Relativistic DFT Response Theory for Molecular Magnetic and Symmetry-Violating Properties

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Ardhmeri Alija

Supervisor:

Dr.Konstantin Gaul

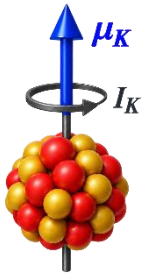
Many-Body Theory: Nuclear Physics Meets Quantum Chemistry

August 24, 2026 to September 4, 2026

From Nuclear Properties to Molecular Parity Violation

Nuclear properties

- Nuclear magnetic moment $\boldsymbol{\mu_K}$



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  Chemical shift δ
  $\delta = \sigma - \sigma_{ref}$
- Indirect nuclear spin–spin coupling (J-coupling)

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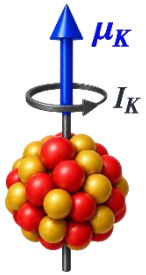

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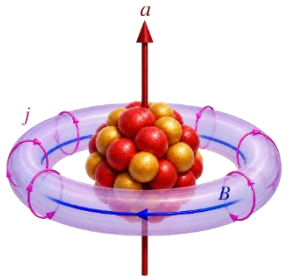

➢ Nuclear-spin-dependent PV interaction

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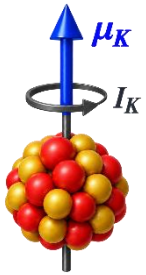

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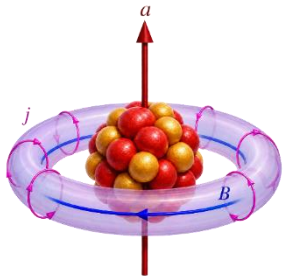

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Parity and chirality

Parity: inversion of all spatial coordinates

$\hat{P}$: r⟶ −r

Electromagnetic and strong interactions **conserve P**

Weak interaction: **violates P**

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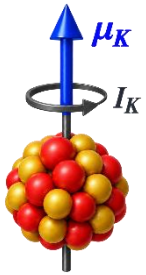

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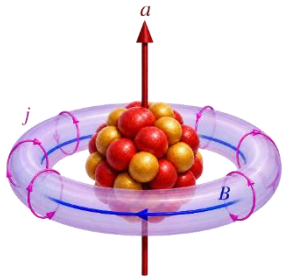

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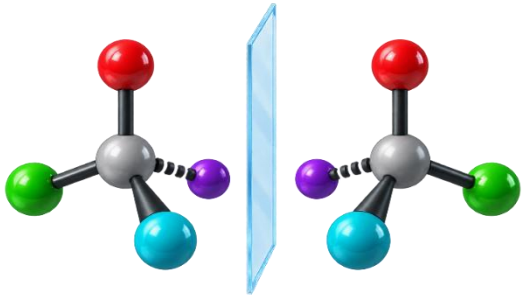

Enantiomers:
Non-superimposable mirror-image molecules

$$R \overset{\hat{P}}{\leftrightarrow} S$$

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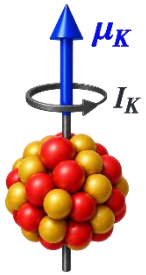

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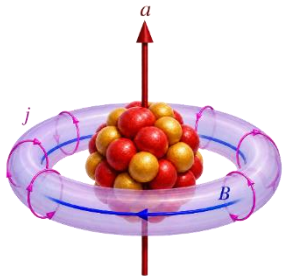

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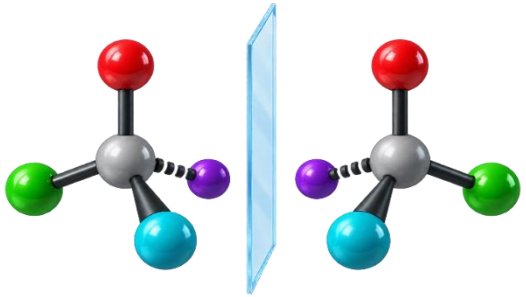

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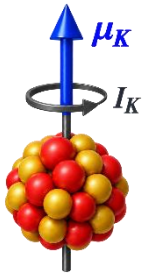

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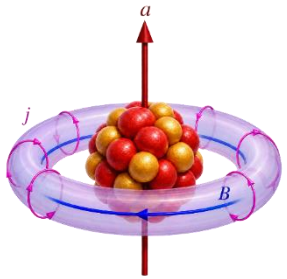

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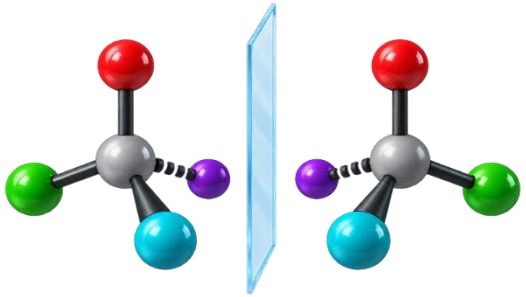

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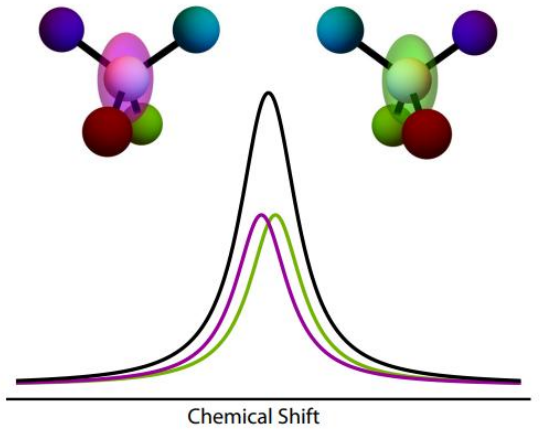
Can this mirror-image difference be detected by NMR?

Detecting Molecular Parity Violation by NMR

J. Eills et al., Phys. Rev. A (2017), 96, 042119



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- PV ⇒ splitting of enantiomers
  $\Delta\nu_{PV} \lesssim mHz$
- Typical NMR linewidth $> 0.5\ Hz$

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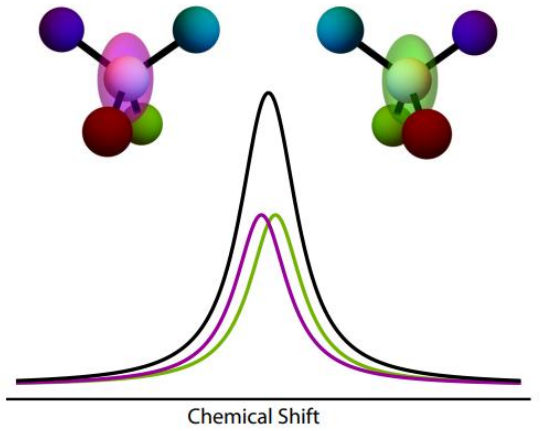

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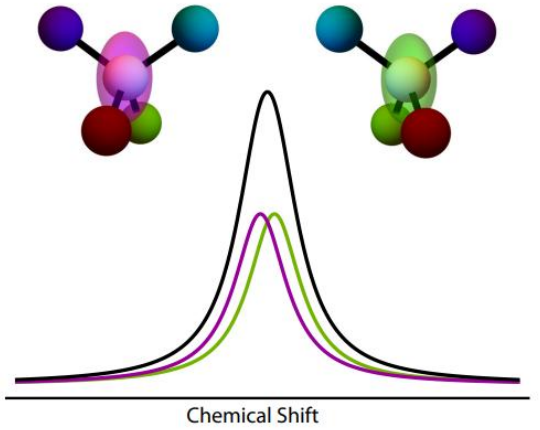

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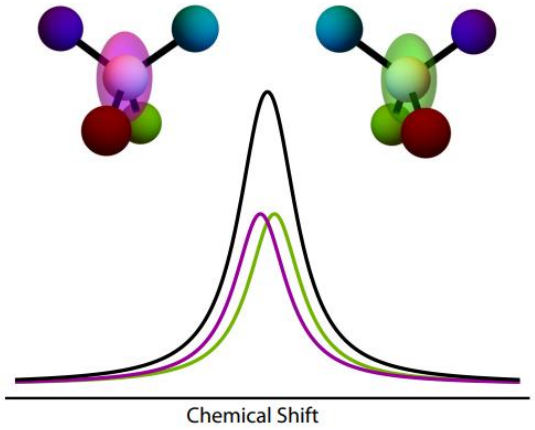

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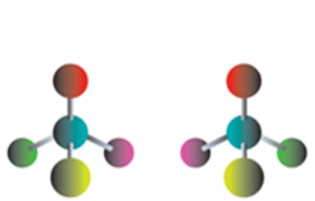
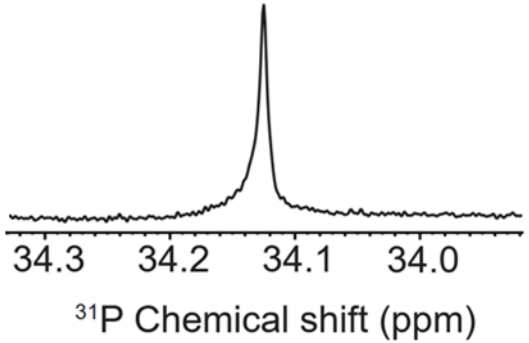
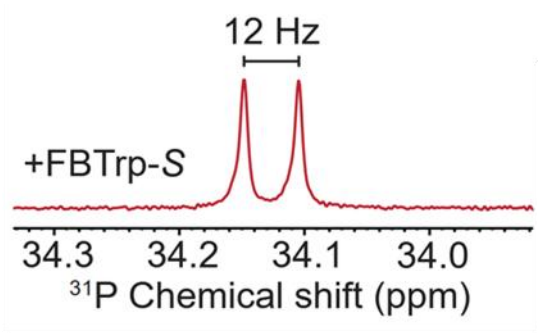
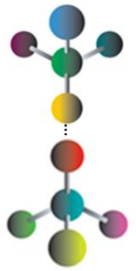
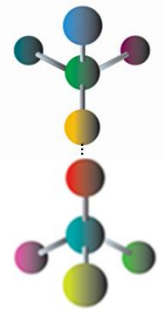







R,R


R,S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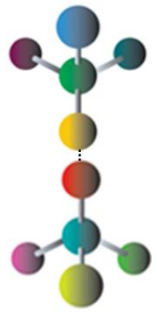
S,R

Diastereomers

-stereoisomers that are not mirror images

R,R↔R,S
R,R↔S,R
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E. Van Dyke et al., Phys. Chem. Chem. Phys. (2025), 27, 6092–6103

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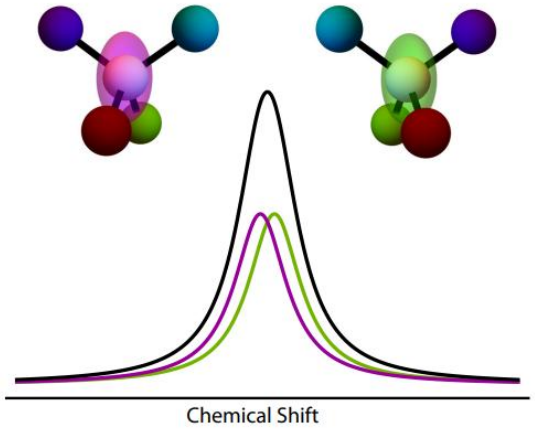

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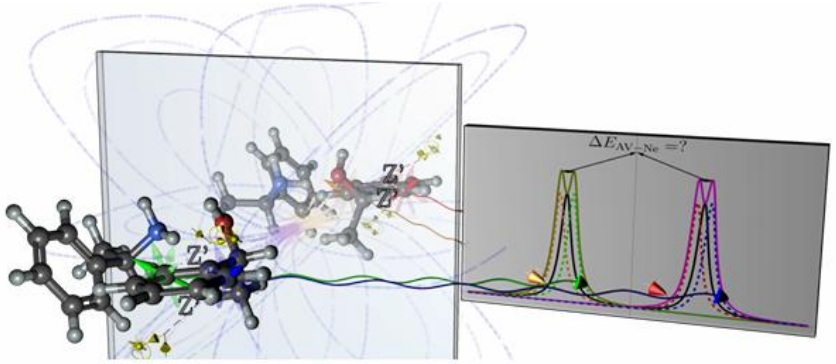

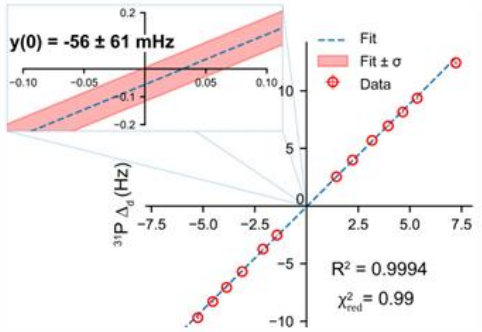

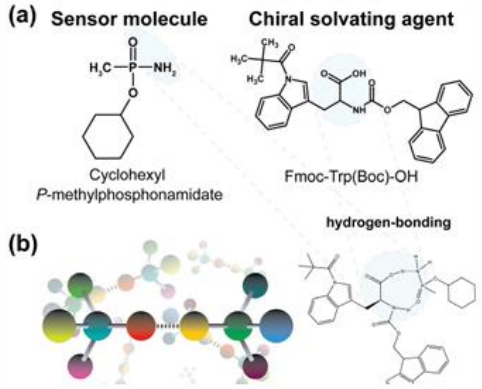

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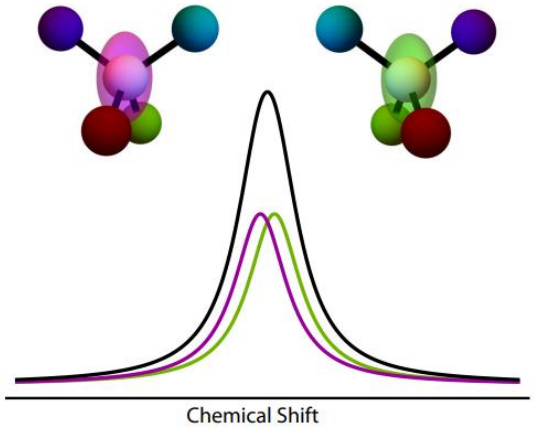

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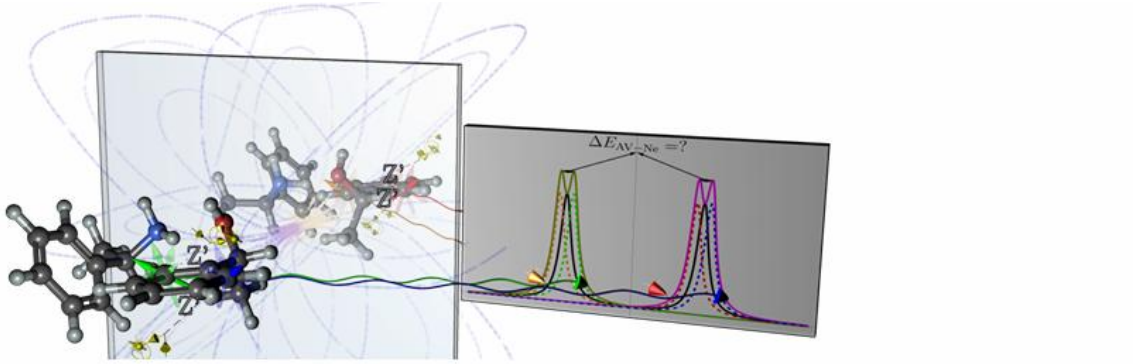

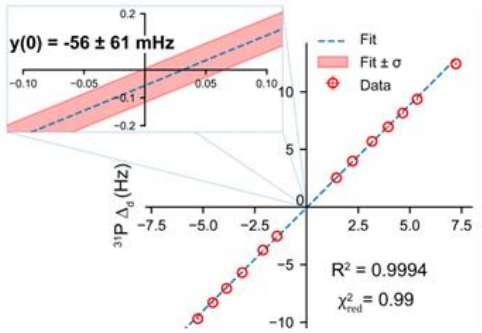

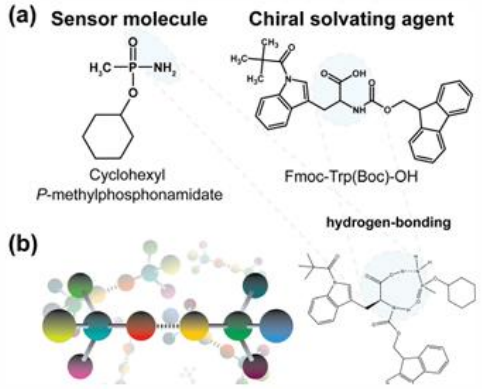

Requirements

- ✓ Soluble compound
- ✓ Few relevant conformers
- ✓ Heavy, NMR-sensitive nucleus
- ✓ High signal-to-noise ratio
- ✓ Narrow linewidth
- ✓ Resolvable diastereomeric interaction
- ✓ PV shifts (mHz)

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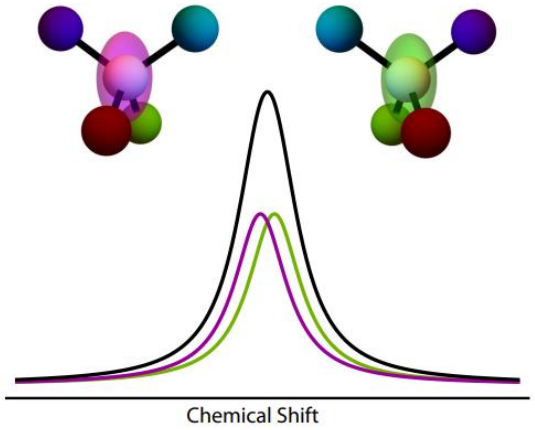

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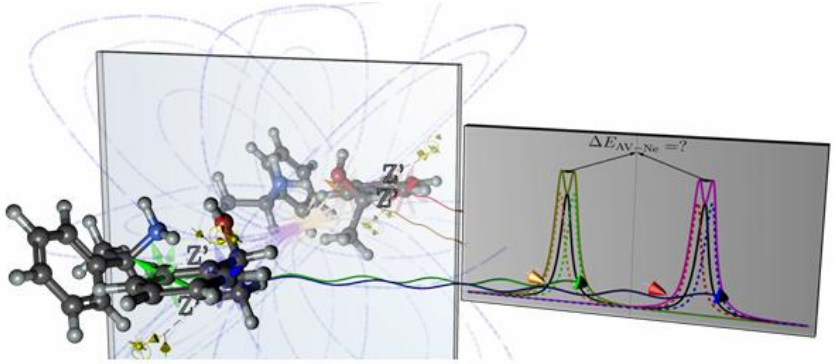

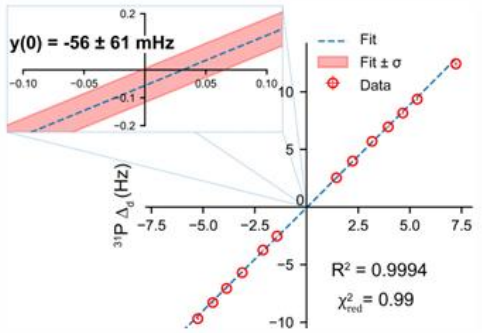

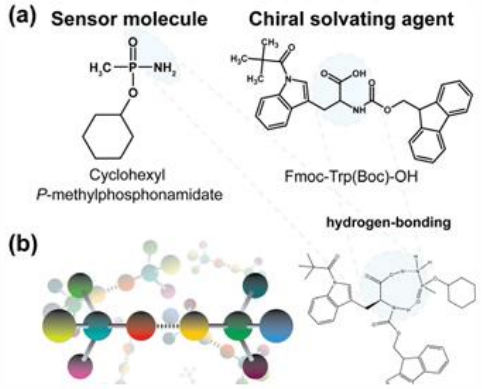

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PV effect → stronger relativistic effects

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Relativistic two-component DFT framework

- **Four-component Dirac theory**
  Fundamental relativistic reference

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

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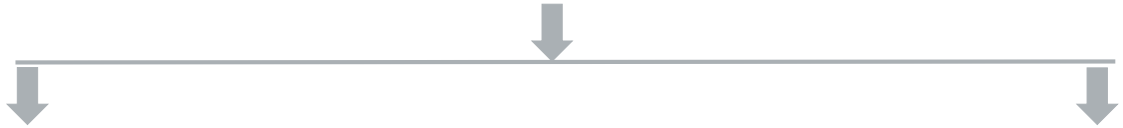

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- **X2C (Exact Two-Component)**

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ZORA (Zeroth-Order Regular Approximation)

Eliminate the small component by expanding the energy dependence as a power series.

Exact relation:

$$\psi^{\mathrm{S}}(\vec{\mathrm{r}})=\frac{c}{2m_ec^2-V(\vec{r})}\left(1+\frac{E}{2m_ec^2-V(\vec{r})}\right)^{-1}\left(\vec{\sigma}\cdot\hat{\vec{\mathrm{p}}}\right)\psi^{\mathrm{L}}(\vec{\mathrm{r}})$$

Power series expansion:

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ZORA approximation (zeroth-order):

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where

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- ω is a position-dependent factor that controls relativity locally

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X2C (Exact Two-Component)

Solve the full 4c problem in a finite basis, then construct the decoupling matrix from the positive-energy eigenvectors

Diagonalize the Dirac matrix:

$$\begin{pmatrix}H_{LL} & H_{Lp}\\ H_{pL} & H_{pp}\end{pmatrix}\begin{pmatrix}C_{L-} & C_{L+}\\ C_{p-} & C_{p+}\end{pmatrix}=\begin{pmatrix}S_{LL} & 0\\ 0 & S_{pp}\end{pmatrix}\begin{pmatrix}C_{L-} & C_{L+}\\ C_{p-} & Cp_{+}\end{pmatrix}\begin{pmatrix}E_{--} & 0\\ 0 & E_{++}\end{pmatrix}$$

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Unrenormalized X2C Hamiltonian:

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Final renormalized Hamiltonian:

$$H_{rX2C}=R^{\dagger}H_{X2C}R$$

Relativistic two-component DFT framework

Four-component Dirac theory

Fundamental relativistic reference

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

ZORA (Zeroth-Order Regular Approximation)

Eliminate the small component by expanding the energy dependence as a power series.

Exact relation:

$$\psi^{\mathrm{S}}(\vec{\mathrm{r}})=\frac{c}{2m_ec^2-V(\vec{r})}\left(1+\frac{E}{2m_ec^2-V(\vec{r})}\right)^{-1}(\vec{\sigma}\cdot\hat{\vec{\mathrm{p}}})\,\psi^{\mathrm{L}}(\vec{\mathrm{r}})$$

Power series expansion:

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$$\psi^{\mathrm{S}}(\vec{\mathrm{r}})\approx c\omega^{\mathrm{ZORA}}(\vec{\mathrm{r}})(\vec{\sigma}\cdot\hat{\vec{\mathrm{p}}})\,\psi_{\mathrm{i}}^{\mathrm{ZORA}}(\vec{\mathrm{r}})$$

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K. Gaul, arXiv:2605.31203 [physics.chem-ph] (2026).

Molecular properties as response functions

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NMR shielding

Perturbations

$$B_0 \ , m_K$$

External magnetic field B_0 and magnetic moment of the nucleus K

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The NMR chemical shift

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PV-NMR response

Perturbations

$$B_0 \ , m_K \ , \lambda_{PV}$$

External magnetic field, magnetic moment of nucleus K, and nuclear-spin-dependent weak interaction

$$\left.\frac{\partial^3 E}{\partial \lambda_{PV} \partial m_{K;\mu} \partial B_{0;\nu}}\right|_{\lambda_{PV}=m_{K;\mu}=B_{0;\nu}=0} = \left\langle\left\langle \hat{H}_{B_{0;\nu}} ; \hat{H}_{\lambda_{PV};m_{K;\mu}} \right\rangle\right\rangle = \upsilon^{PV}_{K;\mu\nu}$$

Experimental meaning

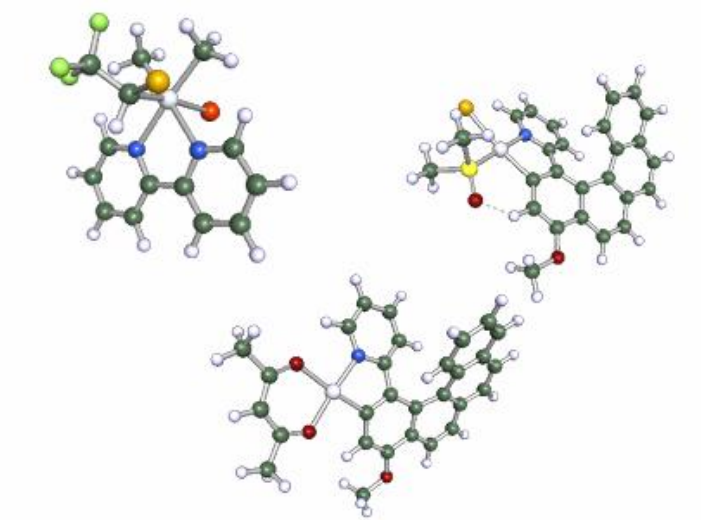
$$\Delta\nu_{PV} = \nu_R - \nu_S$$

Enantiomer-dependent NMR frequency difference

Theory-guided design of a molecular PV-NMR experiment

Candidate selection requires a large PV response and a narrow linewidth

PV effects increase strongly with nuclear charge



Why Platinum?

- ✓ Heavy element: $Z_{Pt} = 78$
- ✓ NMR-active $195Pt$
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E. Van Dyke et al., Phys. Chem. Chem. Phys. (2025), 27, 6092–6103

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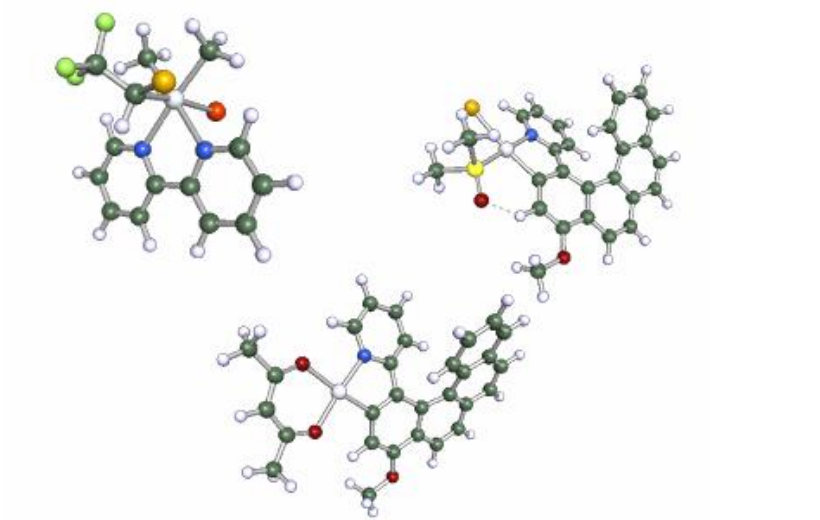

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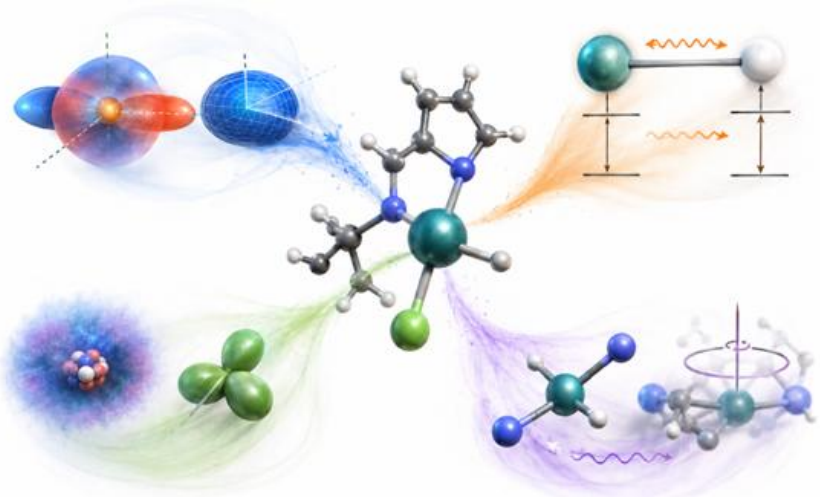
Towards understanding linewidth in heavy-element NMR

First-principles calculation of relaxation-relevant properties



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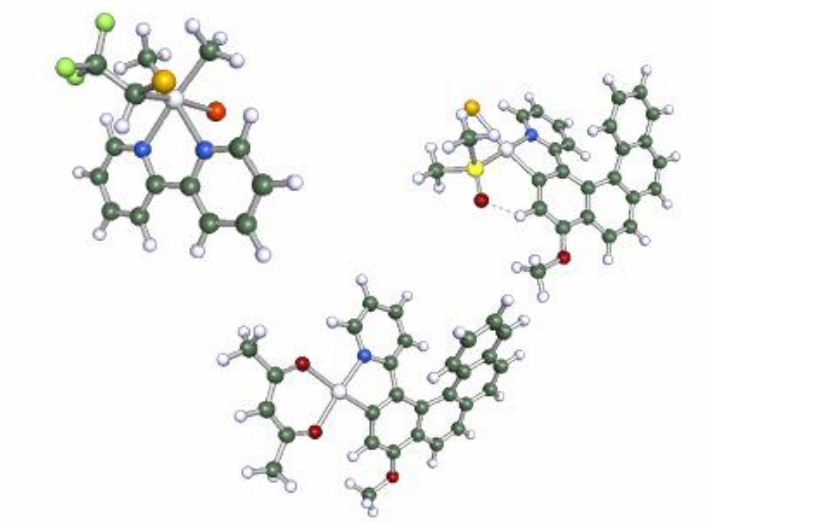

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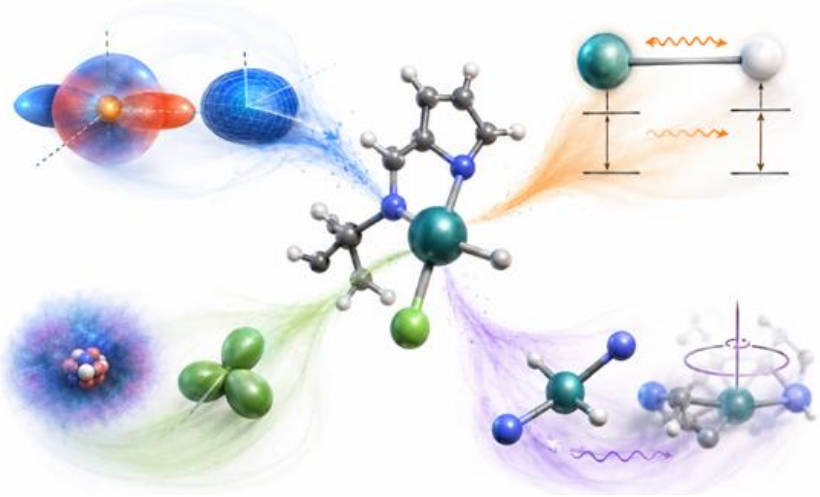
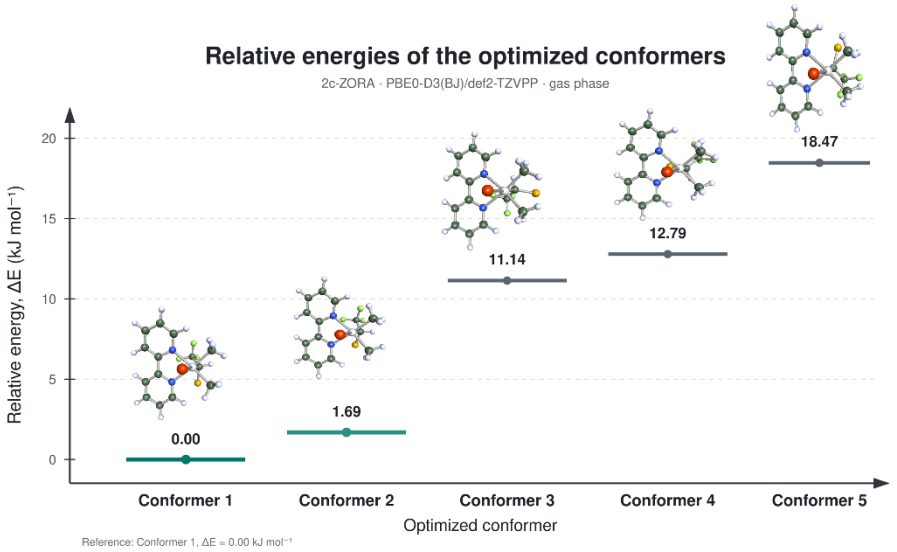


Is CSA the dominant source of line broadening?

E. Van Dyke et al., Phys. Chem. Chem. Phys. (2025), 27, 6092–6103

Representative case study: relativistic ^{195}Pt NMR and PV-NMR properties



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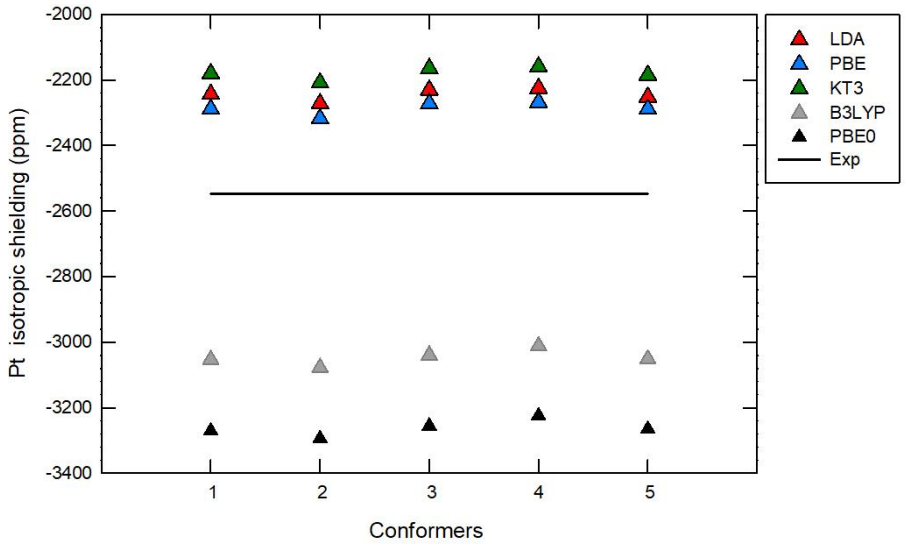

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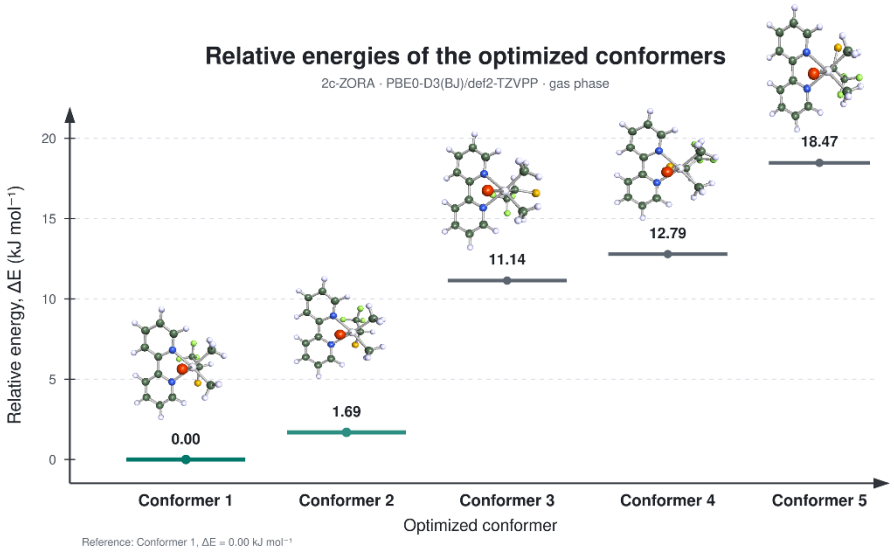

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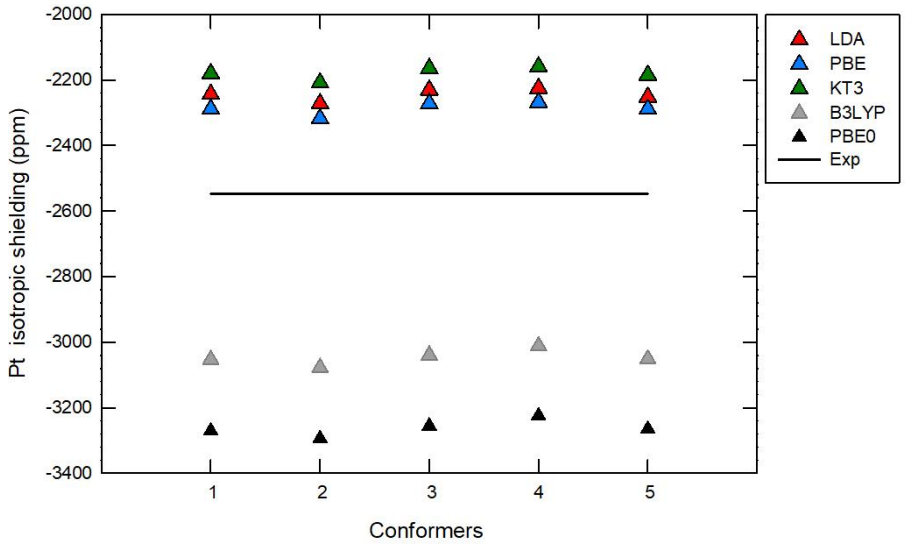

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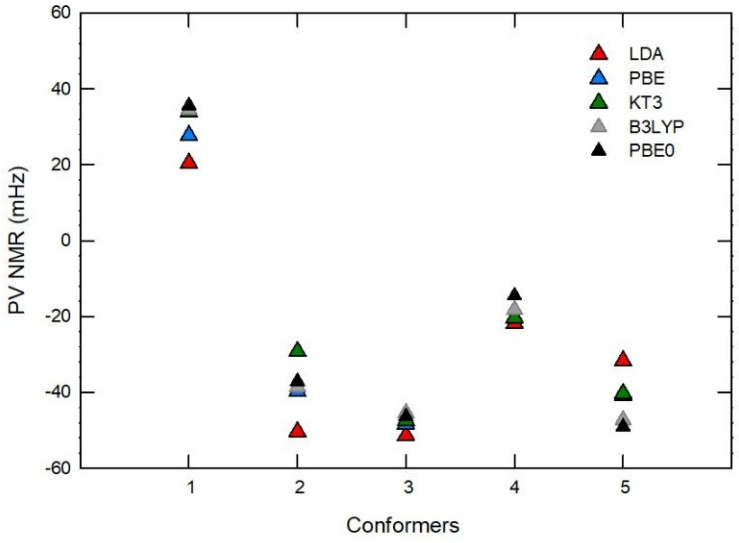
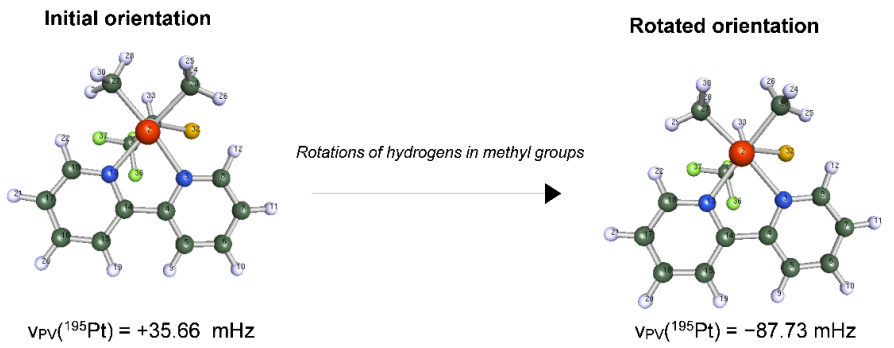


Methyl-Group Rotation in Conformer 1



Current Challenges for Reliable Magnetic Response

Current-density treatment

$j_p(r)$ *-paramagnetic current density*

$J_{ia}(r)$ *-spin-current density*

$L(r)$ *-orbital angular-momentum density*

Existing approaches:

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- Limited consistency under strong SOC

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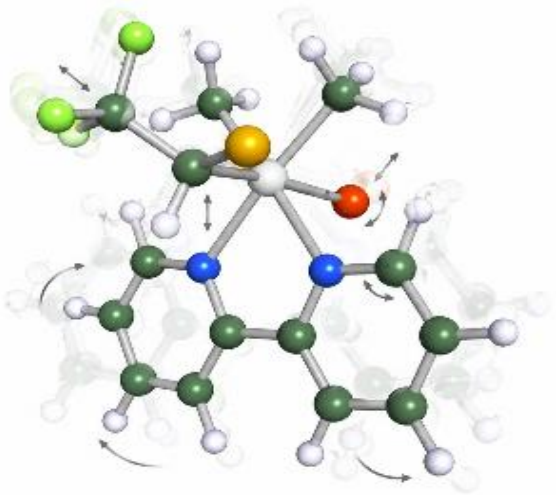

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- Analytic gradients: $(3N)$ property calculations

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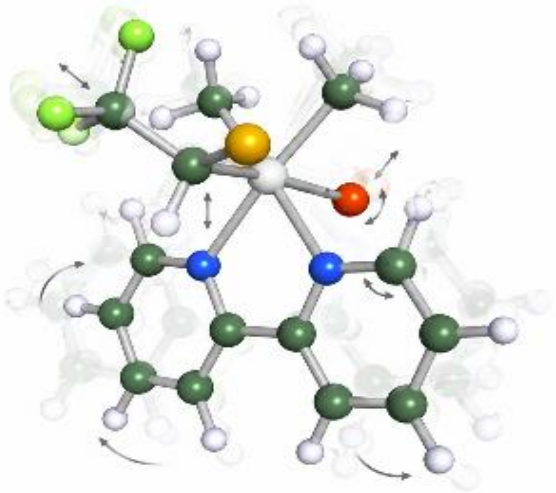

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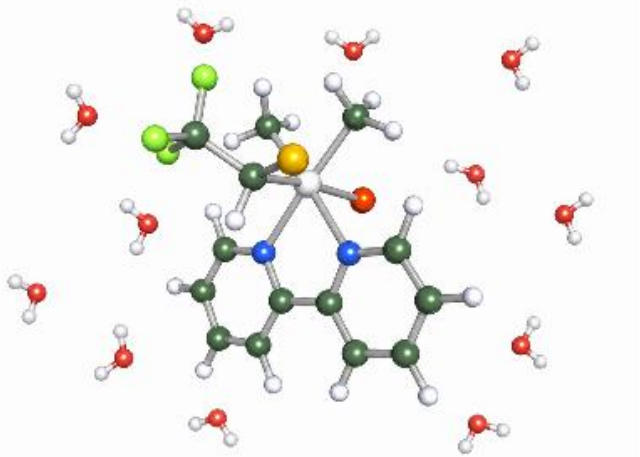
Solvent effects

$|\Delta J_{solv}| \sim$ *a few percent*



- Implicit solvent treatment using PCM
- Assess solvent screening of J- couplings
- Validation for ZULF-NMR systems

Goal: Realistic predictions in solution

Conclusions & Outlook

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