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

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

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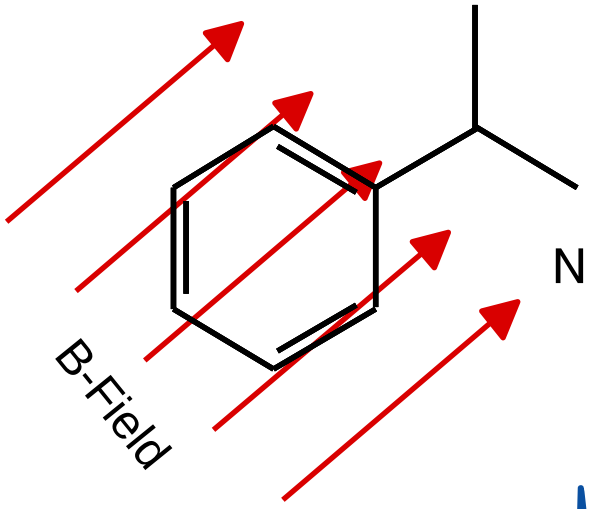
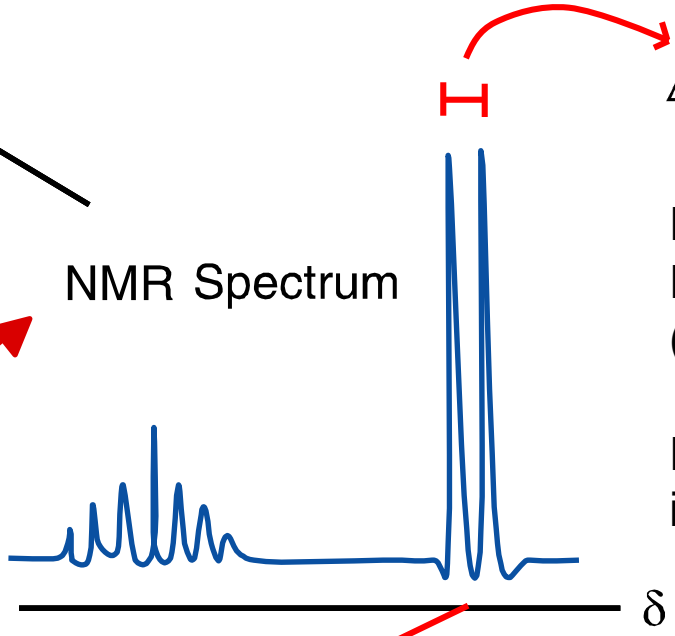
- NBO analysis of EFG tensors





$$\Delta E = \boldsymbol{\mu}_A \ddot{K}_{AB} \boldsymbol{\mu}_B$$

Fine Structure: Indirect Nuclear spin—spin coupling ("*J*-coupling")

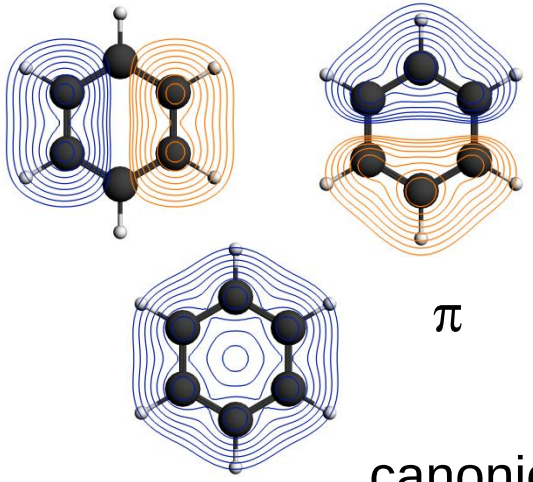
Reduced coupling tensor **K** independent of γ's

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

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

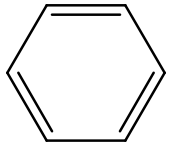
From theory: $\ddot{\sigma}_A = \left. \frac{\mathrm{d}^2 E}{\mathrm{d}\boldsymbol{\mu}_A \mathrm{d}\boldsymbol{\mathcal{B}}} \right|_{\substack{\boldsymbol{\mu}_A = 0 \\ \boldsymbol{\mathcal{B}} = 0}}$; $\ddot{K}_{AB} = \left. \frac{\mathrm{d}^2 E}{\mathrm{d}\boldsymbol{\mu}_A \mathrm{d}\boldsymbol{\mu}_B} \right|_{\substack{\boldsymbol{\mu}_A = 0 \\ \boldsymbol{\mu}_B = 0}}$

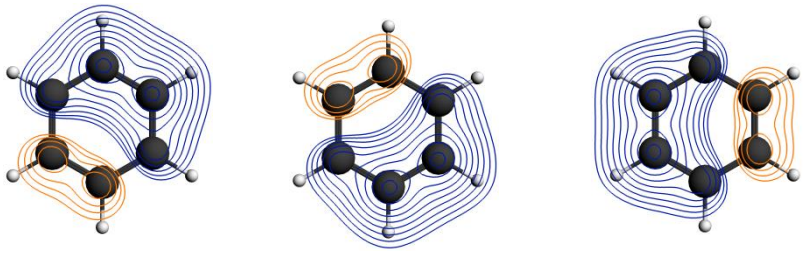
NMR parameters, EFG, and many other properties depend on local features of the electronic structure
⇒ use a localized description for analysis



π

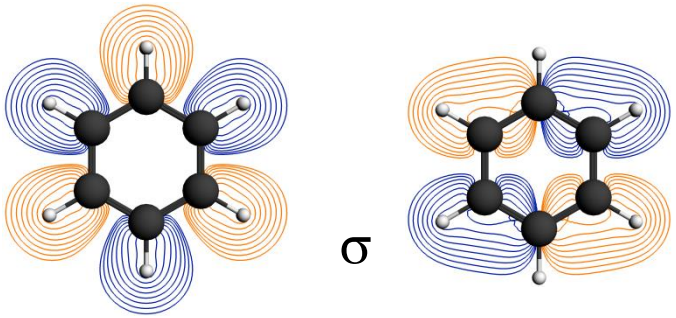
canonical/
delocalized





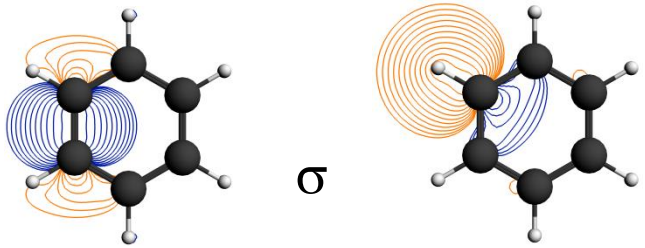
π

localized
shown here: NLMOs



σ

etc…

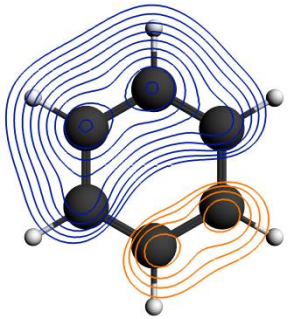


σ

etc…

NLMOs versus NBOs

NLMO = $a_{j,j}$·NBO + delocalization tail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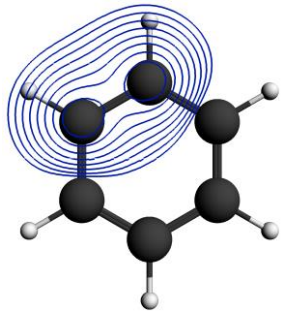
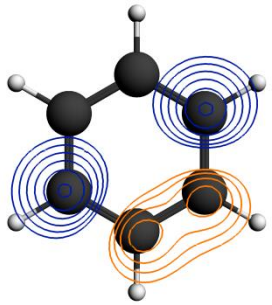

+


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

Localized
"Lewis" (L)

Not Localized
"Non-Lewis" (NL)

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

Status Quo (ca. 2007)

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):
Wilkens 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

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

two-component MOs

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

scalar relativistic MOs (“external”)

we write: $$\vec{\Phi}_i = \sum_{k}^{\text{ext}} \varphi_k \vec{Q}_{k,i}$$

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

$$\Rightarrow \quad \mathbf{C} = \mathbf{BWT}$$

Second-derivative property:

$$P^{(1,1)} = 2\,\mathrm{Re}\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} h_{i,a}^{(0,1)} A_{a,i}^{(1,0)} + \sum_{i}^{\mathrm{occ}} h_{i,i}^{(1,1)}$$

$$P^{(1,1)} = \sum_{j}^{\mathrm{NLMO}}\sum_{n}^{\mathrm{NBO}}\sum_{i}^{\mathrm{occ}}\sum_{k}^{\mathrm{ext\ MO}}\sum_{r}^{\mathrm{AO}}\sum_{s}^{\mathrm{AO}}\sum_{\gamma,\gamma'}^{\mathrm{spin}} \Big\{ 2\,\mathrm{Re}\Big[Q_{k,i}^{\gamma *} h_{r,s}^{(0,1),\gamma,\gamma'} \times \sum_{a}^{\mathrm{unocc}} E_{s,a}^{\gamma'} A_{a,i}^{(1,0)} \Big] + Q_{k,i}^{\gamma *} h_{r,s}^{(1,1),\gamma,\gamma'} E_{s,i}^{\gamma'} \Big\} \cdot \left[B_{r,n}\, W_{n,j}\, T_{j,k} \right]$$

JCP 127 (2007), 124106
JCP 128 (2008), 164112

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

With GIAOs there are additional occ-occ terms

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

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

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

and the matrix elements contain a few more terms

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

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

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

Scalar ZORA *J*(Tl-I)

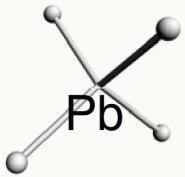
NLMO j	(L)	(NL)	Parent NBO (occup.) label
1:	-3733.7	0.0	(2.00000) BD (1)Tl 1- I 2
6:	-110.8	0.0	(1.99996) CR (5)Tl 1
18:	-192.0	0.6	(1.99988) CR (17)Tl 1
53:	-77.8	-0.1	(1.99995) CR (13) I 2
64:	441.0	-64.5	(1.99943) LP (1)Tl 1
65:	2702.8	119.1	(1.99889) LP (1) I 2
Sum listed:	-970.5	55.0	
(L) + (NL)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

Spin-orbit ZORA (units: 1E19T^2/J)

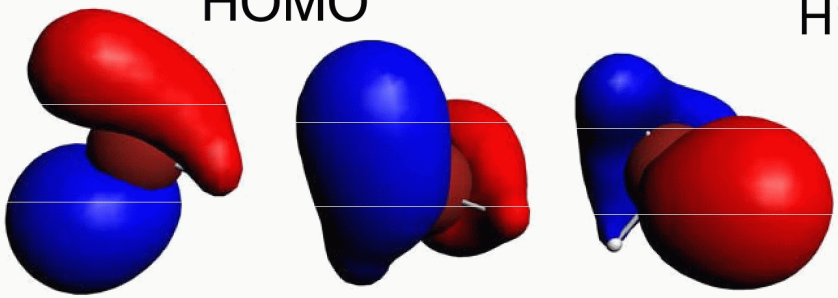
NLMO j	(L)	(NL)	Parent NBO (occup.) label
1:	-5738.7	0.0	(2.00000) BD (1)Tl 1- I 2
6:	-160.2	0.0	(1.99996) CR (5)Tl 1
18:	-154.8	1.2	(1.99988) CR (17)Tl 1
53:	-198.6	-0.1	(1.99995) CR (13) I 2
64:	-541.2	-23.0	(1.99943) LP (1)Tl 1
65:	3603.4	124.6	(1.99889) LP (1) I 2
66:	-324.9	-67.7	(1.92243) LP (2)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

NBO analysis of J-coupling

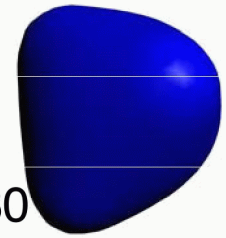
ZSC Canonical MOs



HOMO



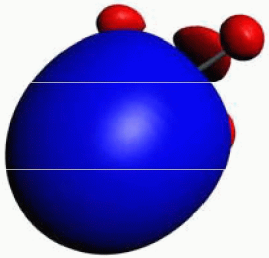
K = 132 / 0 233 / 216 40 / 85



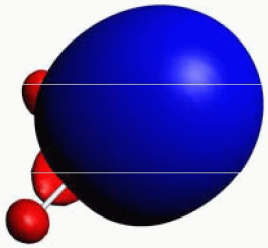
HOMO-1

K = 828 / 830

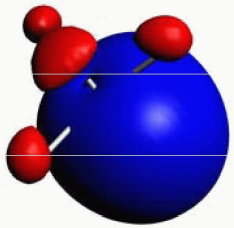
ZSC NLMOs



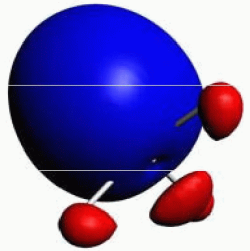
1912 / 1836



-309 / -304



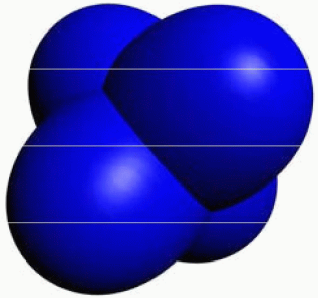
-309 / -304



-309 / -304

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

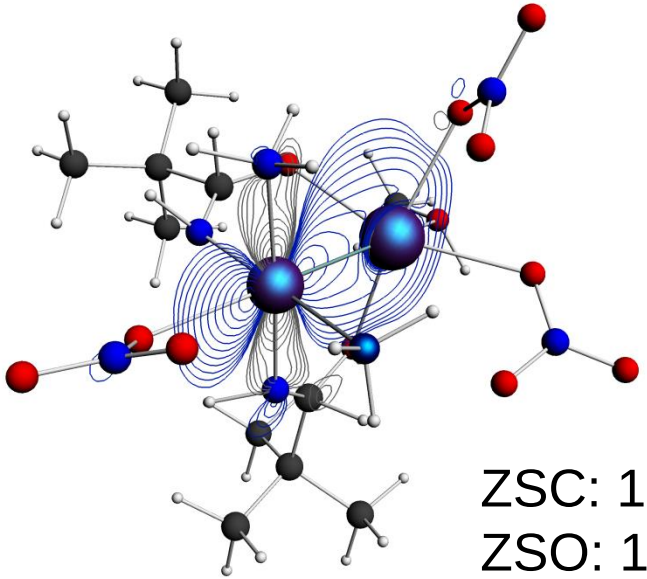
(units: 10^{19} kg m^{-2} C^{-2},
isosurface values: 0.030, 0.024 a.u.)

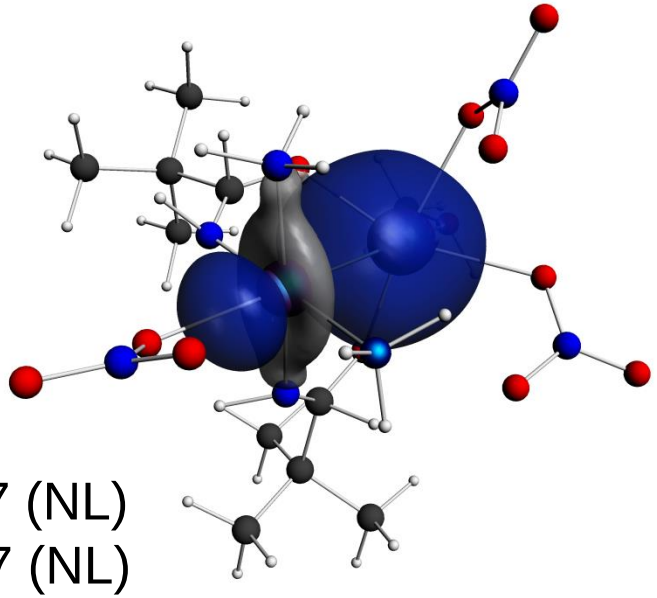


Total K = 1240 / 1150

(~ +240 from Pb 5s)

Pt-Tl coupling constants

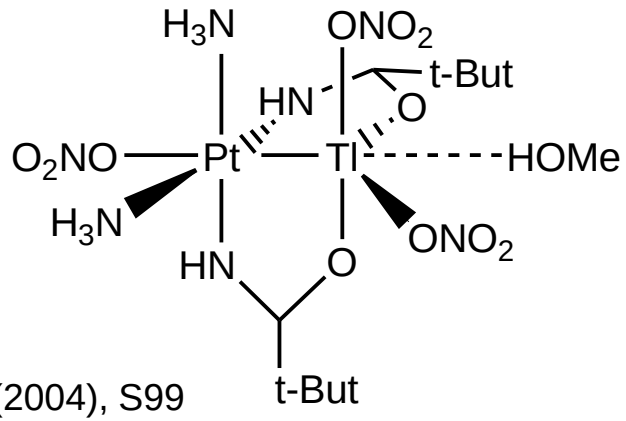




ZSC: 14228 (L) -4397 (NL)
ZSO: 14728 (L) -4507 (NL)

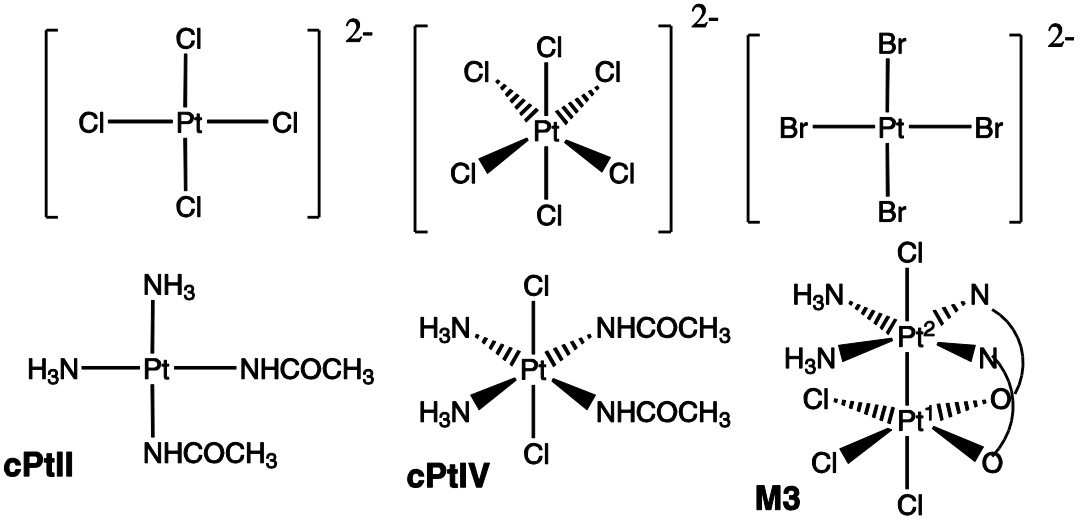
9% Pt 6s, 87% Tl 6s

K(Pt-Tl):expt[a] 9,658 (*J* = 147 kHz)
scalar ZORA 9,621
SO ZORA 10,408



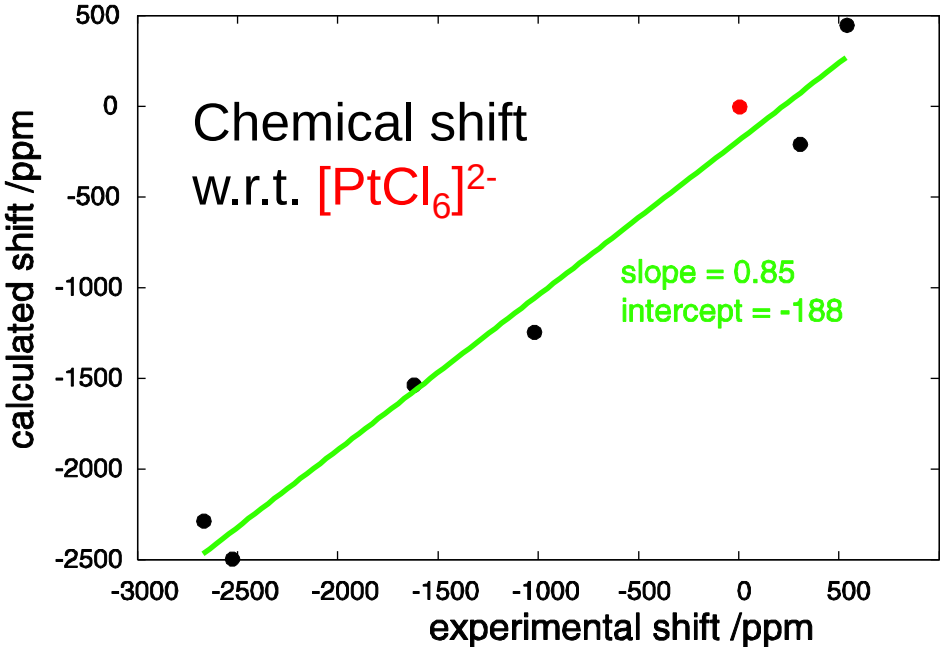
a) B. Le Guennic, K. Masumoto, JA, Magn. Reson. Chem. 42 (2004), S99
in units of 10^{20} kg $m^{-2}C^{-2}$

Pt complexes, chemical shift analysis



Analysis of chemical shifts in Pt complexes,

with focus on nonbonding Pt 5d orbitals



JCP 128 (2008), 164112
Magn. Reson. Chem. 46 (2008), S48

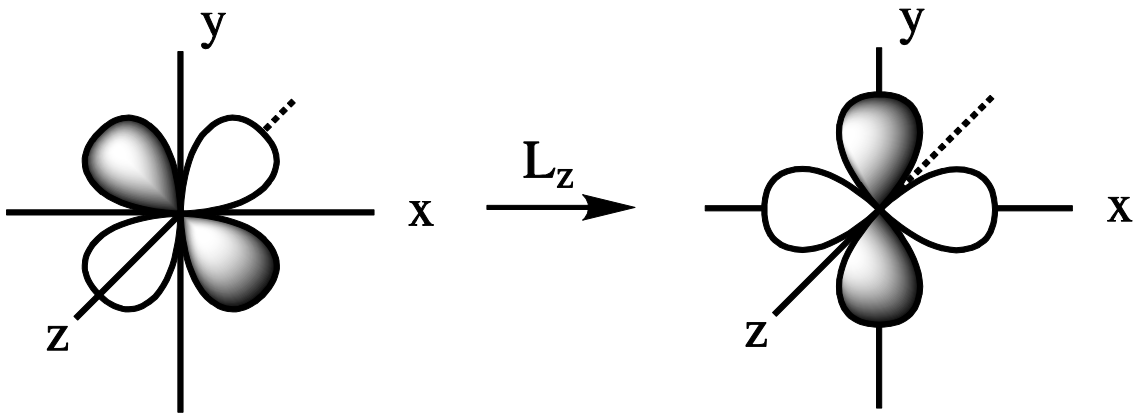
$[PtCl_4]^{2-}$ vs. $[PtCl_6]^{2-}$

	PtCl4	PtCl6	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	
σ(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

JCP 128 (2008), 164112

$$\sigma^{p}_{u,v} = \text{const.} \cdot \text{Re} \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{\langle \varphi_i | \hat{k}^{B}_{u} \hat{l}_{u} + \hat{\Delta}_{u} | \varphi_a \rangle \langle \varphi_a | \hat{k}^{\mu}_{v} \hat{l}^{A}_{v} | \varphi_i \rangle}{\varepsilon_i - \varepsilon_a}$$



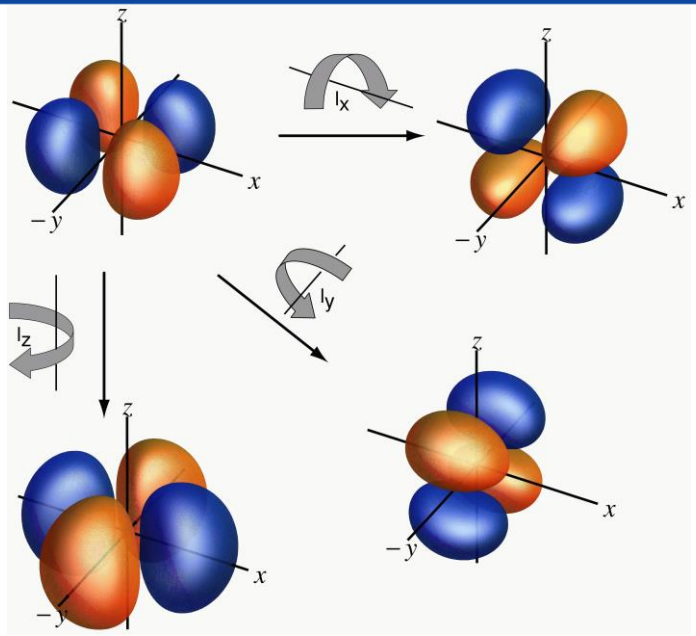
angular term Ω	$\hat{l}_x \Omega$	$\hat{l}_y \Omega$	$\hat{l}_z \Omega$
xy	$-xz$	yz	$x^2 - y^2$
xz	xy	$z^2 - x^2$	$-yz$
yz	$y^2 - z^2$	$-xy$	xz
$x^2 - y^2$	$2yz$	$2xz$	$-4xy$
$2z^2 - x^2 - y^2$	$6yz$	$-6xz$	0

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

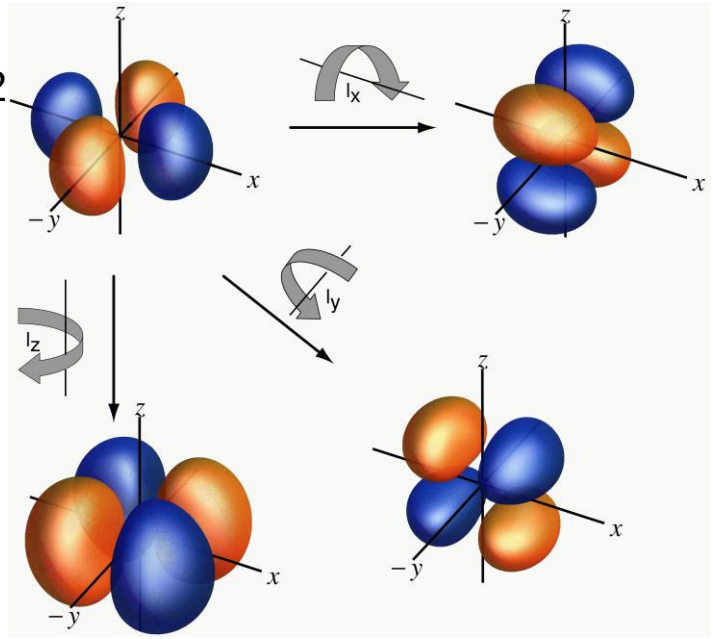
See also: Jameson & Gutowsky, JCP 40 (1964), 1714

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

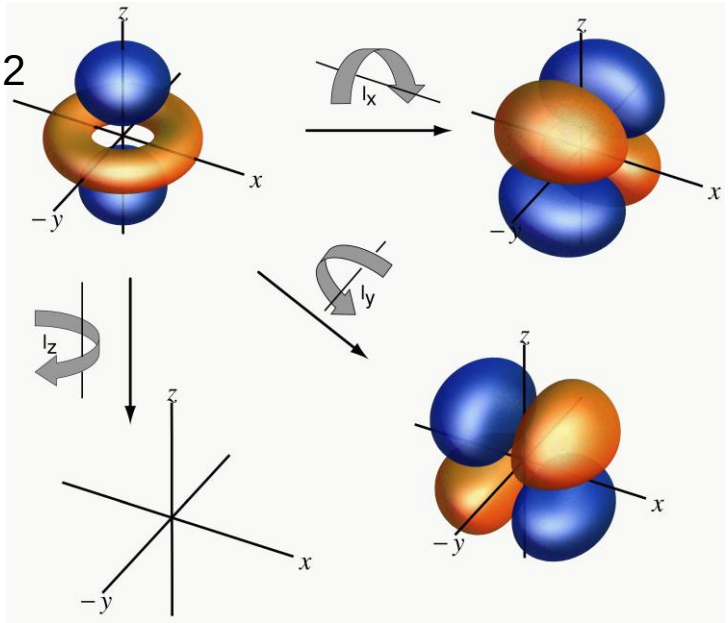
d_{xy}



d_{x2-y2}



d_{z2}

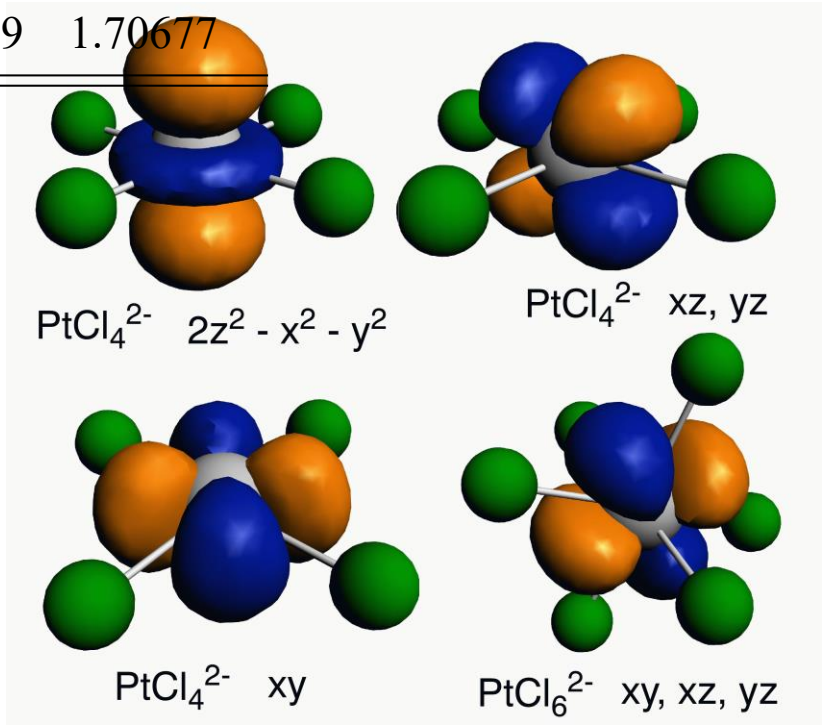


$[PtCl_4]^{2-}$ vs. $[PtCl_6]^{2-}$

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
σ(Pt-Cl) av.	-133	-53	-187	88.6	1.77576
		$[PtCl_6]^{2-}$			
xz, yz, xy	-3136	-42	-3179	99.7	1.99459
σ(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 $PtCl_4^{2-}$ vs. $PtBr_4^{2-}$ reveals spin-orbit mechanisms (mainly NHD)



JCP 128 (2008), 164112
Magn. Reson. Chem. 46 (2008), S48

- 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 $V_{uv} = \frac{\partial^2 V}{\partial r_u \partial r_v} \quad u, v \in \{x, y, z\}$

Electronic contribution

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

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

Electronic contribution

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

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

Nuclear charge contribution

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

Lots of cancellation of terms! Undesirable

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

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

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

⇓

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

analysis of principal components

NL MO/NBO or other partitioning straightforward

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

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 an p_y are equivalent

Filled p-shell (unperturbed): [(-2) + (+1) + (+1)] const. = 0

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

Tensor properties (here: rank-2)

$$A^{\text{iso}} = \frac{1}{3}(A_{1,1} + A_{2,2} + A_{3,3})$$

$$\mathbf{A} = \begin{pmatrix} A_{1,1} & A_{1,2} & A_{1,3} \\ A_{2,1} & A_{2,2} & A_{2,3} \\ A_{3,1} & A_{3,2} & A_{3,3} \end{pmatrix}$$

Examples: shielding tensor, *J*-coupling tensor

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

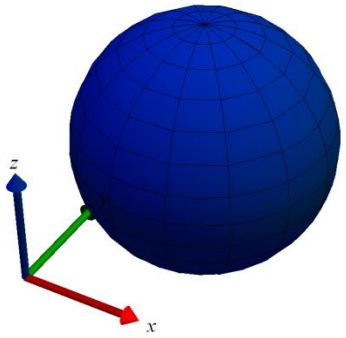
Rewrite as: $f(r, \theta, \phi) = r^2 \cdot g(\theta, \phi)$

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

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

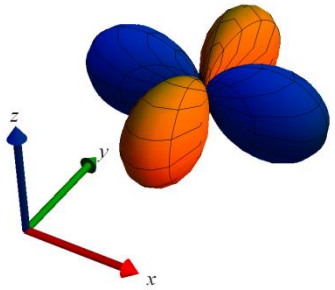
This is a ***polar plot*** of the rank-2 tensor

Polar plots of rank-2 tensors



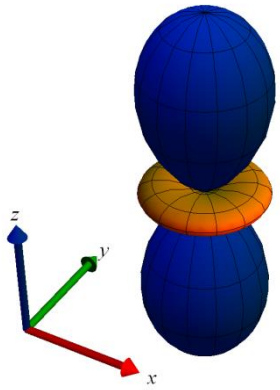
isotropic

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



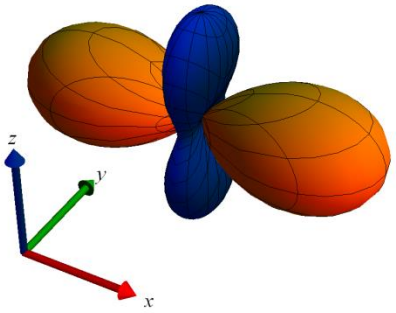
two large opposite components

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



one large, two smaller opposite components

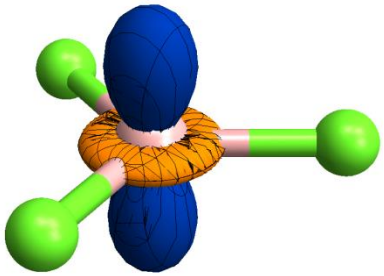
$$\begin{pmatrix} 0.5 & 0 & 0 \\ 0 & 0.5 & 0 \\ 0 & 0 & 1.5 \end{pmatrix}$$

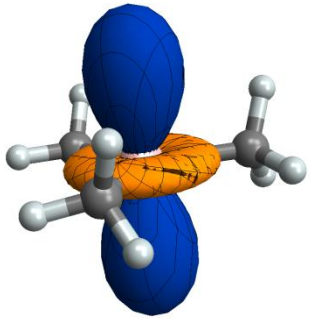


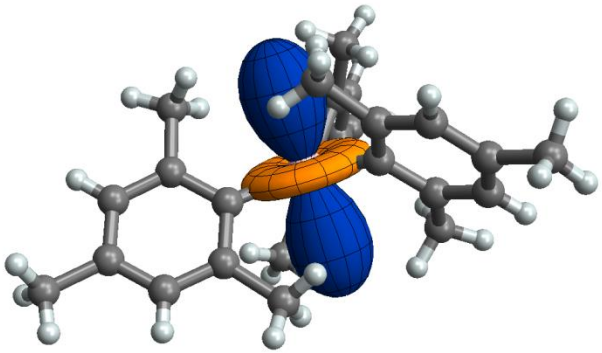
intermediate situation

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

^{27}Al EFG tensors







	$AlCl_3$	$Al(Me)_3$	$Al(Mes)_3$
revPBE/TZP computed results			
$V_{zz} = V_{33}$:	0.796	1.400	1.472
C_Q/Hz	similar to ^{2}P atom (0.57) [a]		48.42 (expt: 48.2(1) [a])

[a] Tang et al, ChemPhysChem 7 (2006), 117

$AlCl_3$ analysis

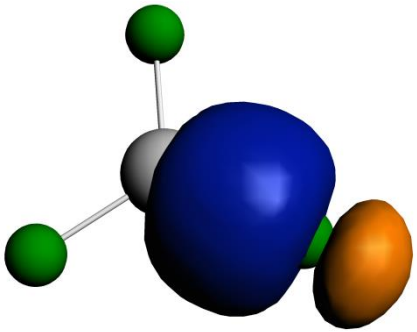
V33	Al-Cl bonding (L)	NL	Al 2P core (L)	NL
	0.23	-0.032	27.658	0.039
	0.231	-0.031	-55.152	0.134
	0.23	-0.032	27.658	0.039
Sum	0.691	-0.095	0.164	0.212
Printed L + NL	0.596		0.376	

$AlMe_3$ analysis

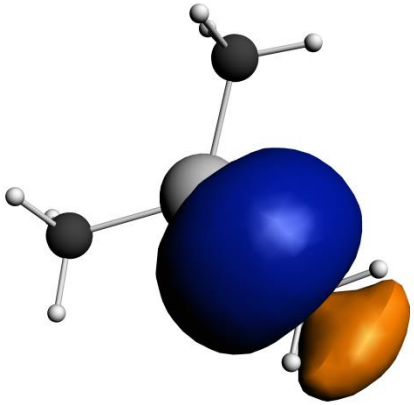
V33	Al-C bonding (L)	NL	Al 2P core (L)	NL
	0.271	-0.029	7.131	0.109
	0.273	-0.029	-26.657	0.173
	0.274	-0.028	19.875	0.082
Sum	0.818	-0.086	0.349	0.364
Printed L + NL	0.732		0.713	

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

^{27}Al EFG tensors



$AlCl_3$



$Al(Me)_3$

σ bond NLMO	on Al side:	σ bond NLMO	on Al side:
	54% s		57% s
	44% p		42% p
occ Cl $2p_z$	1.91		
occ. $3p_z^*$	0.25	occ. $3p_z^*$	0.00

Tang et al. argued that in AlX_3 there is some X-Al pi donation which reduces V_{zz} for $AlCl_3$. This is clearly seen in the NBO occupations but not clearly in the NLMO contributions to EFG $\Longrightarrow$ Analysis per NBO instead

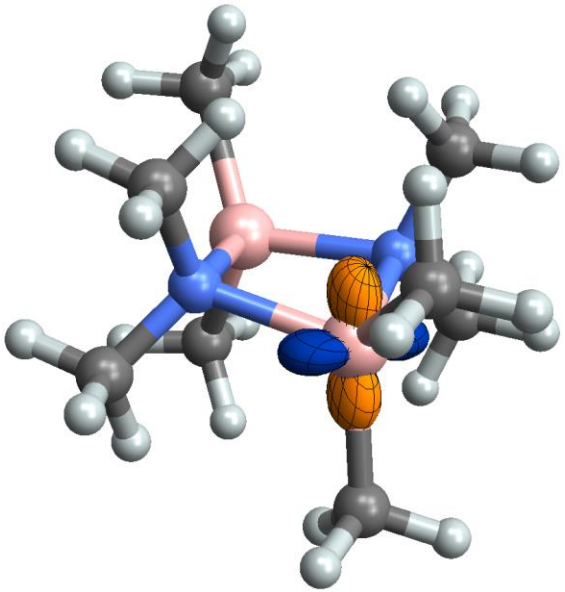
$AlCl_3$ EFG decomposition per NBO

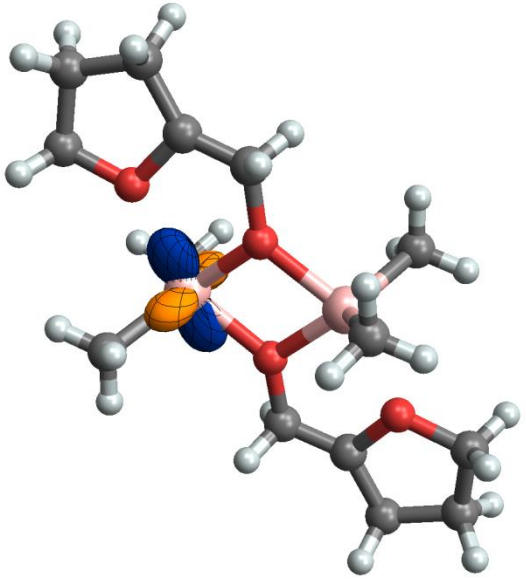

```
================================
NBO contributions to 1e Property  ***  EFG Atom    1 Principal component 3  ***
================================

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

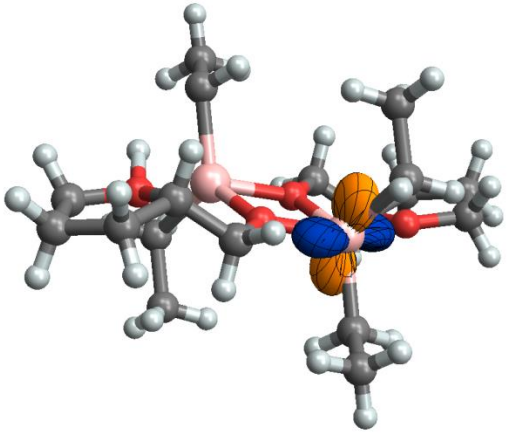
Difference between $AlCl_3$ and $AlMe_3$ from bonds (1/4), back-bonding (1/4), and differences in core polarization (1/2)

Some other bonding environments:



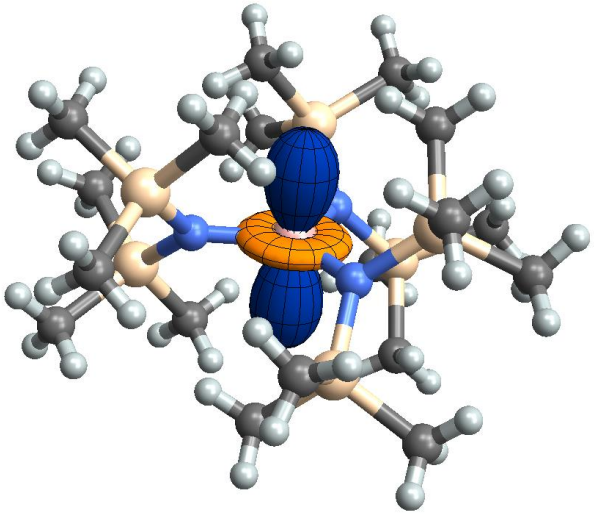


4-coordinate



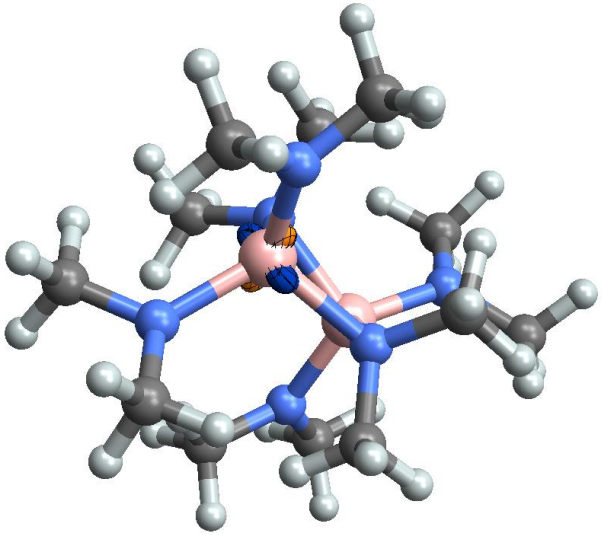
These and many other examples are discussed in detail in
Autschbach, Zheng & Schurko, Concepts Magn. Reson. 36A (2010), 84-126.

planar, 3 Nitrogens

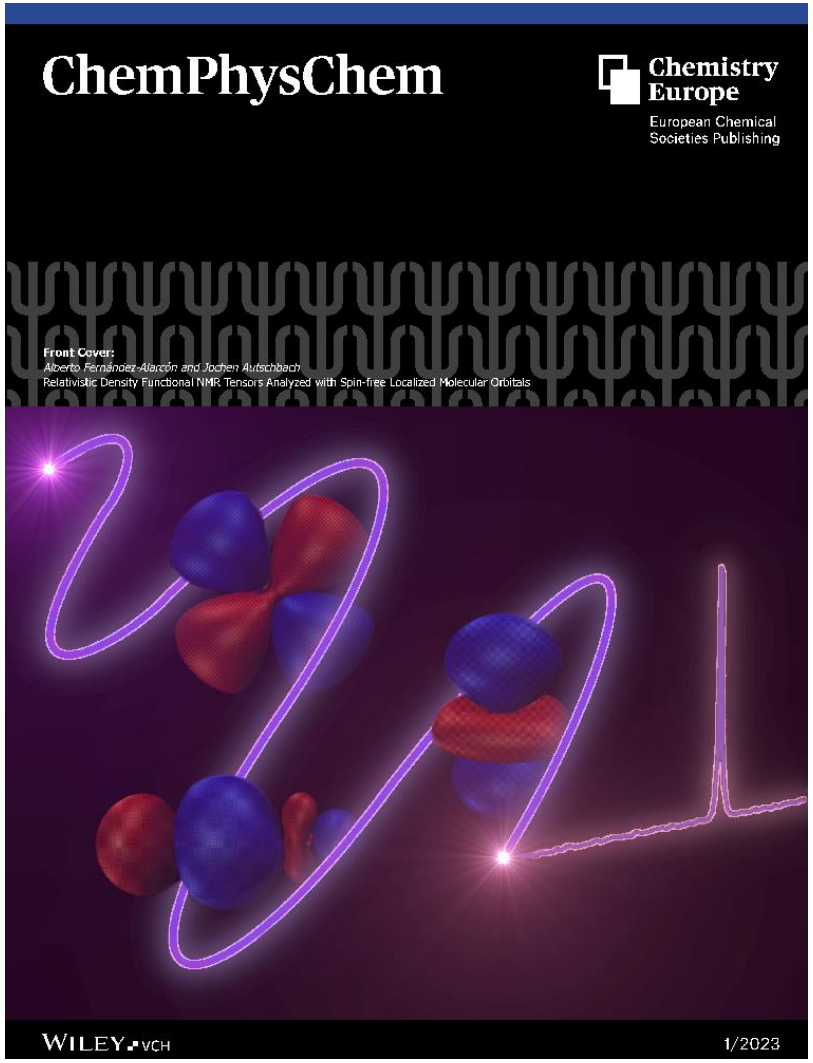


V_{33} =1.05

almost tetrahedral,
4 nitrogens



V_{33} =0.34



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