-coupling
- NBO analysis of EFG tensors



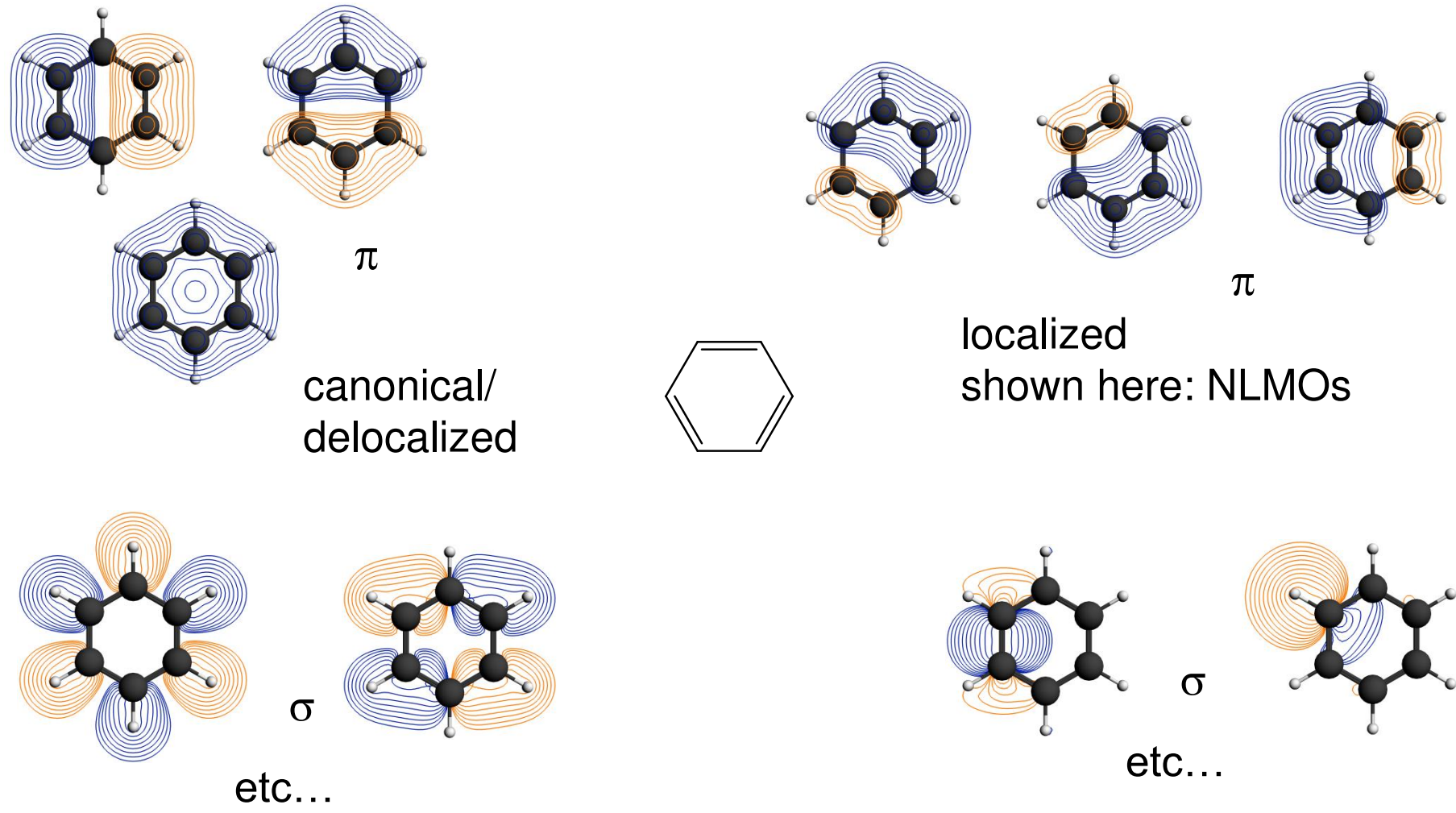
Chemical shift $\delta_A = \sigma_A^{\text{ref}} - \sigma_A^{\text{probe}}$

$$\Delta E = -\mu_A (1 - \ddot{\sigma}_A) \mathcal{B}$$

From theory:

$$\ddot{\sigma}_A = \left. \frac{d^2 E}{d\mu_A d\mathcal{B}} \right|_{\substack{\mu_A=0 \\ \mathcal{B}=0}} ; \quad \ddot{K}_{AB} = \left. \frac{d^2 E}{d\mu_A d\mu_B} \right|_{\substack{\mu_A=0 \\ \mu_B=0}}$$

NMR parameters, EFG, and many other properties depend on **local** features of the electronic structure
⇒ use a **localized** description for analysis



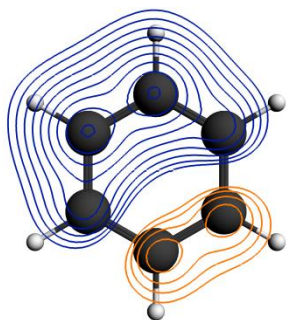
NLMO

=

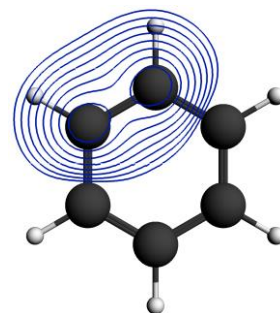
$a_{j,j}$ NBO

+

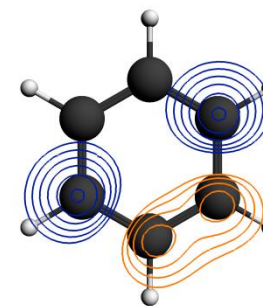
delocalization
tail



=



+



ϕ_j^{NLMO}

=

$\Omega_j a_{j,j}$

+

$$\sum_{n=j}^{\text{NBO}} \Omega_n a_{n,j}$$

Localized
“Lewis” (L)

Not Localized
“Non-Lewis” (NL)

(here, $a_{j,j} = 0.83$)

Nonrelativistic NBO analysis for nuclear shielding (with GIAOs):
Bohman et al., JCP 104 (1997), 1173

Nonrelativistic NBO analysis for FC term of J-coupling (finite-field):
Wilkins et al., JACS 123 (2001), 12026

Missing features (ca. 2007):

- a) Analysis for all NMR nuclei (light and heavy)
- b) J-coupling with analytic derivatives, incl. all terms
- c) General relativistic treatment (incl. spin-orbit coupling)
- d) EFG analyses

See also:

J-coupling analyses (using analytic derivatives), JA et al.:
JACS 125 (2003), 1028 (ADF's FOs)
Magn. Res. Chem. 42 (2004), S99 (FOs, Boys LMOs)
J. Chem. Educ. 84 (2007), 156 (FOs, Boys LMOs)

Cremer et al.,
JCP (many)

Analysis features for molecular properties
(presently in the ADF code) in terms of:

- NBOs/NLMOs (today's topic)
- Canonical (regular) MOs and MO energies
- Boys Localized MOs
- “Property density” functions (spatial contributions)

Based on DFT computations applicable to elements from all over
the periodic table (ZORA relativistic approach, scalar or spin-orbit)

Examples chosen from our work on heavy atom NMR

How do we do this for two-component orbitals?

(NBO 5.0 has ~ 30k lines of code, re-write for two-component orbitals is undesirable)

⇒ Analyze property in terms of scalar relativistic orbitals

$$\vec{\Phi}_i = \sum_{\mu}^{\text{AO}} \chi_{\mu} \vec{E}_{\mu,i} = \sum_{\mu}^{\text{AO}} \chi_{\mu} \begin{pmatrix} E_{\mu,i}^{\alpha} \\ E_{\mu,i}^{\beta} \end{pmatrix}$$

two-component MOs

$$\varphi_k^{\text{MO}} = \sum_{\mu}^{\text{AO}} \chi_{\mu} C_{\mu,k}$$

scalar relativistic MOs (“external”)

we write:

$$\vec{\Phi}_i = \sum_k^{\text{ext}} \varphi_k \vec{Q}_{k,i}$$

$$\Rightarrow \vec{Q} = \mathbf{C}^{\dagger} \mathbf{S} \vec{E}$$

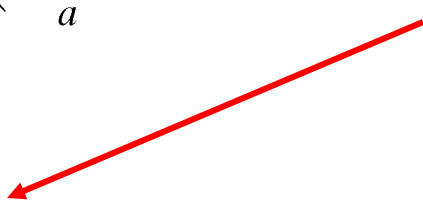
$$\Rightarrow \mathbf{C} = \mathbf{B} \mathbf{W} \mathbf{T}$$

Second-derivative property:

$$P^{(1,1)} = 2 \operatorname{Re} \sum_i^{\text{occ}} \sum_a^{\text{unocc}} h_{i,a}^{(0,1)} A_{a,i}^{(1,0)} + \sum_i^{\text{occ}} h_{i,i}^{(1,1)}$$

$$P^{(1,1)} = \sum_j^{\text{NLMO}} \sum_n^{\text{NBO}} \sum_i^{\text{occ}} \sum_k^{\text{ext MO}} \sum_r^{\text{AO}} \sum_s^{\text{AO}} \sum_{\gamma,\gamma'}^{\text{spin}} \left\{ 2 \operatorname{Re} \left[Q_{k,i}^{\gamma*} h_{r,s}^{(0,1),\gamma,\gamma'} \right. \right. \\ \left. \left. \times \sum_a^{\text{unocc}} E_{s,a}^{\gamma'} A_{a,i}^{(1,0)} \right] + Q_{k,i}^{\gamma*} h_{r,s}^{(1,1),\gamma,\gamma'} E_{s,i}^{\gamma'} \right\} \cdot [B_{r,n} \ W_{n,j} \ T_{j,k}]$$

$$P^{(1,1)} = \sum_j^{\text{NLMO}} \sum_n^{\text{NBO}} \sum_i^{\text{occ}} \sum_k^{\text{ext MO}} \sum_r^{\text{AO}} \sum_s^{\text{AO}} \sum_{\gamma, \gamma'}^{\text{spin}} \left\{ 2 \operatorname{Re} \left[Q_{k,i}^{\gamma*} h_{r,s}^{(0,1), \gamma, \gamma'} \right. \right. \\ \left. \left. \times \left(\sum_a^{\text{unocc}} E_{s,a}^{\gamma'} A_{a,i}^{(u,0)} + \sum_l^{\text{occ}} E_{s,l}^{\gamma'} A_{l,i}^{(u,0)} \right) \right] + Q_{k,i}^{\gamma*} h_{r,s}^{(1,1), \gamma, \gamma'} E_{s,i}^{\gamma'} \right\} \cdot [B_{r,n} \ W_{n,j} \ T_{j,k}]$$



$$A_{k,i}^{(u,0)} = -\frac{1}{2} \mathcal{S}_{k,i}^{(u,0)} \quad k, i \in \text{occ}$$

With GIAOs there are additional occ-occ terms

$$S_{r,s}^{(u,0)} = \frac{i}{2c} \langle \chi_r | [\mathbf{r} \times (\mathbf{R}_s - \mathbf{R}_r)]_u | \chi_s \rangle$$

$$A_{a,i}^{(u,0)} = \frac{\mathcal{F}_{a,i}^{(u,0)} - \varepsilon_i \mathcal{S}_{a,i}^{(u,0)}}{\varepsilon_i - \varepsilon_a} \quad a \in \text{unocc}, i \in \text{occ}$$

and the matrix elements contain a few more terms \longrightarrow

$$F_{r,s}^{(u,0)} = \langle \chi_r | \hat{h}^{(u,0)} | \chi_s \rangle + \sum_{t,w} P_{t,w}^{(u,0)} [f_{HXC}]_{r,s,t,w}$$

$$- \frac{i}{2c} \langle \chi_r | (\mathbf{r} \times \mathbf{R}_r)_u \hat{F} | \chi_s \rangle$$

$$+ \frac{i}{2c} \langle \chi_r | \hat{F} (\mathbf{r} \times \mathbf{R}_s)_u | \chi_s \rangle$$

Scalar ZORA

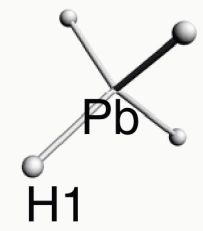
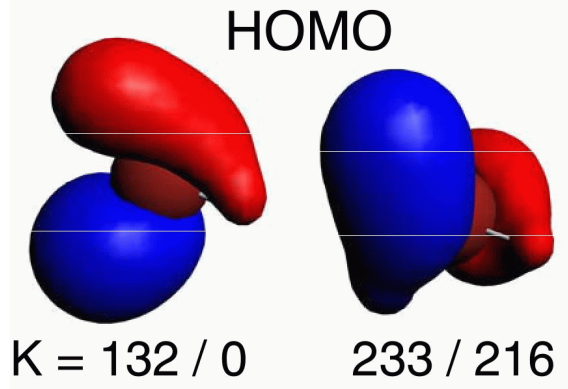
 $J(\text{TI-I})$

Spin-orbit ZORA (units: 1E19T²/J)

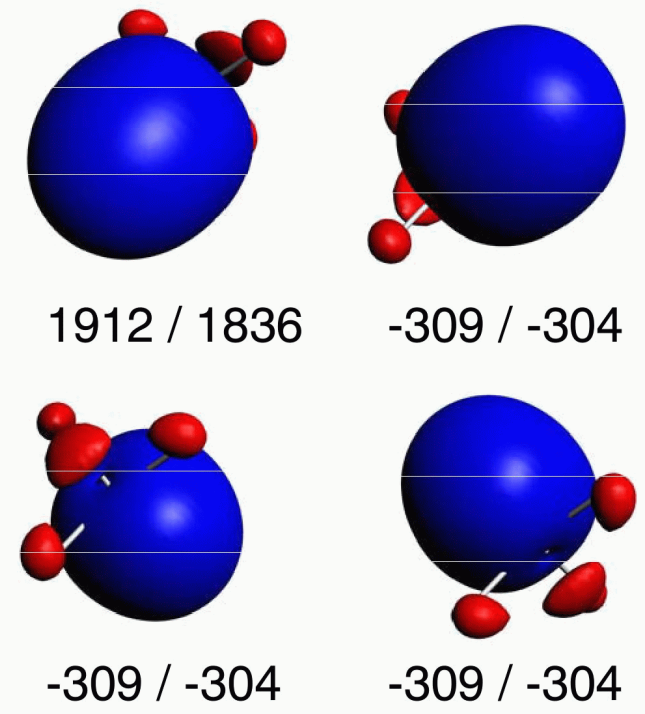
NLMO j	(L)	(NL)	Parent NBO (occup.)	label
1:	-3733.7	0.0	(2.00000)	BD (1)TI 1- I 2
6:	-110.8	0.0	(1.99996)	CR (5)TI 1
18:	-192.0	0.6	(1.99988)	CR (17)TI 1
53:	-77.8	-0.1	(1.99995)	CR (13) I 2
64:	441.0	-64.5	(1.99943)	LP (1)TI 1
65:	2702.8	119.1	(1.99889)	LP (1) I 2
Sum listed: -970.5 55.0				
(L) + (NL) listed: -915.5				
Total computed: -882.5				

NLMO j	(L)	(NL)	Parent NBO (occup.)	label
1:	-5738.7	0.0	(2.00000)	BD (1)TI 1- I 2
6:	-160.2	0.0	(1.99996)	CR (5)TI 1
18:	-154.8	1.2	(1.99988)	CR (17)TI 1
53:	-198.6	-0.1	(1.99995)	CR (13) I 2
64:	-541.2	-23.0	(1.99943)	LP (1)TI 1
65:	3603.4	124.6	(1.99889)	LP (1) I 2
66:	-324.9	-67.7	(1.92243)	LP (2) I 2
67:	-324.9	-67.7	(1.92243)	LP (3) I 2
68:	-38.1	50.6	(0.07764)	LP*(2)TI 1
69:	-38.1	50.6	(0.07764)	LP*(3)TI 1
221:	276.3	-0.4	(0.00196)	BD*(1)TI 1- I 2
Sum listed: -3639.9 68.0				
(L) + (NL) listed: -3571.9				
Total computed: -3849.5				

ZSC Canonical MOs

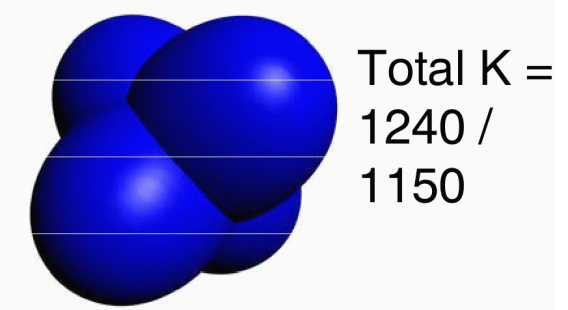


ZSC NLMOs

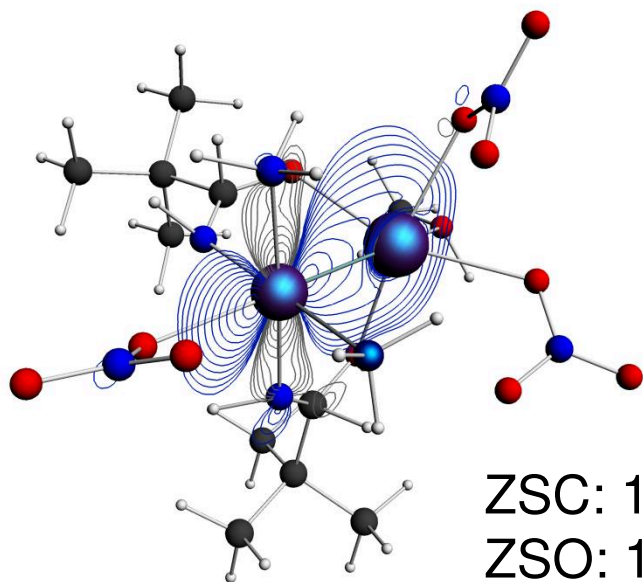


Total K = 1240 (ZSC) / 1150 (ZSO)

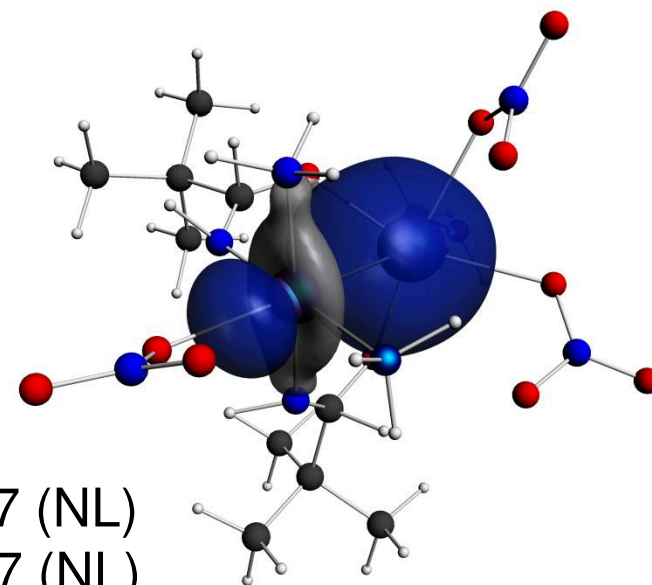
(units: $10^{19} \text{ kg m}^{-2} \text{ C}^{-2}$,
isosurface values: 0.030, 0.024 a.u.)



(~ +240 from Pb 5s)

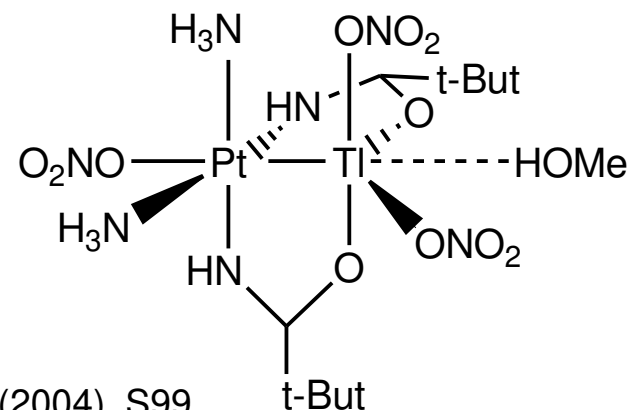


ZSC: 14228 (L) -4397 (NL)
 ZSO: 14728 (L) -4507 (NL)

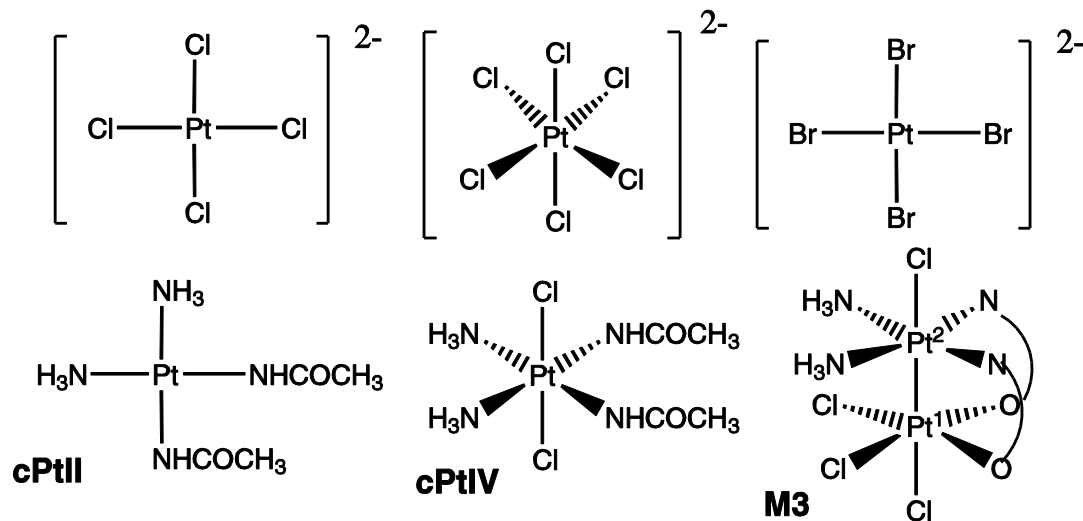


9% Pt 6s, 87% Tl 6s

$K(\text{Pt-Tl})\text{:expt}^{\text{a}}$	9,658 ($J = 147$ kHz)
scalar ZORA	9,621
SO ZORA	10,408

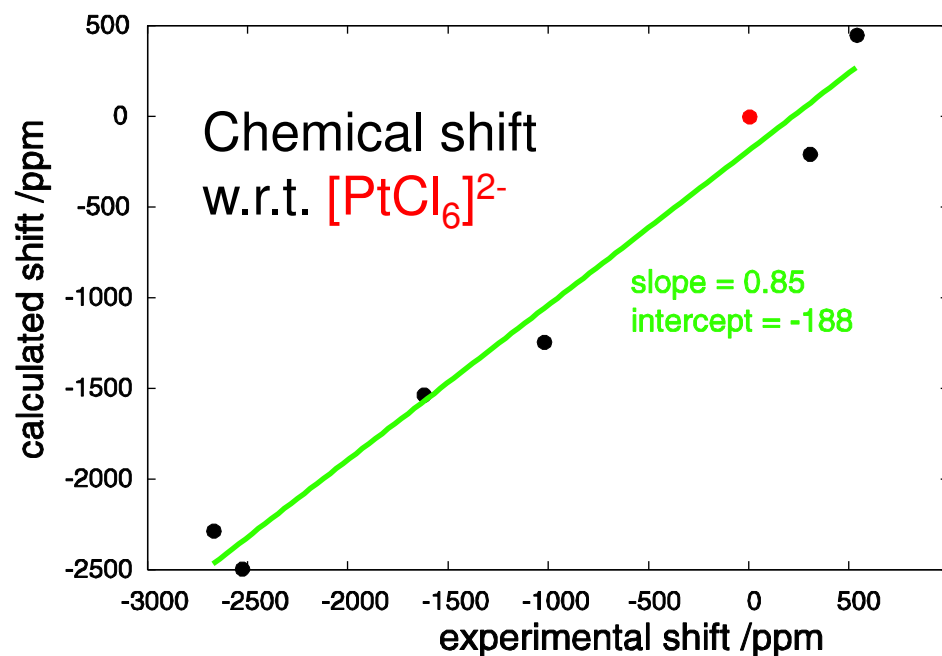


a) B. Le Guennic, K. Masumoto, JA, Magn. Reson. Chem. 42 (2004), S99
 in units of $10^{20} \text{ kg m}^{-2} \text{C}^{-2}$



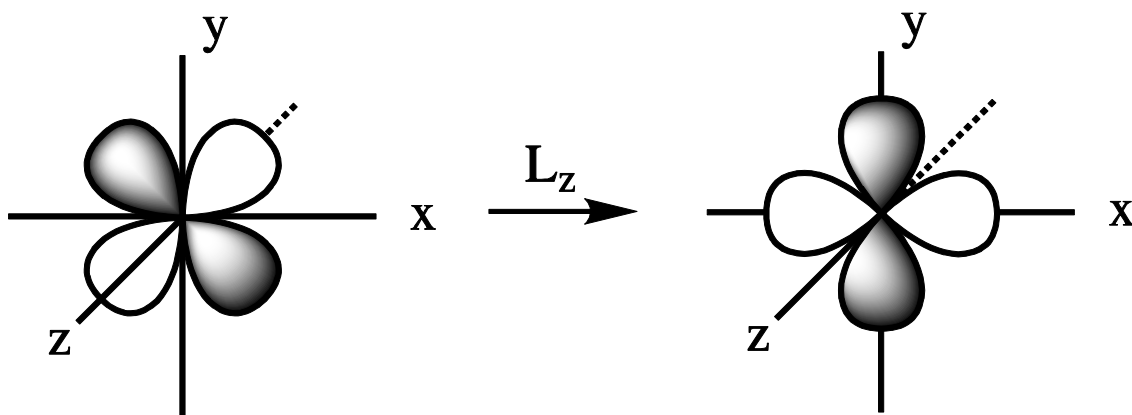
Analysis of chemical shifts
in Pt complexes,

with focus on nonbonding
Pt 5d orbitals



	PtCl ₄	PtCl ₆	shift
Pt Core s	7596.43	7624.58	28.15
Pt Core p	2548.81	2379.03	-169.77
Pt Core d	1610.27	1553.91	-56.36
Pt Core f	597.38	595.22	-2.16
Pt Core total	12352.88	12152.74	-200.14
diamag. total	9600.97	9594.43	-6.55
$\sigma(\text{Pt-Cl})$	-748.99	-373.53	375.45
Pt LP	-7594.48	-9537.00	-1942.53 ***
Cl LP	-33.59	186.96	220.56
Cl Core	-0.422	0.408	0.83
\sum unocc	-349.65	-335.85	13.81
\sum analysis ^a	3625.76	2093.73	-1532.02
shift obtained from Pt lone-pairs and Pt-Cl bonds			-1567.08
total calculated	3625.75	2093.74	-1532.01
^a sum of listed NLMO contributions			

$$\sigma_{u,v}^p = \text{const.} \cdot \text{Re} \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\langle \varphi_i | \hat{k}_u^B \hat{l}_u + \hat{\Delta}_u | \varphi_a \rangle \langle \varphi_a | \hat{k}_v^\mu \hat{l}_v^A | \varphi_i \rangle}{\varepsilon_i - \varepsilon_a}$$



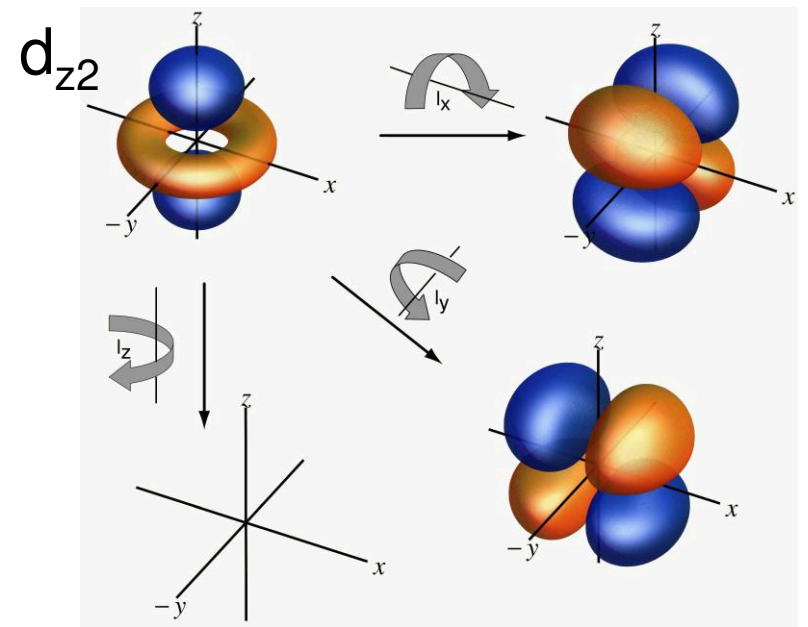
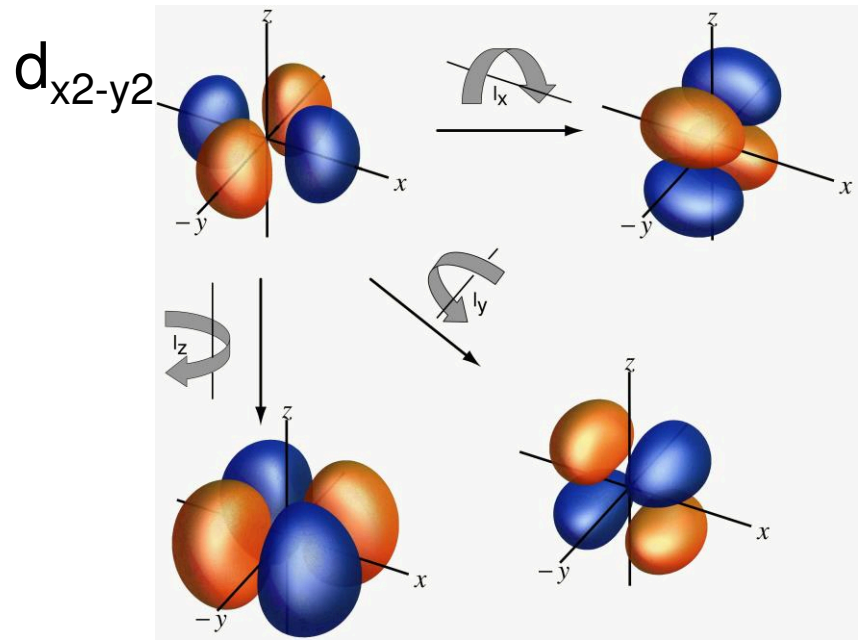
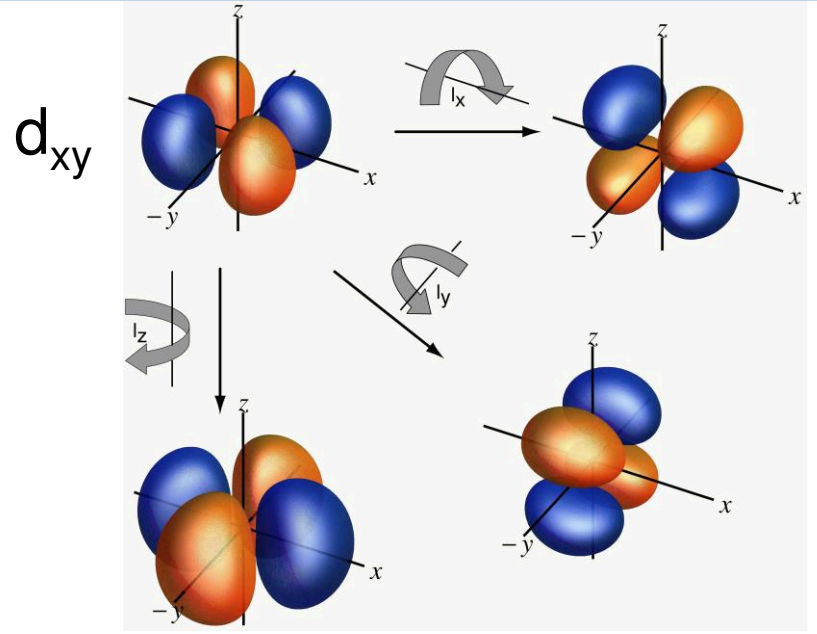
angular term Ω	$\hat{l}_x \Omega$	$\hat{l}_y \Omega$	$\hat{l}_z \Omega$
xy	$-xz$	yz	$x^2 - y^2$
xz	xy	$z^2 - x^2$	$-yz$
yz	$y^2 - z^2$	$-xy$	xz
$x^2 - y^2$	$2yz$	$2xz$	$-4xy$
$2z^2 - x^2 - y^2$	$6yz$	$-6xz$	0

Magn. Reson. Chem. 46 (2008), S48

See also: Jameson & Gutowsky,
 JCP 40 (1964), 1714

d-orbital "rotations"

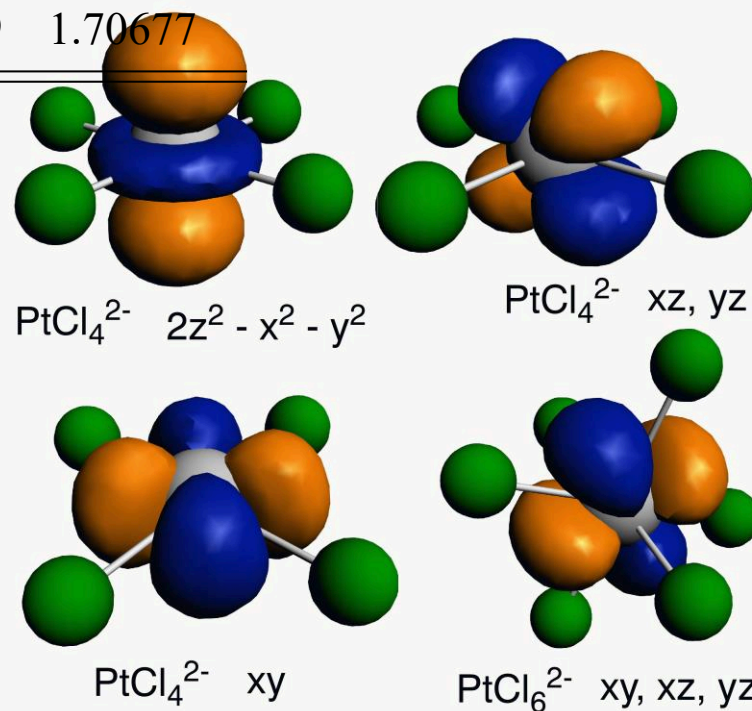
angular term Ω	$\hat{l}_x \Omega$	$\hat{l}_y \Omega$	$\hat{l}_z \Omega$
xy	$-xz$	yz	$x^2 - y^2$
xz	xy	$z^2 - x^2$	$-yz$
yz	$y^2 - z^2$	$-xy$	xz
$x^2 - y^2$	$2yz$	$2xz$	$-4xy$
$2z^2 - x^2 - y^2$	$6yz$	$-6xz$	0



NLMO	(L)	(NL)	(L)+(NL)	% NBO, occup.	
				[PtCl ₄] ²⁻	
$3z^2 - r^2$	98	-21	76	99.8	1.99675
xz, yz	-1583	-15	-1599	99.7	1.99307
xy	-4377	-95	-4473	99.5	1.98990
$\sigma(\text{Pt-Cl})$ av.	-133	-53	-187	88.6	1.77576
				[PtCl ₆] ²⁻	
xz, yz, xy	-3136	-42	-3179	99.7	1.99459
$\sigma(\text{Pt-Cl})$ av.	-38	-23	-62	84.9	1.70677

d-orbital contributions also yield most of the computed shielding tensor anisotropy

NLMO analysis for PtCl₄²⁻ vs. PtBr₄²⁻ reveals spin-orbit mechanisms (mainly NHD)



- NBO / NLMO analysis of NMR shielding & J-coupling
- NBO analysis of EFG tensors

NQCC versus EFG

$$C_Q = \frac{eQV_{33}}{h}$$

Hessian matrix of electric potential $V_{uv} = \frac{\partial^2 V}{\partial r_u \partial r_v}$ $u, v \in \{x, y, z\}$

Electronic contribution

$$V_{uv}^{\text{el}}(\mathbf{R}_A) = \int d\mathbf{r} \cdot \rho(\mathbf{r}) \hat{V}_{uv}^{\text{el}}(\mathbf{r}, \mathbf{R}_A)$$

$$\text{with } \hat{V}_{uv}^{\text{el}}(\mathbf{r}, \mathbf{R}_A) = -\frac{3(\mathbf{r} - \mathbf{R}_A)_u(\mathbf{r} - \mathbf{R}_A)_v - \delta_{u,v}|\mathbf{r} - \mathbf{R}_A|^2}{|\mathbf{r} - \mathbf{R}_A|^5}$$

Electronic contribution

$$V_{uv}^{\text{el}}(\mathbf{R}_A) = \int d\mathbf{r} \cdot \rho(\mathbf{r}) \hat{V}_{uv}^{\text{el}}(\mathbf{r}, \mathbf{R}_A)$$

$$\text{with } \hat{V}_{uv}^{\text{el}}(\mathbf{r}, \mathbf{R}_A) = -\frac{3(\mathbf{r} - \mathbf{R}_A)_u(\mathbf{r} - \mathbf{R}_A)_v - \delta_{u,v}|\mathbf{r} - \mathbf{R}_A|^2}{|\mathbf{r} - \mathbf{R}_A|^5}$$

Nuclear charge contribution

$$V_{uv}^{\text{nuc}}(\mathbf{R}_A) = \sum_{B=A} \frac{3(\mathbf{R}_B - \mathbf{R}_A)_u(\mathbf{R}_B - \mathbf{R}_A)_v - \delta_{u,v}|\mathbf{R}_B - \mathbf{R}_A|^2}{|\mathbf{R}_B - \mathbf{R}_A|^5}$$

Lots of cancellation of terms! Undesirable

$$V_{uv}^{\text{nuc}}(\mathbf{R}_A) = \sum_{B=A} \frac{3(\mathbf{R}_B - \mathbf{R}_A)_u(\mathbf{R}_B - \mathbf{R}_A)_v - \delta_{u,v}|\mathbf{R}_B - \mathbf{R}_A|^2}{|\mathbf{R}_B - \mathbf{R}_A|^5}$$

Unified treatment (and analysis) of el and nuc terms:

$$\hat{V}_{uv}^{\text{nuc}}(\mathbf{r}, \mathbf{R}_A) = \frac{1}{N} V_{uv}^{\text{nuc}}(\mathbf{R}_A) \quad \text{yields density weighted nuclear contribution}$$



$$V_{uv}(\mathbf{R}_A) = \int d\mathbf{r} \cdot \rho(\mathbf{r}) \left\{ \hat{V}_{uv}^{\text{el}}(\mathbf{r}, \mathbf{R}_A) + \hat{V}_{uv}^{\text{nuc}}(\mathbf{r}, \mathbf{R}_A) \right\}$$

analysis of
principal
components

NL MO/NBO or other partitioning straightforward

$$\rho(\mathbf{r}) = \sum_j n_j \phi_j^{*,\text{NLMO}} \phi_j^{\text{NLMO}}$$

$$\text{with } \phi_j^{\text{NLMO}} = \Omega_j W_{j,j} + \sum_{n=j}^{\text{NBO}} \Omega_n W_{n,j}$$

Qualitative aspects: p-orbitals

$$V_{zz}^{\text{el}}(\vec{R}_A = 0) = \frac{1}{r^3} - 3\frac{z^2}{r^5}$$

p_z orbital:
-2 const.

p_x, p_y orbitals:
+1 const.

with respect to z axis, p_x and p_y are equivalent

Filled p-shell (**unperturbed**): $[(-2) + (+1) + (+1)] \text{ const.} = 0$

Same for all filled atomic shells at nucleus A , **if unperturbed**
by environment

Tensor properties (here: rank-2)

$$A^{\text{iso}} = \frac{1}{3}(A_{1,1} + A_{2,2} + A_{3,3}) \quad \mathbf{A} = \begin{pmatrix} A_{1,1} & A_{1,2} & A_{1,3} \\ A_{2,1} & A_{2,2} & A_{2,3} \\ A_{3,1} & A_{3,2} & A_{3,3} \end{pmatrix}$$

Examples: shielding tensor, J -coupling tensor

Define: $f(x, y, z) = A_{1,1} \cdot xx + A_{1,2} \cdot xy + A_{1,3} \cdot xz + \dots + A_{3,3} \cdot zz$

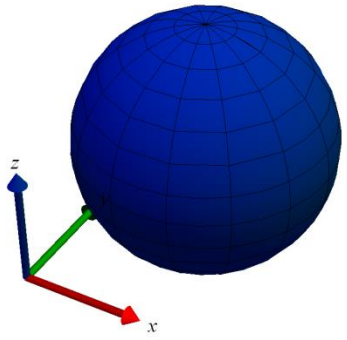
Rewrite as: $f(r, \theta, \phi) = r^2 \cdot g(\theta, \phi)$

and plot in a 3D coordinate system the surface parameterized as

$$r = g(\theta, \phi)$$

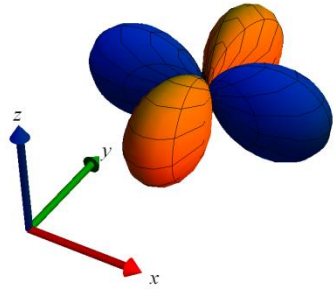
This is a **polar plot** of the rank-2 tensor

Polar plots of rank-2 tensors



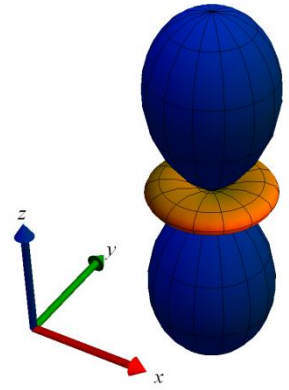
isotropic

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



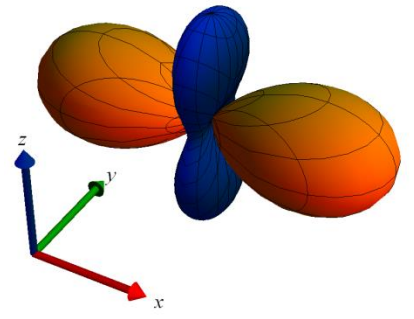
two large opposite components

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



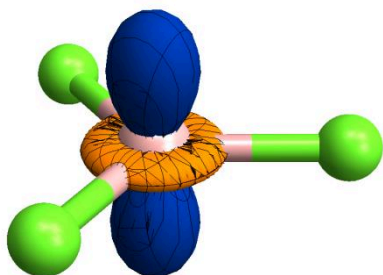
one large, two smaller opposite components

$$\begin{pmatrix} 0.5 & 0 & 0 \\ 0 & 0.5 & 0 \\ 0 & 0 & 1.5 \end{pmatrix}$$

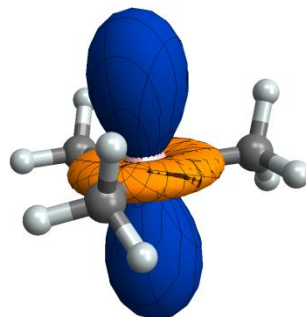


intermediate situation

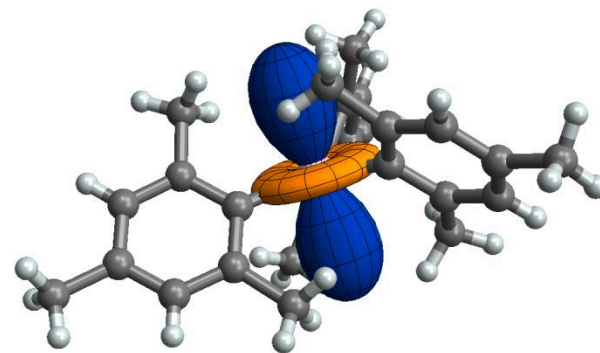
$$\begin{pmatrix} 1.475 & 0 & 0 \\ 0 & 0.339 & 0 \\ 0 & 0 & 0.904 \end{pmatrix}$$



AlCl_3



$\text{Al}(\text{Me})_3$



$\text{Al}(\text{Mes})_3$

revPBE/TZP computed results

$V_{zz} = V_{33}$:
 C_Q/Hz

0.796

1.400

1.472

48.42

(expt: 48.2(1) ^a)

similar
to ^{27}P
atom
(0.57) ^a

^a Tang et al, ChemPhysChem 7 (2006), 117

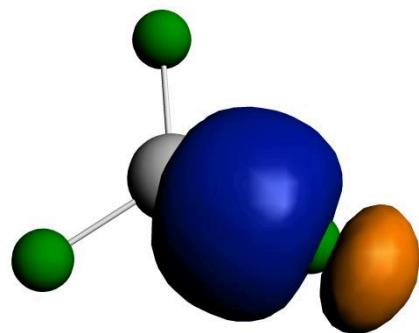
AlCl₃ analysis

V33	Al-Cl bonding (L)	NL	Al 2P core (L)	NL
	0.23	-0.032	27.658	0.039
	0.231	-0.031	-55.152	0.134
	0.23	-0.032	27.658	0.039
Sum	0.691	-0.095	0.164	0.212
Printed L + NL	0.596		0.376	

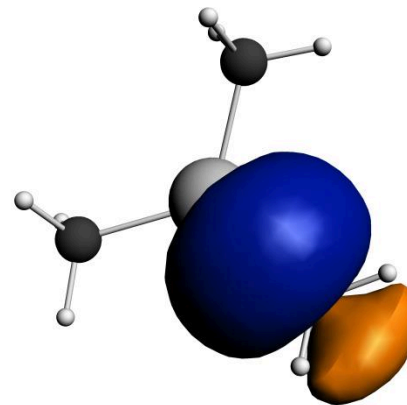
AlMe₃ analysis

V33	Al-C bonding (L)	NL	Al 2P core (L)	NL
	0.271	-0.029	7.131	0.109
	0.273	-0.029	-26.657	0.173
	0.274	-0.028	19.875	0.082
Sum	0.818	-0.086	0.349	0.364
Printed L + NL	0.732		0.713	

sum of contributions not identical to total, but the trend is reproduced



AlCl₃



Al(Me)₃

σ bond NLMO on Al side:

54% s

44% p

occ Cl 2p_z 1.91

occ. 3p_z^{*} 0.25

σ bond NLMO on Al side:

57% s

42% p

occ. 3p_z^{*} 0.00

Tang et al. argued that in AlX₃ there is some X-Al pi donation which reduces V_{zz} for AlCl₃. This is clearly seen in the NBO occupations but not clearly in the NLMO contributions to EFG ⇒ Analysis [per NBO](#) instead

```
=====
NBO contributions to 1e Property *** EFG Atom 1 Principal component 3 ***
=====
```

Print threshold 0.040 atomic units
In the following, i is the index of an
NBO as characterized in the NBO program output

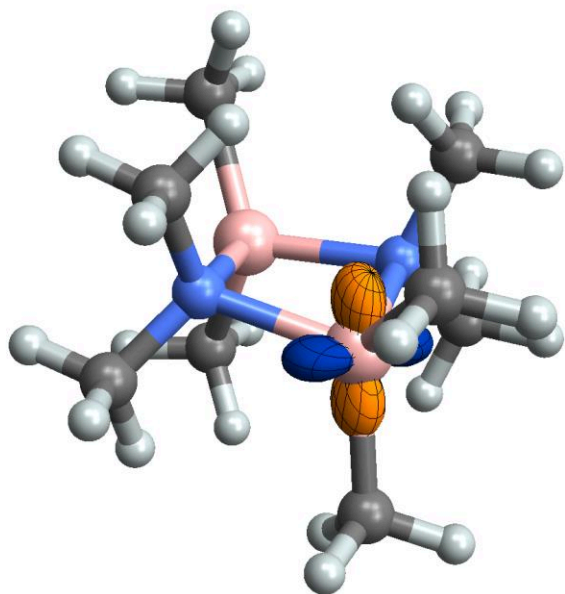
i	contribution to Property in a.u.	NBO label
1:	0.230	1. (1.97788) BD (1)Al 1-Cl 2
2:	0.230	2. (1.97792) BD (1)Al 1-Cl 3
3:	0.230	3. (1.97788) BD (1)Al 1-Cl 4
6:	27.569	6. (1.99993) CR (3)Al 1
7:	-54.975	7. (1.99980) CR (4)Al 1
8:	27.569	8. (1.99993) CR (5)Al 1
33:	-0.181	33. (0.24735) LP*(1)Al 1

```
total Property from NBO decomposition : 0.7948846415
sum of printed NBO contributions : 0.6728894786
```

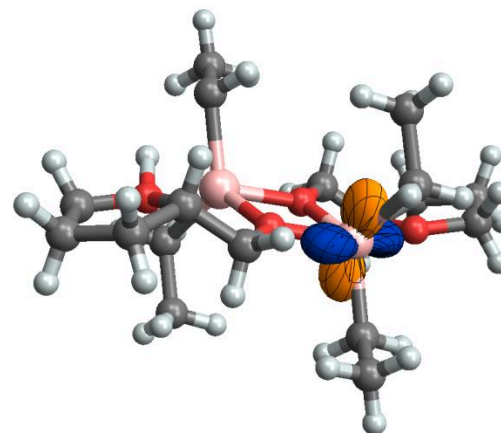
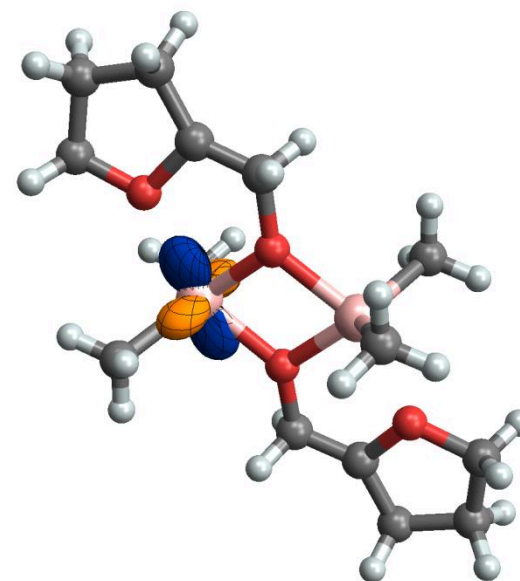
⇒ The $3p_z$ occupation does reduce the field gradient, but not so much

Difference between AlCl_3 and AlMe_3 from bonds (1/4), back-bonding (1/4), and differences in core polarization (1/2)

Some other bonding environments:

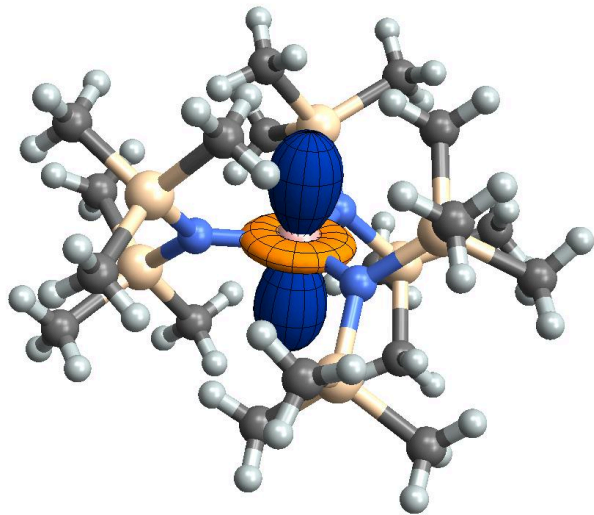


4-coordinate



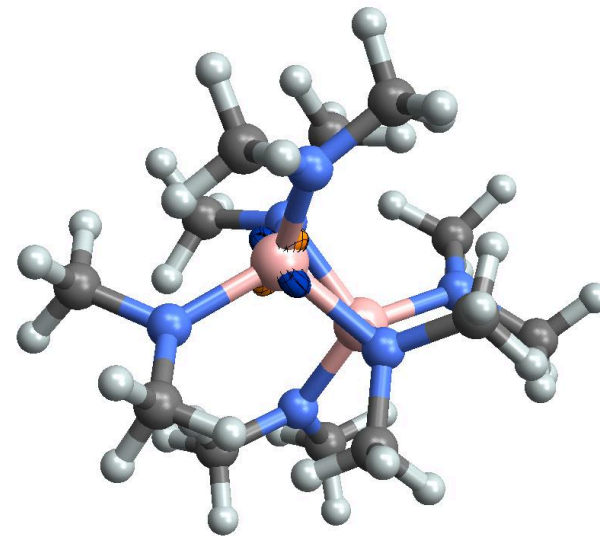
These and many other examples are discussed in detail in
[Autschbach, Zheng & Schurko, Concepts Magn. Reson. 36A \(2010\), 84-126.](#)

planar, 3 Nitrogens

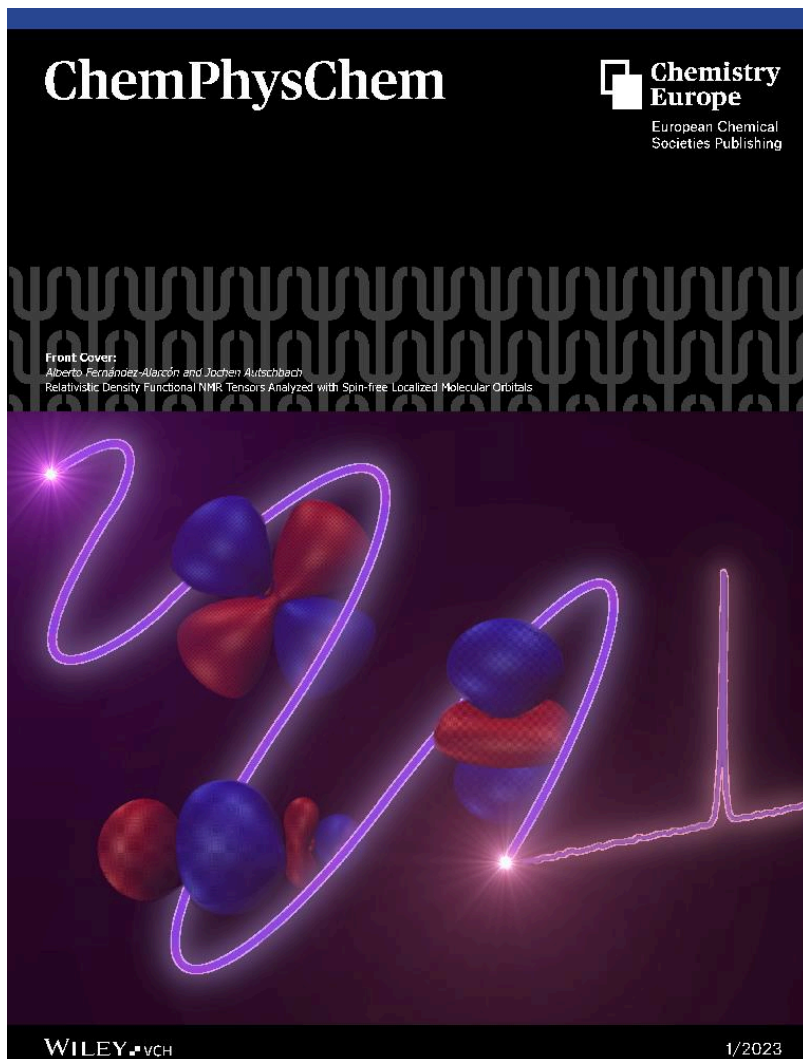


$$V_{33} = 1.05$$

almost tetrahedral,
4 nitrogens



$$V_{33} = 0.34$$



Acknowledgments:

DOE grant DE-SC0022310

Dr. Alberto Fernandez-Alarcon

Prof. Rob Schurko

ChemPhysChem **2023**, *24*, e202200667