

Introduction to Computational Quantum Chemistry

Relativistic calculation

Why relativistic quantum chemistry

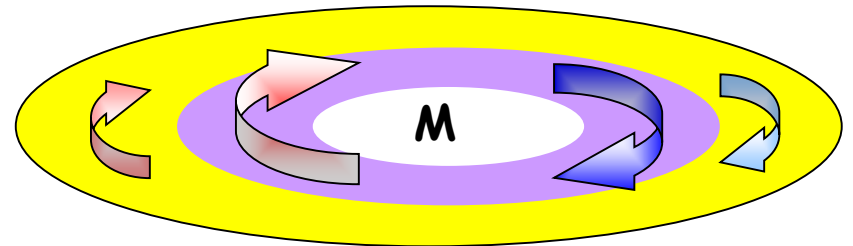
■ Relativistic Effects

- Nonrelativistic Hamiltonian of the Schrödinger equation is

$$\hat{H}^{nrel} = \sum_i \frac{\hat{p}_i^2}{2} + \sum_i V_{Ni} + V_{ee} + V_{nuc}$$

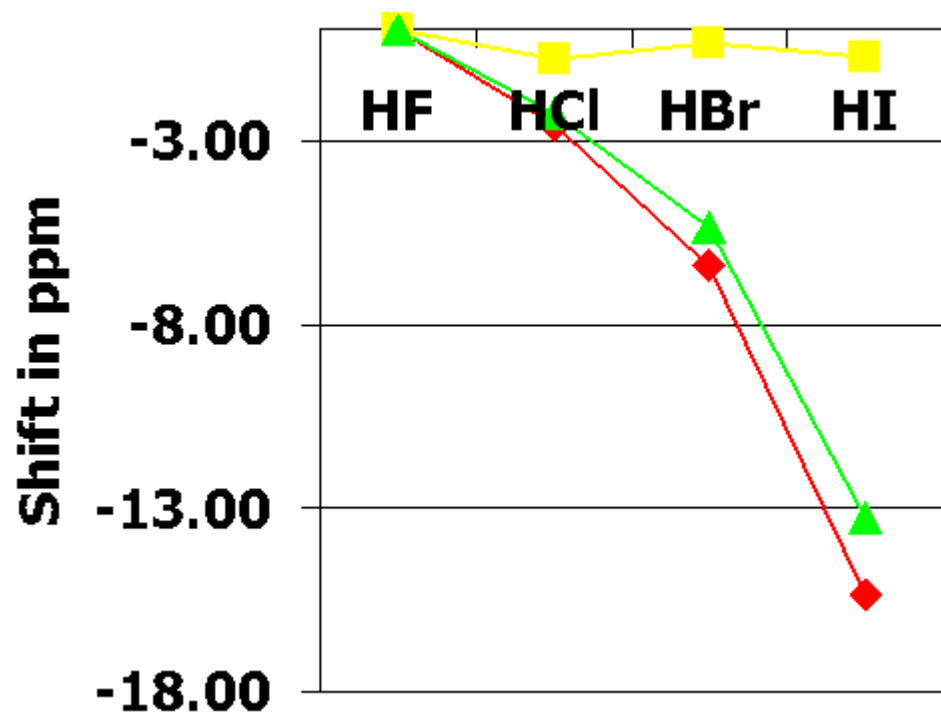
- In heavy elements the inner shell electrons move with a speed comparable with speed of light. So the core electrons of heavy atoms show sizable relativistic effect.

$$m_{rel} = \sqrt{\frac{m_0}{\left(1 - \frac{v^2}{c^2}\right)}}$$

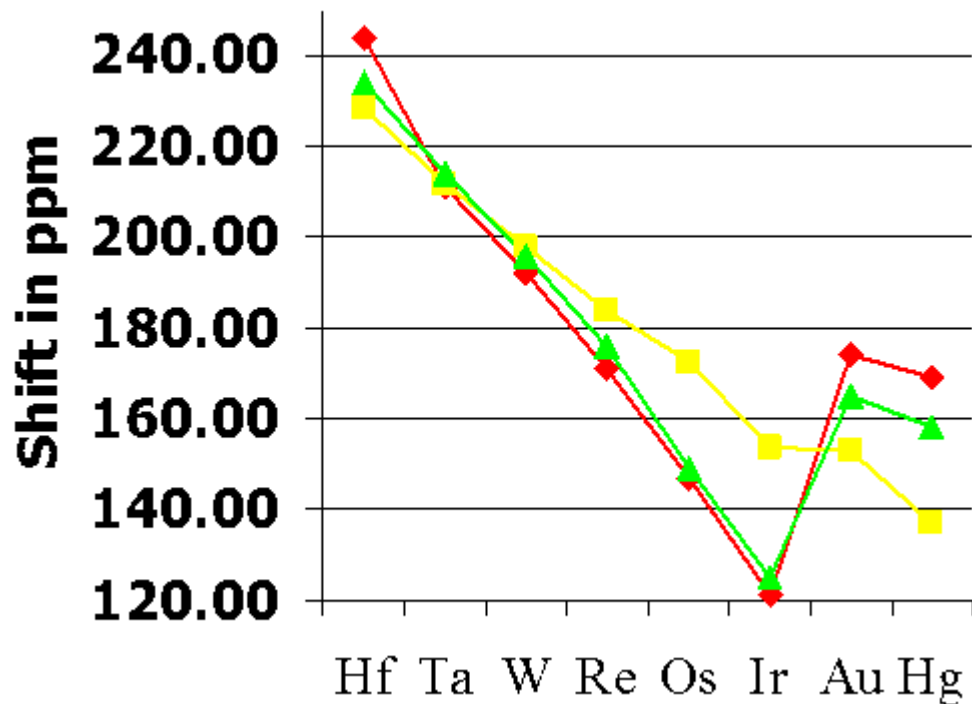


- Properties like NMR are very sensitive to this

Why it is important??



H^1 NMR



C^{13} NMR

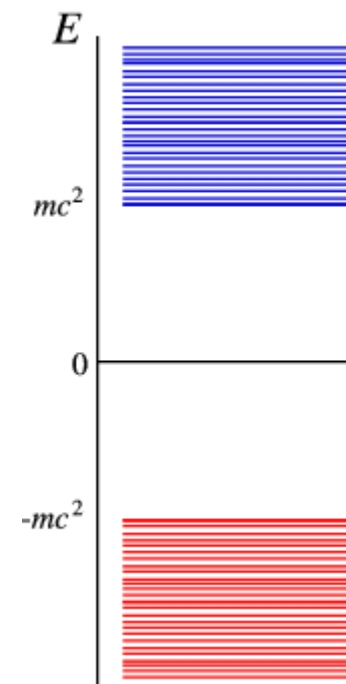
Dirac equation

Four-component Dirac equation

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

σ is the Pauli spin-matrix

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$



The main difference here is kinetic energy operator. It takes into account the relativistic increase of electron mass due to high velocities, it includes the electron's rest mass energy, it incorporates the electron spin also causes the spin orbit coupling.

Two-component relativistic methods

- High computational cost of four-component relativistic calculations.
- Solution contains negative energy spectrum.
- Many transformations that eliminate the small component wave functions to form two-component Hamiltonian have been developed.
- Two-component relativistic Hamiltonians (involving only positive-energy orbitals) : pseudopotential and all-electron methods

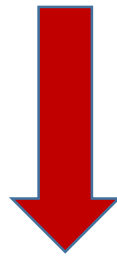
ZORA: accurate and efficient relativistic DFT

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.

Four-component Dirac Hamiltonian

$$\begin{aligned} V\phi + c(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\chi &= E\phi \\ c(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\phi + (V - 2mc^2)\chi &= E\chi \end{aligned}$$

ϕ : Large component
 χ : Small component



4c-2c transformation

Two-component zeroth order regular approximation

$$\begin{aligned} H^{ZORA} \phi_{ZORA} &= E_{ZORA} \phi_{ZORA} \\ H^{ZORA} &= \left(\frac{c^2 \hat{\mathbf{p}}^2}{2mc^2 - V} + \frac{2c^2}{(2mc^2 - V)^2} - \frac{Z\hat{S} \cdot \hat{I}}{r^3} + V \right) \end{aligned}$$

Amsterdam Density Functional

- Very fast code
- Uses **Slater-type** basis functions
- All electron relativistic basis sets for all elements
- Available for most spectroscopic properties
- Include relativistic effects on structure and reactivity
- Functionalities:
 - Optimizations
 - Response properties (NMR, EPR, UV-VIS, IR, Mössbauer..)
 - NOCV
 - EDA
 - COSMO model of solvation
 - ZORA scalar and spin-orbit relativistic approach**

Advantages

- Many quantum-chemical tools implemented
- Relativistic effects included via ZORA
- Good powerful GUI (ADFView)

Disadvantages

- Slow geometry optimization
- Sometimes cryptic error messages
- Sometimes serious convergence problems

NMR calculations

- Calculate the NMR properties of hydrogen in HI and HCl
- Write the molecular geometry in same format as .xyz (Å)
- Use the following parameters
- Bond lengths:
 - HCl(scalar): 1.276930
 - HI(scalar) : 1.606797
 - HCl(SO): 1.276467
 - HI(SO): 1.609681
- For relativity use **ZORA Scalar** and **ZORA Spin-Orbit** Approximation in ADF
- Compare the Experimental, Nonrelativistic, ECP, and Two component approach
- Chemical shielding for benzene 1H nuclei:

ReSpect

There are two parts of ReSpect calculation

- SCF module- Calculation of unperturbed ground state MO Coefficient.
- MAG module- Calculation of the magnetic properties .
- Each part requires a specific input file (.inp and .M)

List of properties

EPR

- G-tensor
- Hyperfine coupling tensor

NMR

- NMR shielding tensor
- Nuclear spin-rotation coupling tensor
- Indirect nuclear spin-spin coupling tensor

Functional:

PBE, BP86, PBE0 etc

Solvent: PCM, CPCM model (not available for NMR properties)

- Calculate the NMR chemical shielding of H in HI using ReSpect
- Use the prepared input files distributed in IS.
- Three input file required.
 - Initial guess, guess.inp
 - Run using the command
respect --np=4 --inp=guess
 - Restart the calculation at 4 component level from the initial guess
respect --np=4 --inp=4c --restart=guess
 - Calculate the NMR parameters using .M file.
respect --np=4 --inp=4c --M=CS