Reduced Density Matrix Functional Theory

Kasia Pernal

Lodz University of Technology, Poland

Atomic units

Throughout the lecture atomic units are used

$$\begin{aligned} h/2\pi &= 1[a.u.] = 1.0546 \times 10^{-34}[Js] \\ m_e &= 1[a.u.] = 9.1095 \times 10^{-31}[kg] \\ e &= 1[a.u.] = 1.6022 \times 10^{-19}[C] \end{aligned}$$

Energy

$$1[a.u.] = 1[Hartree] = 4.3598 \times 10^{-18}[J] = 27.211[eV]$$

Length

$$1[a.u] = 1[bohr] = 5.2918 \times 10^{-11}[m] = 0.52918[\mathring{A}]$$

Born-Oppenheimer approximation

For molecules we consider only the electronic Hamiltonian, i.e. the Born-Oppenheimer approximation is used

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N}\sum_{I=1}^{M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{j}^{N}\sum_{i>j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where N-number of electrons, M-number of nuclei, $\{\mathbf{r}_i\}$-electronic coordinates, $\{\mathbf{R}_I\}$-nuclear coordinates.

The Schrödinger equation

- The time-dependent Schrödinger equation for an N-electron system

  $$i\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\psi(x,t)$$

  $$x = (x_1, \ldots, x_N)$$

  $$x_i = (\mathbf{r}_i, \sigma_i)$$

  for a time-independent Hamiltonian reduces to

  $$\hat{H}\Psi_n(x_1, \ldots, x_N) = E_n\Psi_n(x_1, \ldots, x_N)$$

  and the solutions to the time-dependent equation are given by

  $$\psi(x,t) = e^{-iE_nt}\Psi_n(x_1, \ldots, x_N)$$

- Let Ψ_0 be a ground state wavefunction and E_0 a corresponding **ground state energy**, i.e.

  $$\forall_{n\neq 0} \quad E_0 \leq E_n$$

Wavefunction-based methods

- Many quantum chemistry methods rely on a specific ansatz (parameterization) for the wavefunction

  $$\Psi_0 \approx \tilde{\Psi}$$

  e.g. the Hartree-Fock method (HF), Configuration Interaction methods (CI, MR-CI, MC-SCF, CAS-SCF, etc.), Coupled Cluster methods (CCSD, CCSD(T), CCSDT, etc.).
- In variational methods (so not in the CC methods) the energy is obtained as the expectation value of the Hamiltonian

  $$E_0 \approx \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$$

Variational wavefunction-based methods

- The variational principle reads

$$E_0 \leq \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$$

where $\tilde{\Psi}$ is a trial, normalized wavefunction.

- In case of the **variational methods**, e.g. HF, CI, or SCF, the optimal parameters $\mathbf{C}$ in $\tilde{\Psi}$ follow from optimizing the expectation value of the Hamiltonian

$$E_0 \leq \tilde{E}_0 = \min_{\mathbf{C}} \left\{ \langle \tilde{\Psi}(\mathbf{C}) | \hat{H} | \tilde{\Psi}(\mathbf{C}) \rangle : \quad \tilde{\Psi}(\mathbf{C}) - \text{normalized} \right\}$$

One-electron reduced density matrix (1-RDM)

Consider the expectation value of the kinetic energy operator

$$\hat{T} = \sum_{i=1}^{N} \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \right] = \sum_{i=1}^{N} \hat{t}(\mathbf{r}_i)$$

One-electron reduced density matrix (1-RDM)

Consider the expectation value of the kinetic energy operator

$$\hat{T} = \sum_{i=1}^{N} \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \right] = \sum_{i=1}^{N} \hat{t}(\mathbf{r}_i)$$

$$T = \int \Psi(x_1, \ldots, x_N)^* \left[\sum_{i=1}^{N} \hat{t}(\mathbf{r}_i) \right] \Psi(x_1, \ldots, x_N) \; dx_1 \ldots dx_N$$

$$= N \int \Psi(x_1, \ldots, x_N)^* \hat{t}(\mathbf{r}_1) \Psi(x_1, \ldots, x_N) \; dx_1 \ldots dx_N$$

$$= \int \delta(x_1 - x_1') \hat{t}(\mathbf{r}_1) \left[N \int \Psi(x_1', \ldots, x_N)^* \Psi(x_1, \ldots, x_N) dx_2 \ldots dx_N \right] \; dx_1' dx_1$$

$$= \int \delta(x_1 - x_1') \hat{t}(\mathbf{r}_1) \Gamma^{(1)}(x_1, x_1') \; dx_1' dx_1$$

One-electron reduced density matrix (1-RDM)

Consider the expectation value of the kinetic energy operator

$$\hat{T} = \sum_{i=1}^{N} \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \right] = \sum_{i=1}^{N} \hat{t}(\mathbf{r}_i)$$

$$\begin{aligned} T &= \int \Psi(x_1, \ldots, x_N)^* \left[\sum_{i=1}^{N} \hat{t}(\mathbf{r}_i) \right] \Psi(x_1, \ldots, x_N)\ dx_1 \ldots dx_N \\ &= N \int \Psi(x_1, \ldots, x_N)^* \hat{t}(\mathbf{r}_1) \Psi(x_1, \ldots, x_N)\ dx_1 \ldots dx_N \\ &= \int \delta(x_1 - x_1') \hat{t}(\mathbf{r}_1) \left[N \int \Psi(x_1', \ldots, x_N)^* \Psi(x_1, \ldots, x_N) dx_2 \ldots dx_N \right]\ dx_1' dx_1 \\ &= \int \delta(x_1 - x_1') \hat{t}(\mathbf{r}_1) \Gamma^{(1)}(x_1, x_1')\ dx_1' dx_1 \end{aligned}$$

$\Gamma^{(1)}$ is a **one-electron reduced density matrix (1-RDM)** defined as

$$\Gamma^{(1)}(x_1, x_1') = N \int \Psi(x_1', x_2, \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_2 \ldots dx_N$$

Electron density

Consider the expectation value of the external potential operator

$$\hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i)$$

$$\begin{aligned}
V_{ext} &= \int \Psi(x_1, \ldots, x_N)^* \left[\sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) \right] \Psi(x_1, \ldots, x_N)\ dx_1 \ldots dx_N \\
&= N \int \Psi(x_1, \ldots, x_N)^* v_{ext}(\mathbf{r}_1) \Psi(x_1, \ldots, x_N)\ dx_1 \ldots dx_N \\
&= \int v_{ext}(\mathbf{r}_1) \left[N \int \Psi(x_1, \ldots, x_N)^* \Psi(x_1, \ldots, x_N) dx_2 \ldots dx_N \right]\ dx_1 \\
&= \int v_{ext}(\mathbf{r}_1) \rho(x_1) dx_1
\end{aligned}$$

Electron density

Consider the expectation value of the external potential operator

$$\hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i)$$

$$\begin{aligned}
V_{ext} &= \int \Psi(x_1, \ldots, x_N)^* \left[\sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) \right] \Psi(x_1, \ldots, x_N) \; dx_1 \ldots dx_N \\
&= N \int \Psi(x_1, \ldots, x_N)^* v_{ext}(\mathbf{r}_1) \Psi(x_1, \ldots, x_N) \; dx_1 \ldots dx_N \\
&= \int v_{ext}(\mathbf{r}_1) \left[N \int \Psi(x_1, \ldots, x_N)^* \Psi(x_1, \ldots, x_N) dx_2 \ldots dx_N \right] \; dx_1 \\
&= \int v_{ext}(\mathbf{r}_1) \rho(x_1) dx_1
\end{aligned}$$

where the **electron density** $\rho(x_1)$ is related to $\Gamma^{(1)}(x_1, x_1')$

$$\rho(x_1) = N \int \Psi(x_1, \ldots, x_N)^* \Psi(x_1, \ldots, x_N) dx_2 \ldots dx_N = \Gamma^{(1)}(x_1, x_1)$$

Two-electron reduced density matrix (2-RDM)

The electron-electron interaction operator is a two-body operator

$$\hat{V}_{ee} = \frac{1}{2}\sum_{i\neq j}^{N} |\mathbf{r}_i - \mathbf{r}_j|^{-1} = \frac{1}{2}\sum_{i\neq j}^{N} r_{ij}^{-1}$$

and its expectation value reads

$$\begin{aligned} V_{ee} &= \int \Psi(x_1,\ldots,x_N)^* \left[\frac{1}{2}\sum_{i\neq j}^{N} r_{ij}^{-1}\right] \Psi(x_1,\ldots,x_N)\ dx_1\ldots dx_N \\ &= \frac{N(N-1)}{2}\int \Psi(x_1,\ldots,x_N)^* r_{12}^{-1}\Psi(x_1,\ldots,x_N)\ dx_1\ldots dx_N \\ &= \int r_{12}^{-1}\left[\int \frac{N(N-1)}{2}\Psi(x_1,\ldots,x_N)^*\Psi(x_1,\ldots,x_N)\ dx_3\ldots dx_N\right] dx_1 dx_2 \\ &= \int r_{12}^{-1}\Gamma^{(2)}(x_1,x_2;x_1,x_2) dx_1 dx_2 \end{aligned}$$

$\Gamma^{(2)}(x_1, x_2; x_1, x_2)$ is an element of the **two-electron reduced density matrix (2-RDM)** defined as

$$\Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{N(N-1)}{2} \times \int \Psi(x_1', x_2', x_3, \ldots, x_N)^* \Psi(x_1, x_2, x_3, \ldots, x_N) dx_3 \ldots dx_N$$

Expectation value of the electronic Hamiltonian

The expectation value of the electronic Hamiltonian is given in terms of one-electron and two-electron reduced density matrices

$$\hat{H} = \sum_{i=1}^{N} \hat{t}(\mathbf{r}_i) + \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N} \left| \mathbf{r}_i - \mathbf{r}_j \right|^{-1}$$

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= \int \delta(x_1 - x_1') \hat{t}(\mathbf{r}_1) \Gamma^{(1)}(x_1, x_1') \; dx_1' dx_1 + \int v_{ext}(\mathbf{r}_1) \Gamma^{(1)}(x_1, x_1) dx_1 \\ &+ \int \left| \mathbf{r}_1 - \mathbf{r}_2 \right|^{-1} \Gamma^{(2)}(x_1, x_2; x_1, x_2) dx_1 dx_2 \end{aligned}$$

Two-electron density matrix functional

- Since the 2-RDM determines 1-RDM

$$\Gamma^{(1)}(x_1, x_1') = \frac{2}{N-1} \int \Gamma^{(2)}(x_1, x_2; x_1', x_2) dx_2$$

then the energy is an explicit functional of 2-RDM

$$E = E[\Gamma^{(2)}]$$

Two-electron density matrix functional

- Since the 2-RDM determines 1-RDM

$$\Gamma^{(1)}(x_1, x_1') = \frac{2}{N-1}\int \Gamma^{(2)}(x_1, x_2; x_1', x_2)\,dx_2$$

then the energy is an explicit functional of 2-RDM

$$E = E[\Gamma^{(2)}]$$

- Does the exact energy result from the minimization

$$E_0 \overset{?}{=} \min_{\Gamma^{(2)}} E[\Gamma^{(2)}]$$

Yes, if the domain is restricted to the so called N-representable $\Gamma^{(2)}$.

N-representability of 2-RDM

- $\Gamma^{(2)}$ is called **N-representable** if it corresponds to some antisymmetric wavefunction Ψ (or a ensemble of wavefunctions)

$$\exists\Psi \quad \Gamma^{(2)}(x_1,x_2;x_1',x_2') =$$

$$\frac{N(N-1)}{2}\int\Psi(x_1',x_2',\ldots,x_N)^*\Psi(x_1,x_2,\ldots,x_N)dx_3\ldots dx_N$$

N-representability of 2-RDM

- $\Gamma^{(2)}$ is called **N-representable** if it corresponds to some antisymmetric wavefunction Ψ (or a ensemble of wavefunctions)

$$\exists\Psi \quad \Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{N(N-1)}{2}\int \Psi(x_1', x_2', \ldots, x_N)^*\Psi(x_1, x_2, \ldots, x_N)dx_3 \ldots dx_N$$

- Some sufficient N-representability conditions for $\Gamma^{(2)}$ are known but they are too restrictive (A. J. Coleman and V. I. Yukalov, [1]).

N-representability of 2-RDM

- $\Gamma^{(2)}$ is called **N-representable** if it corresponds to some antisymmetric wavefunction Ψ (or a ensemble of wavefunctions)

$$\exists\Psi \quad \Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{N(N-1)}{2}\int \Psi(x_1', x_2', \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_3 \ldots dx_N$$

- Some sufficient N-representability conditions for $\Gamma^{(2)}$ are known but they are too restrictive (A. J. Coleman and V. I. Yukalov, [1]).
- Imposing only necessary conditions on 2-RDM results in too low energy [1,2], i.e.

$$\min_{\tilde{\Gamma}^{(2)}} E[\tilde{\Gamma}^{(2)}] < E_0$$

where $\tilde{\Gamma}^{(2)}$ are 2-RDM's satisfying some known necessary N-representability conditions.

Different representations of RDM's

1- and 2-RDM's may be expanded in a given orthonormal basis set $\{\chi_p(x)\}$ as

$$\Gamma^{(1)}(x,x') = \sum_{pq} \Gamma^{(1)}_{pq} \chi_p(x) \chi_q(x')^*$$

$$\Gamma^{(2)}(x_1,x_2;x_1',x_2') = \sum_{pqrs} \Gamma^{(2)}_{pqrs}\ \chi_p(x_1)\chi_q(x_2)\chi_r(x_1')^*\chi_s(x_2')^*$$

Different representations of RDM's

1- and 2-RDM's may be expanded in a given orthonormal basis set $\{\chi_p(x)\}$ as

$$\Gamma^{(1)}(x,x') = \sum_{pq} \Gamma^{(1)}_{pq} \chi_p(x)\chi_q(x')^*$$

$$\Gamma^{(2)}(x_1,x_2;x_1',x_2') = \sum_{pqrs} \Gamma^{(2)}_{pqrs}\ \chi_p(x_1)\chi_q(x_2)\chi_r(x_1')^*\chi_s(x_2')^*$$

1- and 2-RDM's are the expectation values of the reduced density matrix operators

$$\Gamma^{(k)}(x,x') = \left\langle \Psi|\hat{\Gamma}^{(k)}(x,x')|\Psi \right\rangle$$

Reduced density matrix operators

- The RDM operators are defined in terms of the creation $\left\{\hat{c}_p^+\right\}$ and annihilation $\left\{\hat{c}_p\right\}$ operators, in a given basis set, i.e.

$$\hat{\Gamma}^{(1)}(x,x') = \sum_{pq} \hat{c}_q^+ \hat{c}_p \; \chi_p(x)\chi_q(x')^*$$

$$\hat{\Gamma}^{(2)}(x_1,x_2;x_1',x_2') = \frac{1}{2}\sum_{pqrs} \hat{c}_r^+ \hat{c}_s^+ \hat{c}_q \hat{c}_p \; \chi_p(x_1)\chi_q(x_2)\chi_r(x_1')^*\chi_s(x_2')^*$$

Reduced density matrix operators

- The RDM operators are defined in terms of the creation $\left\{\hat{c}_p^+\right\}$ and annihilation $\left\{\hat{c}_p\right\}$ operators, in a given basis set, i.e.

$$\hat{\Gamma}^{(1)}(x,x') = \sum_{pq} \hat{c}_q^+ \hat{c}_p \; \chi_p(x)\chi_q(x')^*$$
$$\hat{\Gamma}^{(2)}(x_1,x_2;x_1',x_2') = \frac{1}{2}\sum_{pqrs} \hat{c}_r^+ \hat{c}_s^+ \hat{c}_q \hat{c}_p \; \chi_p(x_1)\chi_q(x_2)\chi_r(x_1')^*\chi_s(x_2')^*$$

- Consequently,

$$\Gamma_{pq}^{(1)} = \left\langle \Psi \middle| \hat{c}_q^+ \hat{c}_p \middle| \Psi \right\rangle$$
$$\Gamma_{pqrs}^{(2)} = \frac{1}{2}\left\langle \Psi \middle| \hat{c}_r^+ \hat{c}_s^+ \hat{c}_q \hat{c}_p \middle| \Psi \right\rangle$$

Some trivial necessary N-rep conditions for RDM's

- Hermiticity

$$\Gamma^{(1)}_{pq} = \Gamma^{(1)*}_{qp} \;, \quad \Gamma^{(2)}_{pqrs} = \Gamma^{(2)*}_{rspq}$$

- Antisymmetricity of 2-RDM

$$\Gamma^{(2)}_{pqrs} = -\Gamma^{(2)}_{qprs} = -\Gamma^{(2)}_{pqsr} = \Gamma^{(2)}_{qpsr}$$

- Trace conditions

$$\sum_p \Gamma^{(1)}_{pp} = N \;, \quad \sum_{pq} \Gamma^{(2)}_{pqpq} = \frac{N(N-1)}{2}$$

- Sum rule for 1-RDM and 2-RDM

$$\sum_q \Gamma^{(2)}_{pqrq} = \frac{N-1}{2}\Gamma^{(1)}_{pr}$$

Some less trivial necessary N-rep conditions for 2-RDM

The following P, Q, and G matrices must be positive semidefinite (P, Q, G conditions)

$$\begin{aligned}
P_{pqrs} &= \left\langle \hat{c}_r^+ \hat{c}_s^+ \hat{c}_q \hat{c}_p \right\rangle = 2\Gamma^{(2)}_{pqrs} \\
Q_{pqrs} &= \left\langle \hat{c}_r \hat{c}_s \hat{c}_q^+ \hat{c}_p^+ \right\rangle \\
&= \delta_{sq}\delta_{rp} - \delta_{rq}\delta_{sp} - \delta_{sq}\Gamma^{(1)}_{rp} + \delta_{rq}\Gamma^{(1)}_{sp} - \delta_{rp}\Gamma^{(1)}_{sq} + \delta_{sp}\Gamma^{(1)}_{rq} + 2\Gamma^{(2)}_{rspq} \\
G_{pqrs} &= \left\langle \hat{c}_r^+ \hat{c}_s \hat{c}_q^+ \hat{c}_p \right\rangle \\
&= \delta_{sq}\Gamma^{(1)}_{pr} - 2\Gamma^{(2)}_{psrq}
\end{aligned}$$

There are more conditions (T1, T2, T1', T2'). (M. Nakata et al. [3], Z. Zhao et al. [4]).

Variation of the 2-RDM functional

The approximate ground state may be obtained by minimizing the 2-RDM functional

$$E_0 = \min_{\Gamma^{(1)},\Gamma^{(2)}} \left\{ \sum_{pq} h_{pq} \Gamma^{(1)}_{qp} + \sum_{pqrs} \langle pq|rs\rangle \, \Gamma^{(2)}_{rspq} \right\}$$

where

$$h_{pq} = \int \chi_p(x)^* \left[\hat{t}(\mathbf{r}) + v_{ext}(\mathbf{r})\right] \chi_q(x) dx$$

$$\langle pq|rs\rangle = \int \chi_p(x_1)^* \chi_q(x_2)^* \left|\mathbf{r}_1 - \mathbf{r}_2\right|^{-1} \chi_r(x_1)\chi_s(x_2) dx_1 dx_2$$

subject to the necessary conditions listed before.
See papers by Mazziotti [5], Nakata et al. [3], Zhao et al. [4], D. van Neck et al. [6], and the work of Eugene DePrince et al. [27]-[28].

Variation of the 2-RDM functional

- **Pros**
  - no need to handle *N*-electron wavefunction
  - high accuracy of the ground state energies; comparable to high-level methods like CCSD(T) or better for multireference states
- **Cons**
  - expensive constrained optimization algorithms are needed (semidefinite programming SDP) - high computational cost!!!
  - wrong dissociation products of diatomic molecules

Talk to Eugene DePrince to learn more (everything).

Coming back to 1-RDM ...

Can we find a ground state energy without a knowledge of 2-RDM?

Coming back to 1-RDM ...

Can we find a ground state energy without a knowledge of 2-RDM?
In principle... YES.

- In 1975 T. L. Gilbert proved the existence of the energy 1-RDM functional for a local or nonlocal external potential [7].
- Gilbert theorem: a ground state wavefunction is determined by the v-representable one-electron reduced density matrix, $\Gamma^{(1)} \longrightarrow \Psi_0$.

Note that the expectation value of the nonlocal potential is given by 1-RDM, i.e.

$$\upsilon = \int \upsilon(x, x')\Gamma^{(1)}(x, x')dxdx'$$

Proof of Gilbert theorem

Assume two different (by more than a constant) nonlocal potentials $\hat{v}_1$ and $\hat{v}_2$ giving rise to two different wavefunctions Ψ_1 and Ψ_2 yielding the same 1-RDM's $\Gamma_1^{(1)} = \Gamma_2^{(1)} = \Gamma^{(1)}$.

Proof of Gilbert theorem

Assume two different (by more than a constant) nonlocal potentials $\hat{v}_1$ and $\hat{v}_2$ giving rise to two different wavefunctions Ψ_1 and Ψ_2 yielding the same 1-RDM's $\Gamma_1^{(1)} = \Gamma_2^{(1)} = \Gamma^{(1)}$.
On one hand, due to the variational theorem

$$E_0^1 = \left\langle \Psi_1 \middle| \hat{H}_1 \middle| \Psi_1 \right\rangle < \left\langle \Psi_2 \middle| \hat{H}_1 \middle| \Psi_2 \right\rangle$$
$$E_0^2 = \left\langle \Psi_2 \middle| \hat{H}_2 \middle| \Psi_2 \right\rangle < \left\langle \Psi_1 \middle| \hat{H}_2 \middle| \Psi_1 \right\rangle$$

Proof of Gilbert theorem

Assume two different (by more than a constant) nonlocal potentials $\hat{v}_1$ and $\hat{v}_2$ giving rise to two different wavefunctions Ψ_1 and Ψ_2 yielding the same 1-RDM's $\Gamma_1^{(1)} = \Gamma_2^{(1)} = \Gamma^{(1)}$.
On one hand, due to the variational theorem

$$
\begin{aligned}
E_0^1 &= \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle \\
E_0^2 &= \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle < \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle
\end{aligned}
$$

and

$$\Delta E = \left(\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle - E_0^1 \right) + \left(\langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle - E_0^2 \right) > 0$$

On the other hand, since $\hat{H}_1 - \hat{H}_2 = \hat{v}_1 - \hat{v}_2$ then

$$\begin{aligned}
\Delta E &= \left\langle \Psi_2 \middle| \hat{H}_1 - \hat{H}_2 \middle| \Psi_2 \right\rangle + \left\langle \Psi_1 \middle| \hat{H}_2 - \hat{H}_1 \middle| \Psi_1 \right\rangle \\
&= \int \left[v_1(x,x') - v_2(x,x') \right] \Gamma(x,x') dx dx' \\
&+ \int \left[v_2(x,x') - v_1(x,x') \right] \Gamma(x,x') dx dx' \\
&= 0
\end{aligned}$$

On the other hand, since $\hat{H}_1 - \hat{H}_2 = \hat{v}_1 - \hat{v}_2$ then

$$
\begin{aligned}
\Delta E &= \left\langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \right\rangle + \left\langle \Psi_1 | \hat{H}_2 - \hat{H}_1 | \Psi_1 \right\rangle \\
&= \int \left[v_1(x,x') - v_2(x,x') \right] \Gamma(x,x') dx dx' \\
&+ \int \left[v_2(x,x') - v_1(x,x') \right] \Gamma(x,x') dx dx' \\
&= 0
\end{aligned}
$$

So one obtains contradicting equations

$$
\begin{aligned}
\Delta E &> 0 \\
\Delta E &= 0
\end{aligned}
$$

which proves the Gilbert theorem.

Energy functional

- Gilbert theorem establishes the existence of the energy functional for v-representable 1-RDM's

  $$E[\Gamma^{(1)}] = \mathrm{Tr}\left[(\hat{t} + \hat{v}_{ext})\Gamma^{(1)}\right] + F[\Gamma^{(1)}]$$

  where $F[\Gamma^{(1)}]$ is a universal functional.

Energy functional

- Gilbert theorem establishes the existence of the energy functional for υ-representable 1-RDM's

$$E[\Gamma^{(1)}] = \mathrm{Tr}\left[(\hat{t} + \hat{\upsilon}_{ext})\Gamma^{(1)}\right] + F[\Gamma^{(1)}]$$

  where $F[\Gamma^{(1)}]$ is a universal functional.

- Levy proposed a functional defined for all pure state N-representable 1-RDM's as follows [8]

$$E[\Gamma_p^{(1)}] = \mathrm{Tr}\left[(\hat{t} + \hat{\upsilon}_{ext})\Gamma_p^{(1)}\right] + \min_{\Psi \rightarrow \Gamma_p^{(1)}} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

Energy functional

- A given density matrix $\Gamma^{(1)}$ is **pure state N-representable** (N-rep) if there exists an antisymmetric N-electron wavefunction Ψ such that

$$\Gamma_p^{(1)} \in N\text{-rep if}$$

$$\exists\Psi \quad \Gamma^{(1)}(x_1, x_1') = N \int \Psi(x_1', x_2, \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_2 \ldots dx_N$$

Energy functional

- A given density matrix $\Gamma^{(1)}$ is **pure state N-representable** (N-rep) if there exists an antisymmetric N-electron wavefunction Ψ such that

$$\Gamma_p^{(1)} \in N\text{-rep if}$$

$$\exists \Psi \quad \Gamma^{(1)}(x_1, x_1') = N \int \Psi(x_1', x_2, \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_2 \ldots dx_N$$

- Density matrix variational principle for Levy's functional

$$\forall \; \Gamma_p^{(1)} \in N\text{-rep} \quad E_0 \leq E[\Gamma_p^{(1)}]$$

Energy functional

- A given density matrix $\Gamma^{(1)}$ is **pure state *N*-representable** (*N*-rep) if there exists an antisymmetric *N*-electron wavefunction Ψ such that

$$\Gamma_p^{(1)} \in N\text{-rep if}$$

$$\exists\Psi \quad \Gamma^{(1)}(x_1, x_1') = N \int \Psi(x_1', x_2, \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_2 \ldots dx_N$$

- Density matrix variational principle for Levy's functional

$$\forall\ \Gamma_p^{(1)} \in N\text{-rep} \quad E_0 \leq E[\Gamma_p^{(1)}]$$

- Pure state *N*-representability conditions for 1-RDM have been presented recently [29]-[30]. They are impractical for real systems [31]. Talk to **Christian Schilling** and **Julia Liebert**.

Ensemble N-representable 1-RDM's

- A given density matrix $\Gamma^{(1)}$ is **ensemble *N*-representable** if there exists an ensemble-state N-particle density matrix

$$\Gamma^{(N)}(x_1', \ldots, x_N'; x_1, \ldots, x_N) = \sum_i \omega_i \Psi_i(x_1', \ldots, x_N')^* \Psi_i(x_1, \ldots, x_N)$$

$$\sum_i \omega_i = 1$$

$$\forall i \quad \omega_i \geq 0$$

such that

$$\Gamma^{(1)}(x_1, x_1') = N \sum_i \omega_i \int \Psi_i(x_1', \ldots, x_N)^* \Psi_i(x_1, \ldots, x_N) dx_2 \ldots dx_N$$

- The necessary and sufficient ensemble N-representability conditions for 1-RDM's are known and they are easy to be imposed.

Spectral representation of 1-RDM

Consider a Hermitian and normalized 1-RDM

$$\Gamma^{(1)}(x,x') = \sum_{pq} \Gamma^{(1)}_{pq} \chi_p(x) \chi_q(x')^*$$

$$\Gamma^{(1)}(x,x') = \Gamma^{(1)}(x',x)^*, \quad \Gamma^{(1)}_{pq} = \Gamma^{(1)^*}_{qp}$$

$$\int \Gamma^{(1)}(x,x) dx = \sum_{pp} \Gamma^{(1)}_{pp} = N$$

Spectral representation of 1-RDM

Consider a Hermitian and normalized 1-RDM

$$\Gamma^{(1)}(x,x') = \sum_{pq} \Gamma^{(1)}_{pq} \chi_p(x) \chi_q(x')^*$$

$$\Gamma^{(1)}(x,x') = \Gamma^{(1)}(x',x)^*, \quad \Gamma^{(1)}_{pq} = \Gamma^{(1)^*}_{qp}$$

$$\int \Gamma^{(1)}(x,x) dx = \sum_{pp} \Gamma^{(1)}_{pp} = N$$

Hermiticity of reduced density matrix allows for its spectral representation

$$\Gamma^{(1)}(x,x') = \sum_{p} n_p \ \varphi_p(x) \varphi_p(x')^*$$

where the numbers $\{n_p\}$ are eigenvalues of $\Gamma^{(1)}$ while the functions $\{\varphi_p(x)\}$ are the corresponding eigenfunctions

$$\int \Gamma^{(1)}(x,x') \varphi_p(x') dx' = n_p \ \varphi_p(x)$$

Properties of natural occupation numbers and natural spinorbitals

- $\{n_p\}$ - natural occupation numbers
- $\{\varphi_p(x)\}$ - natural spinorbitals
- For a Hermitian and normalized 1-RDM the following properties are satisfied
    - orthonormality of natural spinorbitals

$$\int \varphi_p(x)^* \varphi_q(x) dx = \delta_{pq}$$

    - natural occupation numbers are real and sum up to N

$$\sum_p n_p = N$$

Necessary N-representability conditions for 1-RDM

Assume $\Gamma^{(1)}$ to be pure state N-representable, i.e. there exists a wavefunction $|\Psi\rangle$ such that

$$\Gamma^{(1)}(x, x') = \left\langle \Psi | \hat{\Gamma}^{(1)}(x, x') | \Psi \right\rangle$$

Necessary N-representability conditions for 1-RDM

Assume $\Gamma^{(1)}$ to be pure state N-representable, i.e. there exists a wavefunction $|\Psi\rangle$ such that

$$\Gamma^{(1)}(x,x') = \left\langle \Psi | \hat{\Gamma}^{(1)}(x,x') | \Psi \right\rangle$$

Using the natural spinorbitals as a basis set the 1-RDM operator reads

$$\hat{\Gamma}^{(1)}(x,x') = \sum_{pq} \hat{c}_q^{+} \hat{c}_p \ \varphi_p(x) \varphi_q(x')^*$$

Necessary N-representability conditions for 1-RDM

Assume $\Gamma^{(1)}$ to be pure state N-representable, i.e. there exists a wavefunction $|\Psi\rangle$ such that

$$\Gamma^{(1)}(x,x') = \left\langle \Psi|\hat{\Gamma}^{(1)}(x,x')|\Psi \right\rangle$$

Using the natural spinorbitals as a basis set the 1-RDM operator reads

$$\hat{\Gamma}^{(1)}(x,x') = \sum_{pq} \hat{c}_q^+ \hat{c}_p \ \varphi_p(x)\varphi_q(x')^*$$

and

$$\begin{aligned}\Gamma^{(1)}(x,x') &= \sum_{pq} \langle \Psi|\hat{c}_q^+ \hat{c}_p|\Psi\rangle \ \varphi_p(x)\varphi_q(x')^* \\ &= \sum_{p} n_p \ \varphi_p(x)\varphi_p(x')^*\end{aligned}$$

Necessary N-representability conditions for 1-RDM

Assume $\Gamma^{(1)}$ to be pure state N-representable, i.e. there exists a wavefunction $|\Psi\rangle$ such that

$$\Gamma^{(1)}(x,x') = \left\langle \Psi | \hat{\Gamma}^{(1)}(x,x') | \Psi \right\rangle$$

Using the natural spinorbitals as a basis set the 1-RDM operator reads

$$\hat{\Gamma}^{(1)}(x,x') = \sum_{pq} \hat{c}_q^+ \hat{c}_p \;\; \varphi_p(x)\varphi_q(x')^*$$

and

$$\begin{aligned}\Gamma^{(1)}(x,x') &= \sum_{pq} \langle \Psi | \hat{c}_q^+ \hat{c}_p | \Psi \rangle \;\; \varphi_p(x)\varphi_q(x')^* \\ &= \sum_{p} n_p \;\; \varphi_p(x)\varphi_p(x')^*\end{aligned}$$

Consequently,

$$\langle \Psi | \hat{c}_q^+ \hat{c}_p | \Psi \rangle = n_p \delta_{pq}$$

Necessary N-representability conditions for 1-RDM

We obtained

$$n_p = \langle \Psi | \hat{N}_p | \Psi \rangle$$

where

$$\hat{N}_p = \hat{c}_p^+ \hat{c}_p$$

Necessary N-representability conditions for 1-RDM

We obtained

$$n_p = \langle \Psi | \hat{N}_p | \Psi \rangle$$

where

$$\hat{N}_p = \hat{c}_p^+ \hat{c}_p$$

Since (use $\hat{c}_p \hat{c}_p^+ + \hat{c}_p^+ \hat{c}_p = 1$ and $\hat{c}_p \hat{c}_p = 0$)

$$\hat{N}_p^2 = \hat{c}_p^+ \hat{c}_p \hat{c}_p^+ \hat{c}_p = \hat{c}_p^+ \hat{c}_p - \hat{c}_p^+ \hat{c}_p^+ \hat{c}_p \hat{c}_p = \hat{c}_p^+ \hat{c}_p = \hat{N}_p$$

$\hat{N}_p$ is a projection operator.

Necessary N-representability conditions for 1-RDM

We obtained

$$n_p = \langle \Psi | \hat{N}_p | \Psi \rangle$$

where

$$\hat{N}_p = \hat{c}_p^+ \hat{c}_p$$

Since (use $\hat{c}_p \hat{c}_p^+ + \hat{c}_p^+ \hat{c}_p = 1$ and $\hat{c}_p \hat{c}_p = 0$)

$$\hat{N}_p^2 = \hat{c}_p^+ \hat{c}_p \hat{c}_p^+ \hat{c}_p = \hat{c}_p^+ \hat{c}_p - \hat{c}_p^+ \hat{c}_p^+ \hat{c}_p \hat{c}_p = \hat{c}_p^+ \hat{c}_p = \hat{N}_p$$

$\hat{N}_p$ is a projection operator.
The expectation value of the projection operator is nonnegative and not greater than 1 so

$$0 \leq n_p \leq 1$$

Necessary and sufficient ensemble N-representability conditions for 1-RDM

- The **necessary conditions** for pure or ensemble *N*-representability conditions of $\Gamma^{(1)}$ read

$$\begin{aligned} {\Gamma^{(1)}}^{+} &= \Gamma^{(1)} \\ \mathrm{Tr}[\Gamma^{(1)}] &= N \\ 0 \leq n_p &\leq 1 \end{aligned}$$

- A. J. Coleman proved that these are also **sufficient conditions** for ensemble *N*-representability (for a proof see [2] or a book by R. G. Parr and W. Yang [9], p.43].

Necessary and sufficient ensemble N-representability conditions for 1-RDM

- The **necessary conditions** for pure or ensemble N-representability conditions of $\Gamma^{(1)}$ read

$$\begin{aligned} {\Gamma^{(1)}}^{+} &= \Gamma^{(1)} \\ \mathrm{Tr}[\Gamma^{(1)}] &= N \\ 0 \leq n_p &\leq 1 \end{aligned}$$

- A. J. Coleman proved that these are also **sufficient conditions** for ensemble N-representability (for a proof see [2] or a book by R. G. Parr and W. Yang [9], p.43].

As opposed to $\Gamma^{(2)}$ there is no N-representability problem for $\Gamma^{(1)}$!

Energy functional for ensemble N-representable density matrices

- S. M. Valone extended Levy construction of the density matrix functional to ensemble N-representable density matrices [10]

$$E[\Gamma_e^{(1)}] = \mathrm{Tr}\left[(\hat{t} + \hat{v}_{ext})\hat{\Gamma}_e^{(1)}\right] + \min_{\Gamma^{(N)} \to \Gamma_e^{(1)}} \mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right]$$

where $\Gamma_e^{(1)}$ stands for ensemble N-representable 1-RDM, the minimization is performed with respect to ensemble-state density matrices that reduce to a given $\Gamma_e^{(1)}$, and

$$\mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right] = \sum_i \omega_i \left\langle \Psi_i \middle| \hat{V}_{ee} \middle| \Psi_i \right\rangle$$

Energy functional for ensemble N-representable density matrices

- S. M. Valone extended Levy construction of the density matrix functional to ensemble N-representable density matrices [10]

$$E[\Gamma_e^{(1)}] = \mathrm{Tr}\left[(\hat{t} + \hat{v}_{ext})\hat{\Gamma}_e^{(1)}\right] + \min_{\Gamma^{(N)} \to \Gamma_e^{(1)}} \mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right]$$

  where $\Gamma_e^{(1)}$ stands for ensemble N-representable 1-RDM, the minimization is performed with respect to ensemble-state density matrices that reduce to a given $\Gamma_e^{(1)}$, and

$$\mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right] = \sum_i \omega_i \left\langle \Psi_i \middle| \hat{V}_{ee} \middle| \Psi_i \right\rangle$$

- One can show that

$$E_0 \leq E[\Gamma_e^{(1)}]$$

  so the ground state may be achieved by searching the space of ensemble N-representable density matrices.

Reduced density matrix functional theory (RDMFT)

Reduced density matrix functional theory (RDMFT)

- The functional exists but, unlike for 2-RDM functional, the form of the electron-electron interaction term is not known (similarly to DFT).

Reduced density matrix functional theory (RDMFT)

- The functional exists but, unlike for 2-RDM functional, the form of the electron-electron interaction term is not known (similarly to DFT).
- The kinetic energy functional is given explicitly (unlike in DFT).

Reduced density matrix functional theory (RDMFT)

- The functional exists but, unlike for 2-RDM functional, the form of the electron-electron interaction term is not known (similarly to DFT).
- The kinetic energy functional is given explicitly (unlike in DFT).
- The necessary and sufficient ensemble N-representability conditions for $\Gamma^{(1)}$ are known and they are rather easy to impose.

Reduced density matrix functional theory (RDMFT)

- The functional exists but, unlike for 2-RDM functional, the form of the electron-electron interaction term is not known (similarly to DFT).
- The kinetic energy functional is given explicitly (unlike in DFT).
- The necessary and sufficient ensemble *N*-representability conditions for $\Gamma^{(1)}$ are known and they are rather easy to impose.
- Thus, having a density matrix functional, the ground state is found by minimizing the functional with respect to *N*-rep 1-RDM

$$E_0 = \min_{N\text{-rep } \Gamma^{(1)}} E[\Gamma^{(1)}]$$

Constructing approximate density matrix functionals

How to construct an approximate functional?

- Insights from wavefunction theories.
- Reconstructions of diagonal part of 2-RDM in terms of 1-RDM.
- Proposing a simple form that involves some parameters and finding the parameters empirically.

Hartree-Fock density matrix

- One-electron density matrix assumes a simple form for a single N-electron determinant.
- In fact one can show that [11]

$$\Psi(x_1,\ldots,x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \ldots & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & \ldots & \varphi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(x_1) & \varphi_N(x_2) & \ldots & \varphi_N(x_N) \end{vmatrix}$$

$$\iff \quad \Gamma^{(1)}(x,x') = \sum_{p=1}^{N} \varphi_p(x)\varphi_p(x')^*$$

Hartree-Fock density matrix

- One-electron density matrix assumes a simple form for a single N-electron determinant.
- In fact one can show that [11]

$$\Psi(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \ldots & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & \ldots & \varphi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(x_1) & \varphi_N(x_2) & \ldots & \varphi_N(x_N) \end{vmatrix}$$

$$\iff \quad \Gamma^{(1)}(x, x') = \sum_{p=1}^{N} \varphi_p(x)\varphi_p(x')^*$$

- $\Longrightarrow$ The occupation numbers of 1-RDM corresponding to a Slater wavefunction are integer

$$\begin{aligned} \forall p \leq N \quad & n_p = 1 \\ \forall p > N \quad & n_p = 0 \end{aligned}$$

Occupation numbers for uncorrelated and correlated wavefunction

- $\Longleftarrow$ A density matrix whose all occupation numbers are integer (0 or 1) is pure state N-representable and a Slater determinant is the corresponding wavefunction.

Occupation numbers for uncorrelated and correlated wavefunction

- $\Longleftarrow$ A density matrix whose all occupation numbers are integer (0 or 1) is pure state N-representable and a Slater determinant is the corresponding wavefunction.
- A density matrix for a multideterminantal wavefunction possesses fractional occupation numbers, $0 < n_p < 1$.

Occupation numbers for uncorrelated and correlated wavefunction

- $\Longleftarrow$ A density matrix whose all occupation numbers are integer (0 or 1) is pure state N-representable and a Slater determinant is the corresponding wavefunction.
- A density matrix for a multideterminantal wavefunction possesses fractional occupation numbers, $0 < n_p < 1$.
- Are all occupation numbers fractional for a correlated wavefunction in case of electronic 3D systems? There are some arguments that for H_2 molecule at some values of interatomic distances there exists $n_p = 0$ (J. Cioslowski and K. Pernal [20]).

Occupation numbers for uncorrelated and correlated wavefunction

- $\Longleftarrow$ A density matrix whose all occupation numbers are integer (0 or 1) is pure state N-representable and a Slater determinant is the corresponding wavefunction.
- A density matrix for a multideterminantal wavefunction possesses fractional occupation numbers, $0 < n_p < 1$.
- Are all occupation numbers fractional for a correlated wavefunction in case of electronic 3D systems? There are some arguments that for H_2 molecule at some values of interatomic distances there exists $n_p = 0$ (J. Cioslowski and K. Pernal [20]).
- Note that an ensemble of Slater determinants leads to 1-RDM with fractional occupation numbers.

Hartree-Fock energy expression in terms of 1-RDM

- For a single determinantal wavefunction 2-RDM is explicitly given in terms of 1-RDM

$$\Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{1}{2}[\Gamma^{(1)}(x_1, x_1')\Gamma^{(1)}(x_2, x_2') \\ - \Gamma^{(1)}(x_1, x_2')\Gamma^{(1)}(x_2, x_1')]$$

Hartree-Fock energy expression in terms of 1-RDM

- For a single determinantal wavefunction 2-RDM is explicitly given in terms of 1-RDM

$$\begin{aligned}\Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{1}{2}[&\Gamma^{(1)}(x_1, x_1')\Gamma^{(1)}(x_2, x_2') \\ &- \Gamma^{(1)}(x_1, x_2')\Gamma^{(1)}(x_2, x_1')]\end{aligned}$$

- So the expression for the energy

$$\begin{aligned}E = &\int \delta(x_1 - x_1')[\hat{t}(\mathbf{r}_1) + v_{ext}(\mathbf{r}_1)]\Gamma^{(1)}(x_1, x_1')\ dx_1' dx_1 \\ &+ \int r_{12}^{-1}\Gamma^{(2)}(x_1, x_2; x_1, x_2) dx_1 dx_2\end{aligned}$$

takes form

$$\begin{aligned}E^{HF} &= \int \delta(x_1 - x_1')[\hat{t}(\mathbf{r}_1) + v_{ext}(\mathbf{r}_1)]\Gamma^{(1)}(x_1, x_1')\; dx_1' dx_1 \\ &+ \frac{1}{2}\int r_{12}^{-1}\Gamma^{(1)}(x_1, x_1)\Gamma^{(1)}(x_2, x_2) dx_1 dx_2 \\ &- \frac{1}{2}\int r_{12}^{-1}\Gamma^{(1)}(x_1, x_2)\Gamma^{(1)}(x_2, x_1) dx_1 dx_2\end{aligned}$$

1. The first term in the energy is the so-called **one-particle energy** term

$$E_{one}[\Gamma^{(1)}] = E_{kin}[\Gamma^{(1)}] + E_{ext}[\Gamma^{(1)}]$$

2. The 2nd term is called **Hartree** (or Coulomb repulsion) energy

$$\begin{aligned} E_H[\Gamma^{(1)}] &= \frac{1}{2}\int |\mathbf{r}_1 - \mathbf{r}_2|^{-1}\,\Gamma^{(1)}(x_1, x_1)\Gamma^{(1)}(x_2, x_2)\,dx_1\,dx_2 \\ &= \frac{1}{2}\int |\mathbf{r}_1 - \mathbf{r}_2|^{-1}\,\rho(x_1)\rho(x_2)\,dx_1\,dx_2 \end{aligned}$$

3. The 3rd term is an **exchange** interaction

$$E_X[\Gamma^{(1)}] = -\frac{1}{2}\int |\mathbf{r}_1 - \mathbf{r}_2|^{-1}\,|\Gamma^{(1)}(x_1, x_2)|^2\,dx_1\,dx_2$$

Hartree-Fock density matrix functional

The simplest explicit density matrix functional may be defined as

$$E^{HF}[\Gamma^{(1)}] = E_{one}[\Gamma^{(1)}] + E_H[\Gamma^{(1)}] + E_X[\Gamma^{(1)}]$$

Hartree-Fock density matrix functional

The simplest explicit density matrix functional may be defined as

$$E^{HF}[\Gamma^{(1)}] = E_{one}[\Gamma^{(1)}] + E_H[\Gamma^{(1)}] + E_X[\Gamma^{(1)}]$$

Let E^{HF} be a Hartree-Fock energy (obtained from solving Hartree-Fock equations).

Hartree-Fock density matrix functional

The simplest explicit density matrix functional may be defined as

$$E^{HF}[\Gamma^{(1)}] = E_{one}[\Gamma^{(1)}] + E_H[\Gamma^{(1)}] + E_X[\Gamma^{(1)}]$$

Let E^{HF} be a Hartree-Fock energy (obtained from solving Hartree-Fock equations).
Obviously, $E^{HF}[\Gamma^{(1)}]$ is not smaller than E^{HF} for any $\Gamma^{(1)}$ with integer occupation numbers.

Hartree-Fock density matrix functional

The simplest explicit density matrix functional may be defined as

$$E^{HF}[\Gamma^{(1)}] = E_{one}[\Gamma^{(1)}] + E_H[\Gamma^{(1)}] + E_X[\Gamma^{(1)}]$$

Let E^{HF} be a Hartree-Fock energy (obtained from solving Hartree-Fock equations).
Obviously, $E^{HF}[\Gamma^{(1)}]$ is not smaller than E^{HF} for any $\Gamma^{(1)}$ with integer occupation numbers.
E. Lieb showed that it is true for any N-representable 1-RDM [12], i.e.

$$\forall N\text{-rep } \Gamma^{(1)} \quad E^{HF} \leq E^{HF}[\Gamma^{(1)}]$$

Hartree-Fock density matrix functional

The simplest explicit density matrix functional may be defined as

$$E^{HF}[\Gamma^{(1)}] = E_{one}[\Gamma^{(1)}] + E_{H}[\Gamma^{(1)}] + E_{X}[\Gamma^{(1)}]$$

Let E^{HF} be a Hartree-Fock energy (obtained from solving Hartree-Fock equations).
Obviously, $E^{HF}[\Gamma^{(1)}]$ is not smaller than E^{HF} for any $\Gamma^{(1)}$ with integer occupation numbers.
E. Lieb showed that it is true for any N-representable 1-RDM [12], i.e.

$$\forall N\text{-rep } \Gamma^{(1)} \quad E^{HF} \leq E^{HF}[\Gamma^{(1)}]$$

Therefore minimization of $E^{HF}[\Gamma^{(1)}]$ leads to the same solution as Hartree-Fock equations

$$\min_{N\text{-rep } \Gamma^{(1)}} E^{HF}[\Gamma^{(1)}] = E^{HF}$$

We do not gain anything over the Hartree-Fock method, the optimal 1-RDM is the same as the one obtained from the HF wavefunction (integer occupation numbers)!

Two-electron system in a singlet spin state

Consider a real-valued singlet wavefunction for a two-electron system [13]

$$^{1}\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \sum_{pq} C_{pq} \begin{vmatrix} \chi_p(\mathbf{r}_1)\alpha(1) & \chi_p(\mathbf{r}_2)\alpha(2) \\ \chi_q(\mathbf{r}_1)\beta(1) & \chi_q(\mathbf{r}_2)\beta(2) \end{vmatrix}$$

where α and β are spin functions.

Two-electron system in a singlet spin state

Consider a real-valued singlet wavefunction for a two-electron system [13]

$$^{1}\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \sum_{pq} C_{pq} \begin{vmatrix} \chi_p(\mathbf{r}_1)\alpha(1) & \chi_p(\mathbf{r}_2)\alpha(2) \\ \chi_q(\mathbf{r}_1)\beta(1) & \chi_q(\mathbf{r}_2)\beta(2) \end{vmatrix}$$

where α and β are spin functions.
The spin symmetry

$$\hat{S}^2\Psi = 0$$

imposes the symmetry on the real matrix $\mathbf{C}$ (see for example [14])

$$\mathbf{C}^T = \mathbf{C}$$

Two-electron system in a singlet spin state

Consider a real-valued singlet wavefunction for a two-electron system [13]

$$^{1}\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \sum_{pq} C_{pq} \begin{vmatrix} \chi_p(\mathbf{r}_1)\alpha(1) & \chi_p(\mathbf{r}_2)\alpha(2) \\ \chi_q(\mathbf{r}_1)\beta(1) & \chi_q(\mathbf{r}_2)\beta(2) \end{vmatrix}$$

where α and β are spin functions.
The spin symmetry

$$\hat{S}^2\Psi = 0$$

imposes the symmetry on the real matrix $\mathbf{C}$ (see for example [14])

$$\mathbf{C}^T = \mathbf{C}$$

The normalization of $^{1}\Psi$ implies

$$\sum_{pq} C_{pq}^2 = 1$$

The wavefunction can be rewritten as follows

$$^{1}\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \sum_{pq} C_{pq}\chi_p(\mathbf{r}_1)\chi_q(\mathbf{r}_2)$$

The wavefunction can be rewritten as follows

$$^{1}\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \sum_{pq} C_{pq}\chi_p(\mathbf{r}_1)\chi_q(\mathbf{r}_2)$$

The matrix **C** is symmetric so it can be diagonalized

$$\mathbf{C} = \mathbf{U}^T\mathbf{c}\mathbf{U}$$

where **c** is a diagonal matrix, **U** is unitary and

$$\sum_p c_p^2 = 1$$

The wavefunction can be rewritten as follows

$$^1\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \sum_{pq} C_{pq}\chi_p(\mathbf{r}_1)\chi_q(\mathbf{r}_2)$$

The matrix **C** is symmetric so it can be diagonalized

$$\mathbf{C} = \mathbf{U}^T\mathbf{c}\mathbf{U}$$

where **c** is a diagonal matrix, **U** is unitary and

$$\sum_p c_p^2 = 1$$

The wavefunction in a diagonal form reads

$$^1\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \sum_p c_p\varphi_p(\mathbf{r}_1)\varphi_p(\mathbf{r}_2)$$

$$\varphi_p(\mathbf{r}) = \sum_q U_{pq}\chi_q(\mathbf{r})$$

A corresponding one-electron density matrix follows immediately as

$$\begin{aligned}\Gamma^{(1)}(x_1, x_1') &= 2\int \Psi(x_1', x_2)\Psi(x_1, x_2)dx_2 \\ &= \sum_p c_p^2[\varphi_p(\mathbf{r}_1)\alpha(1)\varphi_p(\mathbf{r}_1')\alpha(1') + \varphi_p(\mathbf{r}_1)\beta(1)\varphi_p(\mathbf{r}_1')\beta(1')]\end{aligned}$$

A corresponding one-electron density matrix follows immediately as

$$\begin{aligned}\Gamma^{(1)}(x_1, x_1') &= 2\int \Psi(x_1', x_2)\Psi(x_1, x_2)dx_2 \\ &= \sum_p c_p^2[\varphi_p(\mathbf{r}_1)\alpha(1)\varphi_p(\mathbf{r}_1')\alpha(1') + \varphi_p(\mathbf{r}_1)\beta(1)\varphi_p(\mathbf{r}_1')\beta(1')]\end{aligned}$$

The spinorbitals $\{\varphi_p\alpha, \varphi_p\beta\}$ are the natural spinorbitals and $\left\{c_p^2\right\}$ are the natural occupation numbers

$$c_p^2 = n_{p\alpha} = n_{p\beta}$$
$$\sum_p \left(n_{p\alpha} + n_{p\beta}\right) = 2$$

The exact 1-RDM functional for singlet two-el systems

- The expression for energy for a singlet wavefunction in a representation of the natural spinorbitals takes a simple form

$$E^{2-el} = \left\langle {}^1\Psi \middle| \hat{H} \middle| {}^1\Psi \right\rangle = 2\sum_p c_p^2 h_{pp} + \sum_{pq} c_p c_q \left\langle \varphi_p \varphi_q \middle| \varphi_q \varphi_p \right\rangle$$

$$h_{pp} = \int \varphi_p(\mathbf{r}) \left[\hat{t}(\mathbf{r}) + v_{ext}(\mathbf{r})\right] \varphi_p(\mathbf{r}) d\mathbf{r}$$

$$\left\langle \varphi_p \varphi_q \middle| \varphi_q \varphi_p \right\rangle = \int \varphi_p(\mathbf{r}_1)\varphi_q(\mathbf{r}_2) \left|\mathbf{r}_1 - \mathbf{r}_2\right|^{-1} \varphi_q(\mathbf{r}_1)\varphi_p(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

The exact 1-RDM functional for singlet two-el systems

- The expression for energy for a singlet wavefunction in a representation of the natural spinorbitals takes a simple form

$$E^{2-el} = \langle {}^1\Psi | \hat{H} | {}^1\Psi \rangle = 2\sum_p c_p^2 h_{pp} + \sum_{pq} c_p c_q \langle \varphi_p \varphi_q | \varphi_q \varphi_p \rangle$$

$$h_{pp} = \int \varphi_p(\mathbf{r}) \left[\hat{t}(\mathbf{r}) + v_{ext}(\mathbf{r})\right] \varphi_p(\mathbf{r}) d\mathbf{r}$$

$$\langle \varphi_p \varphi_q | \varphi_q \varphi_p \rangle = \int \varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2) \left|\mathbf{r}_1 - \mathbf{r}_2\right|^{-1} \varphi_q(\mathbf{r}_1) \varphi_p(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- The exact ground state energy is obtained by minimizing E^{2-el} with respect to orbitals and $\{c_p\}$ coefficients subject to conditions $\sum_p c_p^2 = 1$.

Since $\sqrt{n_p} = \pm c_p$ it is possible to define an implicit density matrix functional [15]

$$\begin{aligned} E^{2-el}[\Gamma^{(1)}] &= E^{2-el}[\{n_p\}, \{\varphi_p(\mathbf{r})\}] \\ &= 2\sum_p n_p h_{pp} + \min_{\{f_r\}} \sum_{pq} f_p f_q \sqrt{n_p n_q} \left\langle \varphi_p \varphi_q \middle| \varphi_q \varphi_p \right\rangle \end{aligned}$$

where 1-RDM is assumed to be N-representable, i.e.

$$\int \varphi_p(\mathbf{r}) \varphi_q(\mathbf{r}) d\mathbf{r} = \delta_{pq}$$

$$\sum_p n_p = 1$$

$$0 \leq n_p \leq 1$$

and

$$\forall p \quad f_p = \pm 1$$

An almost exact functional for singlet two-el systems

Numerical experience shows that after minimization of the energy the sign of the c_1 coefficient corresponding to mostly occupied orbital is opposite to the sign of the rest [16]

$$\begin{aligned} \forall p > 1 \quad & c_1 c_p < 0 \\ \forall p, q > 1 \quad & c_q c_p > 0 \end{aligned}$$

An almost exact functional for singlet two-el systems

Numerical experience shows that after minimization of the energy the sign of the c_1 coefficient corresponding to mostly occupied orbital is opposite to the sign of the rest [16]

$$\begin{aligned} \forall p > 1 &\quad c_1 c_p < 0 \\ \forall p, q > 1 &\quad c_q c_p > 0 \end{aligned}$$

The functional for two-electron system reads then

$$E^{2-el}[\{n_p\},\{\varphi_p(\mathbf{r})\}] = 2\sum_p n_p h_{pp} + n_1 \langle \varphi_1\varphi_1|\varphi_1\varphi_1\rangle$$
$$-2\sum_{p>1}\sqrt{n_p n_1}\langle \varphi_p\varphi_1|\varphi_1\varphi_p\rangle + \sum_{p>1,q>1}\sqrt{n_p n_q}\langle \varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

An almost exact functional for singlet two-el systems

Numerical experience shows that after minimization of the energy the sign of the c_1 coefficient corresponding to mostly occupied orbital is opposite to the sign of the rest [16]

$$\forall p > 1 \quad c_1 c_p < 0$$
$$\forall p, q > 1 \quad c_q c_p > 0$$

The functional for two-electron system reads then

$$E^{2-el}[\{n_p\}, \{\varphi_p(\mathbf{r})\}] = 2\sum_p n_p h_{pp} + n_1 \langle \varphi_1\varphi_1|\varphi_1\varphi_1\rangle$$
$$-2\sum_{p>1} \sqrt{n_p n_1} \langle \varphi_p\varphi_1|\varphi_1\varphi_p\rangle + \sum_{p>1,q>1} \sqrt{n_p n_q} \langle \varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

A two-electron case is a paradigm in RDMFT.

Approximate density matrix functionals

- Approximate functionals proposed so far are of the form

$$
\begin{aligned}
E[\{n_p\},\{\varphi_p(x)\}] = \sum_p n_p h_{pp} + E_H[\{n_p\},\{\varphi_p(x)\}] \\
+ E_{xc}[\{n_p\},\{\varphi_p(x)\}]
\end{aligned}
$$

Approximate density matrix functionals

- Approximate functionals proposed so far are of the form

$$E\left[\{n_p\},\{\varphi_p(x)\}\right] = \sum_p n_p h_{pp} + E_H\left[\{n_p\},\{\varphi_p(x)\}\right] + E_{xc}\left[\{n_p\},\{\varphi_p(x)\}\right]$$

- The Hartree term in terms of the natural occupation numbers and the natural spinorbitals reads

$$E_H\left[\{n_p\},\{\varphi_p(x)\}\right] = \frac{1}{2}\sum_{pq} n_p n_q \langle \varphi_p\varphi_q|\varphi_p\varphi_q\rangle$$

Approximate density matrix functionals

- Approximate functionals proposed so far are of the form

$$E\left[\{n_p\},\{\varphi_p(x)\}\right] = \sum_p n_p h_{pp} + E_H\left[\{n_p\},\{\varphi_p(x)\}\right] + E_{xc}\left[\{n_p\},\{\varphi_p(x)\}\right]$$

- The Hartree term in terms of the natural occupation numbers and the natural spinorbitals reads

$$E_H\left[\{n_p\},\{\varphi_p(x)\}\right] = \frac{1}{2}\sum_{pq} n_p n_q \langle \varphi_p\varphi_q|\varphi_p\varphi_q\rangle$$

- The exchange-correlation functional involves only exchange integrals

$$E_{xc}\left[\{n_p\},\{\varphi_p(x)\}\right] = \frac{1}{2}\sum_{pq} G(n_p,n_q)\langle \varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

$$G(x,y) = G(y,x)$$

Power functional

In case of the Hartree-Fock functional (no correlation) the G function takes form

$$G(n_p, n_q) = -n_p n_q$$

Power functional

In case of the Hartree-Fock functional (no correlation) the G function takes form

$$G(n_p, n_q) = -n_p n_q$$

The simplest step beyond HF would be

$$G(n_p, n_q) = -\left(n_p n_q\right)^{\alpha}$$

$$\alpha < 1$$

How to choose α?

Power functional

In case of the Hartree-Fock functional (no correlation) the G function takes form

$$G(n_p, n_q) = -n_p n_q$$

The simplest step beyond HF would be

$$G(n_p, n_q) = -\left(n_p n_q\right)^{\alpha}$$

$$\alpha < 1$$

How to choose α?

Note that the electron-electron repulsion functional reads

$$E_{ee}\left[\{n_p\}, \{\varphi_p(x)\}\right] = \frac{1}{2}\sum_{pq} n_p n_q \left\langle \varphi_p \varphi_q | \varphi_p \varphi_q \right\rangle - \frac{1}{2}\sum_{pq} \left(n_p n_q\right)^{\alpha} \left\langle \varphi_p \varphi_q | \varphi_q \varphi_p \right\rangle$$

On the other hand, the exact E_{ee} energy expression involves 2-RDM

$$E_{ee} = \sum_{pqrs} \Gamma^{(2)}_{rspq} \left\langle \varphi_p \varphi_q | \varphi_r \varphi_s \right\rangle$$

Power functional

A comparison of $E_{ee}[\{n_p\},\{\varphi_p(x)\}]$ with the exact E_{ee} would suggest

$$\Gamma^{(2)}_{rspq} = \frac{1}{2}[n_p n_q \delta_{pr}\delta_{qs} - (n_p n_q)^{\alpha}\delta_{qr}\delta_{ps}]$$

Power functional

A comparison of $E_{ee}[\{n_p\},\{\varphi_p(x)\}]$ with the exact E_{ee} would suggest

$$\Gamma^{(2)}_{rspq} = \frac{1}{2}[n_p n_q \delta_{pr}\delta_{qs} - (n_p n_q)^{\alpha}\delta_{qr}\delta_{ps}]$$

Power functional

A comparison of $E_{ee}[\{n_p\},\{\varphi_p(x)\}]$ with the exact E_{ee} would suggest

$$\Gamma^{(2)}_{rspq} = \frac{1}{2}\left[n_p n_q \delta_{pr}\delta_{qs} - (n_p n_q)^{\alpha}\delta_{qr}\delta_{ps}\right]$$

- The antisymmetry condition

$$\Gamma^{(2)}_{rspq} = -\Gamma^{(2)}_{rsqp} = -\Gamma^{(2)}_{srpq} \quad \Rightarrow \quad \alpha = 1$$

- The sum rule

$$\sum_q \Gamma^{(2)}_{pqrq} = \frac{N-1}{2}\Gamma^{(1)}_{pr} = \frac{N-1}{2} n_p \delta_{pr} \quad \Rightarrow \quad \alpha = \frac{1}{2}$$

Power functional

A comparison of $E_{ee}\left[\{n_p\},\{\varphi_p(x)\}\right]$ with the exact E_{ee} would suggest

$$\Gamma^{(2)}_{rspq} = \frac{1}{2}\left[n_p n_q \delta_{pr}\delta_{qs} - (n_p n_q)^{\alpha}\,\delta_{qr}\delta_{ps}\right]$$

- The antisymmetry condition

$$\Gamma^{(2)}_{rspq} = -\Gamma^{(2)}_{rsqp} = -\Gamma^{(2)}_{srpq} \quad \Rightarrow \quad \alpha = 1$$

- The sum rule

$$\sum_q \Gamma^{(2)}_{pqrq} = \frac{N-1}{2}\Gamma^{(1)}_{pr} = \frac{N-1}{2} n_p \delta_{pr} \quad \Rightarrow \quad \alpha = \frac{1}{2}$$

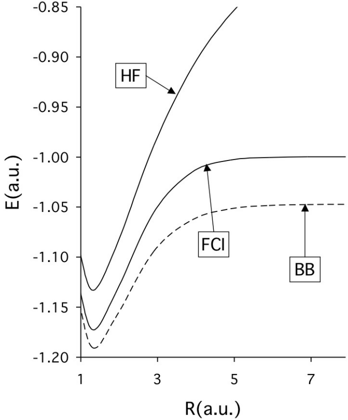
- Other choices of α would violate both conditions for the underlying $\Gamma^{(2)}$.

BB functional

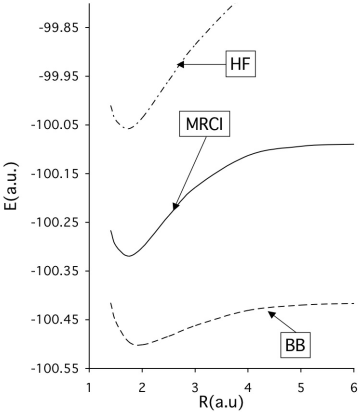
The choice of $\alpha = \frac{1}{2}$ leads to the so-called Buijse-Baerends [17] functional also known as Müller [18] or corrected Hartree functional [19]

$$E_{xc}[\{n_p\}, \{\varphi_p(x)\}] = -\frac{1}{2}\sum_{pq}(n_p n_q)^{1/2}\langle\varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

It is known that BB produces too much correlation energy [19, 21].



H2 molecule



FH molecule

HF: Hartree-Fock, FCI: full configuration interaction, MRCI: multireference configuration interaction, BB: $\alpha = 1/2$ power functional.

Empirical power functional

It has been found that $\alpha = 0.578$ works best for the correlation energy of molecules and $\alpha = 0.55$ reproduces well correlation energy of the homogeneous electron gas (N.N. Lathiotakis et al., [22])

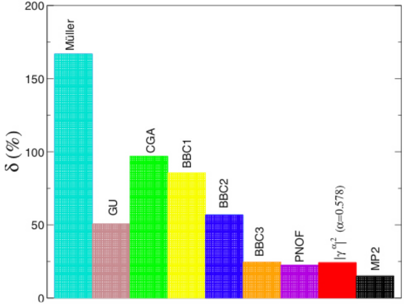


FIG. 2. (Color online) Percentage deviation of the correlation energy, obtained using various 1-RDM functionals, from the exact CCSD(T) results.

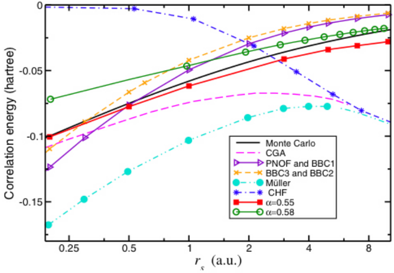


FIG. 1. (Color online) Correlation energy as a function of the Wigner-Seitz radius for the homogeneous electron gas. RDMFT results are obtained using various approximations to the xc functional. Monte Carlo results are taken from Ref. [21] (see also Ref. [22]).

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of
    - strongly occupied (**occ**) orbitals; $1 - n_p \ll 1$,

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of
  - strongly occupied (**occ**) orbitals; $1 - n_p \ll 1$,
  - weakly occupied (**virt**), $n_p \ll 1$,

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of
    - strongly occupied (**occ**) orbitals; $1 - n_p \ll 1$,
    - weakly occupied (**virt**), $n_p \ll 1$,
    - frontier (**frn**) that includes bonding and antibonding orbitals.

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of
  - strongly occupied (**occ**) orbitals; $1 - n_p \ll 1$,
  - weakly occupied (**virt**), $n_p \ll 1$,
  - frontier (**frn**) that includes bonding and antibonding orbitals.

BBC3 functional

- Based on the knowledge of a density matrix functional for two-electron system a number of corrections to the BB ($\alpha = 1/2$) functional has been proposed (O.V. Gritsenko et al. [21]) resulting in the BBC3 functional.
- In BBC3 the natural orbitals are divided into sets of
  - strongly occupied (**occ**) orbitals; $1 - n_p \ll 1$,
  - weakly occupied (**virt**), $n_p \ll 1$,
  - frontier (**frn**) that includes bonding and antibonding orbitals.

$$G^{BBC3}(n_p, n_q) = \begin{cases} \sqrt{n_p n_p} \ , & (p \neq q;\ \ p, q \in \mathrm{virt}) \\ -n_p n_q \ , & (p \neq q;\ \ p, q \in \mathrm{occ}) \\ & \vee \quad (p \in \mathrm{occ}\ ,\ \ q \in \mathrm{frn}) \\ & \vee \quad (q \in \mathrm{occ}\ ,\ \ p \in \mathrm{frn}) \\ -n_p^2 \ , & (p = q;\ \ p \notin \mathrm{frn}) \\ -\sqrt{n_p n_q} \ , & \mathrm{otherwise} \end{cases}$$

AC3 functional

- Special treatment of frontier orbitals leads to the proper description of the molecules with stretched bonds.

AC3 functional

- Special treatment of frontier orbitals leads to the proper description of the molecules with stretched bonds.
- BBC3 requires selecting frontier orbitals prior to calculations. It leads to numerical problems.

AC3 functional

- Special treatment of frontier orbitals leads to the proper description of the molecules with stretched bonds.
- BBC3 requires selecting frontier orbitals prior to calculations. It leads to numerical problems.
- To select the orbitals automatically (based on their occupation number) a damping function was introduced leading to the AC3 functional (D. R. Rohr et al., [23])

$$G^{AC3}(n_p, n_q) = f_{pq}\sqrt{n_p n_q}[1 - D_{pq}(n_p, n_q)] - n_p n_q D_{pq}(n_p, n_q)$$

$$f_{pq} = \begin{cases} +1\ , & (p \neq q;\ p, q > N/2) \\ -1\ , & \text{otherwise} \end{cases}$$

where it is assumed that the orbitals are ordered according to the descending occupation numbers.

AC3 functional

- Special treatment of frontier orbitals leads to the proper description of the molecules with stretched bonds.
- BBC3 requires selecting frontier orbitals prior to calculations. It leads to numerical problems.
- To select the orbitals automatically (based on their occupation number) a damping function was introduced leading to the AC3 functional (D. R. Rohr et al., [23])

$$G^{AC3}(n_p, n_q) = f_{pq}\sqrt{n_p n_q}[1 - D_{pq}(n_p, n_q)] - n_p n_q D_{pq}(n_p, n_q)$$

$$f_{pq} = \begin{cases} +1\,, & (p \neq q;\ p, q > N/2) \\ -1\,, & \text{otherwise} \end{cases}$$

  where it is assumed that the orbitals are ordered according to the descending occupation numbers.
- The damping function includes two empirical parameters optimized for HF and H_2O molecules.

Piris natural orbital functionals (PNOFi)

In Hartree-Fock theory the 2-RDM is given by the antisymmetrized product of 1-RDM, i.e.

$$^{HF}\Gamma^{(2)}_{pqrs} = \Gamma^{(1)}_{pr}\Gamma^{(1)}_{qs} - \Gamma^{(1)}_{ps}\Gamma^{(1)}_{qr}$$

Piris natural orbital functionals (PNOFi)

In Hartree-Fock theory the 2-RDM is given by the antisymmetrized product of 1-RDM, i.e.

$$ {}^{HF}\Gamma^{(2)}_{pqrs} = \Gamma^{(1)}_{pr}\Gamma^{(1)}_{qs} - \Gamma^{(1)}_{ps}\Gamma^{(1)}_{qr} $$

The missing part in the exact 2-RDM is called a cumulant density matrix, $\boldsymbol{\lambda}$

$$ \Gamma^{(2)}_{pqrs} = \Gamma^{(1)}_{pr}\Gamma^{(1)}_{qs} - \Gamma^{(1)}_{ps}\Gamma^{(1)}_{qr} + \lambda_{pqrs} $$

Piris natural orbital functionals (PNOFi)

In Hartree-Fock theory the 2-RDM is given by the antisymmetrized product of 1-RDM, i.e.

$$^{HF}\Gamma^{(2)}_{pqrs} = \Gamma^{(1)}_{pr}\Gamma^{(1)}_{qs} - \Gamma^{(1)}_{ps}\Gamma^{(1)}_{qr}$$

The missing part in the exact 2-RDM is called a cumulant density matrix, $\boldsymbol{\lambda}$

$$\Gamma^{(2)}_{pqrs} = \Gamma^{(1)}_{pr}\Gamma^{(1)}_{qs} - \Gamma^{(1)}_{ps}\Gamma^{(1)}_{qr} + \lambda_{pqrs}$$

M. Piris et al. have proposed a number of approximations to $\boldsymbol{\lambda}$ in terms of the occupation numbers that resulted in a series of natural orbital functionals **PNOFi** (i$= 0, 1, 2, 3, 4, 5, 6, 7$) [24,32].

The approximations satisfy certain necessary N-representability conditions for 2-RDM like the proper antisymmetry, sum rule etc.

Piris natural orbital functionals

- PNOFi is also of the form that is a generalization of the HF functional. It is a functional of the natural orbitals and the occupation numbers, namely

$$
\begin{aligned}
E^{PNOFi}\left[\{n_p\},\{\varphi_p(x)\}\right] = \sum_p n_p h_{pp} + \frac{1}{2}\sum_{pq} n_p n_q \langle \varphi_p\varphi_q|\varphi_p\varphi_q\rangle \\
+ \frac{1}{2}\sum_{pq} G^{PNOFi}_{pq}(\mathbf{n}) \langle \varphi_p\varphi_q|\varphi_q\varphi_p\rangle
\end{aligned}
$$

  where

$$
G^{PNOFi}_{pq}(\mathbf{n}) = -n_p n_q + \Lambda_{pq}(\mathbf{n})
$$

Piris natural orbital functionals

- PNOFi is also of the form that is a generalization of the HF functional. It is a functional of the natural orbitals and the occupation numbers, namely

$$E^{PNOFi}[\{n_p\},\{\varphi_p(x)\}] = \sum_p n_p h_{pp} + \frac{1}{2}\sum_{pq} n_p n_q \langle \varphi_p\varphi_q|\varphi_p\varphi_q\rangle + \frac{1}{2}\sum_{pq} G_{pq}^{PNOFi}(\mathbf{n}) \langle \varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

  where

$$G_{pq}^{PNOFi}(\mathbf{n}) = -n_p n_q + \Lambda_{pq}(\mathbf{n})$$

- PNOF0 functional is defined as [25]

$$G_{pq}^{PNOF0}(\mathbf{n}) = -n_p n_q + \left(f_{pq}\sqrt{n_p n_q} + n_p n_q\right)(1-\delta_{pq})$$

$$f_{pq} = \begin{cases} +1\,, & (p \neq q;\ p,q > N/2) \\ -1\,, & \text{otherwise} \end{cases}$$

Dissociation of molecules with density matrix functionals

The following density matrix functionals are employed to reproduce potential energy curves of a number of molecules:

- AC3 - based on the exact functional for singlet two-electron systems, computationally more practical modification of the BBC3 functional [23],

Dissociation of molecules with density matrix functionals

The following density matrix functionals are employed to reproduce potential energy curves of a number of molecules:

- AC3 - based on the exact functional for singlet two-electron systems, computationally more practical modification of the BBC3 functional [23],
- ML - functional obtained by assuming a general form of the exchange-correlation functional

  $$E_{xc}[\{n_p\},\{\varphi_p(x)\}] = \frac{1}{2}\sum_{pq} G^{ML}(n_p,n_q)\,\langle\varphi_p\varphi_q|\varphi_q\varphi_p\rangle$$

  $$G^{ML}(n_p,n_q) = -\frac{1}{2}n_pn_q\frac{a_0+a_1n_pn_q}{1+b_1n_pn_q}$$

  and finding the empirical parameters $\{a_0,a_1,b_1\}$ by fitting energy to accurate values [26],

Dissociation of molecules with density matrix functionals

The following density matrix functionals are employed to reproduce potential energy curves of a number of molecules:

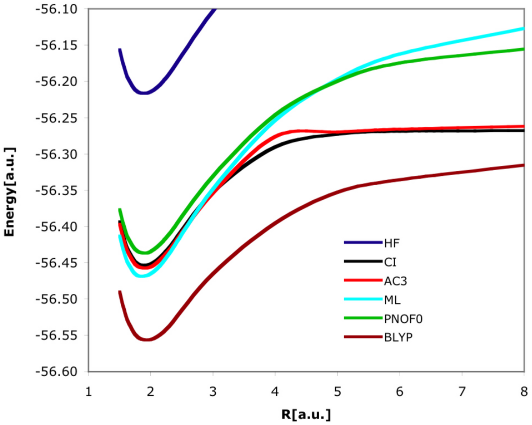
- AC3 - based on the exact functional for singlet two-electron systems, computationally more practical modification of the BBC3 functional [23],
- ML - functional obtained by assuming a general form of the exchange-correlation functional

  $$E_{xc}[\{n_p\}, \{\varphi_p(x)\}] = \frac{1}{2}\sum_{pq} G^{ML}(n_p, n_q) \langle \varphi_p \varphi_q | \varphi_q \varphi_p \rangle$$

  $$G^{ML}(n_p, n_q) = -\frac{1}{2} n_p n_q \frac{a_0 + a_1 n_p n_q}{1 + b_1 n_p n_q}$$

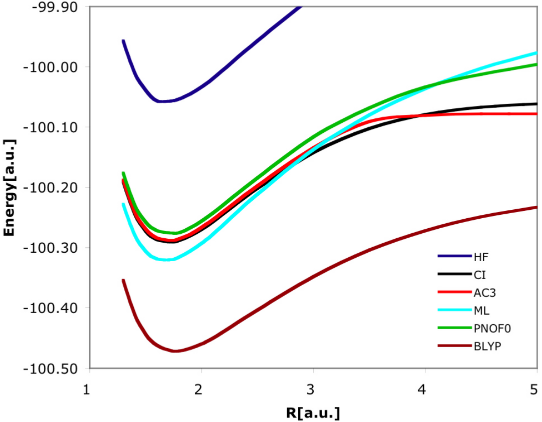
  and finding the empirical parameters $\{a_0, a_1, b_1\}$ by fitting energy to accurate values [26],
- PNOF0 - one of the functionals of Piris, obtained by reconstructing 2-RDM in terms of 1-RDM [25].

Dissociation of a single NH bond of the NH3 molecule [23]



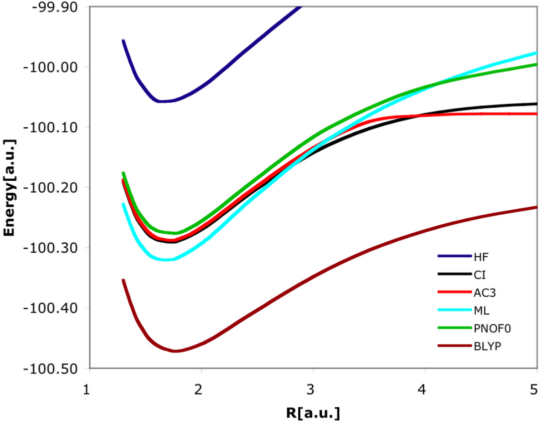
HF - Hartree-Fock; CI - configuration interaction; AC3, ML, PNOF0 - density matrix functionals; BLYP - density functional.

Dissociation of the FH molecule [23]



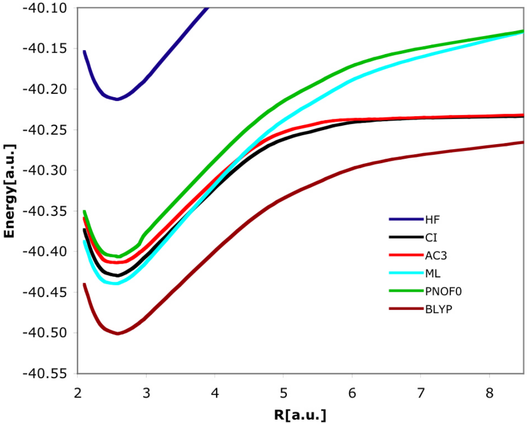
HF - Hartree-Fock; CI - configuration interaction; AC3, ML, PNOF0 - density matrix functionals; BLYP - density functional.

Dissociation of the FH molecule [23]



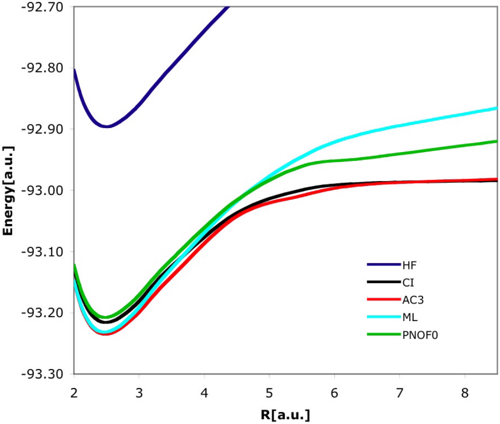
HF - Hartree-Fock; CI - configuration interaction; AC3, ML, PNOF0 - density matrix functionals; BLYP - density functional.

Dissociation of a single CH bond of the CH4 molecule [23]



HF - Hartree-Fock; CI - configuration interaction; AC3, ML, PNOF0 - density matrix functionals; BLYP - density functional.

Dissociation of a single HC bond of the HCN molecule [23]



HF - Hartree-Fock; CI - configuration interaction; AC3, ML, PNOF0 - density matrix functionals; BLYP - density functional.

Challenges for RDMFT

- Conditions for functionals.
- More accurate functionals for molecules.
- Description of open-shell (other spin states than singlets) systems with RDMFT.
- Functionals for excited states.
- Functionals for solids.
- Efficient optimization algorithms for functionals.

References

1. A. J. Coleman and V. I. Yukalov, *Lecture Notes in Chemistry 72: Reduced Density Matrices*, Springer, 2000.
2. A. J. Coleman *Rev. Mod. Phys.* **35**, 668 (1963).
3. M. Nakata, B. J. Braams, K. Fujisawa, M. Fukuda, J. K. Percus, M. Yamashita, Z. Zhao, *J. Chem. Phys.* **128**, 164113 (2008).
4. Z. Zhao, B. J. Braams, M. J. Overton, J. K. Percus, *J. Chem. Phys.* **120**, 2095 (2004).
5. D. A. Mazziotti, *Phys. Rev. A* **65**, 062511 (2002).
6. B. Verstichel, H. van Aggelen, D. van Neck, P. W. Ayers, and P. Bultinck, *J. Chem. Phys.* **132**, 114113 (2010).
7. T. L. Gilbert, *Phys. Rev.* B **12**, 2111 (1975).
8. M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979).
9. R. G. Parr and W. Yang, *Density-functional theory of atoms and molecules*, Oxford University Press 1989.
10. S. M. Valone, *J. Chem. Phys.* **73,** 1344, 4653 (1980).

References

11. E. K. U. Gross, E. Runge, and O. Heinonen, *Many-Particle Theory*, Adam Hilger 1991, chapter 6.
12. E. H. Lieb, *Phys. Rev. Lett.* **46**, 457 (1981).
13. P. O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1956).
14. A. Szabo and N. Ostlund, *Modern Quantum Chemistry*, Dover 1996, chapter 2.5.
15. J. Cioslowski and K. Pernal, *J. Chem. Phys.* **115**, 5784 (2001).
16. S. Goedecker and C. J. Umrigar in *Many-Electron Densities and Reduced Density Matrices*, J. Cioslowski (ed.), Kluwer, New York, 2000.
17. M. A. Buijse and E. J. Baerends, *Mol. Phys.* **100**, 401 (2002).
18. A. M. K. Müller, *Phys. Lett.* **105**A, 446 (1984).
19. V. N. Staroverov and G. E. Scuseria, *J. Chem. Phys.* **117**, 2489 (2002).

References

⑳ J. Cioslowski and K. Pernal, *Chem. Phys. Lett.* **430**, 188 (2006).

㉑ O. V. Gritsenko, K. Pernal, and E.J. Bearends, *J. Chem. Phys.* **122**, 204102 (2005).

㉒ N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. G. Eich, M. A. L. Marques, and E. K. U. Gross , *Phys. Rev.* A **79**, 040501(R) (2009).

㉓ D. R. Rohr, K. Pernal, O.V. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* **129**, 164105 (2008).

㉔ M. Piris, *Int. J. Quantum Chem.* 2012, DOI: 10.1002/qua.24020 and the references there.

㉕ M. Piris, *Int. J. Quantum Chem.* **106**, 1093 (2006).

㉖ M. A. L. Marques and N. N. Lathiotakis, *Phys. Rev.* A **77**, 032509 (2008).

㉗ J. Fosso-Tande, T.S. Nguyen, G. Gidofalvi, A.E. DePrince III, *J. Chem. Theory and Comput.* **12**, 2260 (2016).

㉘ A.E. DePrince III, *WIRE: Computational Molecular Science* **14** , e1702 (2024).

References

㉙ A. Klyachko, *J. Phys. Conf. Ser.* **36**, 72 (2006).

㉚ M. Altunbulak and A. Klyachko, *Commun. Math. Phys.***282**, 287 (2008).

㉛ J. Liebert, Y. Lemke, M. Altunbulak, T. Maciazek, Ch. Ochsenfeld, and Ch. Schilling, *arXiv:2502.15464*, (2025).

㉜ M.Piris *Chem. Sci.* **15**, 17284 (2024).