# Introduction to Computational Quantum Chemistry

Lesson 11 : Relativistic Calculations of NMR Shifts

## Why Relativistic Quantum Chemistry?

- recall the non-relativistic Hamiltonian

$$\hat{H} = \sum_{i=1} \frac{\hat{p}_i^2}{2m} + \sum_i V_{Ni} + V_{ee} + V_{nuc}$$

- $\frac{\hat{p}_i^2}{2m}$ is the non-relativistic kinetic energy operator
- in heavy atoms (HA) the inner shell electrons has a speed comparable with speed of light.
- the core electrons of HA show sizable relativistic effects:

$$m_{rel} = \frac{m_e}{\sqrt{1 - v_e/c_2}}$$

- "magnetic properties" is very sensitive to this effect

# Relativistic Quantum Chemistry

- relativistic corrections to non-relativistic energy value

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

- $-\frac{p^2}{8c^2}$, **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 potential energy

- $+\frac{1}{2c^2}\frac{1}{r}\frac{dv}{dr}\mathbf{1} \cdot s$ **spin-orbit coupling**: interaction of the electron spin and the orientation of electronic motions (orbital angular momentum) accurately described by the "fine structure" splitting of the Hydrogen spectrum (Michelson-Morley, 1887).

# from full Dirac to ZORA equation

- **Two-Component Relativistic Methods**
  - the high computational cost of four-components relativistic calculations has motivated the development of computationally less demanding two-component 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 and can be applied with scalar and spin-orbit corrections.

# from Dirac to ZORA equation

- from Four-component Dirac

$$\begin{bmatrix} V_{nuc} + J\phi\phi - K\phi\phi + J\chi\chi & c\sigma \cdot p - k\phi\chi \\ c\sigma \cdot p - k\chi\phi & -2c_2 + V_{nuc} + J\phi\phi - K\phi\phi + J\chi\chi \end{bmatrix} \cdot \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

$$= E \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

- (after a long derivation) to Two-Component Zeroth Order Approximation

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

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

- scalar and spin-orbit effects

## 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/)

## Activity 1: ADF

- recall, the NMR Shifts [$\delta$] of specific atom ($i$) in a molecule is obtained by subtracting NMR shielding [$\sigma$] constants from a reference:
  $\delta_i = \sigma_{ref} - \sigma_i$
- ADF NMR Shielding calculations
    - 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 job submission works.
    - NOTE: there are two parts of adf calculation, SCF module-calculation and the NMR shielding calculation.

- after the successful NMR run, check the **.out** file, look for the keyword "PARAMAGNETIC (), DIAMAGNETIC () and SPIN ORBIT (NMR SHIELDING TENSOR)" and below the **"isotropic" shielding value(s)** of the atom(s) sought.
- NOTE: PARA eigenvalues is associated with ground and excited state transitions, DIA contribution is only associated with the ground-state (this is beyond the scope of our session).

- after the successful calculations, ZORA Scalar and ZORA Spin-Orbit approximations, compare the values with the experiment, complete this table:

| | Calc. Shielding (ref-TMS) | Calc. Shielding | | Calc. Shielding Total | | | Calc Shift | Exp Shift |
|---|---|---|---|---|---|---|---|---|
| | $\sigma_{ref}$ | para | dia | $\sigma_i$ (para + dia) | $\delta_i$ ($\sigma_{ref}$ - $\sigma_i$) | SO | $\delta_i$ + SO | *$\delta_{exp}$ |
| 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 |

# Activity 2: ReSpect

- ReSpect NMR Shielding Calculations
  - 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

# Activity 2: ReSpect, (Cont.)

- after the successful CS calculation, check the **.out_cs** file and look for the keyword "CHEMICAL SHIELDING FOR NUCLEUS (your ATOM)" and below is the "Principal values of the NMR shielding tensor" where the PARA and DIA part shielding value(s) of the atom(s) sought.
- NOTE: in this full Diract calculation, the "SO effect" is embedded in PARA and DIA, thus we can't isolate the SO effects as opposed to the ADF ZORA calculations.

- after the successful calculation, compare the values with the experiment, complete this table:

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

# Questions

- which system(s) are sensitive to relativistic effects?
- from these activities, which method has the calculated value(s) that corroborates best with experimental $^1$H NMR shifts?
- is it worth choosing a computational method that contains approximations that are cheap and has a practical results?

**END**