Development of an efficient quasi-relativistic two-component DFT and Hartree-Fock program

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What it is all about?

“Quasi-Relativistic”

… means we use (one-particle) Hamiltonians which reproduce only the positive-energy part of the full Dirac spectrum

… this can be achieved to good approximation, or even as a converging series

… in our work, we have used and implemented so far

the **ZORA** (or CPD) Hamiltonian
the Douglas-Kroll-Heß (**DKH**) approximation
effective core potentials (**ECP**s)

“Two-Component”

… means that our orbitals ϕ_i are neither pure α or β spin, but linear combinations thereof. In Pauli notation, this gives two-component one-particle wave functions:

$$\phi_i = \begin{pmatrix} \phi_{i\alpha} \\ \phi_{i\beta} \end{pmatrix}$$

… the need arises because quasirelativistic Hamiltonians “act” on spin because of **spin-orbit coupling**

$$\hat{h}^{(QR)} = \hat{h}^{(0)} + \sigma_x \hat{h}^{(x)} + \sigma_y \hat{h}^{(y)} + \sigma_z \hat{h}^{(z)}$$

“Efficient”

Two-component methods were extensively investigated by Y. S. Lee. They use ECPs and a special version of the four-component program MOLFDIR. **Focus is on small molecules and high level of electron correlation.**

We aim at an implementation applicable to **larger systems**, and concentrate on “simple” **single-configuration** schemes such as Hartree-Fock and DFT.

This also implies that **spin-orbit CI** is no alternative here

- spin-orbit CI cannot be used for (super)heavy p-block Elements anyway -

What has been done?

What has been achieved so far:

1999/2000:	two-component DFT energies
2000/2001:	two-component HF energies
	(includes hybrid functionals à la B3LYP)
2002/2003:	two-component geometry gradients
	(HF, DFT including hybrid functionals)
1999/2002:	ZORA (CPD) matrix elements (incl. gradient)
2003/2004	DKH matrix elements (through 6th order)
	including corrections for two-particle picture change
2004:	ECP spin-orbit matrix elements

Note: DKH & ECP: energy only, no derivative integrals so far

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Efficiency considerations, closed-shell case

Construction of „Fock“ matrix:

exactly the same effort as in the nonrelativistic case using a basis set of the same size

Diagonalization of „Fock“ matrix:

generally, effort grows by a factor of 32 (matrix dimension doubles, complex arithmetic)

(this is a nuisance in parallel calculations, some symmetry exploitation could be incorporated)

Geometry gradient:

exactly the same effort (as in the nonrelativistic case)

Calculation of derivative two-electron integrals

Efficiency considerations, open-shell case

Construction of „Fock“ matrix:

- exactly the same effort for the (costly) Hartree part
- effort doubled for the exchange-correlation part

  non-collinear approximation, magnetization direction is different at each point in space
- effort 4* higher for the „exact exchange“ part

  operators $K^{(0)}$, $K^{(x)}$, $K^{(y)}$, $K^{(z)}$ have both real and imaginary parts

Geometry gradient:

- exactly the same effort (!)

  only construction of density matrices is affected, computation & contraction of two-electron derivative integrals stays the same

What we would like to do!

Future work, or:
What do we want to do with the money we are asking for?

Task A: Hamiltonians

- **Geometry derivative integrals for spin-orbit ECPs**

  Geometry optimization of large systems including 6p elements

  Adsorption of superheavy p-block elements on models of metal surfaces (clusters), including surface relaxation

- Douglas-Kroll integrals for contracted basis functions

- Future work on „model potential“ approximation to the two-electron picture change corrections

Future work, or:
What do we want to do with the money we are asking for?

Task B: Implementation of new methods

- TD-HF and TD-DFT for two-component Hamiltonians

  non-collinear approximation: „new features" even in the non-rel. limit

  spin-orbit effects on electron spectra of large heavy-element compounds, especially if their size prohibits the use of spin-orbit CI methods

Thank you for the attention!

(Please ask questions if anything is still not clear to you)