Reduced Density-Matrix Functional Theory in OCTOPUS
Reduced density-matrix functional theory

\[ \psi(r_1...r_N) \leftrightarrow \gamma(r, r') \]
\[ \gamma(r, r') = N \int d^3r_2...d^3r_N \psi^*(r'...r_N) \psi(r...r_N) \]

- Every ground-state observable is a functional of \( \gamma(r, r') \)

Ground-state energy

\[ E[\gamma] = E_{\text{kin}}[\gamma] + E_{\text{ext}}[\gamma] + E_H[\gamma] + E_{xc}[\gamma] \]
Reduced density-matrix functional theory

Natural orbitals and occupation numbers

\[ \gamma(r, r') = \sum_{j=1}^{\infty} n_j \phi_j^*(r') \phi_j(r) \]

- No non-interacting system at zero temperature due to idempotency
- Minimize total energy with respect to occupation numbers and natural orbitals
- Constraints \(0 \leq n_j \leq 1, \sum_j n_j = N, \langle \phi_j | \phi_k \rangle = \delta_{jk}\)
Direct minimization

Minimization wrt. natural orbitals leads to an equation like

\[ \hat{F}_j \varphi_j(r) = \sum_k \epsilon_{jk} \varphi_k(r) \]

with \( \epsilon_{jk} = \epsilon^*_{kj} \)

- Orbital dependence of \( F \) destroys automatic orthogonality of orbitals
- Explicit orthogonalization during the minimization is a pain on a grid
Finite temperature

- Extend theory to finite temperature (T. Baldsiefen, E.K.U. Gross arXiv)
- Find interacting gs density matrix as gs density matrix of non-interacting system at finite temperature
- Temperature has no physical meaning but can improve convergence
- Two scf cycles
  - Find occupation numbers for fixed natural orbitals
  - Find natural orbitals for fixed occupation numbers
- Müller functional (other approximations very similar)

\[
E_{xc} = -\frac{1}{2} \sum_{j,k=1}^{\infty} \sqrt{n_j n_k} \int \int d^3r d^3r' \frac{\varphi_j(r)\varphi^*_j(r')\varphi_k(r')\varphi^*_k(r)}{|r - r'|}
\]
What is done

- Equation for natural orbitals very similar to Hartree-Fock
- Occupation numbers follow Fermi-Dirac statistics

\[ n_j = \frac{1}{\exp(\epsilon_j - \mu)/k_B T + 1} \]

- Implementation in \texttt{rdmft.F90} in \texttt{/scf}
- \texttt{RDM\_Exchange\_operator} routine in \texttt{/hamiltonian/hamiltonian\_inc.F90}
- Only closed shell implementation
- Occupation numbers can be determined
- Difficulties in setting up the Hamiltonian for natural orbitals