Perspectives on
2- and 4-component relativistic calculations

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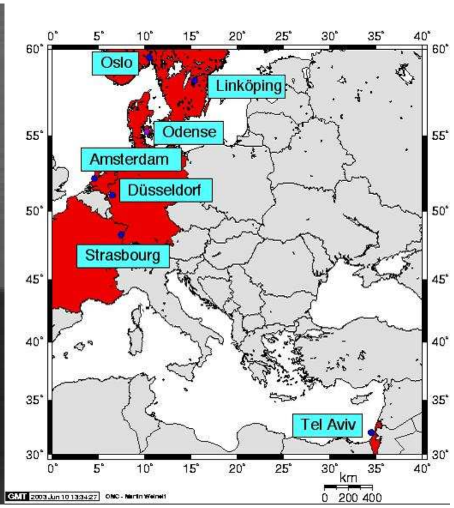
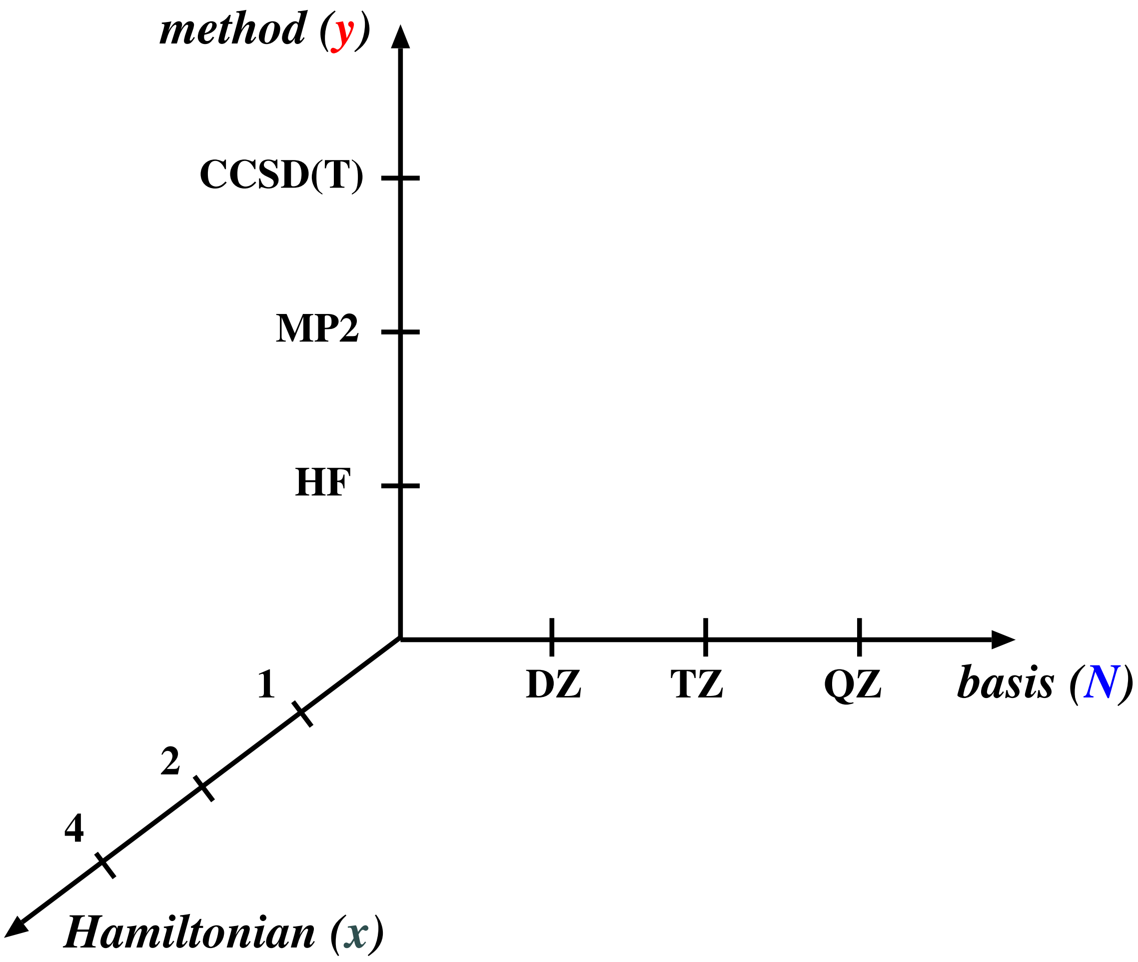
P rogram
• for
A tomic
• and
M olecular

D irect
I terative
R elativistic
A ll-electron
C alculations



http://dirac.chem.sdu.dk

Outline



World Year of Physics 2005

Lanthanide contraction

V.M. Goldschmidt, T. Barth, G. Lunde:

Norske Vidensk. Selsk. Skrifter

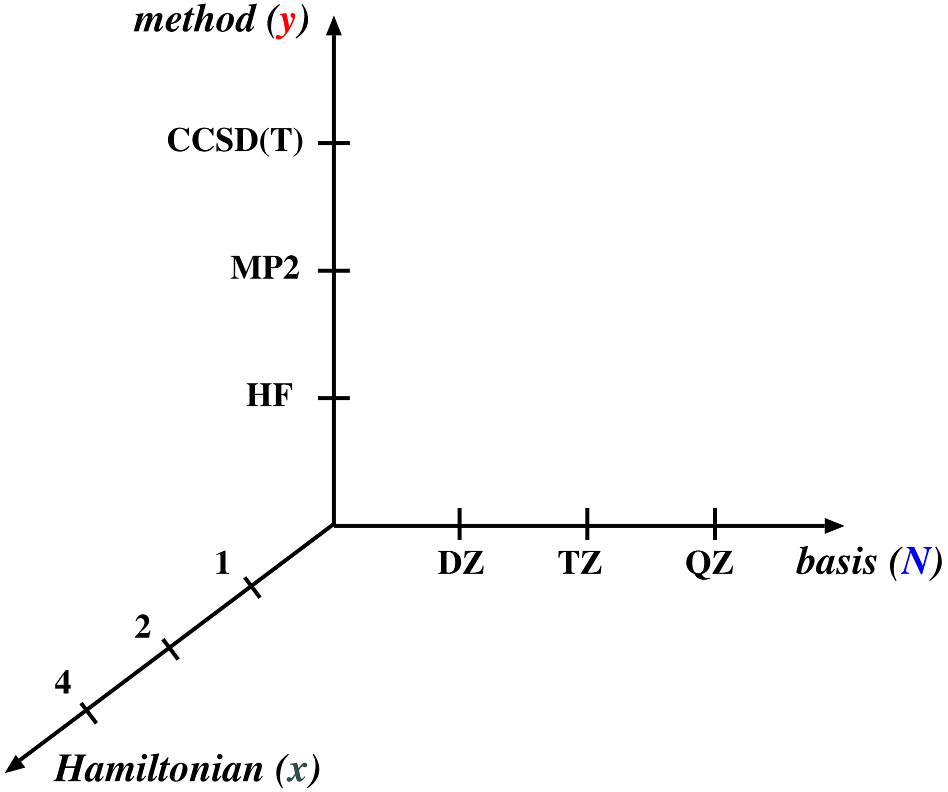
I Mat. Naturv. Kl. **7**, 1 (1925)

Special relativity

A. Einstein:

Ann. Phys. **17** (1905) 891

Theoretical model chemistries



✔ Hamiltonian:

- 1 component:
  scalar relativistic effects
- 2 components:
  spin-orbit interaction
- 4 components:
  complete relaxation of the electronic wave function

The Hamiltonian, relativistic or not, has the same generic form

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2}\sum_{i \neq j} \hat{g}(i,j) + V_{NN}; \quad V_{NN} = \frac{1}{2}\sum_{K \neq L} \frac{Z_K Z_L}{R_{KL}}$$

Computational cost: xN^y

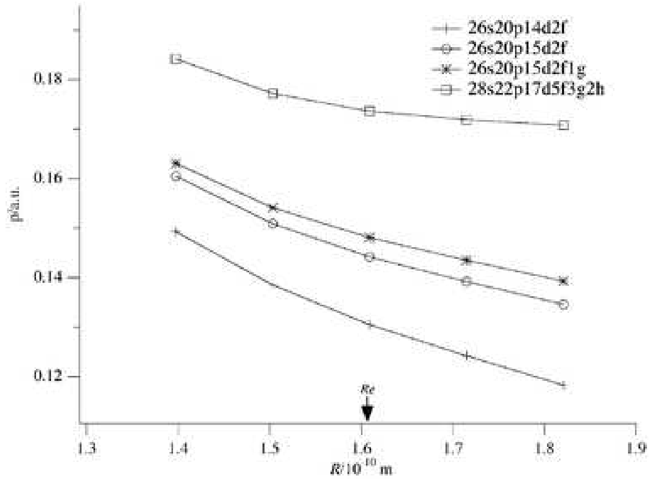
The dipole moment of hydrogen iodine

J. N. P. van Stralen, L. Visscher and J. F. Ogilvie, Phys. Chem. Chem. Phys. **6** (2004) 3779

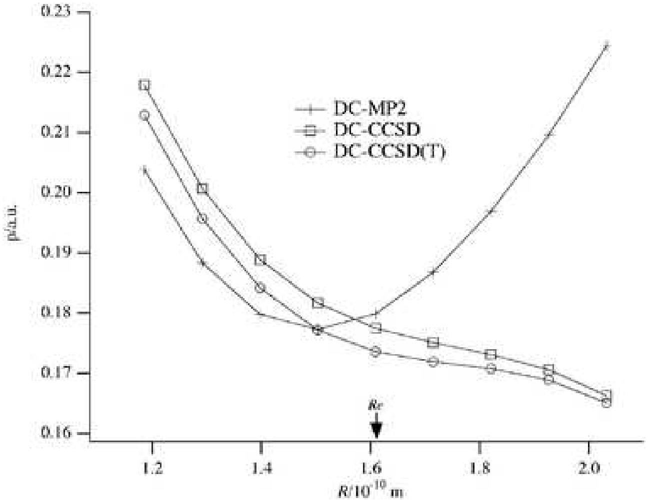
✔ Experiment: $\mu(r_e)$=0.176 au
Dijk and Dymanus, Chem. Phys. Lett. **5** (1970) 387

✔ NR-CCSD(T) + relativistic correction: $\mu(r_e)$= 0.191 au
G. Maroulis, Chem. Phys. Lett. **318** (1996) 1645

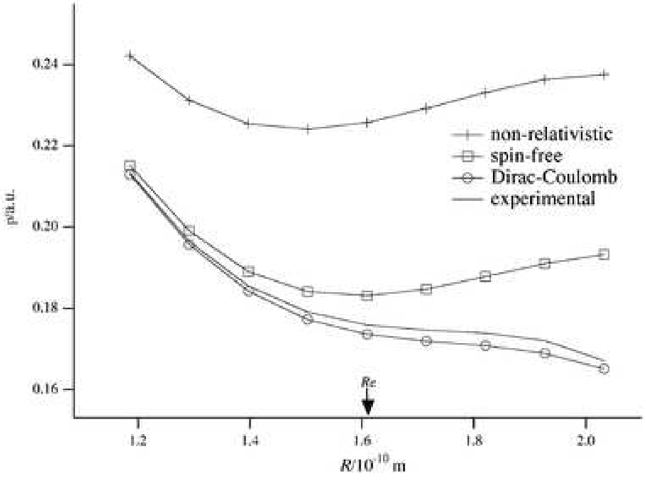
✔ DKH2-CCSD(T) + SO corrections $\mu(r_e)$= 0.154 au
M. Ilias et al., Theor. Chem. Acta **110** (2003) 176



Basis



Method



Hamiltonian

Basis sets

Basis sets

Core correlation becomes increasingly important down the periodic table.

1. Dyall correlation-consistent basis sets: *available from http://dirac.chem.sdu.dk*
    (a) 5d elements: DZ, TZ, QZ
    K. G. Dyall, Theor. Chem. Acc. **112** (2004), 403-409
    (b) 4p/5p/6p elements: DZ, TZ, (QZ)
    K. G. Dyall, Theor. Chem. Acc. **99** (1998) 366, Theor. Chem. Acc. **108** (2002) 365, Theor. Chem. Acc. **108** (2002) 335

2. Fægri 1- and 4-component SCF basis sets (add polarisation !):
available from http://folk.uio.no/knutf/

3. Pseudopotential-based correlation consistent basis sets (K. Peterson *et al.*)
for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements
available from http://tyr0.chem.wsu.edu/~kipeters/basissets/basis.html

Systematic correlation-consistent basis sets for the heavy elements are urgently needed !

Hamiltonian

The 4-component Hamiltonian

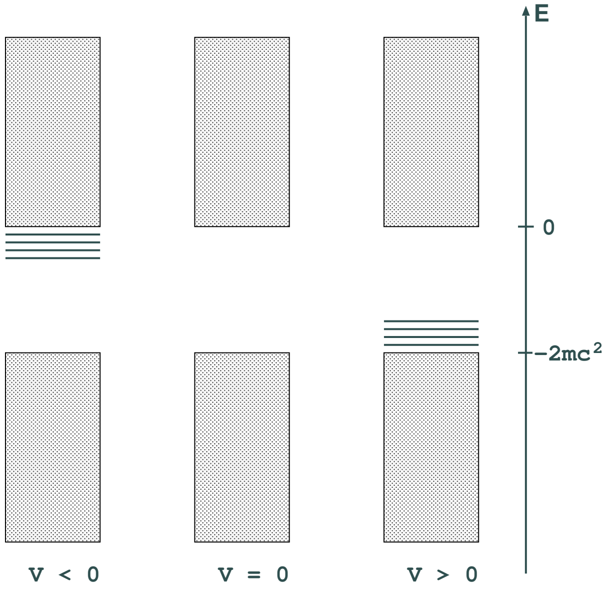
- ✔ One-electron operator: Dirac operator in the molecular field

$$\hat{h}_D(i) = \beta_i' mc^2 + c\,(\boldsymbol{\alpha}_i \cdot \mathbf{p}_i) + \hat{V}_{eN}; \qquad \beta' = \beta - 1$$

- ✔ Two-electron operator: (Coulomb gauge)

$$\begin{aligned} \hat{g}(i,j) &= \frac{1}{r_{ij}} \\ &- \frac{c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j}{c r_{ij}} - \frac{(c\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(c\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j)\, r_{ij}}{2c^2} \\ &+ \ldots \end{aligned}$$

Spectrum of the one-electron operator



The principle of minimal electromagnetic coupling

(M. Gell-Mann, Nuovo Cimento Suppl. **4** (1956) 848)

$$p_\mu \rightarrow p_\mu - qA_\mu \quad \Rightarrow \quad q = -1 \text{ au} \quad \Rightarrow \quad \begin{array}{ccc} \mathbf{p} & \rightarrow & \mathbf{p} + \mathbf{A} \\ E & \rightarrow & E + \phi \end{array}$$

Quaternion forms

T. Saue and H. J. Aa Jensen, J. Chem. Phys. **111** (1999) 6211; L. Visscher and T. Saue, J. Chem. Phys. **113** (2000) 3996

- ✔ Block diagonalization by a quaternion unitary transformation:

$${}^{Q}\widehat{h}_D = \begin{bmatrix} V & 0 \\ 0 & V-2mc^2 \end{bmatrix} - \widehat{\mathbf{i}}c\begin{bmatrix} 0 & \frac{\partial}{\partial z} \\ \frac{\partial}{\partial z} & 0 \end{bmatrix} - \widehat{\mathbf{j}}c\begin{bmatrix} 0 & \frac{\partial}{\partial y} \\ \frac{\partial}{\partial y} & 0 \end{bmatrix} - \widehat{\mathbf{k}}c\begin{bmatrix} 0 & \frac{\partial}{\partial x} \\ \frac{\partial}{\partial x} & 0 \end{bmatrix}$$

- ✔ Modified Dirac equation: $\psi^S = \frac{1}{2mc}(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})\,\phi^S$

$$\begin{bmatrix} \hat{V} & \hat{T} \\ \hat{T} & \frac{1}{4m^2c^2}(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})\,\hat{V}\,(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}) - \hat{T} \end{bmatrix}\begin{bmatrix} \psi^L \\ \phi^S \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & \frac{\hat{T}}{2mc^2} \end{bmatrix}\begin{bmatrix} \psi^L \\ \phi^S \end{bmatrix} E$$

Spin-orbit coupling from: $(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})\,\hat{V}\,(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}) = \widehat{\mathbf{p}}\hat{V}\cdot\widehat{\mathbf{p}} + i\sigma\cdot\left(\widehat{\mathbf{p}}\hat{V}\times\widehat{\mathbf{p}}\right)$

From 4 to 2 components

- ✔ Unitary transformation: decoupling and renormalization

$$\widehat{U}^\dagger \left[\begin{array}{cc} V & c\,(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c\,(\boldsymbol{\sigma}\cdot\mathbf{p}) & V-2mc^2 \end{array} \right] \widehat{U} = \left[\begin{array}{cc} \hat{h}+ & 0 \\ 0 & \hat{h}_- \end{array} \right]; \quad \widehat{U} = \left[\begin{array}{cc} \Omega_+ & -\chi^\dagger\Omega_- \\ \chi\Omega_+ & \Omega_- \end{array} \right]$$

- ✔ Transformation of orbitals:

$$\left[\begin{array}{c} \psi^L \\ \psi^S \end{array} \right] \quad \rightarrow \quad \left[\begin{array}{c} \Omega_+\left[\psi^L + \chi^\dagger\psi^S\right] \\ \Omega_-\left[\psi^S - \chi\psi^L\right] \end{array} \right]$$

- ✔ Positive-energy solutions: χ is the exact coupling of the large and small components

$$\psi^S = \chi\psi^L; \quad \chi = \left(2mc^2 - V + E\right)^{-1} c\,(\boldsymbol{\sigma}\cdot\mathbf{p})$$

2-component relativistic Hamiltonians

- ✔ Pauli Hamiltonian:

$$\chi = \frac{1}{2mc}\left[1+\frac{E-V}{2mc^2}\right]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p}) \sim \frac{1}{2mc}(\boldsymbol{\sigma}\cdot\mathbf{p})$$

- ✔ Regular Approximation:

$$\chi = \frac{c}{2mc^2-V}\left[1+\frac{E}{2mc^2-V}\right]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p}) \sim \frac{c}{2mc^2-V}(\boldsymbol{\sigma}\cdot\mathbf{p})$$

- ✔ Free-particle Foldy-Wouthuysen transformation followed by:

1. decoupling in V: Douglas-Kroll-Heß(DKH) transformation
2. decoupling in c^{-1}: Barysz-Sadlej-Snijders (BSS) transformation

Decoupling the easy way

1. Transform the AO matrix representation of the Dirac operator in the molecular field to free-particle MO-basis (RKB embedded)

2. Let

$$U = \left[\begin{array}{cc} Y_{++} & Y_{+-} \\ Y_{-+} & Y_{--} \end{array} \right]$$

   diagonalize the Dirac Hamiltonian in the molecular field, then

$$Y_{-+} = \chi Y_{++}$$

3. Use this to transform to the infinite-order BSS Hamiltonian for the positive-energy spectrum

4. Backtransform to renormalized large component AO-basis and store on file

Infinite-order 2-component (IOTC) relativistic Hamiltonian

H. J. Aa. Jensen , M. Ilias and T. Saue, in preparation

- reproduces exactly the positive-energy spectrum of the Dirac Hamiltonian
- all matrix manipulations; no new operators to program
- explicit representation of transformation matrix;
  any property operator can be transformed on the fly, no picture change errors

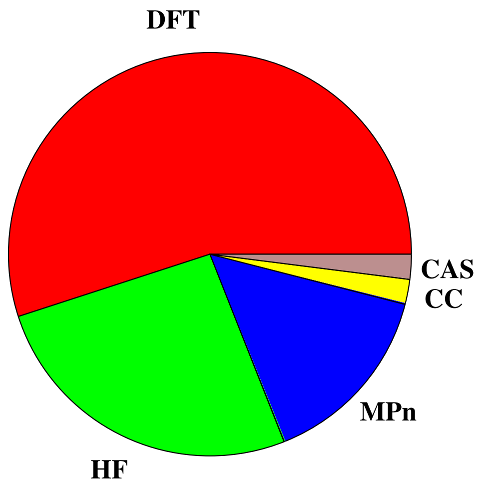
Fock-space CCSD calculations. All values in cm^{-1}				Chlorine		Thallium	
	sr	so	sso	FSS	EA	FSS	IP
DC	∞	∞	∞	928.5	28665	7354	48031
IOTC+AMFI	∞	∞	1	928.3	28667	7328	48006
IOTC	∞	∞	0	1084.4	28616	7590	48212
DKH	2	2	0	1084.4	28616	7542	48210
DKH+AMFI	2	1	1	929.2	28666	8018	48819
DKH	2	1	0	1085.3	28615	8290	49034
exp.	∞	∞	∞	882.4	29152	7793	49264

Methods

“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational. If mathematical analysis should every hold a prominent place in chemistry — an aberration which is happily impossible — it would occasion a rapid and widespread degradation of that science."

A. COMTE (1838)

Density Functional Theory



S. Grimme,

Nachrichten aus der Chemie,

49 (2001) 340

✔ The Dirac-Coulomb Hamiltonian, in the absence of external vector potentials, describes only charge-charge interactions.

⇒ The energy is a functional of the charge density only.

✔ Relativistic corrections have been developed for functionals at the LDA and GGA level, but their effect on spectroscopic constants are negligible, see

- M. Mayer, O. D. Häberlen et N. Rösch, Phys. Rev. A **54** (1996) 4775
- S. Varga, E. Engel, W.-D. Sepp et B. Fricke, Phys. Rev. A **59** (1999) 4288

✔ non-relativistic functionals used:
tested for valence properties, must be checked for core properties

✔ atomic size adjustments in numerical integration

- O. Fossgaard, O. Gropen, M. Corral Valero and T. Saue,
  J. Chem. Phys. **118** (2003) 10418

✔ extensions to TD-DFT and linear reponse

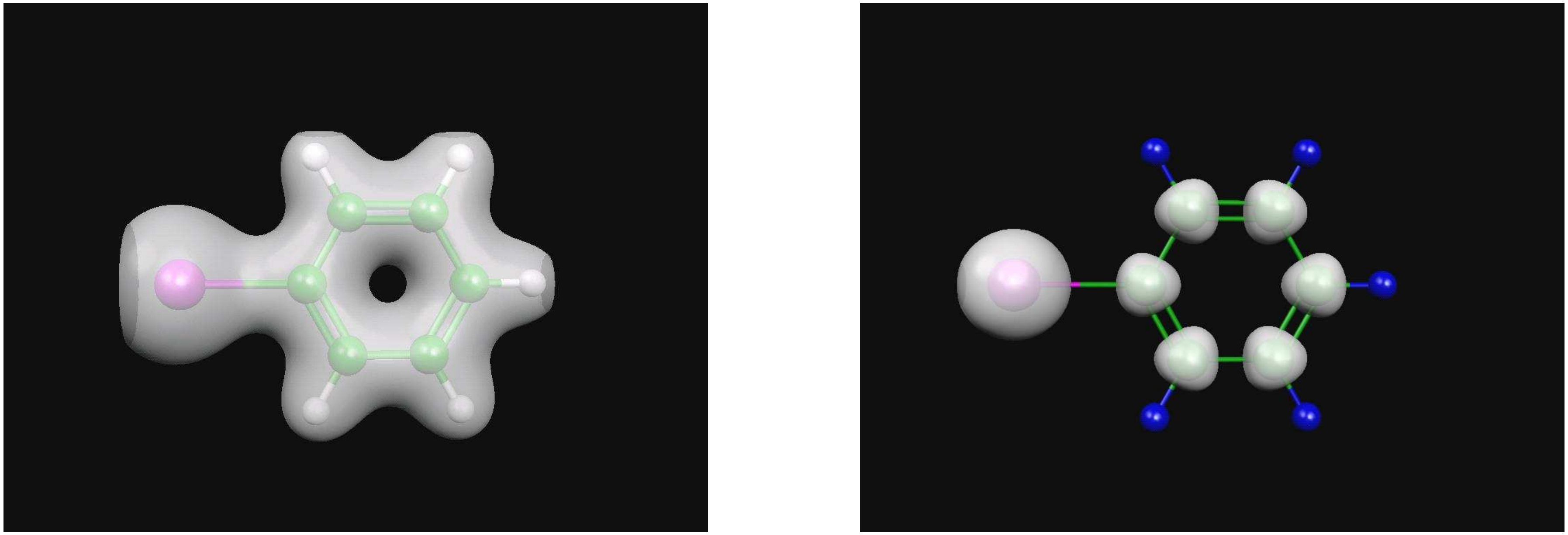
Computational cost: CCSD

	Non-relativistic	**4c Spinfree**
A	$\frac{1}{8}aN^4$	$\frac{1}{2}\left(N_L^4 + 2N_S^2N_L^2 + N_S^4\right)$
B	$\frac{1}{2}nN^4 + \frac{1}{2}n^2N^3$	$\frac{1}{2}n\left(N_L^4 + 4N_S^2N_L^2 + 4N_S^4\right)$ $+\frac{1}{2}n^2\left(N_L^3 + 4N_SN_L^2 + 4N_S^3\right)$
C	$\frac{1}{2}n^3N^2 + \frac{1}{2}n^4N$	$\frac{1}{2}n^3\left(N_L^2 + 4N_S^2\right) + \frac{1}{2}n^4\left(N_L + 4N_S\right)$
D	$\frac{1}{4}n_o^4n_v^2 + 4n_o^4n_v^2 + \frac{1}{2}n_o^2n_v^4$	$\frac{1}{4}n_o^4n_v^2 + 4n_o^4n_v^2 + \frac{1}{2}n_o^2n_v^4$
	2c full $(\infty, 0)$	**4c full**
A	$\frac{1}{2}aN^4$	$\frac{1}{2}\left(N_L^4 + 2N_S^2N_L^2 + N_S^4\right)$
B	$2nN^4 + 8n^2N^3$	$2n\left(N_L^4 + N_S^2N_L^2 + N_S^4\right)$ $+8n^2\left(N_L^3 + N_SN_L^2 + N_S^3\right)$
C	$4n^3N^2 + 16n^4N$	$4n^3\left(N_L^2 + N_S^2\right) + 16n^4\left(N_L + N_S\right)$
D	$8n_o^4n_v^2 + 128n_o^4n_v^2 + 16n_o^2n_v^4$	$8n_o^4n_v^2 + 128n_o^4n_v^2 + 16n_o^2n_v^4$

$n = N; \quad N_S = 2N_L$		4c spf	2c full	4c full
A: Hartree-Fock	N^4	~ 100	~ 4	~ 100
B: Integral transformation I	N^5	~ 61	~ 10	~ 130
C: Integral transformation II	N^5	~ 13	~ 20	~ 68
D: CCSD	N^6	1	32	32

n — number of active orbitals, N_L/N_S — number of large/small basis functions

Hartree-Fock/Kohn-Sham/MP2



ρ^L(iso=0.01) ρ^S(iso=0.0001)

- ✔ Three two-electron integral classes arise from the Coulomb term:

$$(\mathrm{LL}\,|\,\mathrm{LL})\,,(\mathrm{LL}\,|\,\mathrm{SS})\,,(\mathrm{SS}\,|\,\mathrm{SS})$$

- ✔ The Simple Coulombic Correction: $E\left[(\mathrm{SS}\,|\,\mathrm{SS})\right] \approx \frac{1}{2}\sum_{A\neq B}\frac{q_A^S q_B^S}{R_{AB}}$

  L. Visscher, Theor. Chem. Acc. **98** (1997) 68

- ✔ What's next ? Fast Multipole Method (FMM) combined with density fitting

The relativistic framework:

The fundamental interactions of chemistry are electromagnetic.

Electromagnetic interactions are manifestly relativistic.

A closer look at the spin density

- ✔ Magnetization (spin part from Gordon decomposition):

$$\mathbf{M} = \sum_i \psi_i^\dagger \beta \boldsymbol{\Sigma} \psi_i$$

- ✔ Collinear approach:

$$s = M_z \quad \overset{\text{NR}}{\longrightarrow} \quad \rho^\alpha - \rho^\beta$$

- ✔ Non-collinear approach:

$$s = |\mathbf{M}|$$

- ✔ Kramers-unrestricted formulation: spin up/down replaced by moment up/down

Spin density from magnetic neutron scattering

L. L. Hirst, Rev. Mod. Phys. **69** (1997) 607,

P. F. de Chatel and K. Ayuel, Physica B **266** (1999) 256, Phys. Rev. B **61** (2000) 15213

✔ Interaction with external electromagnetic fields

(K. Schwarzschild, Gött. Nach. Math.-Phys. Kl. (1903) 126)

$$H_{\text{int}} = -\int j_\mu A_\mu d\tau = \int \rho(\mathbf{r})\phi(\mathbf{r}) - \mathbf{j}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\tau$$

✔ Getting the spin density from scattering amplitudes:

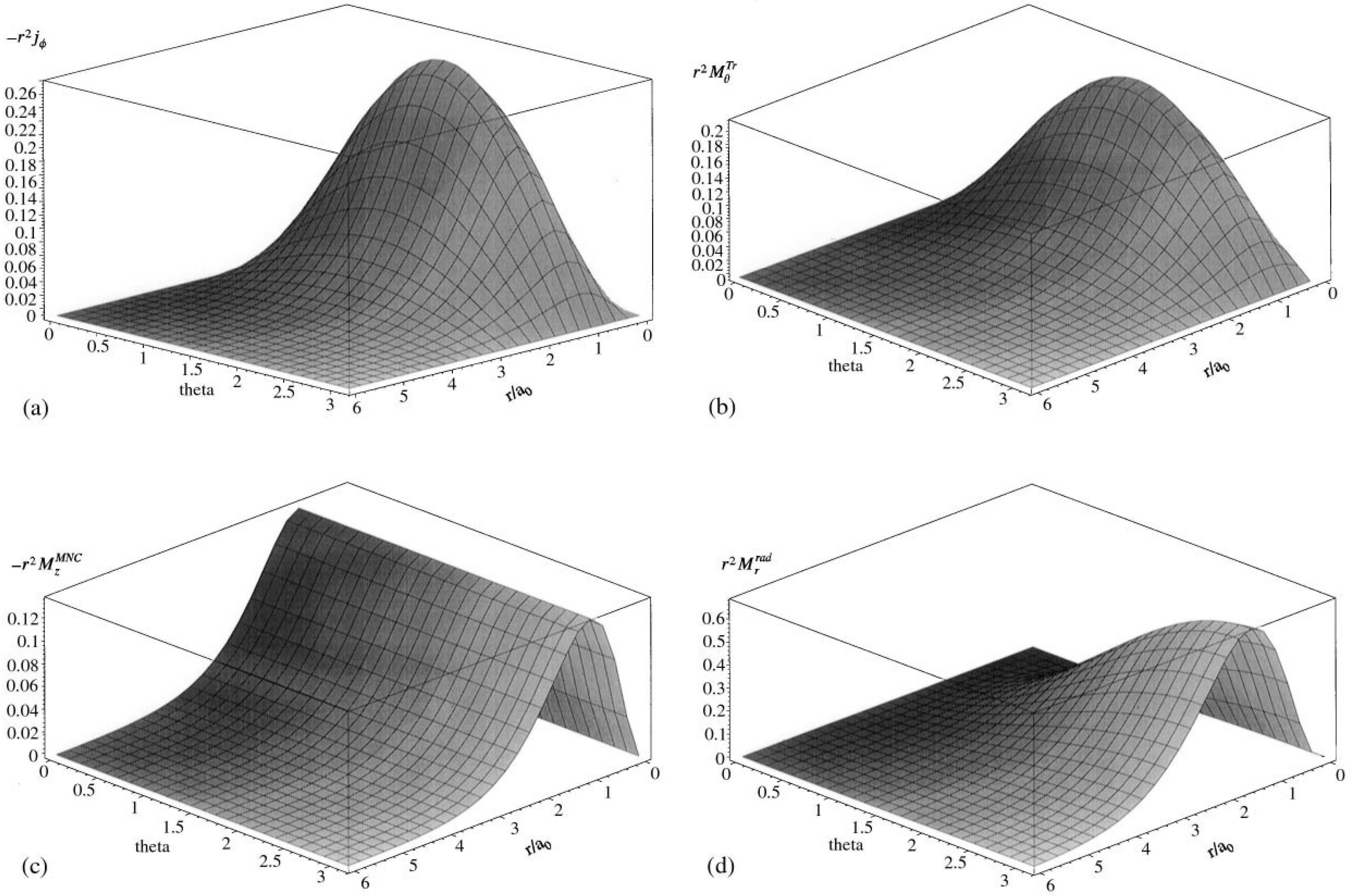
$$\text{amplitudes}(\mathbf{k}) \rightarrow \mathbf{j}(\mathbf{r}) \rightarrow \mathbf{M}(\mathbf{r}) \rightarrow s(\mathbf{r})$$

✔ Problems:

- the neutron "sees" a current density, making no distinction between spin and orbital contributions
- gauge freedom of magnetization: $\mathbf{j} = \boldsymbol{\nabla} \times \mathbf{M}$

Gauge freedom of the magnetization

P. F. Chatel and K. Ayuel, Physica B 266 (1999) 256



Current density and magnetization with three different gauges for the ground state of the hydrogen atom

CDFT in a relativistic framework

- ✔ The mathematical form of the relativistic current density

$$\mathbf{j}^R = -ec\psi^\dagger \boldsymbol{\alpha}\psi$$

is much simpler than the corresponding non-relativistic expression

$$\mathbf{j}^{NR} = -\frac{e}{2m}\{\psi^*\mathbf{p}\psi - \psi\mathbf{p}\psi^*\} - \frac{e^2}{m}\psi^*\mathbf{A}\psi - \frac{e}{m}\boldsymbol{\nabla}\times\{\psi^*\boldsymbol{\sigma}\psi\}$$

- ✔ The charge and current density, as part of the 4-current, are mixed through a Lorentz transformation. This strongly suggests that charge and current density functionals should have the same mathematical form in the relativistic domain.

Conclusions

- ✔ Overall relativistic quantum chemistry is in good shape !
- ✔ Systematic basis sets for the heavy elements are urgently needed.
- ✔ 2-component relativistic Hamiltonians give important computational savings at the HF/DFT/MP2 level, but not at the CC/CI level.
- ✔ The atomic nature of the small component density can be exploited to give computational savings at the 4-component level.
- ✔ Efficiency of CI/CC with spin-orbit must be improved.
- ✔ Spin density is not well defined in both experiment and relativity and should be replaced by current density
- ✔ Do not forget molecular properties !