Density matrix functional theory vis-á-vis density functional theory

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March 14, 2007

Outline

Background on the density matrix and energy functionals

Example calculations with approximate functionals

Theory of effective noninteracting systems

Basics of the Density Matrix

Pure state

$$|\Psi\rangle = c_1 |\phi_1\rangle + c_2 |\phi_2\rangle + \cdots$$

$$\begin{aligned}\left\langle \hat{A} \right\rangle &= \left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle \\ &= \sum_a a \left| \langle a | \Psi \rangle \right|^2 \\ &= \sum_a a \langle a | \Psi \rangle \langle \Psi | a \rangle\end{aligned}$$

Mixed state

$$\hat{\rho} = \sum_i w_i |\Psi_i\rangle \langle \Psi_i|$$

$$\begin{aligned}\left\langle \hat{A} \right\rangle &= \sum_i w_i \left\langle \Psi_i \left| \hat{A} \right| \Psi_i \right\rangle \\ &= \sum_a a \langle a | \underbrace{\sum_i w_i |\Psi_i\rangle \langle \Psi_i|}_{\hat{\rho}} | a \rangle \\ &= Tr\left(\hat{\rho}\, \hat{A}\right)\end{aligned}$$

One-particle Reduced Density Matrix

Many-particle density matrix

$$\rho(r_1, r_2, ..r_N | r_1', r_2', ..r_N') = \sum_i w_i \, \Psi_i(r_1, r_2, \ldots r_N) \, \Psi_i^*(r_1', r_2', \ldots r_N')$$

One-particle density matrix ("1-matrix")

$$\rho_1(x|x') = N \int dr_2 \ldots dr_N \;\; \rho(x, r_2, \ldots r_N | x', r_2, \ldots r_N)$$

$$\rho_1(x|x') = Tr\Big(\hat{\rho} \quad \underbrace{\hat{\psi}^\dagger(x')\hat{\psi}(x)}_{\text{density operator}} \quad \Big) \quad \hat{\rho}_1$$

Electronic Hamiltonian

N electrons in an external potential $v(r)$

$$\hat{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} v(r_i) + \sum_{i,j}^{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$= \hat{T} + \hat{V} + \hat{U}$$

$$E = Tr\left(\hat{\rho}\,\hat{H}\right)$$

The energy is a **linear functional** of the full density matrix $\hat{\rho}$

Energy Functional

Functional of the density (DFT)

$$E[n] = T_s[n] + \int dr\ v(r)n(r) + \frac{e^2}{2}\int\int dr\ dr'\ \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n]$$

Functional of the 1-matrix

$$E[\rho_1] = T[\rho_1] + \int dr\ v(r)n(r) + \frac{e^2}{2}\int\int dr\ dr'\ \frac{n(r)n(r')}{|r-r'|} + \tilde{E}_{xc}[\rho_1]$$

$$\text{density } = n(r) = \rho_1(r,r)$$

KINETIC ENERGY

$$\hat{T} = \int dr \quad \underbrace{\hat{\psi}^\dagger(r)\frac{p^2}{2m}\hat{\psi}(r)}_{\text{kinetic energy density}}$$

$$\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle = \int dr \left\langle \Psi \left| \hat{\psi}^\dagger(r)\frac{p^2}{2m}\hat{\psi}(r) \right| \Psi \right\rangle$$

$$= \int\int dr\, dr' \delta(r-r') \left\langle \Psi \left| \hat{\psi}^\dagger(r')\frac{p^2}{2m}\hat{\psi}(r) \right| \Psi \right\rangle$$

$$= \int\int dr\, dr' \delta(r-r') \left(-\frac{1}{2m}\nabla_r^2\right) \underbrace{\left\langle \Psi \left| \hat{\psi}^\dagger(r')\hat{\psi}(r) \right| \Psi \right\rangle}_{\rho_1(r,r')}$$

Interaction Energy

$$\hat{U} = \frac{e^2}{2} \int \int dr\, dr' \frac{\hat{n}(r)\hat{n}(r')}{|r_i - r_j|}$$
$$= \frac{1}{2} \int \int dr\, dr' \hat{\psi}^\dagger(r)\hat{\psi}(r) \frac{e^2}{|r_i - r_j|} \hat{\psi}^\dagger(r')\hat{\psi}(r')$$

$$\left\langle \Psi \left| \hat{U} \right| \Psi \right\rangle = \frac{e^2}{2} \int \int dr\, dr' \frac{1}{|r_i - r_j|} \underbrace{\left\langle \Psi \left| \hat{\psi}^\dagger(r)\hat{\psi}^\dagger(r')\hat{\psi}(r')\hat{\psi}(r) \right| \Psi \right\rangle}_{\rho_2(r, r'|r, r')}$$

Natural Orbitals

Natural orbitals are eigenstates of the 1-matrix

$$\int dr' \; \rho_1(r, r') \; \chi_i(r') = n_i \; \chi_i(r)$$

Diagonal representation of the 1-matrix

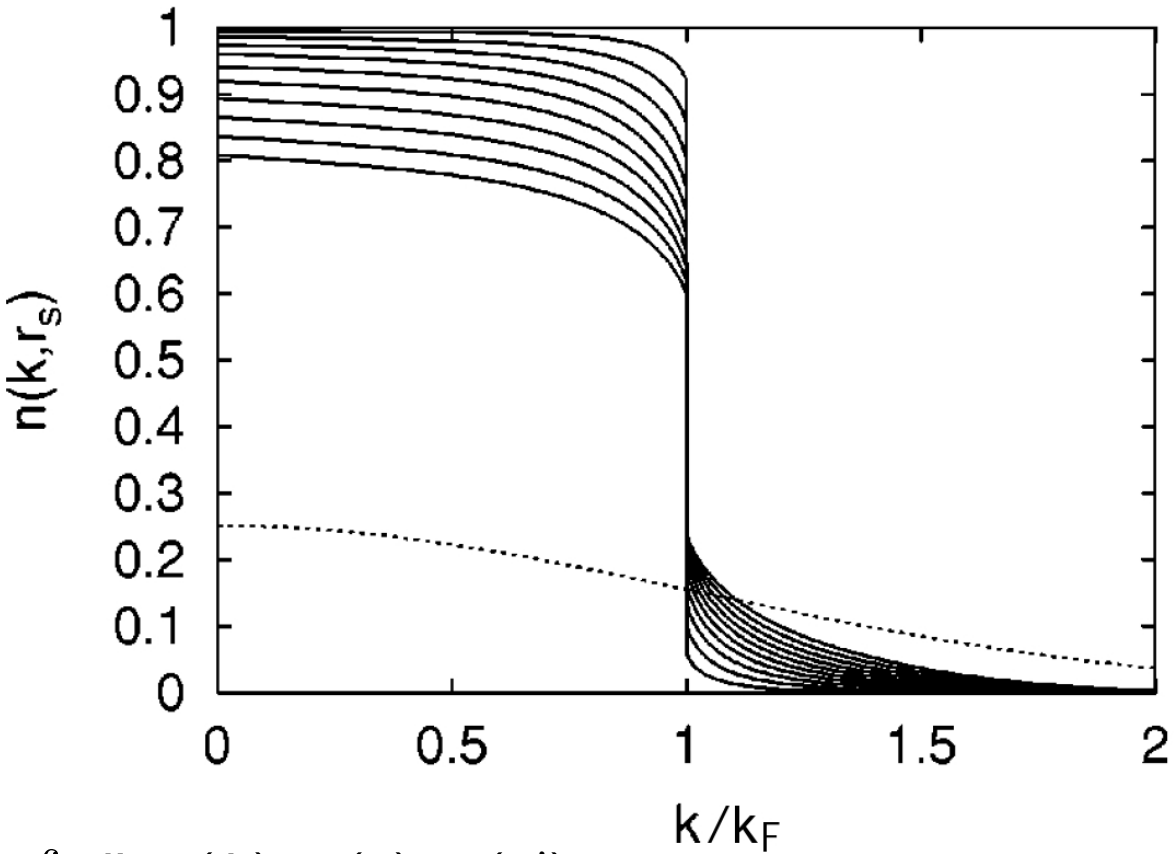
$$\rho_1(r, r') = \sum_i n_i \; \chi_i(r) \; \chi_i^*(r')$$

$n_i =$ Occupation number of χ_i

$0 \leq n_i \leq 1$

EXAMPLE I: HOMOGENEOUS ELECTRON GAS

MOMENTUM DISTRIBUTION [1]



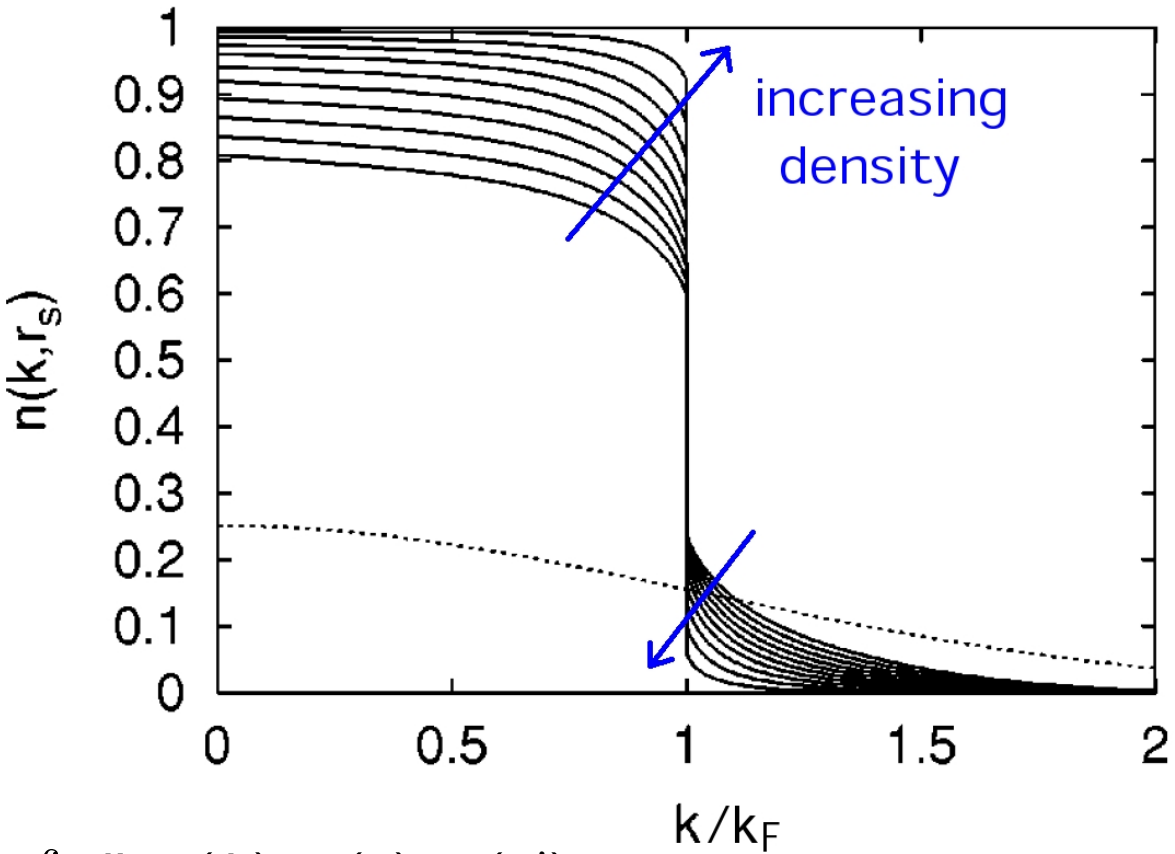
$$\rho_1(r, r') = \int dk\ n(k)\chi_k(r)\chi_k^*(r')$$

$$\chi_k(r) = \frac{1}{\sqrt{V}}\, e^{ikr} \quad \Rightarrow \quad E = E[n(k)], \qquad \frac{V}{N} = \frac{4\pi}{3}\,(r_s a_0)^3$$

[1] P. Gori-Giorgi and P. Ziesche, PRB **66**, 235116 (2002)

EXAMPLE I: HOMOGENEOUS ELECTRON GAS

MOMENTUM DISTRIBUTION [2]



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[2] P. Gori-Giorgi and P. Ziesche, PRB **66**, 235116 (2002)

Müller Energy Functional [3]

$$E[\rho_1] \iff E[n_k, \chi_k]$$

$$E = \sum_i n_i \int dr \phi_i^*(r) \left(\frac{p^2}{2m} + v(r) \right) \phi_i(r) \qquad \leftarrow \text{kinetic and external}$$

$$+ \sum_{i,j} n_i n_j \int \int dr\, dr' \frac{\phi_i^*(r)\phi_j^*(r')\phi_i(r)\phi_j(r')}{|r - r'|} \qquad \leftarrow \text{Hartree}$$

$$+ \sum_{i,j} F(n_i, n_j) \int \int dr\, dr' \frac{\phi_i^*(r)\phi_j^*(r')\phi_j(r)\phi_i(r')}{|r - r'|} \qquad \leftarrow \text{“exchange-like”}$$

[3] A.M.K. Müller, Phys. Lett. **105A**, 446 (1984)

MÜLLER ENERGY FUNCTIONAL

The 2-matrix must satisfy the "sum" rule

$$\int dx_2\ \rho_2(x_1, x_2; x_1', x_2) = (N-1)\rho_1(x_1, x_1')$$

HF approx

$$\rho_2(x_1, x_2; x_1', x_2') = \rho_1(x_1, x_1')\ \rho_1(x_2, x_2') - \rho_1(x_1, x_2')\ \rho_1(x_2, x_1')$$

Müller approx replaces $\hat{\rho}_1 \otimes \hat{\rho}_1 \longrightarrow (\hat{\rho}_1)^{\alpha} \otimes (\hat{\rho}_1)^{1-\alpha}$

HF $\quad F = n_i n_j$

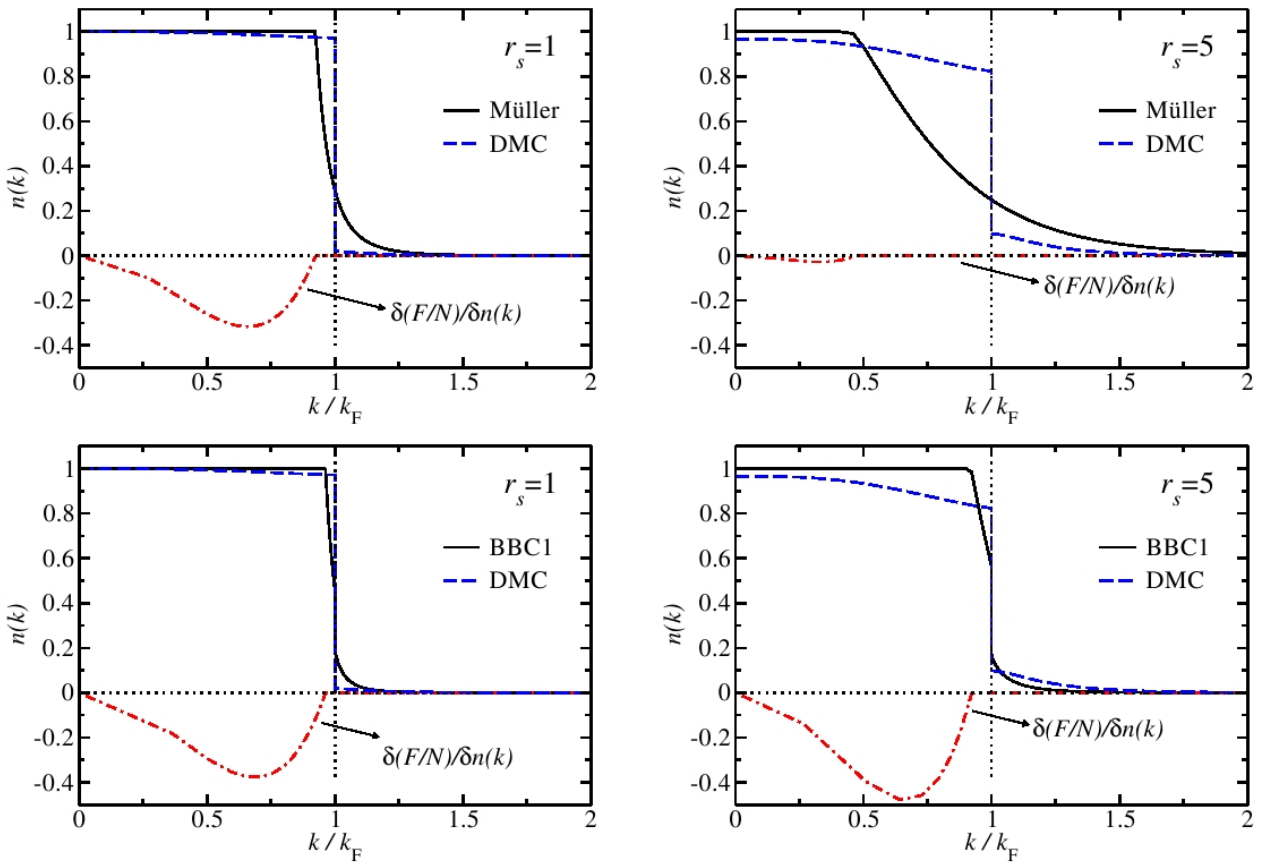
Müller $\quad F = \sqrt{n_i n_j}$

BBC* $\quad F = \begin{cases} -\sqrt{n_i n_j} & \text{if } i,j > \text{threshold} \\ \sqrt{n_i n_j} & \text{otherwise} \end{cases}$

* M.A. Buijse and E.J. Baerends, Mol. Phys. **100**, 401 (2002)

Momentum Distribution of the HEG

Müller approximation[4]



$$E[n(k)] = 2\sum_{k_1} n(k_1)\frac{k_1^2}{2} - \frac{1}{V}\sum_{k_1,k_2} F(n(k_1), n(k_2))\frac{4\pi}{|k_1 - k_2|^2}$$

[4] Lathiotakis, *et. al*, cond-mat/0605531 (2006)

Definition of Correlation Energy

$$E_{corr} = E - E_{HF}$$

Hartree-Fock 1-matrix is pure: $\hat{\rho}_1 \hat{\rho}_1 = \hat{\rho}_1$

$$\psi = \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \dots \\ \phi_2(r_1) & \phi_2(r_2) & \dots \\ \vdots & & \\ \phi_N(r_1) & \dots & \end{vmatrix} + \sum_{\text{configs}} C_{ij\dots z} \begin{vmatrix} \phi_i(r_1) & \phi_i(r_2) & \dots \\ \phi_j(r_1) & \phi_j(r_2) & \dots \\ \vdots & & \\ \phi_z(r_1) & \dots & \dots \end{vmatrix}$$

Exact 1-matrix is **not** pure: $\hat{\rho}_1 \hat{\rho}_1 \neq \hat{\rho}_1$

CORRELATION ENERGY OF THE HEG

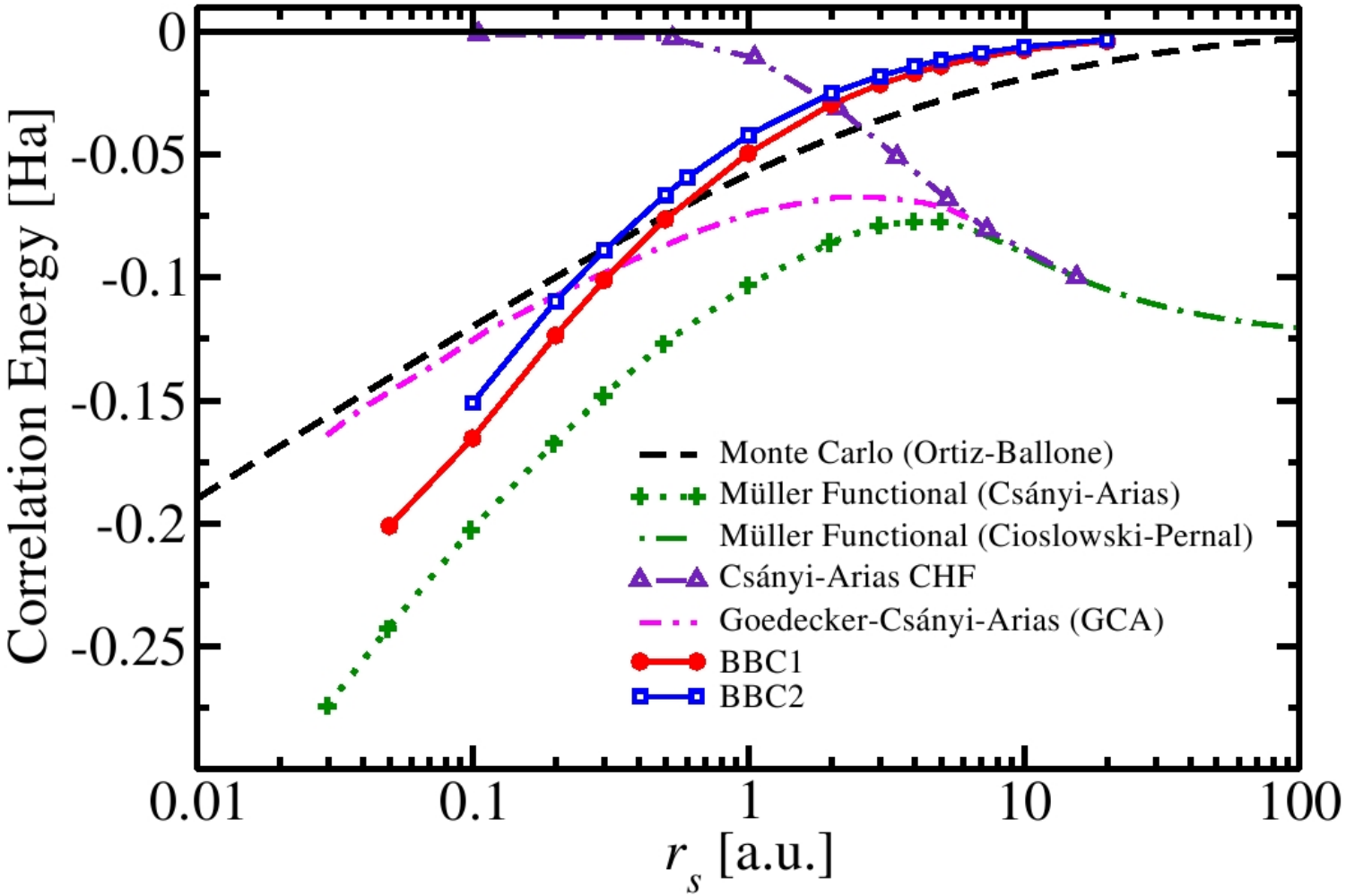


Figure: Correlation energy of the homogeneous electron gas[5]

[5] Lathiotakis, *et. al*, cond-mat/0605531 (2006)

Example II: Beryllium Atom[6]

Method	Energy (a.u.)	% E_{corr}	$n(1s)$	$n(2s)$	$n(2p_z)$
RHF	−14.573 012	0.0	1.0000	1.0000	0.0000
GU	−14.653 435	85.2	1.0000	0.9574	0.0096
FCI	−14.644 757	76.0	0.9985	0.9061	0.0307
Exact[b]	−14.667 36	100.0	0.9982	0.9095	0.0295

Figure: Electronic calculations of the Beryllium atom. GU is Goedecker-Umrigar.

[6] *adapted from* V. N. Staroverov and G. E. Scuseria, J. Chem. Phys. **117**, 2489 (2002); S. Goedecker and C.J. Umrigar, PRL **81**, 866 (1998)

EXAMPLE III: HYDROGEN FLUORIDE

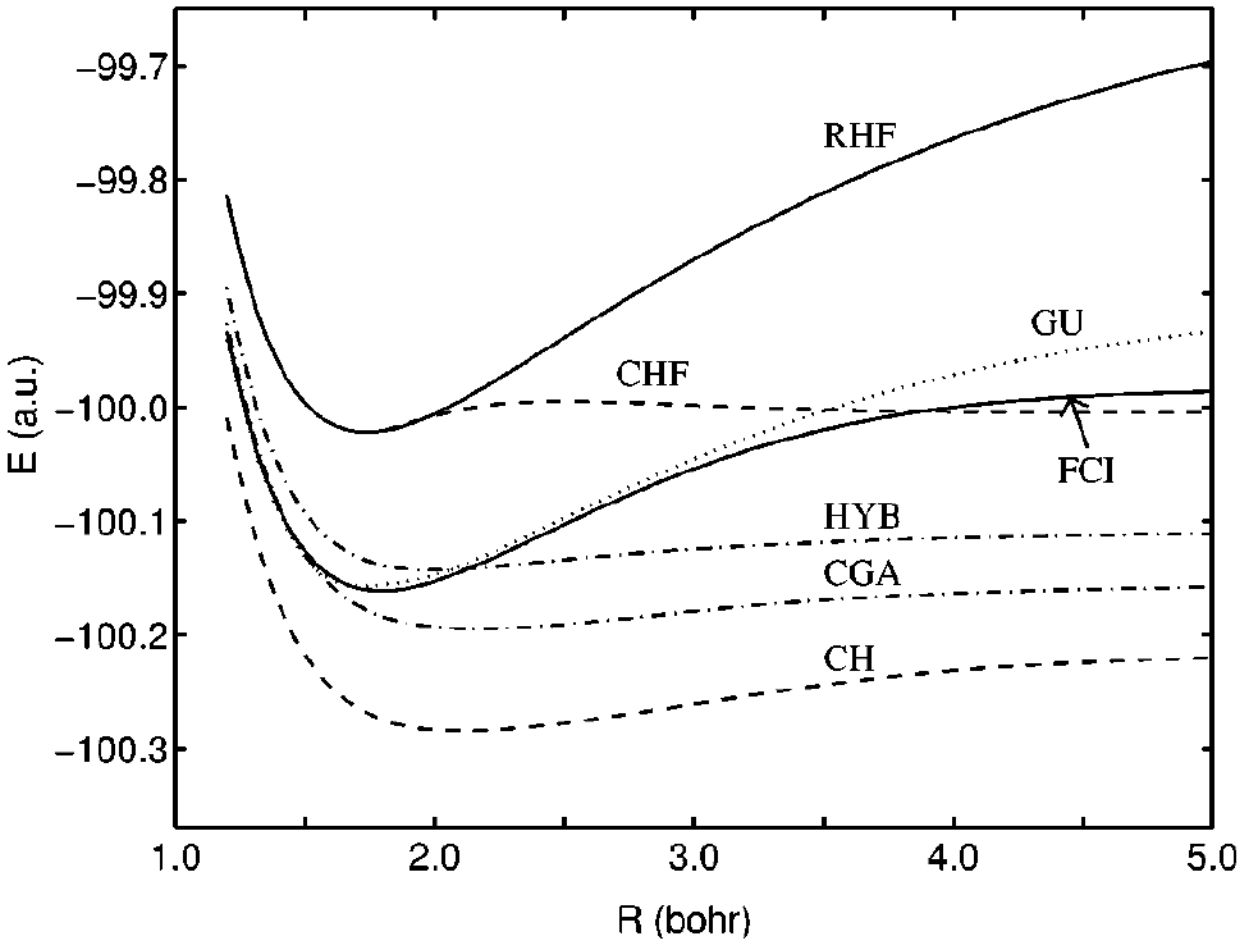


Figure: Energy versus internuclear separation [7]

[7] V. N. Staroverov and G. E. Scuseria, J. Chem. Phys. **117**, 2489 (2002)

Extension of the Hohenberg-Kohn Theorem

Density functional theory

- $E_v[n] = \int dr\ v(r)\ n(r) + F[n]$
- $n(r) \leftrightarrow v(r)$

1-matrix Functional Theory[8]

- $E_v[\rho_1] = \int \int dr\ dr' \left(\hat{t} + v(r, r')\right) \rho_1(r, r') + G[n]$
- $\rho_1(r, r') \leftrightarrow v(r, r')$

[8] T.L. Gilbert, PRB **12**, 2111 (1975)

Stationary Conditions

Variation with respect to ρ_1

$$\mathcal{E}[\rho_1] = E[\rho_1] - \mu\big(Tr(\rho_1) - N\big), \qquad \frac{\delta\mathcal{E}}{\delta\rho_1} = 0$$

Variation with respect to χ_i, n_i

$$\mathcal{E}[\chi_i, n_i] = E - \mu\Big(\sum_i n_i - N\Big) - \sum_{i,j}\lambda_{ij}\big(\langle\chi_i|\chi_j\rangle - \delta_{ij}\big)$$

$$\frac{\delta\mathcal{E}}{\delta\chi_i} = 0, \quad \frac{\partial\mathcal{E}}{\partial n_i} = 0$$

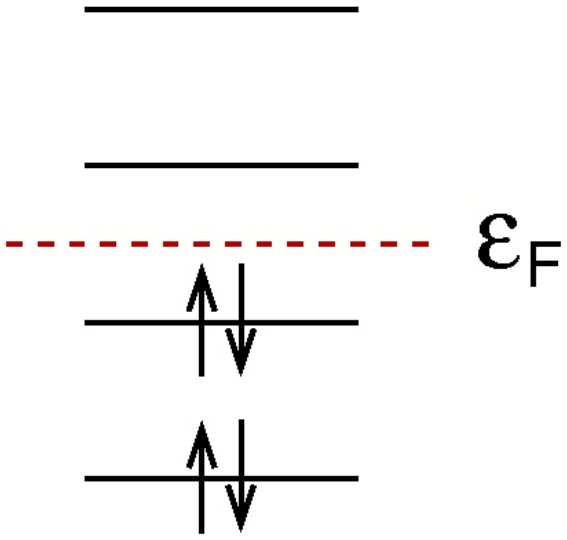
KOHN-SHAM SYSTEM

MAPPING TO A NONINTERACTING SYSTEM

Density functional theory

$$\hat{H} \longrightarrow \hat{h} = -\frac{1}{2m}\nabla^2 + v_s[n](r),$$

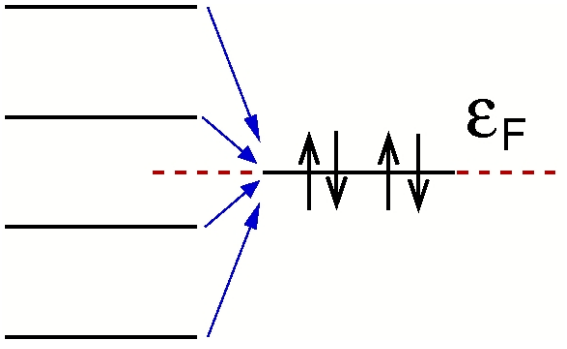
$$n = \sum_i |\phi_i|^2$$



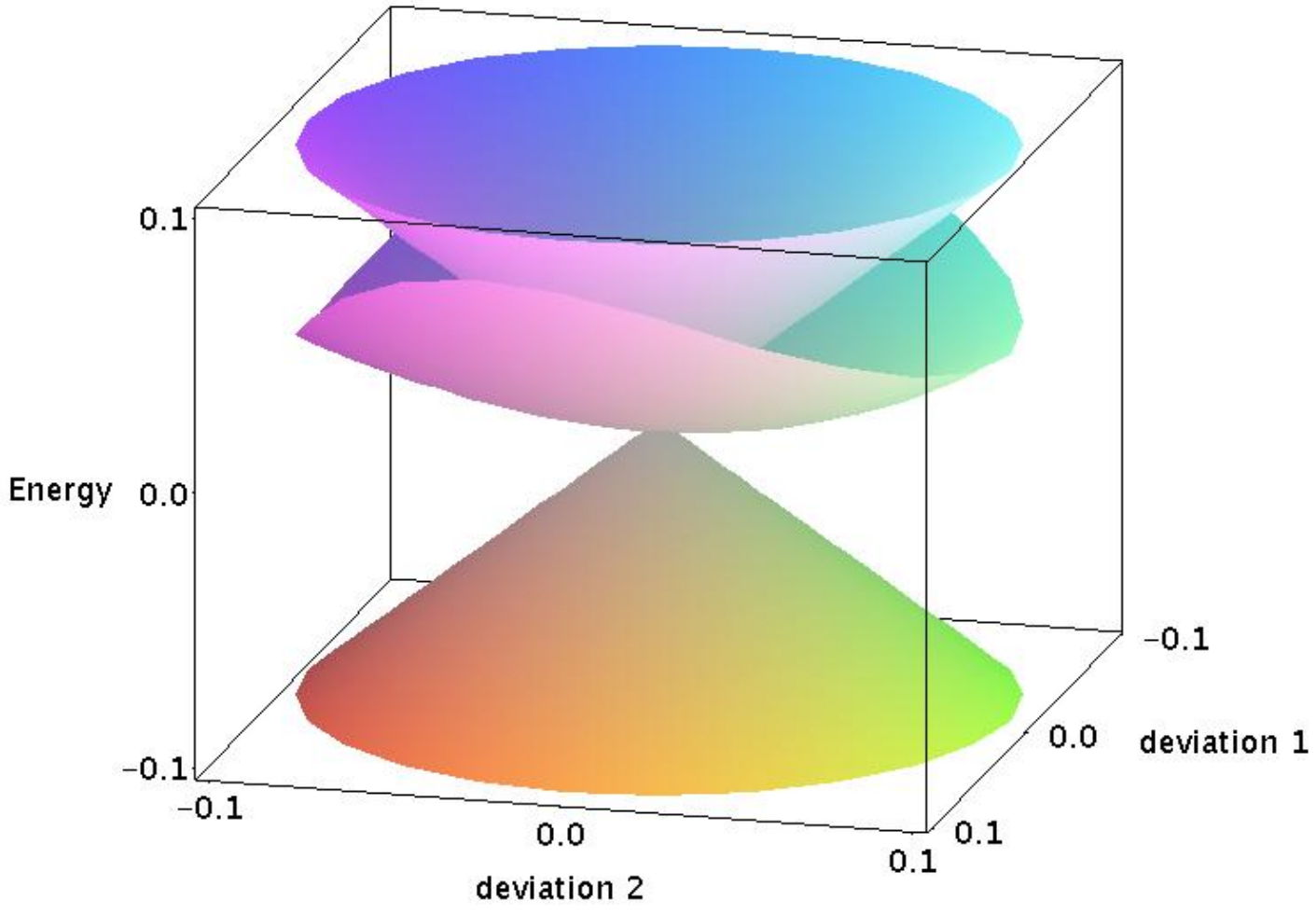
1-matrix functional theory

$$\hat{H} \longrightarrow \hat{h} = -\frac{1}{2m}\nabla^2 + \int dr'\ v_s[\rho_1](r, r')$$

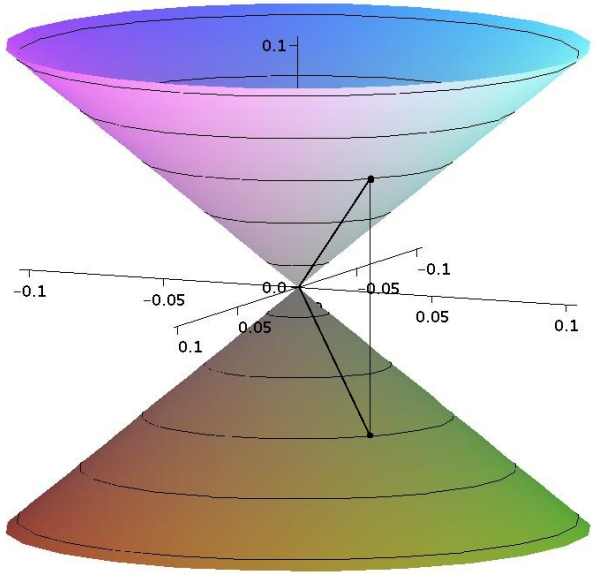
$$\rho_1 = \sum_i n_i\, \chi_i \chi_i^\dagger \qquad \hat{h}\Big|_{\rho_1(gs)} = \mu\, \hat{I}$$

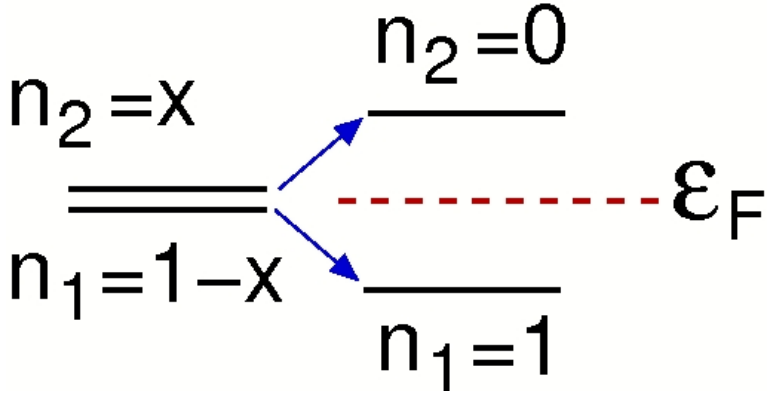


ENERGY SPECTRUM OF THE KOHN-SHAM SYSTEM



QUANTUM RESPONSE OF THE KOHN-SHAM SYSTEM





Linear response $\chi(x,y;x',y') = \frac{\delta\rho_1(x,y)}{\delta v(x',y')}$

We cannot use $\chi = \chi_s + \chi_s(v_c + f_{xc})\chi$

Instead we use $\frac{\delta h}{\delta\rho_1} = -\chi^{-1}$

SUMMARY

- Two descriptions of a quantum state: pure and mixed
- 1-matrix energy functionals... approximations
- The KS system for 1-matrix theory is very different from the conventional KS system