Lesson 11: Relativistic calculation

Why relativistic quantum chemistry

- For accurate predictions of various prperties of chemical system containing heavy elements

$$m_{rel} = \frac{m_0}{\sqrt{1 - \frac{v^2}{C^2}}}$$

- For light element systems we can forget about relativistic correction.

- Schrodinger equation

$$\big[-\frac{1}{2} \bigtriangledown^2 + V(r) \big] \psi(r) = E\psi(r)$$

- Dirac equation

$$\big[c\alpha.p + \beta.mc^2 + V(r) \big] = E\psi(r)$$

$$\psi(r) = \begin{bmatrix} \psi_1(r) \\ \psi_2(r) \\ \psi_3(r) \\ \psi_4(r) \end{bmatrix}$$

Two-component relativistic methods

- High computational cost of four-component 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. 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 equation

Four-component Dirac Hamiltonian

$$\begin{bmatrix} V & c(\sigma.p) \\ c(\sigma.p) & V - 2c^2 \end{bmatrix} \cdot \begin{pmatrix} \phi \\ \chi \end{pmatrix} = E \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

$\Downarrow$ Unitary transformation

Two-component zeroth order regular approximation

$$\big(V(r) + \sigma.p \frac{c^2}{2c^2 - V(r)} \sigma.p\big) \phi_{zora} = E_{zora} \phi_{zora}$$

Amsterdam Density Functional

- "user-friendly DFT software for chemists"
- `https://www.scm.com/`
- Free trial licence for 30 days
- GUI available only at wolf23

Introduction

- Very fast code
- Uses Slater-type basis functions
- Functionalities:
  - Optimizations
  - Response properties (NMR, EPR, UV-VIS, IR, Mössbauer..)
  - NOCV
  - EDA
  - COSMO model of solvation
  - ZORA scalar and spin-orbit relativistic approach

GUI

- Nice and clear interface
- adfinput
- adfview
- adfoutput
- Only single licence

Running ADF jobs

- Input: keywords in blocks
- adf {-n nproc} < input.adf > output.out
- nmr {-n nproc} < input_nmr.adf > output_ nmr.out
- INFINITY takes care of the number of CPUs
- Tape files: binaries containing the orbitals
- `http://www.scm.com/Doc/Doc2014/ADF/ADFUsersGuide/page262.html#keyscheme%20SAVE`

NMR

- TAPE10 is required
- Separate input file with NMR keywords
- `http://www.scm.com/Doc/Doc2014/ADF/ADFUsersGuide/page188.html`

SCF calculations

- Use the prepared input files distributed in IS
- Write the molecular geometry in same format as .xyz (Å)
- Bond lengths:
  - HCl(scalar): 1.276930
  - HI(scalar) : 1.606797
  - HCl(SO): 1.276467
  - HI(SO): 1.609681

NMR calculations

- Calculate the NMR properties of hydrogen in HI and HCl
- For relativity use ZORA Scalar and ZORA Spin-Orbit approximations
- Compare the Experimental, Nonrelativistic, ECP, and Two component approach
- Chemical shielding for benzene ^{1}H nuclei: