Relativistic
Calculations of NMR Shifts

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Why Relativistic Quantum Chemistry?
(Because the periodic table doesn't end with Kr 😊)

➢ Recall the non-relativistic Hamiltonian

$$\widehat{H}^{nrel} = \sum_{i=1} \frac{\widehat{p}_i^2}{2m} + \sum_i V_{N_i} + V_{ee} + Vn_{uc}$$

$\frac{\widehat{p}_i^2}{2m}$ is the non-relativistic kinetic energy operator

➢ In heavy elements the inner shell electrons move with a speed comparable with speed of light.

➢ So the core electrons of heavy atoms show sizable relativistic effect. For accurate predictions of various properties of chemical system containing heavy elements.

$$m_{rel} = \frac{m_o}{\sqrt{1 - v_2/c_2}}$$

➢ **Properties like NMR shift is very sensitive to this effect.**

Relativistic Quantum Theory?

➤ **The marriage of the two greatest concepts of Physics of the 20th century, the Quantum Theory and the Theory of Relativity.**

➤ Dirac labor alone on the problem for 3 years before publishing it in 1928, *The Quantum Theory of the Electron* (https://royalsocietypublishing.org/doi/abs/10.1098/rspa.1928.0023)

➤ If we compare S.E. Hamiltonian from the Dirac Equation, **we can see that there's an α and β term**s, unknown terms in which Dirac introduced to proceed with his labor.

<div style="text-align:center">Schrödinger Equation   Dirac Equation</div>

$$\widehat{H} = -\frac{1}{2}\nabla^2 + v(r) \qquad\qquad \widehat{H} = \alpha \cdot p + \beta c^2 + v(r)$$

➤ These supposed introduction of α and β terms (4 X 4 matrices) naturally suggest its **four component nature** as well as **positive and negative energy solutions.**

Relativistic Quantum Chemistry

➢ Why Relativistic effects matter

$$H^R = H^{NR} - \frac{p^2}{8c^2} + \frac{\Delta v}{8c^2} + \frac{1}{2c^2}\frac{1}{r}\frac{dv}{dr}1 \cdot s$$

mass   Darwin   spin-orbit
-velocity

$-\frac{p^2}{8c^2}$ mass-velocity: variation of the mass with the velocity (affects contraction and stabilization of *s*- and *p* shells; expansion and destabilization of the *d* and *f*-shells)

$+\frac{\Delta v}{8c^2}$ Darwin: correction to the non-local interaction between electron and Coulomb field

$+\frac{1}{2c^2}\frac{1}{r}\frac{dv}{dr}1 \cdot s$ spin-orbit coupling: interaction of the electron spin magnetic moment with magnetic field due to the motion of the (affects the character of orbitals). These part accurately describes with the "fine structure" split of the Hydrogen spectrum, in Michelson-Morley (1887)

From Dirac to ZORA equation

Two-Component Relativistic Methods

➢ High computational cost of **four-components relativistic calculations** has motivated the development of computationally less demanding two-components Hamiltonians.

➢ Two component relativistic Hamiltonians **(involving only positive energy orbitals**): pseudopotential and all-electron methods.

ZORA: accurate and efficient relativistic DFT

➢ The zeroth order regular approximation (ZORA) to the Dirac equation accurately and efficiently treats relativistic effects in chemistry. **ZORA can be applied with spin-orbit coupling or as scalar correction only.**
- Spin Orbit Coupling can be included self consistently
- All electron relativistic basis sets for all elements
- Available for most spectroscopic properties
- Include relativistic effects on structure and reactivity

From Dirac to ZORA

➤ **From** Four-component Dirac

(Fock Matrix)
$$\begin{bmatrix} Vnuc + J\varphi\varphi - K\varphi\varphi + Jxx & c\sigma \cdot p - k\varphi x) \\ c\sigma \cdot p - kx\varphi & -2c_2 + Vnuc + J\varphi\varphi - K\varphi\varphi + Jxx \end{bmatrix} \cdot \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = E \begin{pmatrix} \varphi \\ \chi \end{pmatrix} \quad \Psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix}$$

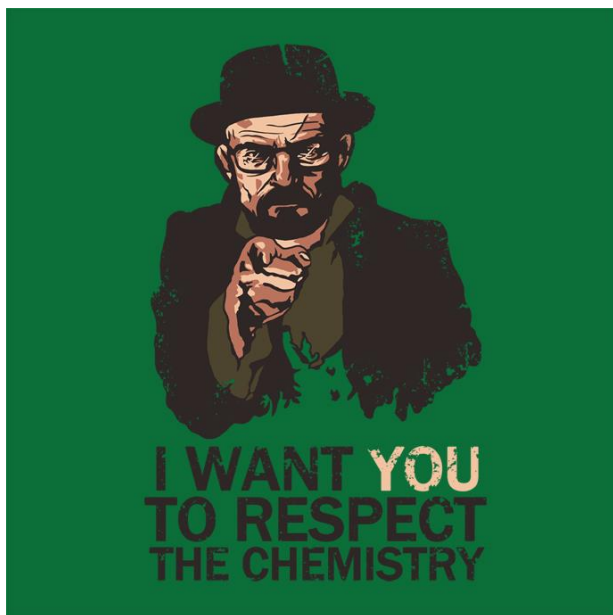➤ **To** two-components zeroth order regular Approximation

After a long derivation

$$H^{ZORA}\Psi^{ZORA} = E^{ZORA}\Psi^{ZORA}$$

$$H^{ZORA} = V + p\frac{c^2}{2c^2 - V}p + \frac{c^2}{(2c^2 - V)^2}\sigma \cdot (\nabla V \times p)$$

➤ The approximation is very convenient as we can now isolate the scalar and spin-orbit effects from the results of the calculation.

ReSpect vs ADF

➢ **ReSpect (RelativisticSpectroscopy**) program enables the prediction and understanding of molecular and material properties using full Dirac Hamiltonian. (http://www.respectprogram.org/)

➢ **ADF (Amsterdam Density Functional)** program enables the prediction and understanding of molecular and material properties using Zeroth Order Approximation (ZORA) (https://www.scm.com/product/adf/)

Exercise (ADF)

Recall: The NMR Shifts [δ] of specific atom (i) in a molecule can be obtained subtracting **NMR shielding [σ]** from its reference

$$\delta_i = \sigma_{ref} - \sigma_i$$

STEP ADF Calc

➢ Calculate the **NMR properties of hydrogen** in HI, HCl, and Benzene

➢ Use the prepared **input files distributed in IS** (HCl_Scalar.inp, nmr.inp, etc)

➢ Take a look at the script **run_adf.sh** to see how adf run works.

NOTE: There are two parts of adf calculation, SCF module-Calculation and the calculation of nmr shielding.

➢ After the successful NMR run. Check the **.out** file, Look for the keyword " **PARAMAGNETIC (), DIAMAGNETIC () and SPIN ORBIT (NMR SHIELDING TENSOR)**" and below it is the **"isotropic"** shielding value(s) of the atom(s) sought.

NOTE: PARA eigenvalues associated with an excited and the ground electronic state, DIA contributions are associated from the ground-state. (this is beyond the scope of our session)

➢ After the successful of ZORA Scalar and ZORA Spin-Orbit Approximations, compare some the values with the experiment, you should be able to **complete this table:**

	Calc. Shielding (ref-TMS)	Calc. Shielding		Calc. Shielding Total				Calc Shift	Exp Shift
	σ_{ref}	para	dia	σ_i (para + dia)	δ_i (σ_{ref} - σ_i)	SO	δ_i + SO		*δ_{exp}
HCl_Scalar	31.35								0.45
HCl_SO	31.41								0.45
HI_Scalar	31.35								13.25
HI_SO	31.41								13.25
Benzene_Scalar	31.35								7.15
Benzene_SO	31.41								7.15

Exercise (ReSpect)

STEP ReSpect Calc

➢ Calculate the **NMR properties of** hydrogen in HI, and HCl
➢ Use the prepared **input files distributed in IS**

➢ Take a look at the script **run_respect.sh** to see how ResPect run works.

NOTE: analogous to ADF, there are two parts of ReSpect calculation

• SCF module-Calculation of unperturbed ground state MO Coefficient, in our case we started a guess SCF from (ks-dkh2/pbe0) to (mdks/pbe0, i.e. Dirac Kohn Sham Implementation)

• CS module-Calculation of the chemical shift properties

➢ After the successful CS. Check the **.out_cs** file Look for the keyword **"CHEMICAL SHIELDING FOR NUCLEUS # (your ATOM)"** and below it is the **"Principal values of the NMR shielding tensor "** where the **PARA and DIA** part shielding value(s) of the atom(s) sought.

NOTE: this is the full Diract calculation, the SO effects are embedded in PARA and DIA, thus we can't isolate the SO effects as opposed to the ZORA calculations.

➤ After the successful of full Dirac calculation, compare some the values with the experiment, you should be able to **complete this table:**

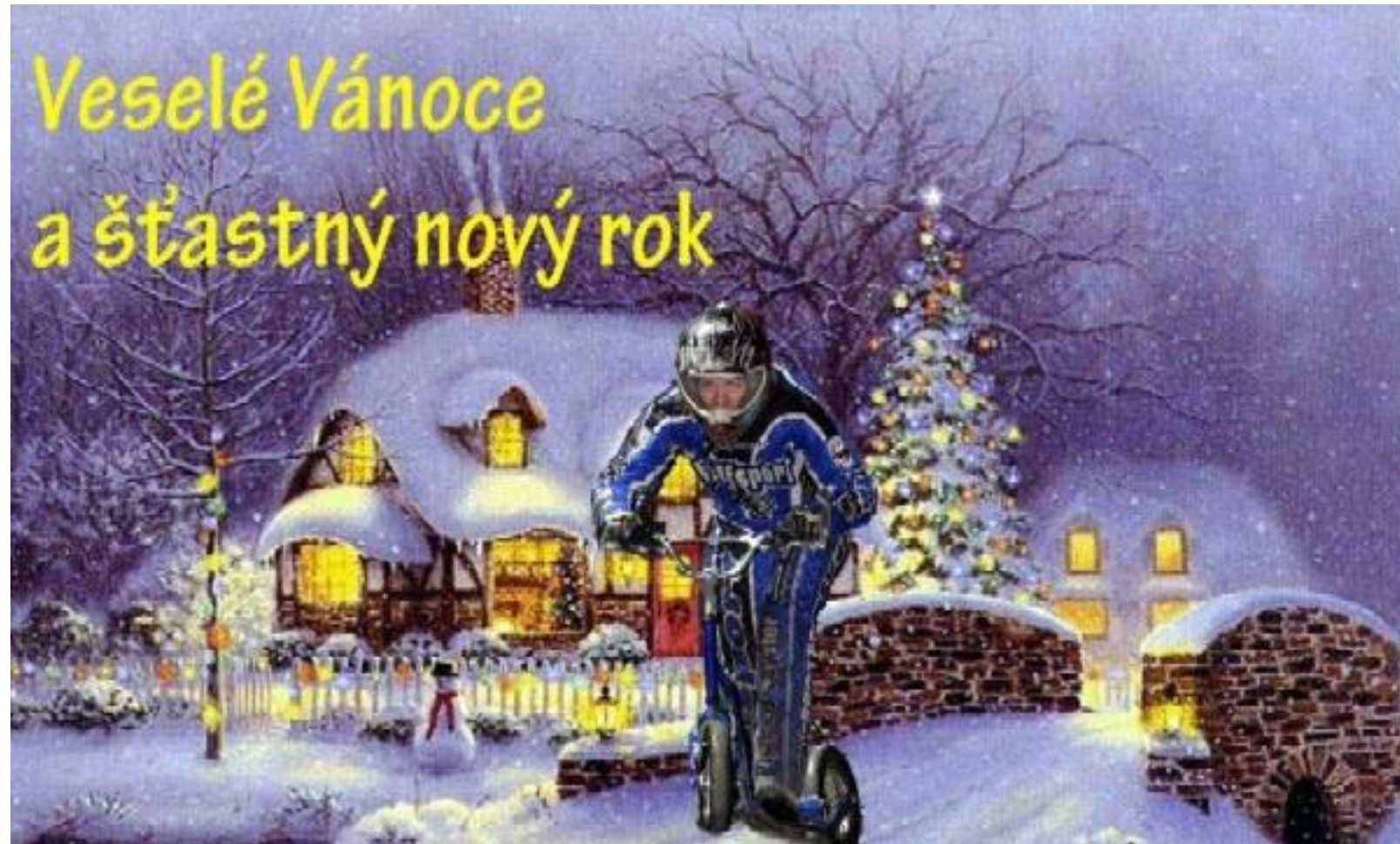|	Calc. Shielding (ref-TMS) σ_{ref}	Calc. Shielding para	Calc. Shielding dia	Calc. Shielding Total σ_i (para + dia)	$-[\delta_i (\sigma_{ref} - \sigma_i)]$	Calc Shift δ_i	Exp Shift $*\delta_{exp}$
HCl_Full	31.41						0.45
HI_Full	31.41						13.25

Questions to Ponder

➢ from this activities, which method has the calculated value(s) that corroborates best with experimental ^1H NMR shifts? On which system did the relativistic effect

➢ is choosing a computational method that contains approximations which lead to quicker and practical results worth it?

Homework (optional task if you have free time hanging out in the wolf room)

➢ Try to calculate heavy metallic systems with experimental NMR datas, such as Platinum (^{195}Pt) NMR Shift using Scalar ZORA, SO ZORA, and full Relativistic DFT calculations.

➢ Try this specie $[Pt(NO2)_4]^{2-}$ with ^{195}Pt experimental shift of – 2187 ppm. Use $PtCl_4^{-2}$ for your reference.

• Use PBE0 functional for optimization and NMR shift calculations, and when it comes to the metal, use specific basis sets optimized for chemical shift calculations. Refer to the website of ADF and ResPect for the complete list.

• ADF (https://www.scm.com/doc/ADF/Input/Basis_sets_and_atomic_fragments.html#available-basis-sets)
• ReSpect (http://www.respectprogram.org/basis.html)

Happy End

Answers

➢ The Complete Table

	Calc. Shielding (ref-TMS)	Calc. Shielding		Calc. Shielding Total			Calc Shift	Exp Shift
	σ_{ref}	para	dia	σ_i (para + dia)	δ_i ($\sigma_{ref} - \sigma_i$)	SO	δ_i + SO	δ_{exp}
HCl_Scalar	31.35	0.83	30.54	31.38	-0.03	**0.00**	**-0.03**	**0.45**
HCl_SO	31.41	0.83	30.56	31.39	0.02	**0.63**	**0.65**	**0.45**
HI_Scalar	31.35	0.63	30.54	31.17	0.18	**0.00**	**0.18**	**13.25**
HI_SO	31.41	0.76	30.67	31.43	-0.02	**9.41**	**9.39**	**13.25**
Benzene_Scalar	31.35	-7.95	31.75	23.80	7.55	**0.00**	**7.55**	**7.15**
Benzene_SO	31.41	-7.95	31.75	23.80	7.61	**-0.02**	**7.59**	**7.15**
	Calc. Shielding (ref-TMS)	Calc. Shielding		Calc. Shielding Total			Calc Shift	Exp Shift
	σ_{ref}	para	dia	σ_i (para + dia)	(-) δ_i ($\sigma_{ref} - \sigma_i$)		δ_i + SO	δ_{exp}
HCl_Full	31.41	2.41	29.29	31.70	0.29		**0.29**	0.45
HI_Full	31.41	16.13	28.63	44.76	13.35		**13.35**	13.25

• The SO effect as we can see here becomes more significant as the system involves atoms larger atoms (HCl to HI). The full Dirac still is the provides the best based on these geometries.