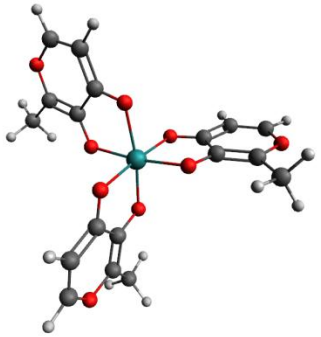
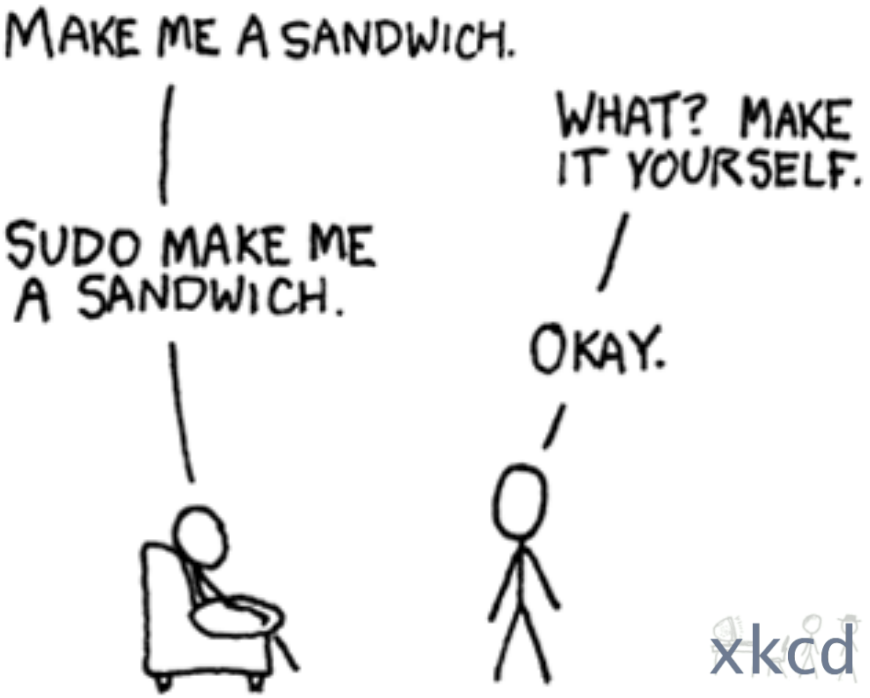
Relativistic calculations of pNMR parameters



Stanislav Komorovský

UiT THE ARCTIC UNIVERSITY OF NORWAY

CTCC
Department of chemistry



the BIG BANG THEORY

22.2. 2014

Content

- Skip motivation
- Progress in relativistic pNMR calculations
- Why is relativity computationally so tough

Quantum physics

1925

$$\left(\frac{1}{2}p^2 + V\right)\varphi = E\varphi \qquad p_k = -i\frac{\partial}{\partial r_k}$$

Gaussian, Turbomole, Dalton,
NWChem, Orca, Molcas, …

1928

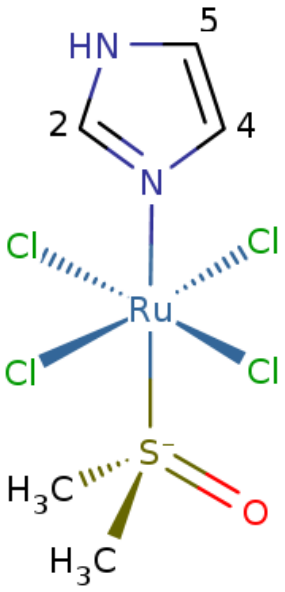
$$\begin{pmatrix} \hat{V}+c^2 & 0 & cp_z & c(p_x-ip_y) \\ 0 & \hat{V}+c^2 & c(p_x+ip_y) & -cp_z \\ cp_z & c(p_x-ip_y) & \hat{V}-c^2 & 0 \\ c(p_x+ip_y) & -cp_z & 0 & \hat{V}-c^2 \end{pmatrix} \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix} = E \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix}$$

ReSpect, Dirac, Bertha, REL4D, BDF, BAGEL

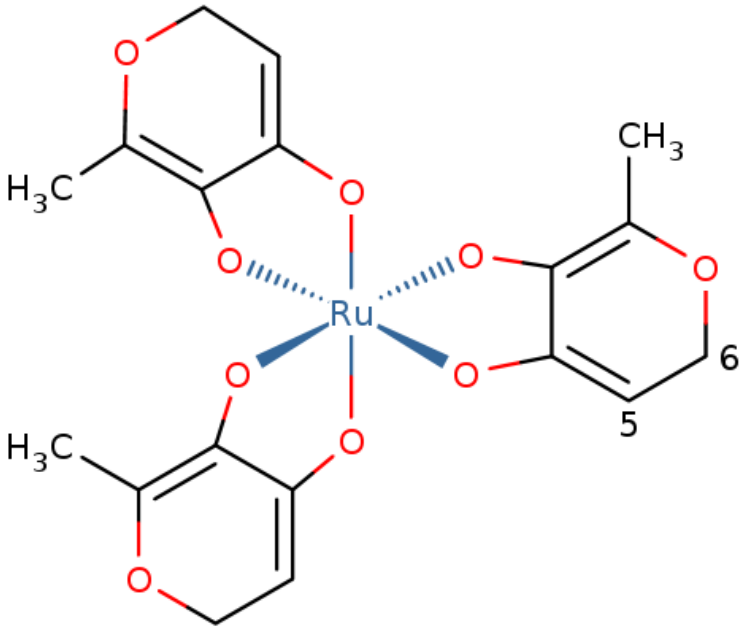
Current progress in our group

Four-component relativistic calculations of pNMR shielding for doublet systems:

S. Komorovsky, M. Repisky, K. Ruud, O. L. Malkina, and V. G. Malkin
J. Phys. Chem. A **117**, 14209 (2013).



NAMI



mer-Ru(ma)$_3$

F. Rastrelli and A. Bagno, *Mag. Res. in Chem.* **48**, S132 (2010).

Traditional way of expressing pNMR shift

$$\delta_M = \delta_M^{orb} + \delta_M^{cs} + \delta_M^{pc}$$

- δ_M^{orb} : orbital shift

$$\delta_M^{orb} = \sigma_M^{ref} - \sigma_M^{orb}$$

- δ_M^{cs} : contact shift

$$\delta_M^{cs} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{3kT} g^{\text{iso}} A_M^{\text{iso}}$$

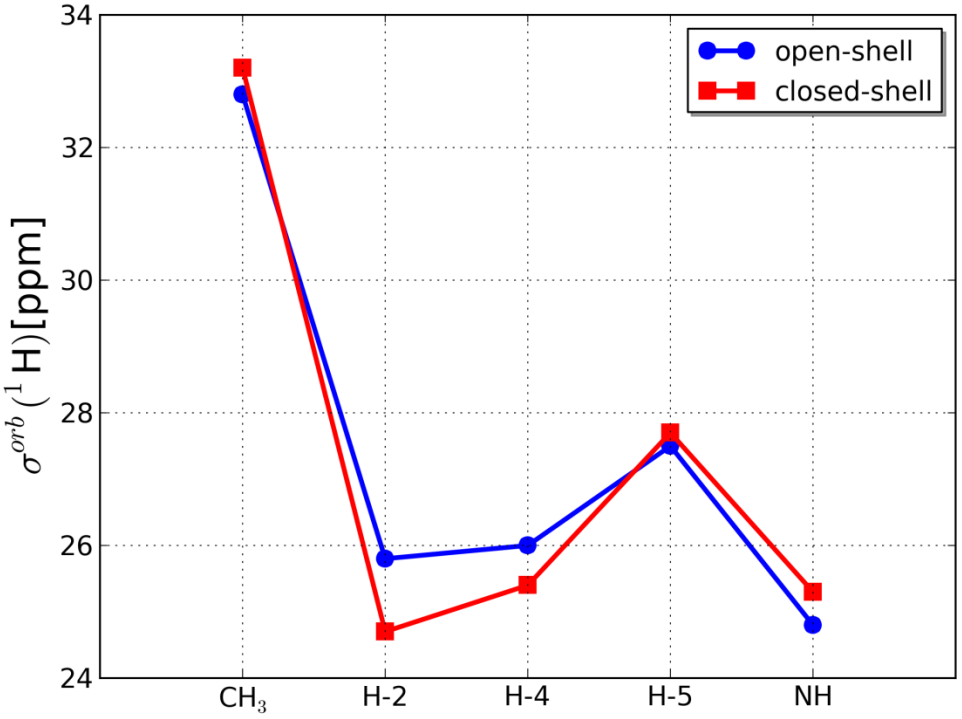
- δ_M^{pc} : pseudocontact shift

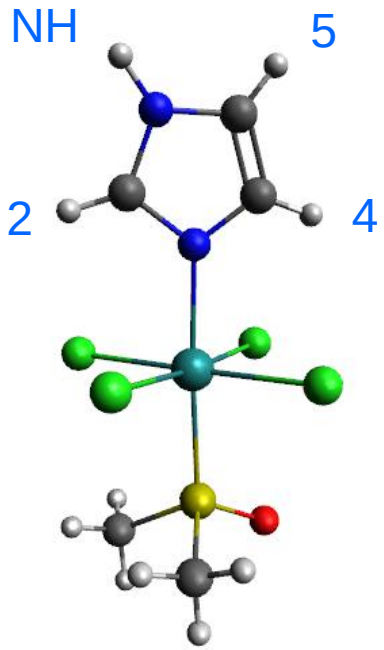
$$\delta_M^{pc} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{9kT} \text{Tr}\left(g^{\text{ani}} A_M^{\text{dip}} \right)$$

Approximation for orbital shift δ^{orb}

Can we use chemical shift of diamagnetic molecule as orbital shift of its paramagnetic counterpart?

Calculated ^{1}H NMR shielding for NAMI and its Ru(II) diamagnetic analogue:





Limitations of expression for δ^{cs}

$$\delta_M^{cs} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{3kT} g^{\text{iso}} A_M^{\text{iso}}$$

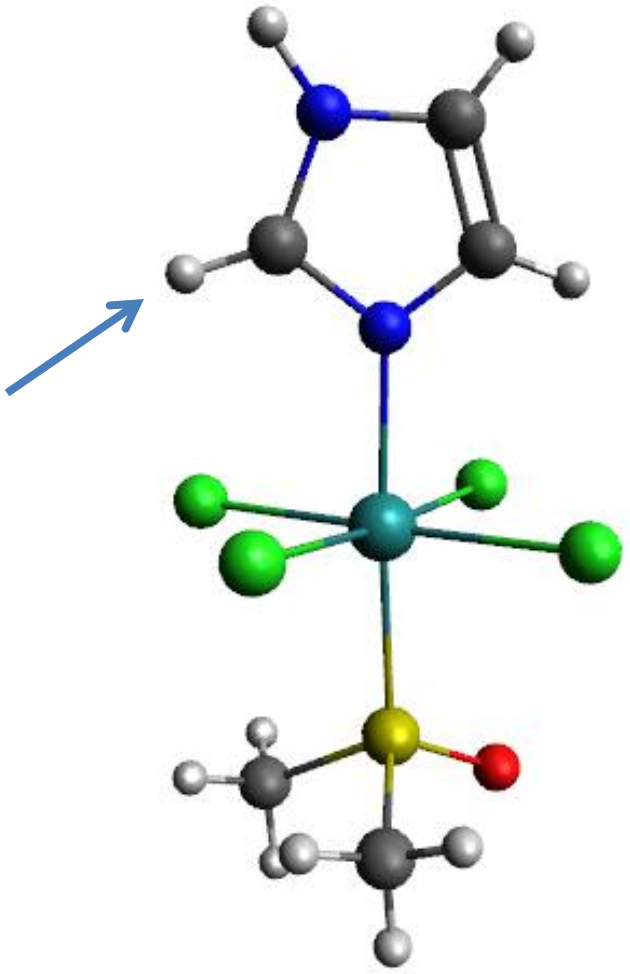
- System must obey Curie law (no spin-orbit coupling effects)
- Holds for single (multiple) electron(s) in an orbital which is well separated from any other excited level

I. Bertini, C. Luchinat, and G. Parigi *Prog. Nucl. Magn. Reson. Spectrosc.* **40**, 249 (2002).

How large can be spin-orbit contribution to δ^{cs}?

$$\delta_M^{cs} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{3kT} g^{iso} A_M^{iso}$$

-1.3



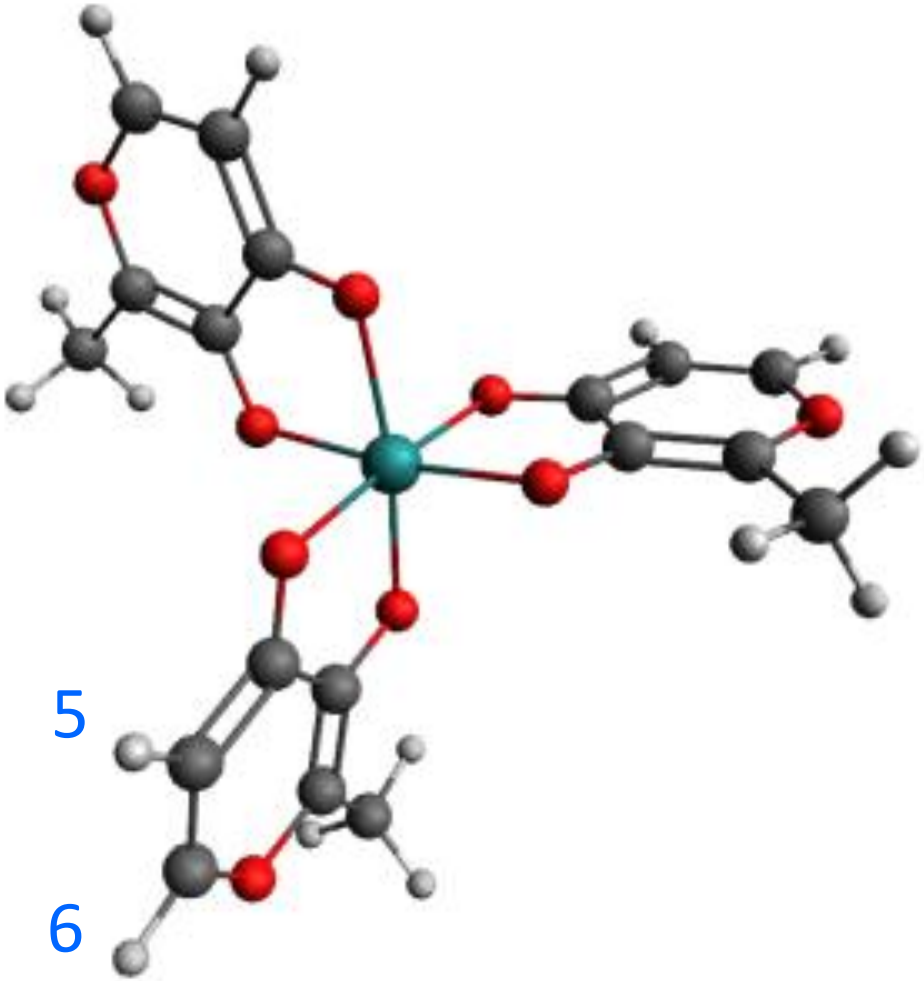
δ^{orb} 5.0

δ^{cs} 6.4 $= 9.5 - 3.1$

δ^{pc} -3.5

δ^{tot} 7.9

How far from metal center will δ^{cs} vanish?



5

6

	δ^{cs}
CH_3(a)	56.4
CH_3(b)	73.8
CH_3(c)	-8.5
H-5a	-7.5
H-6a	-7.9
H-5b	-14.7
H-6b	7.0
H-5c	10.2
H-6c	2.6

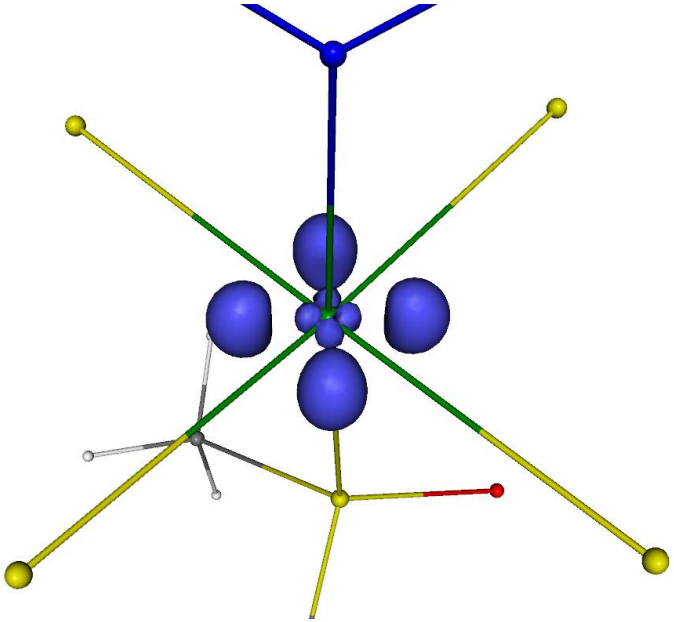
Limitations of expression for δ^{pc}

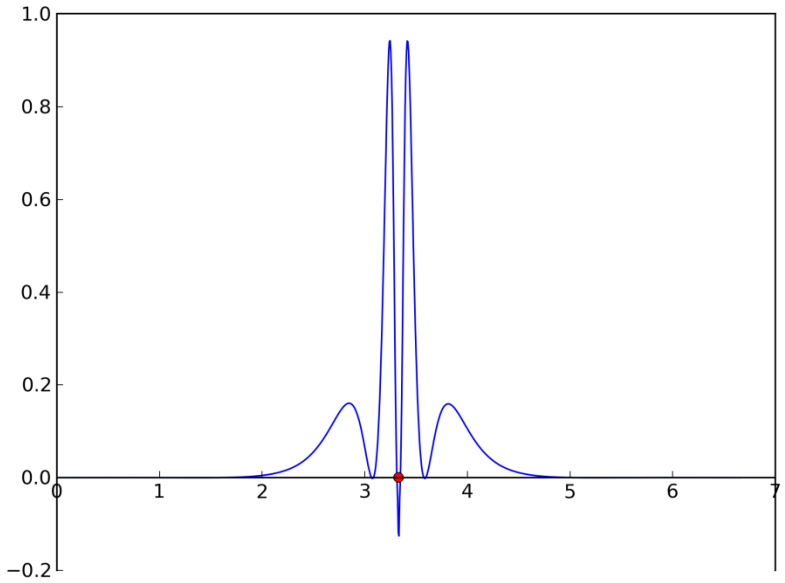
$$\delta_M^{pc} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{9kT} Tr\left(g^{ani} A_M^{dip}\right)$$

- System must obey Curie law (no spin-orbit coupling effects)
- The electron spin on the paramagnetic center can be considered as a point dipole
- No spin-orbit effects ➔ $g^{ani} = 0$ ➔ $\delta_M^{pc} = 0$

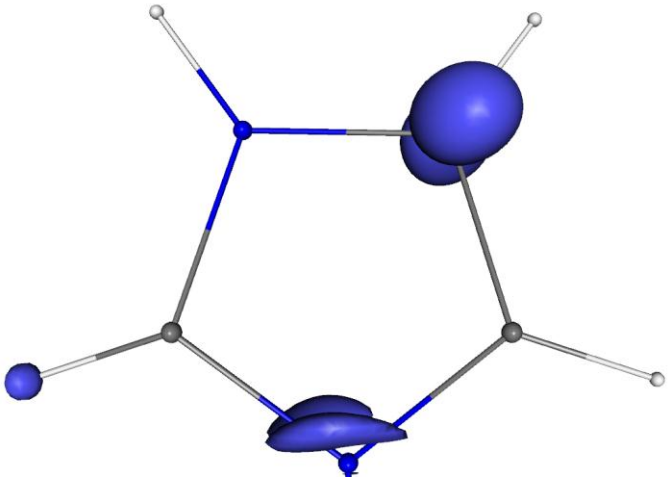
How much of the spin density matter?

$\frac{1}{10}$

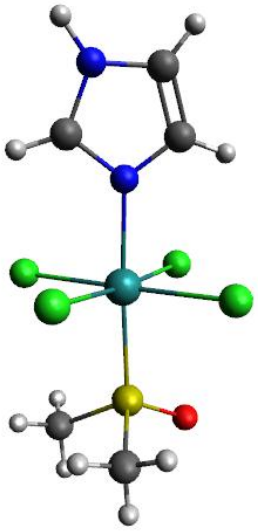




$\frac{1}{10000}$



9.5



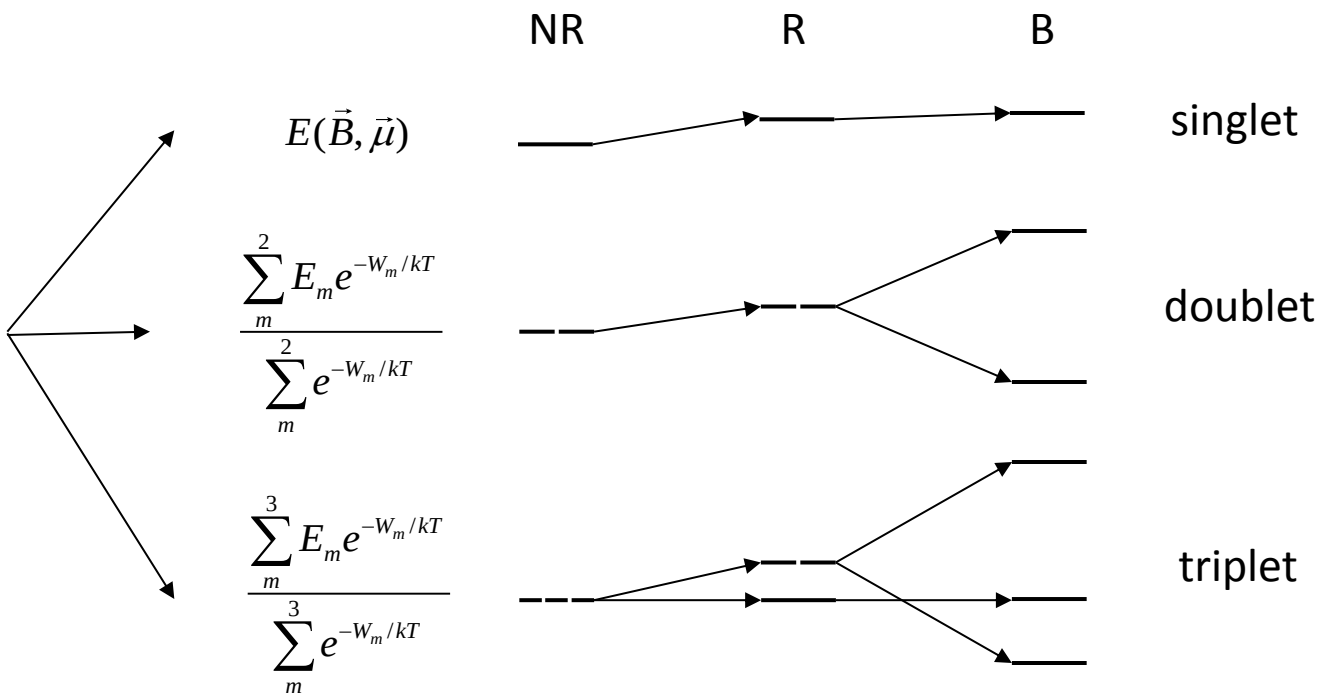
Theoretical considerations

Paramagnetic NMR shielding tensor

NMR shielding tensor for closed-shell systems (singlets): $$\sigma_{uv}^{M} = \frac{\partial^2 E(\vec{B},\vec{\mu})}{\partial B_u \partial \mu_v}$$

NMR shielding tensor for open-shell systems (multiplets): $$\sigma_{uv}^{M} = \frac{\partial^2 \left\langle E(\vec{B},\vec{\mu}) \right\rangle}{\partial B_u \partial \mu_v}$$

$$\left\langle E \right\rangle \equiv \frac{\sum_m E_m e^{-W_m/kT}}{\sum_m e^{-W_m/kT}}$$



Paramagnetic NMR shielding tensor

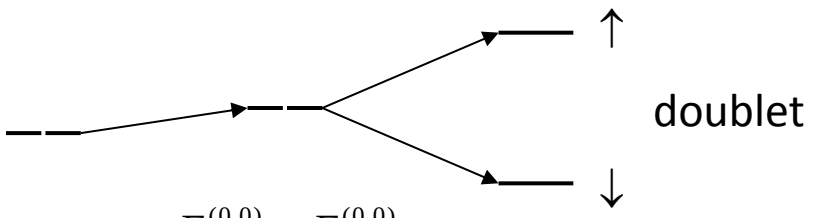
Paramagnetic NMR shielding tensor:

$$\sigma_{uv}^{M} = \frac{\partial^2 \langle E \rangle}{\partial B_u \partial \mu_v} \qquad \langle E \rangle \equiv \frac{\sum_m E_m e^{-W_m/kt}}{\sum_m e^{-W_m/kt}}$$

$$\boldsymbol{\sigma} = \left\langle E^{(\mathbf{B},\boldsymbol{\mu})} \right\rangle_0 - \frac{1}{kT} \left\langle E^{(\mathbf{B},0)} E^{(0,\boldsymbol{\mu})} \right\rangle_0$$

$$\langle X \rangle_0 \equiv \frac{\sum_k X_k e^{-E_k^{(0,0)}/kT}}{\sum_k e^{-E_k^{(0,0)}/kT}}$$

NR R B



$$E_{\uparrow}^{(0,0)} = E_{\downarrow}^{(0,0)}$$

$$E_{\uparrow}^{(\mathbf{B},0)} = -E_{\downarrow}^{(\mathbf{B},0)}$$

$$E_{\uparrow}^{(0,\boldsymbol{\mu})} = -E_{\downarrow}^{(0,\boldsymbol{\mu})}$$

$$E_{\uparrow}^{(\mathbf{B},\boldsymbol{\mu})} = E_{\downarrow}^{(\mathbf{B},\boldsymbol{\mu})}$$

Paramagnetic NMR shielding tensor for doublet:

$$\boldsymbol{\sigma} = E^{(\mathbf{B},\boldsymbol{\mu})} - \frac{1}{kT} E^{(\mathbf{B},0)} E^{(0,\boldsymbol{\mu})}$$

$$\langle X \rangle_0 \equiv \frac{X_{\uparrow} e^{-E_{\uparrow}^{(0,0)}/kT} + X_{\downarrow} e^{-E_{\downarrow}^{(0,0)}/kT}}{e^{-E_{\uparrow}^{(0,0)}/kT} + e^{-E_{\downarrow}^{(0,0)}/kT}} = \frac{1}{2}\left(X_{\uparrow} + X_{\downarrow}\right)$$

Paramagnetic NMR shielding tensor

Paramagnetic NMR shielding tensor for doublet:

$$\boldsymbol{\sigma} = E^{(\mathbf{B},\boldsymbol{\mu})} - \frac{1}{kT} E^{(\mathbf{B},0)} E^{(0,\boldsymbol{\mu})}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\text{orb}} - \frac{\beta_e}{4kTg_I\beta_N} \mathbf{g}\mathbf{A}^{\text{T}}$$

Orbital, contact and pseudocontact contribution:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\text{orb}} + \boldsymbol{\sigma}_{\text{fc}} + \boldsymbol{\sigma}_{\text{pc}}$$

$$\boldsymbol{\sigma}_{\text{fc}} \equiv \mathbf{g}\mathrm{A}_{\text{iso}}^{\text{T}} \qquad \boldsymbol{\sigma}_{\text{pc}} \equiv \mathbf{g}\mathbf{A}_{\text{ani}}^{\text{T}}$$

How to split NMR shielding tensor into different contributions?

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathrm{orb}} - \frac{\beta_e}{4kTg_I\beta_N}\mathbf{g}\mathbf{A}^{\mathrm{T}}$$

$$\mathbf{A} = A^{\mathrm{iso}}\mathbf{1} + \mathbf{A}^{\mathrm{ani}}$$

$$A^{\mathrm{iso}} \equiv \frac{1}{3}\mathrm{Tr}[\mathbf{A}]$$

$$\mathbf{A}^{\mathrm{ani}} \equiv \mathbf{A} - A^{\mathrm{iso}}\mathbf{1}$$

Pseudocontact contribution:

$$H = -\gamma_I I_a \left[\frac{3r_a r_b}{r^5} - \frac{\delta_{ab}}{r^3}\right]\langle\bar{\mu}\rangle_b \longrightarrow \boldsymbol{\sigma}_{\mathrm{pc}} \equiv \mathbf{g}\mathbf{A}_{\mathrm{ani}}^{\mathrm{T}}$$

Contact contribution:

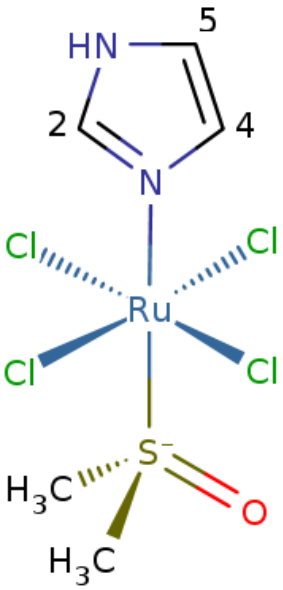
$$H = A\mathbf{S}\cdot\mathbf{I} \longrightarrow \boldsymbol{\sigma}_{\mathrm{fc}} \equiv \mathbf{g}\mathrm{A}_{\mathrm{iso}}^{\mathrm{T}}$$

I. Bertini, C. Luchinat, and G. Parigi *Prog. Nucl. Magn. Reson. Spectrosc.* **40**, 249 (2002).

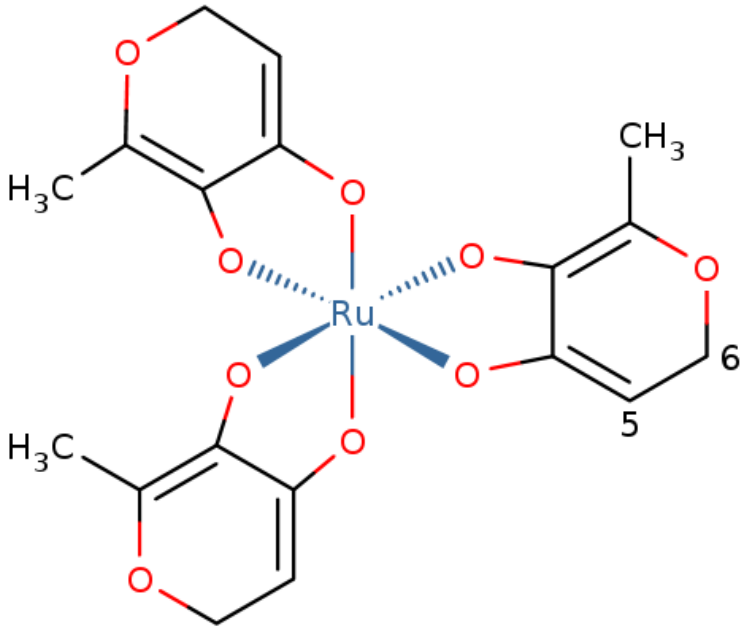
Results

Four-component relativistic calculations of pNMR shielding for doublet systems:

S. Komorovsky, M. Repisky, K. Ruud, O. L. Malkina, and V. G. Malkin
J. Phys. Chem. A **117**, 14209 (2013).



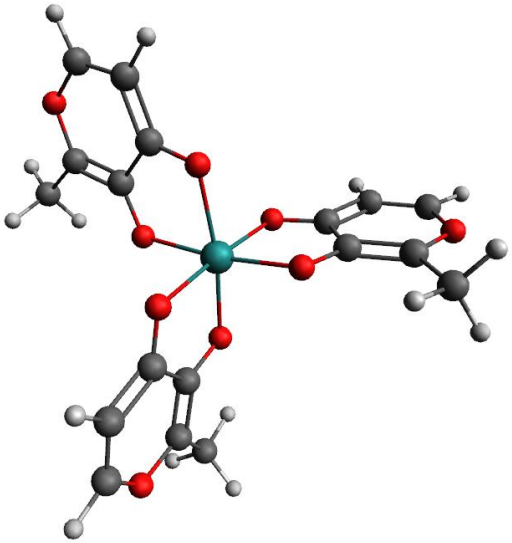
NAMI

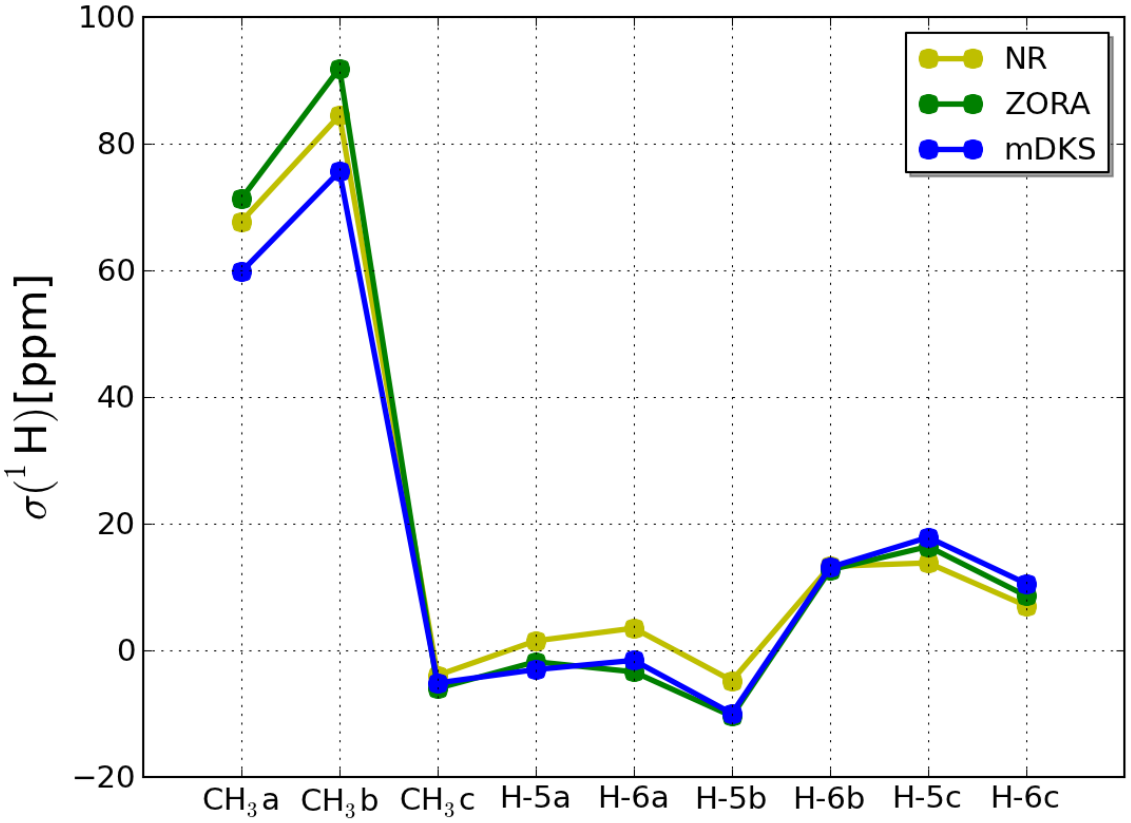


mer-Ru(ma)$_3$

F. Rastrelli and A. Bagno, *Mag. Res. in Chem.* **48**, S132 (2010). → NR and ZORA

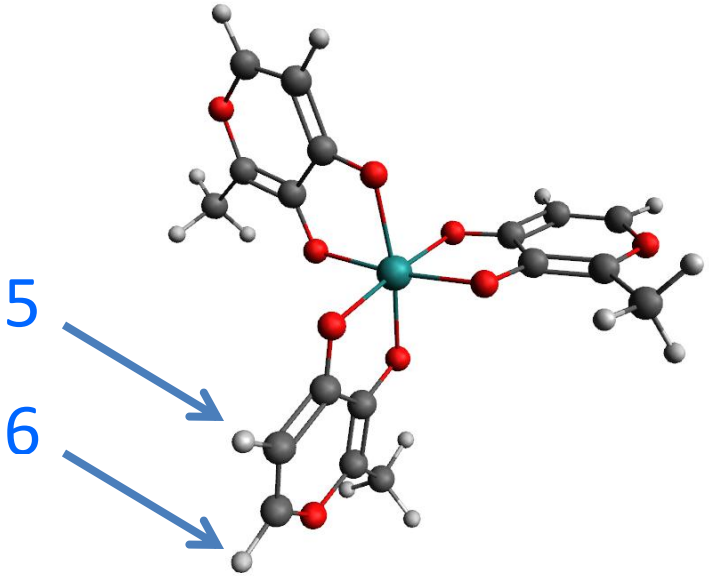
Small relativistic effects in ^{1}H shifts in mer-Ru(ma)$_3$

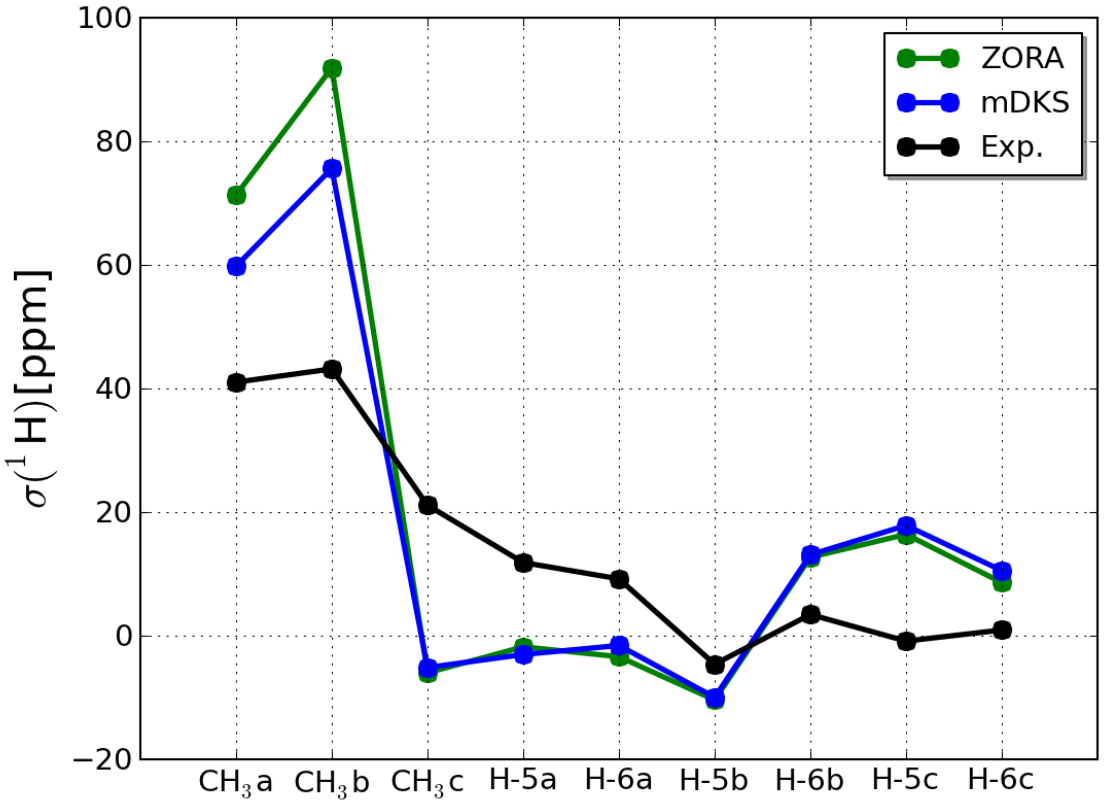




mer-Ru(ma)$_3$	δ_{ZORA}	δ_{mDKS}
CH_3 a	71.3	59.7
CH_3 b	91.9	75.6
CH_3 c	-6.0	-5.2
H-5a	-1.8	-3.0
H-6a	-3.4	-1.6
H-5b	-10.4	-10.0
H-6b	12.7	13.1
H-5c	16.4	17.8
H-6c	8.6	10.5

Calculated and experimental ^{1}H shifts in mer-Ru(ma)$_3$

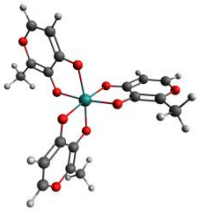


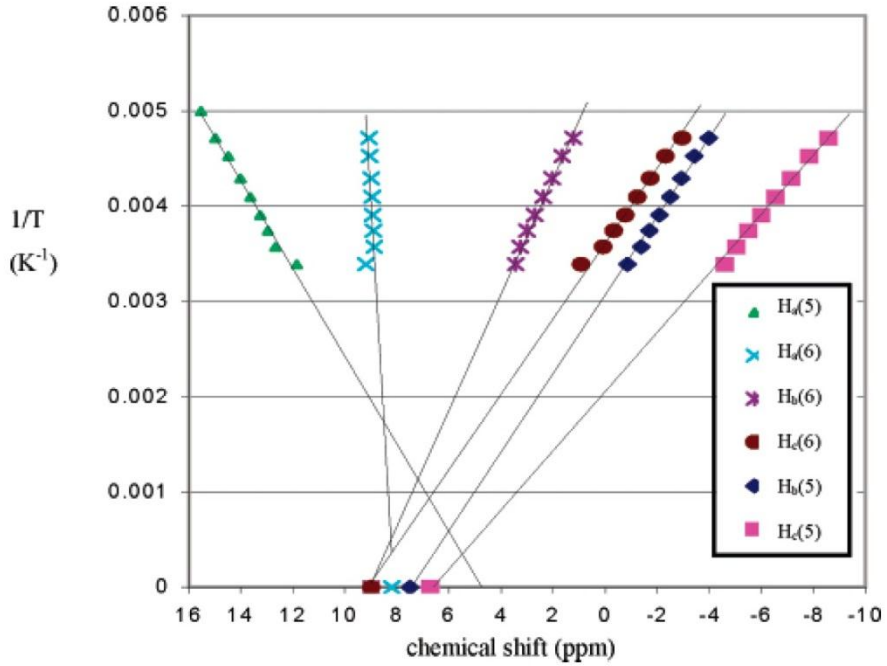


	δ_{ZORA}	δ_{mDKS}	δ_{exp}
mer-Ru(ma)$_3$			
CH$_3$ a	71.3	59.7	41.0
CH$_3$ b	91.9	75.6	43.2
CH$_3$ c	-6.0	-5.2	21.1
H-5a	-1.8	-3.0	11.8
H-6a	-3.4	-1.6	9.2
H-5b	-10.4	-10.0	-4.6
H-6b	12.7	13.1	3.4
H-5c	16.4	17.8	-0.9
H-6c	8.6	10.5	0.9

Experimental assignment of pNMR shifts

D.C. Kennedy, A. Wu, B.O. Patrick, and B.R. James *Inorg. Chem.* **44**, 6529 (2005).





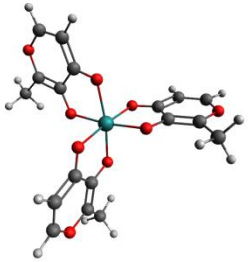
	δ_{theo}^{orb}	δ_{exp}^{orb}
CH_3(a)	2.1	9.0
CH_3(b)	1.5	10.0
CH_3(c)	2.2	14.3
H-5a	5.8	4.9
H-6a	6.7	8.0
H-5b	6.1	6.7
H-6b	6.5	9.0
H-5c	7.2	7.5
H-6c	7.6	9.0

"the extrapolated values ($T \rightarrow \infty$) in every case are within 1.5 ppm of the diamagnetic values measured for free maltol in CD_2Cl_2 [*H*(5) at δ 6.4, and *H*(6) at δ 7.7]"

"The *x* intercepts for the resonances of these groups from the low-temperature ^{1}H NMR data (δ 14.3, δ 10.0 and δ 9.0) do not, however, correlate well with the Me resonance of free maltol (δ 2.4)."

Experimental assignment of pNMR shifts

D.C. Kennedy, A. Wu, B.O. Patrick, and B.R. James *Inorg. Chem.* **44**, 6529 (2005).



"the magnitude of the hyperfine shift for *H*(5) is always greater than that for *H*(6) as expected because *H*(5) is closer to the Ru(III) center."

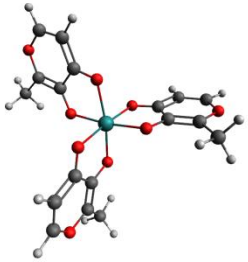
Isotropic hyperfine coupling constants for ^{1}H in *mer*-$Ru(ma)_3$ [MHz]

	5a	6a	5b	6b	5c	6c
FC	-0.232	-0.293	-0.496	0.265	0.333	0.078
PSO	-0.033	0.001	-0.032	-0.002	0.039	0.010
SD	-0.012	-0.001	-0.014	-0.004	0.004	0.009
SUM	-0.277	-0.293	-0.541	0.259	0.376	0.097

	δ^{cs}	δ^{pc}
CH_3(a)	56.4	1.3
CH_3(b)	73.8	0.3
CH_3(c)	-8.5	1.1
H-5a	-7.5	-1.3
H-6a	-7.9	-0.4
H-5b	-14.7	-1.4
H-6b	7.0	-0.4
H-5c	10.2	0.5
H-6c	2.6	0.4

Couplings between H-5 and H-6 protons

D.C. Kennedy, A. Wu, B.O. Patrick, and B.R. James *Inorg. Chem.* **44**, 6529 (2005).



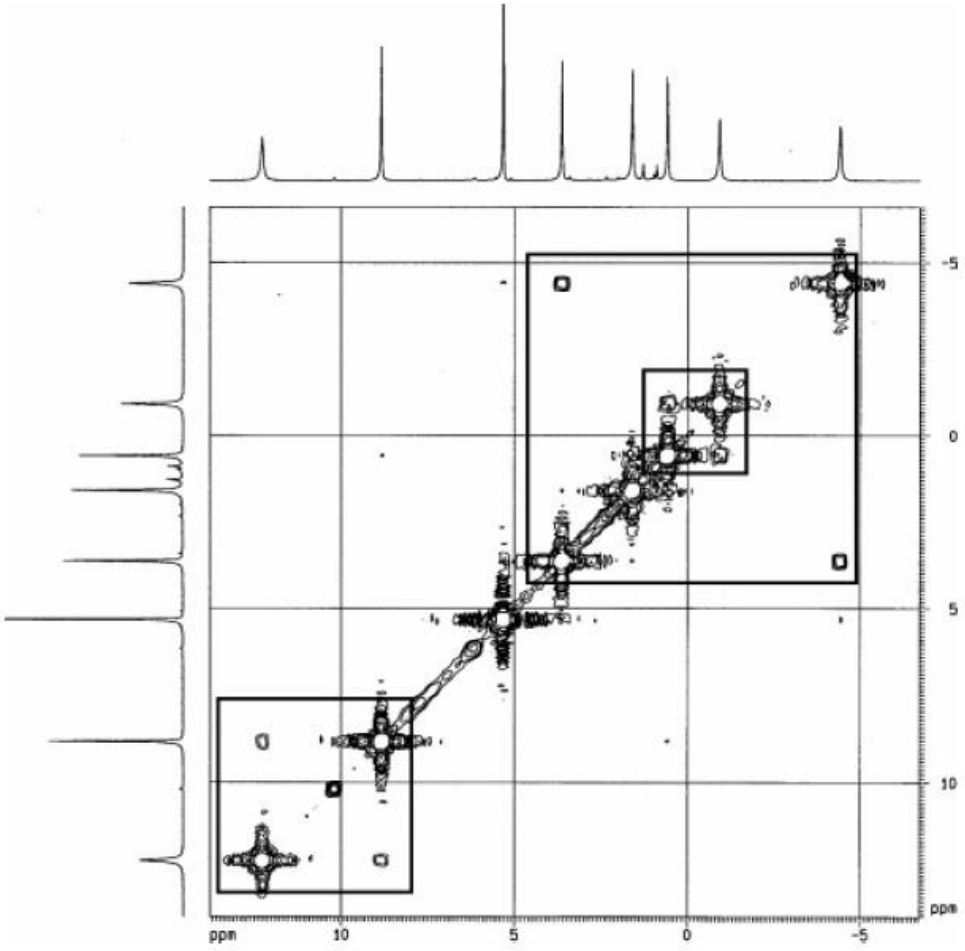
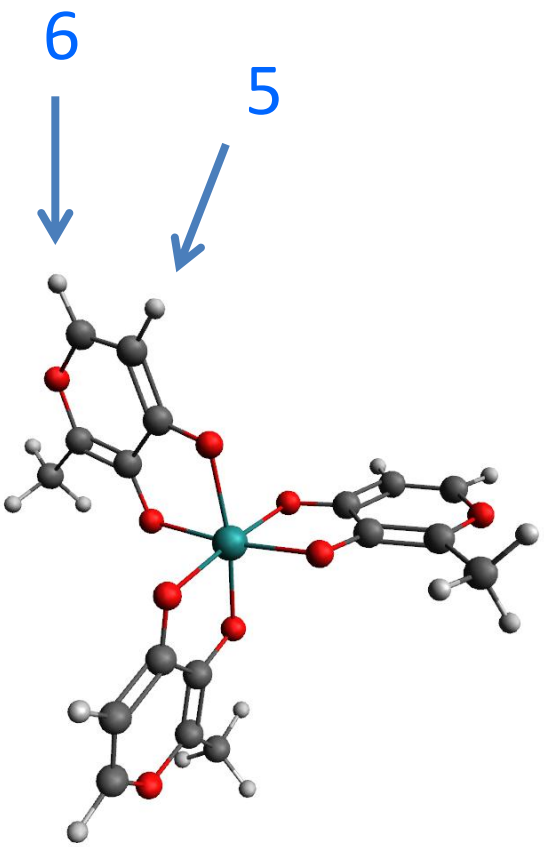
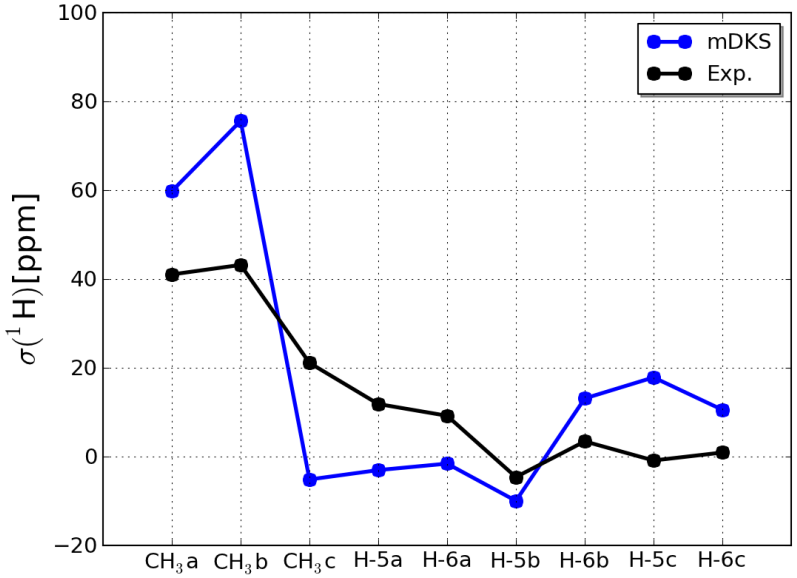
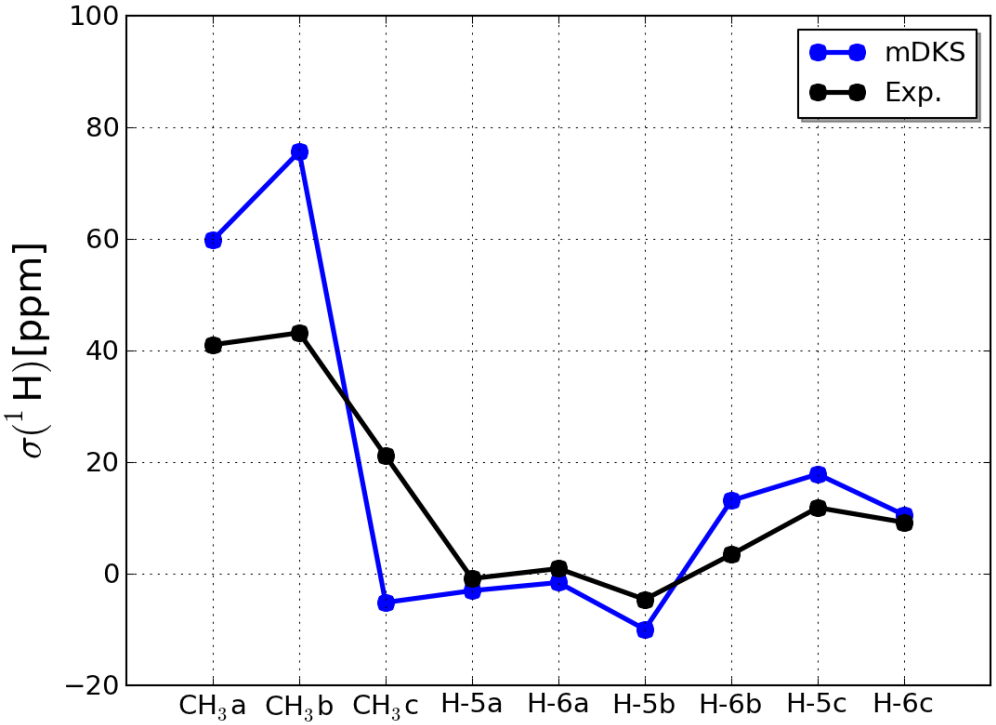


Figure 2. ^{1}H COSY NMR spectrum (300 MHz, CD_2Cl_2) of **1a**. The squares indicate ma *H*(5)/*H*(6) coupling pairs.

Assignment of experimental data to calculated values.

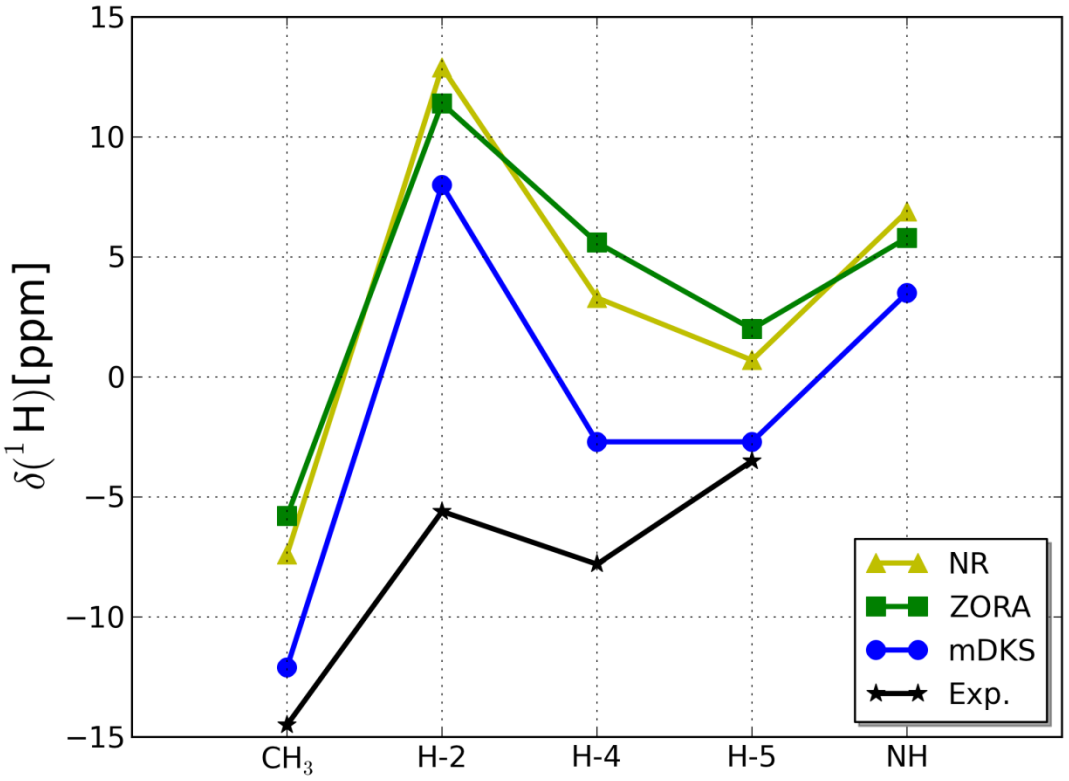


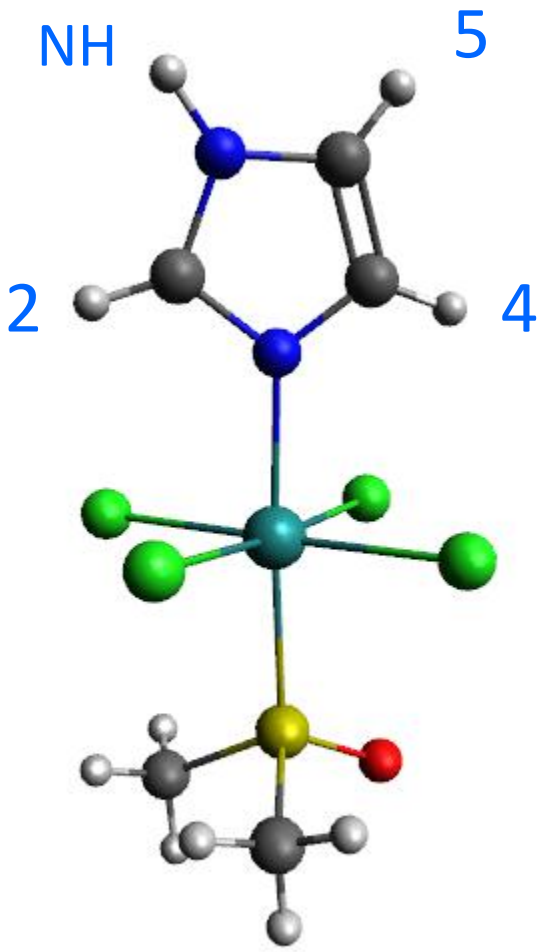




	δ_{nr}	δ_{ZORA}	δ_{mDKS}	δ_{exp}
NAMI				
$O=S(CH_3)_2$	-7.4	-5.8	-12.1	-14.5
H-2	12.9	11.4	8.0	-5.6
H-4	3.3	5.6	-2.7	-7.8
H-5	0.7	2.0	-2.7	-3.5
NH	6.9	5.8	3.5	

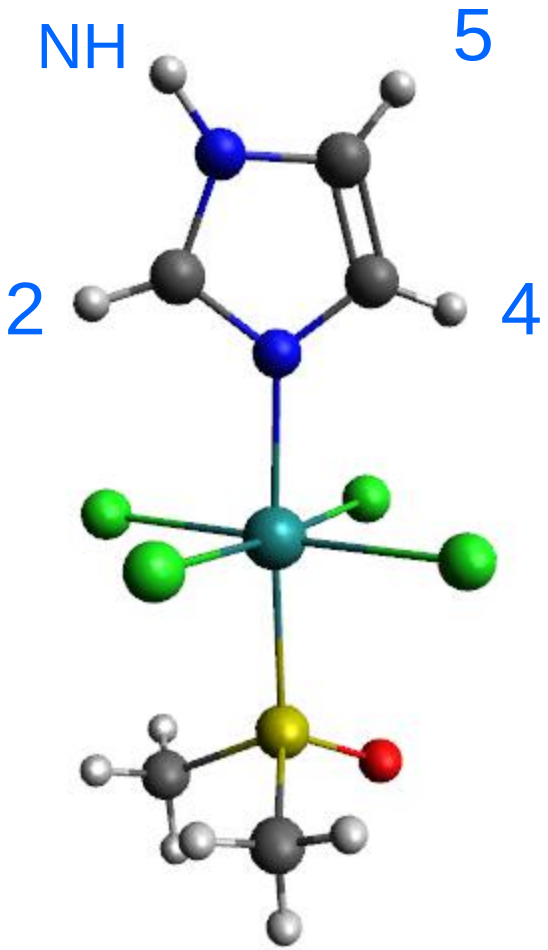
Significant differences between different methods and experimental 1H shifts in NAMI.



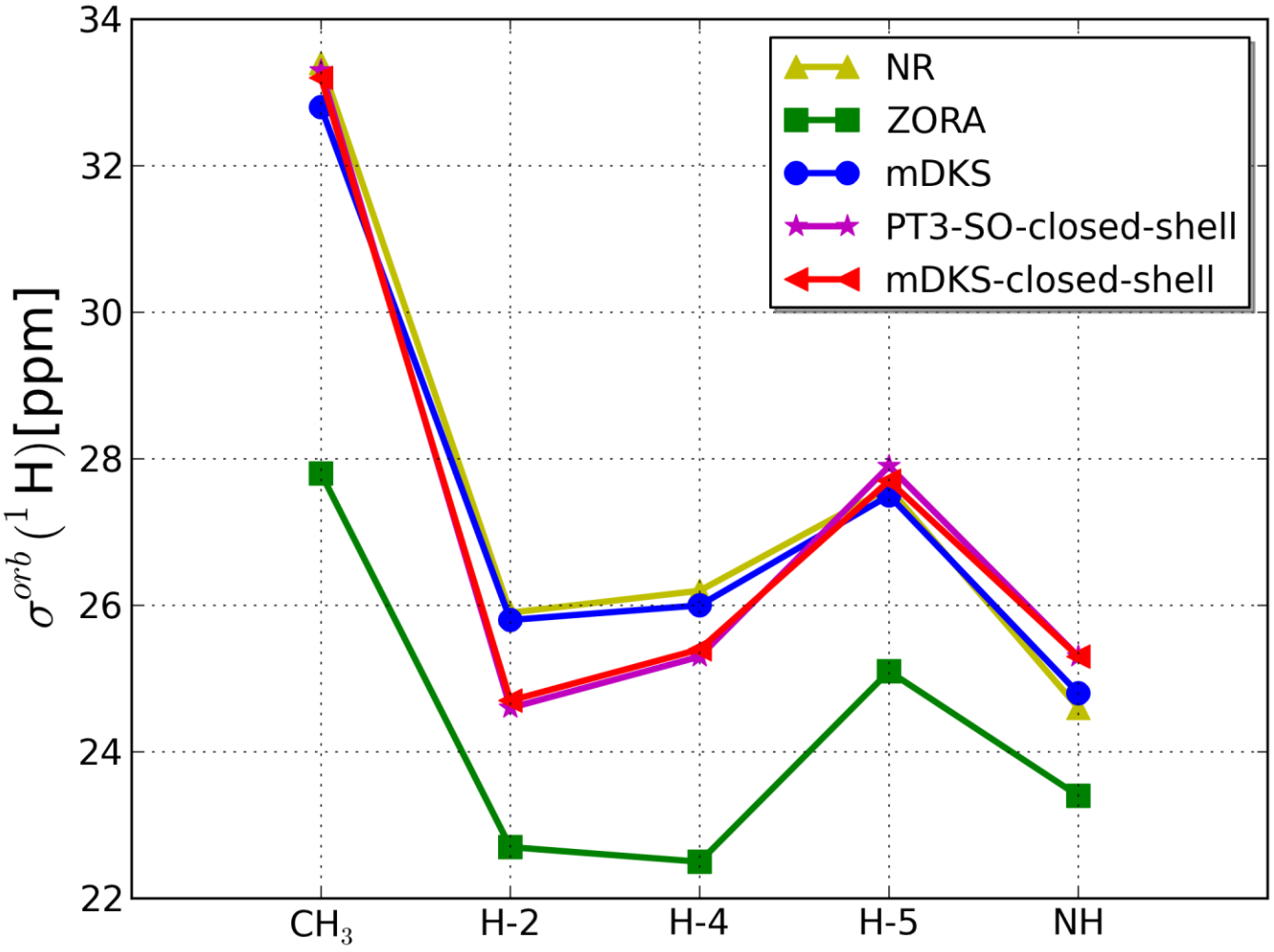


Origin of differences between ZORA and mDKS method for ^{1}H shifts in NAMI.

		σ_{orb}	σ_{fc}	σ_{pc}	σ_{sum}
NAMI					
$O=S(CH_3)_2$	ZORA	27.8	9.4		37.2
	mDKS	32.8	8.0	2.2	43.0
H-2	ZORA	22.7	-2.7		19.9
	mDKS	25.8	-6.4	3.5	22.8
H-4	ZORA	22.5	3.2		25.7
	mDKS	26.0	4.3	3.2	33.5
H-5	ZORA	25.1	4.3		29.4
	mDKS	27.5	4.7	1.3	33.6
NH	ZORA	23.4	2.1		25.5
	mDKS	24.8	1.3	1.3	27.3



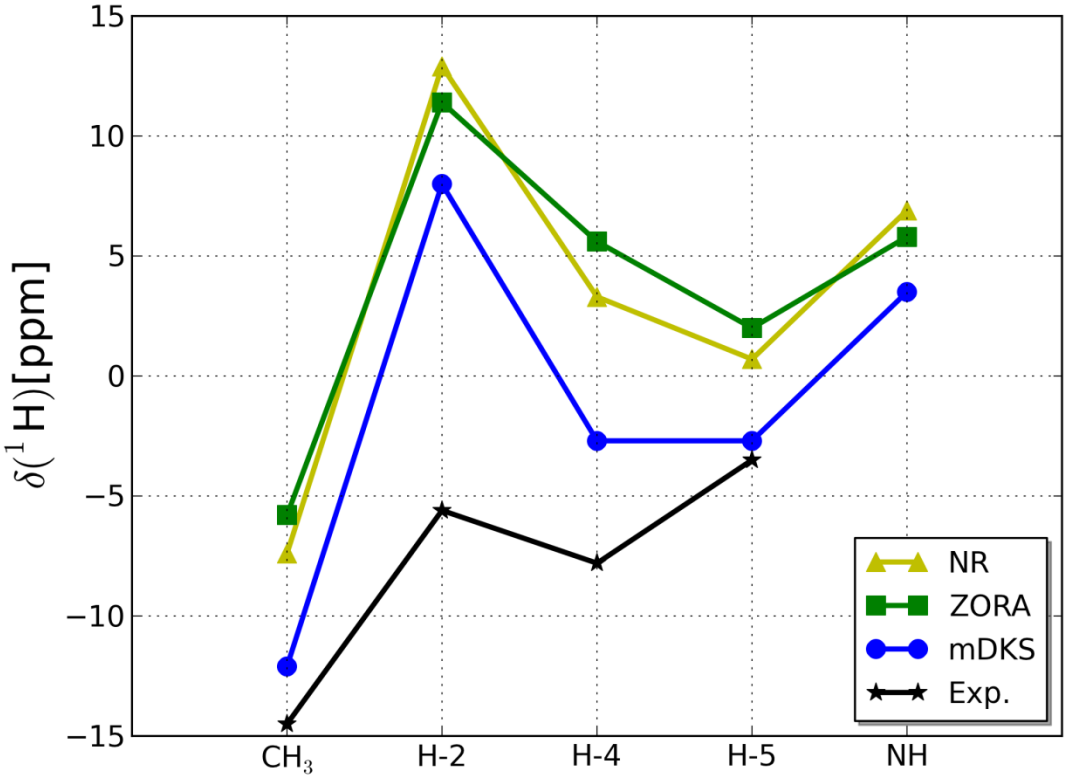
Systematical underestimation of orbital NMR shielding by ZORA method

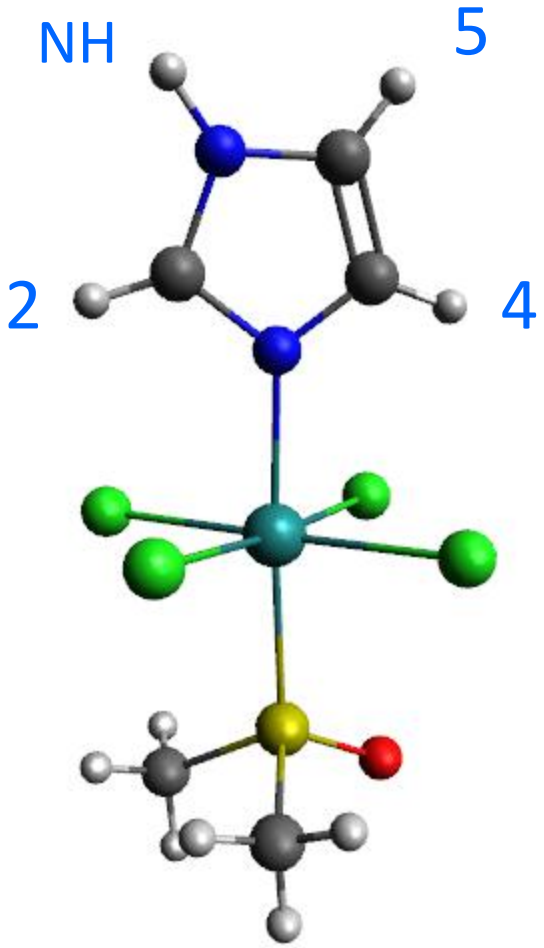


Possible differences between ZORA and mDKS calculations

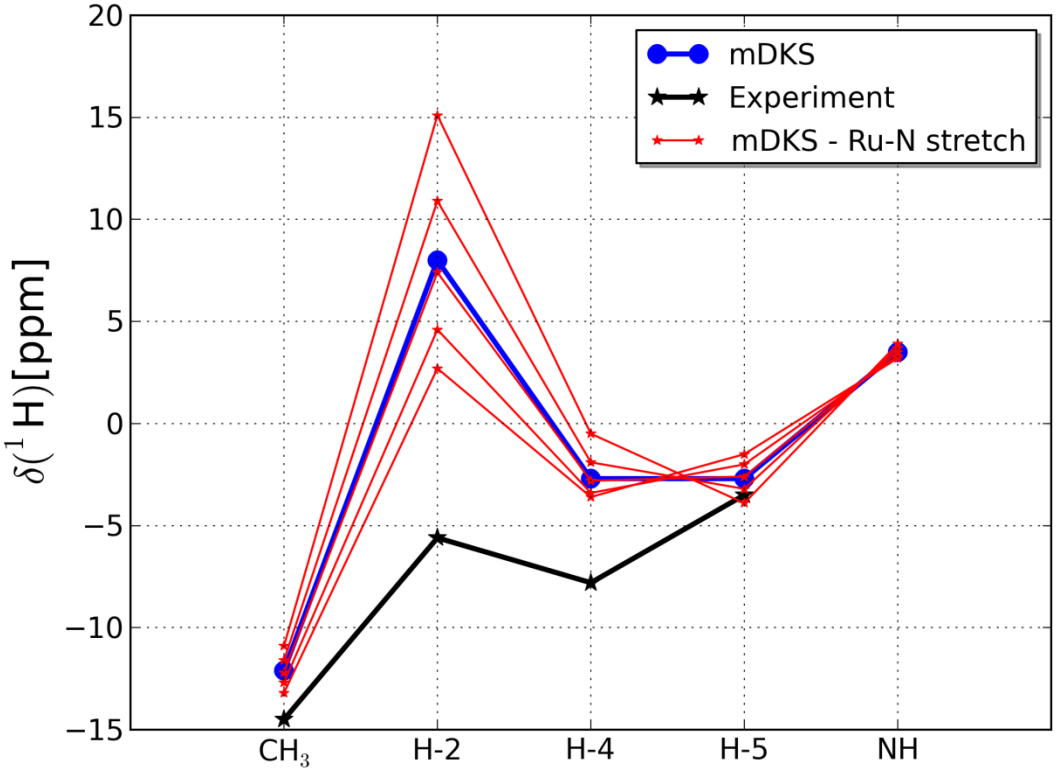
	ZORA	mDKS
Hamiltonian	ZORA Hamiltonian (SO included)	full four-component Dirac-Coulomb Hamiltonian
Basis	STO: TZ2P	GTO: Ru - Dyall vTZ; light elements - upcJ-2
g-tensor, HFCC	SO restricted calculation SR spin-polarized calculation	non-collinear DFT functional
Nuclear shielding	closed-shell analog (Ru(II))	open-shell compound
Fitting	no fitting	fitting of the electron density and spin densities
potential/kernel	BP86/BP86	BP86/SVWN5

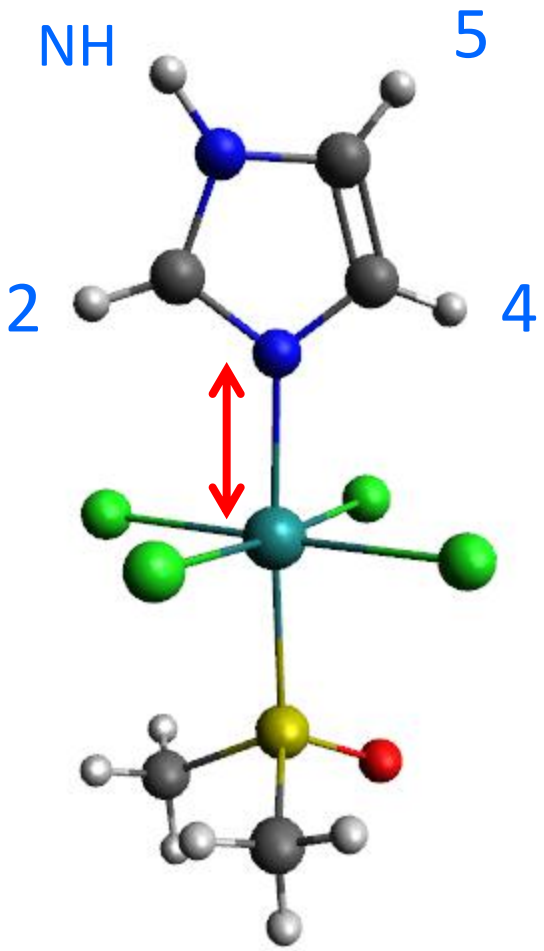
Why there is so big difference for H-2 shift anyway?





First hint: stretching Ru-N bond helps

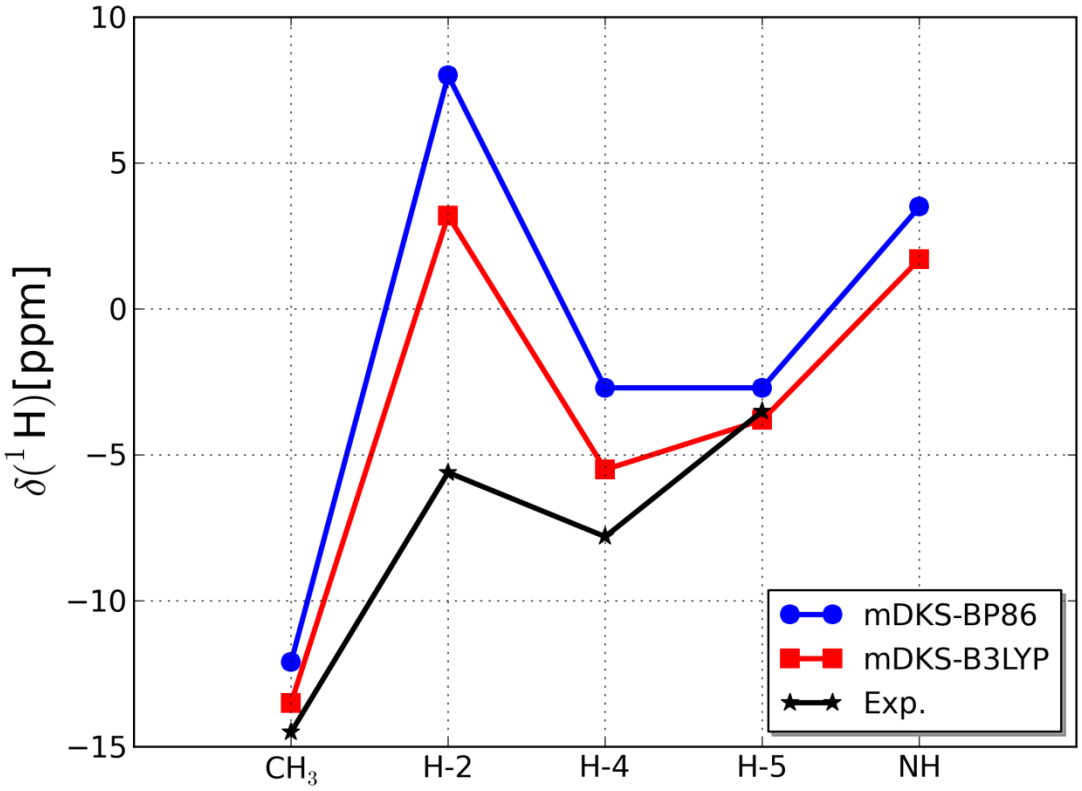


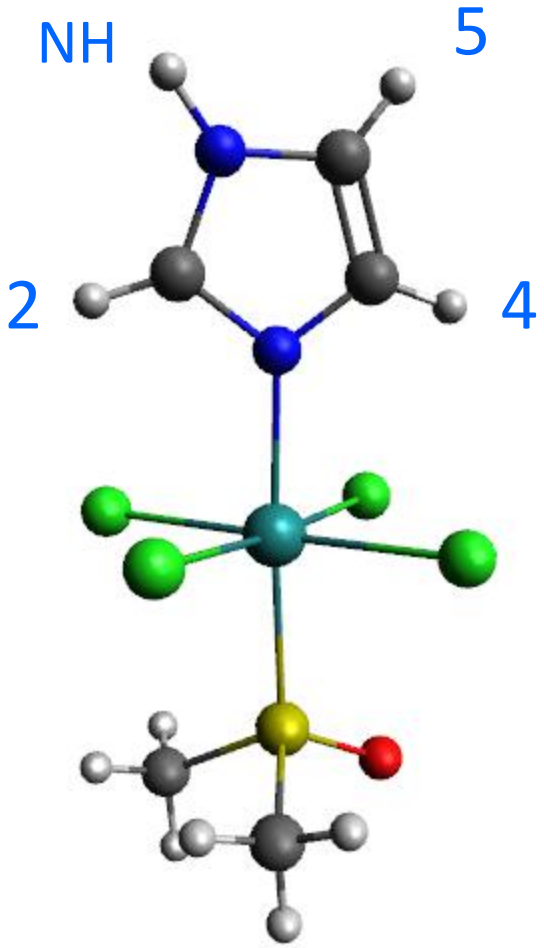


Effect of stretching of Ru−N bond in the interval 1.9−2.3 Å.

Closer to the experimental data are results with longer bonds.

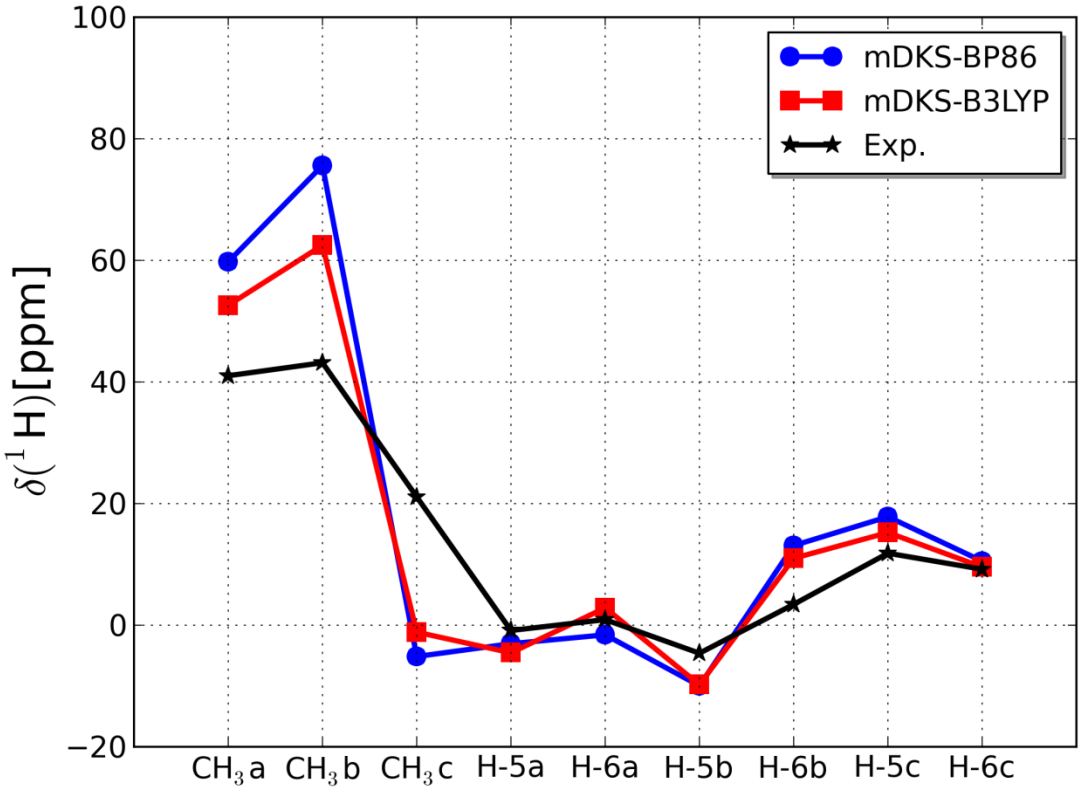
Second hint: hybrid functionals

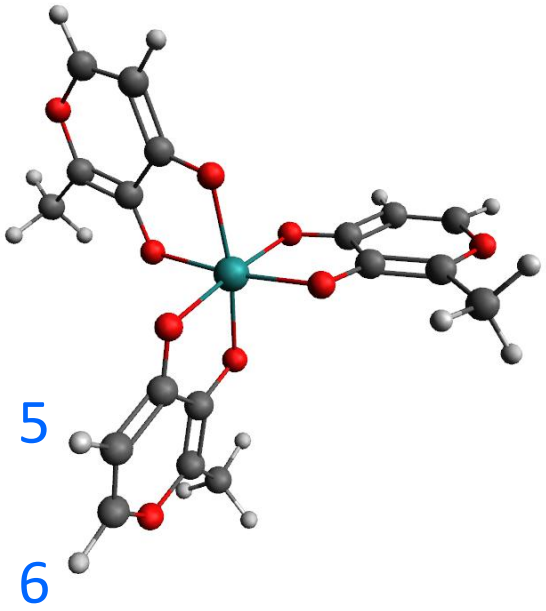




$$\delta_M = \delta_M^{orb} + \delta_M^{cs} + \delta_M^{pc}$$

Using hybrid functionals in *mer*-Ru(ma)$_3$ compound





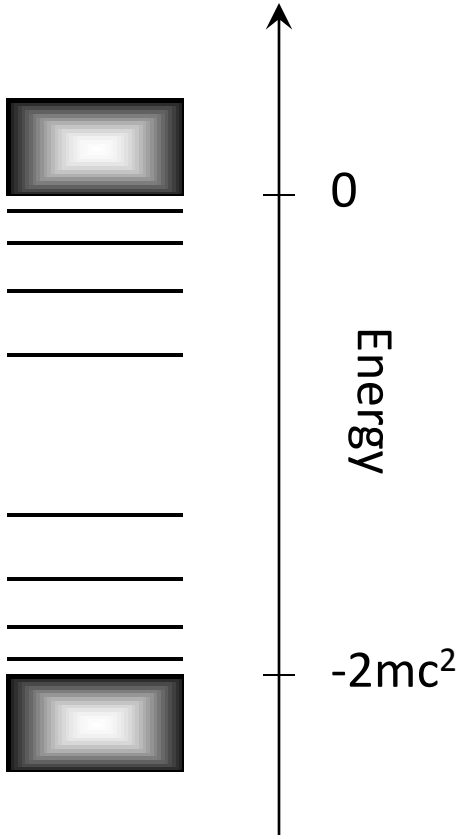
$$\delta_M = \delta_M^{orb} + \delta_M^{cs} + \delta_M^{pc}$$

Why is relativity complicated?

Dirac equation

P. A. M. Dirac, *Proc. R. Soc London* Ser. A **117**, 610 (1928)

- *describes the motion of electron in the external potential*
- *has the 4-component form*
- *describes the spin naturally*
- gives the positive energy (E>0) and negative energy (E<0) solutions



$$\begin{pmatrix} \hat{V} & 0 & cp_z & c(p_x - ip_y) \\ 0 & \hat{V} & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & \hat{V} - 2c^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & \hat{V} - 2c^2 \end{pmatrix} \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix} = E \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix}$$

More compact Dirac notation

$$\begin{pmatrix} \hat{V} & 0 & cp_z & c(p_x - ip_y) \\ 0 & \hat{V} & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & \hat{V} - 2c^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & \hat{V} - 2c^2 \end{pmatrix} \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix} = E \begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix}$$

Pauli matrices: $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\begin{pmatrix} \hat{V} & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & \hat{V} - 2c^2 \end{pmatrix} \begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} = E \begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$$

How small is the small component?

energy states

Positive (electron)

$\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$ large 0.99

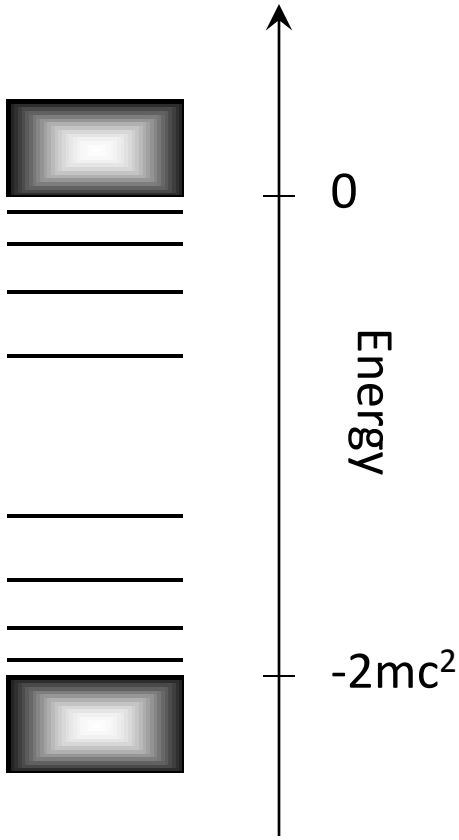
small 0.01

Negative (positron)

$\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$ small

large

$$\langle \varphi | \varphi \rangle = \langle \varphi^L | \varphi^L \rangle + \langle \varphi^S | \varphi^S \rangle = 1$$



Non-relativistic limit of Dirac equation

$$\begin{pmatrix} \hat{V} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}-2c^2 \end{pmatrix}\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} = E\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$$

Non-relativistic limit: $c \to \infty$

$$\left(\tfrac{1}{2}p^2 + \hat{V}\right)\varphi = E\varphi$$

Elimination of the small component:

$$\hat{V}\,\varphi^L + c\vec{\sigma}\cdot\vec{p}\,\varphi^S = E\varphi^L$$

$$c\vec{\sigma}\cdot\vec{p}\,\varphi^L + (\hat{V}-2c^2)\,\varphi^S = E\varphi^S \quad \longrightarrow$$

$$\hat{K} = \left[1 + \frac{E-\hat{V}}{2c^2}\right]^{-1}$$

$$\varphi^S = \frac{1}{2c}\hat{K}\,\vec{\sigma}\cdot\vec{p}\,\varphi^L$$

$$\left[\hat{V} + \frac{1}{2}\vec{\sigma}\cdot\vec{p}\,\hat{K}\,\vec{\sigma}\cdot\vec{p}\right]\varphi^L = E\varphi^L$$

$$\left(\vec{\sigma}\cdot\vec{p}\right)^2 = p^2$$

Wrong non-relativistic limit in finite basis

In QCh we are looking for expansion coefficients: $\varphi = \sum_{\mu=1}^{N} C_\mu \chi_\mu$

- Dirac equation:

$$\begin{pmatrix} \langle\chi|\hat{V}|\chi\rangle & \langle\chi|c\vec{\sigma}\cdot\vec{p}|\chi\rangle \\ \langle\chi|c\vec{\sigma}\cdot\vec{p}|\chi\rangle & \langle\chi|\hat{V}-2c^2|\chi\rangle \end{pmatrix} \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = E \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix}$$

- Non-relativistic limit: $C \longrightarrow \infty$

- Should be Schrodinger equation:

$$\left(\frac{1}{2}\langle\chi|\vec{\sigma}\cdot\vec{p}|\chi\rangle\langle\chi|\vec{\sigma}\cdot\vec{p}|\chi\rangle + \langle\chi|V|\chi\rangle\right)\mathbf{C} = E\,\mathbf{C}$$

Complete (infinite) basis:

$$\xrightarrow[|\chi\rangle\langle\chi|=1]{(\vec{\sigma}\cdot\vec{p})^2 = p^2} \left(\frac{1}{2}\langle\chi|p^2|\chi\rangle + \langle\chi|V|\chi\rangle\right)\mathbf{C} = E\,\mathbf{C}$$

Zero kinetic energy for s orbital!

$$\left(\langle \chi | V | \chi \rangle + \frac{1}{2} \langle \chi | \vec{\sigma} \cdot \vec{p} | \chi \rangle \langle \chi | \vec{\sigma} \cdot \vec{p} | \chi \rangle \right) \mathbf{C} = E \, \mathbf{C}$$

1s orbital in hydrogen atom: $\varphi = \sum_{\mu=1}^{N} C_\mu \, \chi_\mu = \sum_{\mu=1}^{N} C_\mu \, s_\mu$

$s_\mu \rightarrow$ s type functions only

$$\langle \mathbf{s} | \vec{\sigma} \cdot \vec{p} | \mathbf{s} \rangle = -i \begin{pmatrix} \langle \mathbf{s} | \nabla_Z | \mathbf{s} \rangle & \langle \mathbf{s} | \nabla_X - i \nabla_Y | \mathbf{s} \rangle \\ \langle \mathbf{s} | \nabla_X + i \nabla_Y | \mathbf{s} \rangle & -\langle \mathbf{s} | \nabla_Z | \mathbf{s} \rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

Solution: don't use the same basis for φ^L and φ^S

$$\begin{pmatrix} \hat{V} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}-2c^2 \end{pmatrix}\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} = E\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$$

The same basis functions for both components

$$\varphi^L = \sum_{\mu=1}^{N} C_\mu^L \chi_\mu \qquad \varphi^S = \sum_{\mu=1}^{N} C_\mu^S \chi_\mu$$

$$\begin{pmatrix} \langle\boldsymbol{\chi}|\hat{V}|\boldsymbol{\chi}\rangle & \langle\boldsymbol{\chi}|c\vec{\sigma}\cdot\vec{p}|\boldsymbol{\chi}\rangle \\ \langle\boldsymbol{\chi}|c\vec{\sigma}\cdot\vec{p}|\boldsymbol{\chi}\rangle & \langle\boldsymbol{\chi}|\hat{V}-2c^2|\boldsymbol{\chi}\rangle \end{pmatrix}\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = E\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix}$$

Solution: don't use the same basis for φ_L and φ_S

Polar coordinates

Cartesian coordinates

$\varphi(1s)$:

$$\begin{pmatrix} \varphi_\alpha^L \\ \varphi_\beta^L \\ \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix} = \begin{pmatrix} e^{-r} \\ 0 \\ \frac{i}{2c} e^{-r} \cos\theta \\ \frac{i}{2c} e^{-r} \sin\theta e^{i\phi} \end{pmatrix} \rightarrow \begin{pmatrix} \varphi_\alpha^S \\ \varphi_\beta^S \end{pmatrix} = \begin{pmatrix} \frac{i}{2c} \frac{z}{r} e^{-r} \\ \frac{i}{2c} \frac{x^2+y^2}{r} \left(\frac{x}{r} + i \frac{y}{r} \right) e^{-r} \end{pmatrix}$$

$$\frac{1}{2c} \vec{\sigma} \cdot \vec{p} \begin{pmatrix} e^{-r} \\ 0 \end{pmatrix} = -\frac{i}{2c} \begin{pmatrix} \nabla_Z & \nabla_X - i\nabla_Y \\ \nabla_X + i\nabla_Y & -\nabla_Z \end{pmatrix} \begin{pmatrix} e^{-r} \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{i}{2c} \frac{z}{r} e^{-r} \\ \frac{i}{2c} \left(\frac{x}{r} + i \frac{y}{r} \right) e^{-r} \end{pmatrix}$$

Use restricted kinetically balanced basis set:

$$\varphi^L = \sum_{\mu=1}^{N} C_\mu^L \chi_\mu \qquad \varphi^S = \sum_{\mu=1}^{N} C_\mu^S \frac{1}{2c} \vec{\sigma} \cdot \vec{p} \chi_\mu$$

Solution:
use restricted kinetically balanced basis for φ^S

$$\begin{pmatrix} \hat{V} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}-2c^2 \end{pmatrix}\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} = E\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$$

RKB basis for small component:

$$\varphi^L = \sum_{\mu=1}^{N} C_\mu^L \chi_\mu^L \qquad \varphi^S = \sum_{\mu=1}^{N} C_\mu^S \chi_\mu^S = \sum_{\mu=1}^{N} C_\mu^S \tfrac{1}{2c}\vec{\sigma}\cdot\vec{p}\chi_\mu$$

$$\begin{pmatrix} \langle \boldsymbol{\chi}^L | \hat{V} | \boldsymbol{\chi}^L \rangle & \langle \boldsymbol{\chi}^L | c\vec{\sigma}\cdot\vec{p} | \boldsymbol{\chi}^S \rangle \\ \langle \boldsymbol{\chi}^S | c\vec{\sigma}\cdot\vec{p} | \boldsymbol{\chi}^L \rangle & \langle \boldsymbol{\chi}^S | \hat{V}-2c^2 | \boldsymbol{\chi}^S \rangle \end{pmatrix}\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = E\begin{pmatrix} \langle \boldsymbol{\chi}^L | \boldsymbol{\chi}^L \rangle & 0 \\ 0 & \langle \boldsymbol{\chi}^S | \boldsymbol{\chi}^S \rangle \end{pmatrix}\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix}$$

$$\langle \boldsymbol{\chi}^L | c\vec{\sigma}\cdot\vec{p} | \boldsymbol{\chi}^S \rangle = \langle \boldsymbol{\chi} | c\vec{\sigma}\cdot\vec{p} | \tfrac{1}{2c}\vec{\sigma}\cdot\vec{p}\,\boldsymbol{\chi} \rangle = \tfrac{1}{2}\langle \boldsymbol{\chi} | p^2 | \boldsymbol{\chi} \rangle$$

Matrix Dirac equation

$$\begin{pmatrix} \hat{V} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}-2c^2 \end{pmatrix}\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} = E\begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix}$$

$$\varphi^L = \sum_{\mu=1}^{N} C_\mu^L \chi_\mu$$

$$\varphi^S = \sum_{\mu=1}^{N} C_\mu^S \tfrac{1}{2c}\vec{\sigma}\cdot\vec{p}\chi_\mu$$

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W}-\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = E\begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2c^2}\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix}$$

$$\mathbf{T} \equiv \tfrac{1}{2}\langle\boldsymbol{\chi}|\, p^2 \,|\boldsymbol{\chi}\rangle \qquad \mathbf{S} \equiv \langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle$$

$$\mathbf{V} \equiv \langle\boldsymbol{\chi}|\hat{V}|\boldsymbol{\chi}\rangle \qquad \mathbf{W} \equiv \tfrac{1}{4c^2}\langle\boldsymbol{\chi}|\vec{\sigma}\cdot\vec{p}\,\hat{V}\,\vec{\sigma}\cdot\vec{p}|\boldsymbol{\chi}\rangle$$

Dirac-Kohn-Sham equation

P. A. M. Dirac, *Proc. R. Soc London*, Ser. A **117**, 610 (1928)

Dirac one-electron equation:

$$\begin{pmatrix} \hat{V}\hat{1}_{2\times2} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \left(\hat{V}-2c^2\right)\hat{1}_{2\times2} \end{pmatrix}\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = E\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

Dirac-Kohn-Sham equation:

$$\begin{pmatrix} \hat{V}_{2\times2} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}_{2\times2}-2c^2\hat{1}_{2\times2} \end{pmatrix}\begin{pmatrix} \varphi_i^L \\ \varphi_i^S \end{pmatrix} = \varepsilon_i\begin{pmatrix} \varphi_i^L \\ \varphi_i^S \end{pmatrix}$$

$$\hat{V}_{2\times2}\left(\vec{r}\right) = \hat{V}_{nuc}\left(\vec{r}\right)\hat{1}_{2\times2} + \hat{V}_{ee}\left(\vec{r}\right)\hat{1}_{2\times2} + \left(\frac{\delta E\left[\rho\left(\vec{r}'\right)\right]}{\delta\rho\left(\vec{r}\right)}\right)_{2\times2}$$

matrix Dirac-Kohn-Sham (mDKS) equation

$$\begin{pmatrix} \hat{V}_{2\times2} & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & \hat{V}_{2\times2} - 2c^2\hat{1}_{2\times2} \end{pmatrix} \begin{pmatrix} \varphi_i^L \\ \varphi_i^S \end{pmatrix} = \varepsilon_i \begin{pmatrix} \varphi_i^L \\ \varphi_i^S \end{pmatrix}$$

RKB basis: $\varphi^L = \sum_{\mu=1}^{N} C_\mu^L \chi_\mu \qquad \varphi^S = \sum_{\mu=1}^{N} C_\mu^S \frac{1}{2c}\vec{\sigma}\cdot\vec{p}\chi_\mu$

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W}-\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix} = E \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2c^2}\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}^L \\ \mathbf{C}^S \end{pmatrix}$$

$$\mathbf{T} \equiv \tfrac{1}{2}\langle\boldsymbol{\chi}|\, p^2 \,|\boldsymbol{\chi}\rangle \qquad \mathbf{S} \equiv \langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle$$

$$\mathbf{V} \equiv \langle\boldsymbol{\chi}|\hat{V}_{2\times2}|\boldsymbol{\chi}\rangle \qquad \mathbf{W} \equiv \tfrac{1}{4c^2}\langle\boldsymbol{\chi}|\vec{\sigma}\cdot\vec{p}\,\hat{V}_{2\times2}\,\vec{\sigma}\cdot\vec{p}|\boldsymbol{\chi}\rangle$$

Thank you