Reduced Density-Matrix Functional Theory in OCTOPUS

29.03.2012 | I. Theophilou, N. Helbig

Reduced density-matrix functional theory

Reduced density matrix functional theory

$$\Psi(\mathbf{r}_1 ... \mathbf{r}_N) \leftrightarrow \gamma(\mathbf{r}, \mathbf{r}')$$

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int d^3 r_2 ... d^3 r_N \Psi^*(\mathbf{r}' ... \mathbf{r}_N) \Psi(\mathbf{r} ... \mathbf{r}_N)$$

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

Ground-state energy

$$E[\gamma] = E_{\mathrm{kin}}[\gamma] + E_{\mathrm{ext}}[\gamma] + E_H[\gamma] + E_{xc}[\gamma]$$

Reduced density-matrix functional theory

Natural orbitals and occupation numbers

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r})$$

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

Direct minimization

Minimization wrt. natural orbitals leads to an equation like

$$\hat{F}_j \varphi_j(\mathbf{r}) = \sum_k \epsilon_{jk} \varphi_k(\mathbf{r})$$

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)

$$E_{xc} = -\frac{1}{2}\sum_{j,k=1}^{\infty}\sqrt{n_j n_k}\iint d^3r d^3r' \frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')\varphi_k^*(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

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 `rdmft.F90` in `/scf`
- RDM_Exchange_operator routine in `/hamiltonian/hamiltonian_inc.F90`
- Only closed shell implementation
- Occupation numbers can be determined
- Difficulties in setting up the Hamiltonian for natural orbitals