RDMFT implementation in Octopus

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One body reduced density-matrix

RDMFT: energy functional of 1-RDM [1]

$$\gamma(\vec{r},\vec{r'}) = N \int \cdots \int \mathrm{d}\vec{r_2} \ldots \vec{d}\vec{r_N}\, \Psi^*(\vec{r'},\vec{r_2}...\vec{r_N})\Psi(\vec{r},\vec{r_2}...\vec{r_N}) \quad (1)$$

spectral representation of 1-RDM

$$\gamma(\vec{r},\vec{r'}) = \sum_{i=1}^{\infty} n_i \phi_i^*(\vec{r'})\phi_i(\vec{r}), \quad (2)$$

[1] T. L. Gilbert, Phys. Rev. B, **12**, 2111(1975)

RDMFT total energy expression

In RDMFT the total energy is given by

$$E = -\sum_{i=1}^{\infty} n_i \int \mathrm{d}\vec{r}\phi_i^*(\vec{r})\frac{\nabla^2}{2}\phi_i(\vec{r}) + \sum_{i=1}^{\infty} n_i \int \mathrm{d}\vec{r}\, v_{\mathrm{ext}}(\vec{r})|\phi_i(\vec{r})|^2$$
$$+ \frac{1}{2}\sum_{i,j=1}^{\infty} n_i n_j \int \mathrm{d}\vec{r}\mathrm{d}\vec{r}' \frac{|\phi_i(\vec{r})|^2|\phi_j(\vec{r})|^2}{|\vec{r}-\vec{r}'|} + E_{\mathrm{xc}}\left[\{n_j\},\{\phi_j\}\right] \ . \quad (3)$$

- Approximate part E_{xc} comes only from interaction term [2]

$$E_{xc} = -\frac{1}{2}\sum_{i,j=1}^{\infty} \sqrt{n_i n_j}\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}')\phi_j^*(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (4)$$

[2] A.M.K. Mueller, Phys. Lett. A, **105**, 446 (1984)

Conditions

- Closed shell $0 \leq n_i \leq 2$ use $n_i = 2sin^2(2\pi\vartheta_i)$
- Open shell $0 \leq n_i \leq 1$ (not implemented)
- $\sum_i n_i = N$
- Above N-representability conditions[3]
- Orthonormality of orbitals has to be imposed $\langle\phi_i|\phi_j\rangle = \delta_{ij}$

[3] Coleman, A. J., Rev. Mod. Phys. , **35**, 668 (1963)

Two step minimization

$$\Omega\left[N, \{\vartheta_i\}, \{\phi_i(\vec{r})\}\right] = E - \mu\left(\sum_{i=1}^{\infty} 2\sin^2(2\pi\vartheta_i) - N\right) - \sum_{i,j=1}^{\infty} \lambda_{ji}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right) \quad (5)$$

- For fixed natural orbitals energy minimized with respect to occupation numbers.
- μ not known found via bisection
- For fixed occupation numbers energy minimized with respect to natural orbitals.

Piris orbital Minimization

$$\lambda_{ji} = n_i \left\langle \phi_j \left| -\frac{\nabla^2}{2} + v_{\text{ext}} \right| \phi_i \right\rangle + \int \mathrm{d}\vec{r} \frac{\delta E_{\text{Hxc}}}{\delta \phi_i^*(\vec{r})} \phi_j^*(\vec{r}). \quad (6)$$

At the extremum

$$\lambda_{ji} - \lambda_{ij}^* = 0 \ . \quad (7)$$

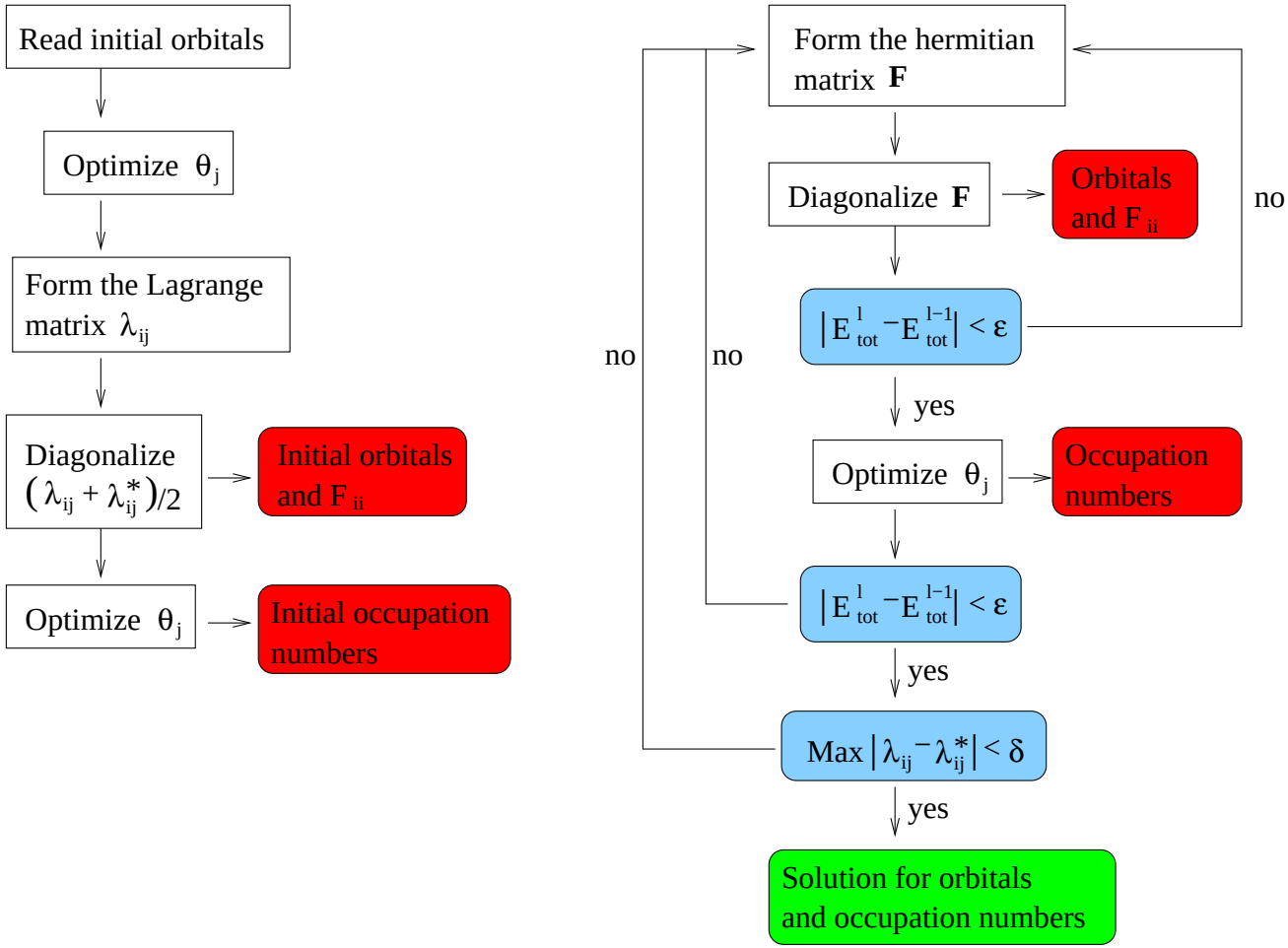
Define non-diagonal elements of **F**

$$F_{ji} = \theta(i-j)(\lambda_{ji} - \lambda_{ij}^*) + \theta(j-i)(\lambda_{ij}^* - \lambda_{ji}), \quad (8)$$

- Diagonalize **F** and use diagonal for next step
- At the solution non-diagonal elements of **F** vanish $\rightarrow$ **F** and γ simultaneously diagonal[4]

[4] M. Piris and J. M. Ugalde, J. Comput. Chem, **13**, 2078 (2009)

Flowchart


Read initial orbitals
Optimize θ_j
Form the Lagrange matrix λ_{ij}
Diagonalize $(\lambda_{ij} + \lambda_{ij}^*)/2$
Initial orbitals and F_{ii}
Optimize θ_j
Initial occupation numbers
Form the hermitian matrix F
Diagonalize F
Orbitals and F_{ii}
no
$|E_{tot}^{l} - E_{tot}^{l-1}| < \varepsilon$
no
no
yes
Optimize θ_j
Occupation numbers
$|E_{tot}^{l} - E_{tot}^{l-1}| < \varepsilon$
yes
Max $|\lambda_{ij} - \lambda_{ij}^*| < \delta$
yes
Solution for orbitals and occupation numbers

Initial guess

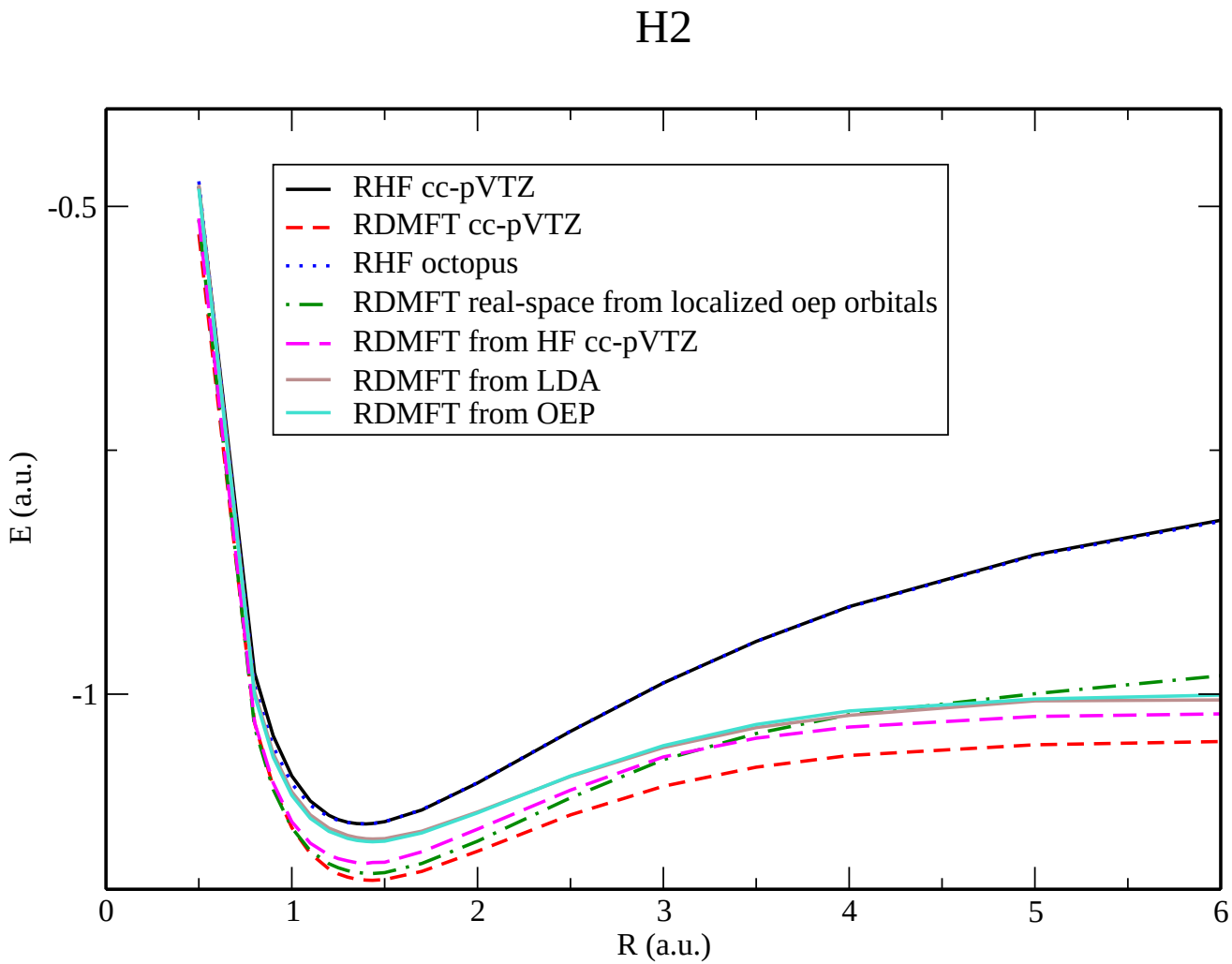
- Hard to find a good initial guess for natural orbitals from a ground state calculation!
- Real-space LDA and HF giving unbound states among unoccupied which are non localized (for example all unoccupied states of H_2 are unbound)
- $\rightarrow$ non localized orbitals bad initial guess for natural orbitals
  $\rightarrow$ converged energy higher
- OEP givess better starting orbitals (for example gives 4 bound states among unoccupied of H_2) but still not good enough
- Gaussian basis codes give more localized unbound states due to the nature of basis set

Initial guess for the moment

- Test: HF orbitals from gaussian calculation on the grid and perform RDMFT with octopus
- Result: comparable energies with gaussian implementation of RDMFT (HIPPO-Lathiotakis[5])
- Take OEP states and multiply unoccupied ones with an exponential sum over the nuclei position to localize them $e^{\alpha((r-R_i)}$
- Problems: system dependent, states needed different localization, degeneracies

[5] N. N. Lathiotakis and M. A. L. Marques, J. Chem. Phys. **18**, 183103 (2008)

H2 dissociation curve



Other problems-open issues

- RDMFT calculation that takes usually a few minutes in gaussian basis sets can take from 15 minutes to two hours in octopus
- Room for improvement in serial and parallelization over states needed
- Make occupation number minimization work with GSL library minimization
- Improving of damping non-diagonal **F**