Introduction to the Reduced Density Matrix Functional Theory

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Outline

1. Connection to Hartree Fock
2. Density matrices
3. Reduced Density Matrix Functional Theory (RDMFT)
4. Functionals and Minimization
5. Application to prototype systems: H_2 dissociation, Homogeneous electron gas
6. Total and atomization energies
7. Fundamental gap
8. Size consistency / Fractional spin

Hartree Fock

- Wave function is one Slater Determinant:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \cdots & \varphi_1(\mathbf{x}_N) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{x}_1) & \varphi_N(\mathbf{x}_2) & \cdots & \varphi_N(\mathbf{x}_N) \end{vmatrix}$$

- We need to minimize:

$$E_{\text{tot}} = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$$

- Minimization chooses N orbitals out an infinite dimension space (or of dimension $M > N$ for practical applications).

Energy in Hartree-Fock

Spin-orbitals $\varphi(\mathbf{x}) = \varphi(\mathbf{r})\alpha(\omega)$. For spin compensated systems:

$$E_{\text{tot}} = 2\sum_{j=1}^{N/2} h^{(1)}_{jj} + 2\sum_{j,k=1}^{N/2} J_{jk} - \sum_{j,k=1}^{N/2} K_{jk}$$

$$h^{(1)}_{jj} = \int d^3\mathbf{r}\,\varphi_j^*(\mathbf{r})\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\varphi_j(\mathbf{r})$$

$$J_{jk} = \int d^3\mathbf{r} \int d^3\mathbf{r}'\,\frac{|\varphi_j(\mathbf{r})|^2\,|\varphi_k(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

$$K_{jk} = \int d^3\mathbf{r} \int d^3\,\mathbf{r}'\,\frac{\varphi_j(\mathbf{r})\,\varphi_j^*(\mathbf{r}')\,\varphi_k(\mathbf{r}')\,\varphi_k^*(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

Energy in Hartree-Fock

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$$E_{\text{tot}} = 2\sum_{j=1}^{\infty} n_j h_{jj}^{(1)} + 2\sum_{j,k=1}^{\infty} n_j n_k\, J_{jk} - \sum_{j,k=1}^{\infty} n_j n_k\, K_{jk}$$

$$h_{jj}^{(1)} = \int d^3\mathbf{r}\, \varphi_j^*(\mathbf{r}) \left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \varphi_j(\mathbf{r})$$

$$J_{jk} = \int d^3\mathbf{r} \int d^3\mathbf{r}'\, \frac{|\varphi_j(\mathbf{r})|^2\, |\varphi_k(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

$$K_{jk} = \int d^3\mathbf{r} \int d^3\mathbf{r}'\, \frac{\varphi_j(\mathbf{r})\, \varphi_j^*(\mathbf{r}')\, \varphi_k(\mathbf{r}')\, \varphi_k^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

Where n_j and n_k occupation numbers

Hartree Fock Functional in RDMFT

$$E_{\text{tot}} = 2\sum_{j=1}^{\infty} n_j \, h_{jj}^{(1)} + 2\sum_{j,k=1}^{\infty} n_j n_k J_{jk} - \sum_{j,k=1}^{\infty} n_j n_k \, K_{jk}$$

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- Assume that this functional is minimized w.r.t. n_j, φ_j.

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- Assume that this functional is minimized w.r.t. n_j, φ_j.
- It is not bound!

  n_j should satisfy extra conditions.

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- Assume that this functional is minimized w.r.t. n_j, φ_j.
- N-representability conditions of Coleman:

$$0 \leq n_j \leq 1, \quad \text{and} \quad 2\sum_{j=1}^{\infty} n_j = N$$

The first reflects the Pauli principle and the second fixes the number of particles.

Hartree Fock Functional in RDMFT

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  The first reflects the Pauli principle and the second fixes the number of particles.

- There no extrema between 0 and 1. It is monotonous selecting either 0 or 1.
- This functional collapses to Hartree-Fock Theory

Density matrices

- N-body density matrix

$$\Gamma^{(N)}(\mathbf{r}_1,\mathbf{r}_2..\mathbf{r}_N;\mathbf{r}'_1,\mathbf{r}'_2..\mathbf{r}'_N) = \Psi^*(\mathbf{r}'_1,\mathbf{r}'_2..\mathbf{r}'_N)\,\Psi(\mathbf{r}_1,\mathbf{r}_2..\mathbf{r}_N)$$

- Reduce the order of the density matrix

$$\Gamma^{(p)}(\mathbf{r}_1,..\mathbf{r}_p;\mathbf{r}'_1,..\mathbf{r}'_p) = \left(\begin{array}{c} N \\ p \end{array}\right)\int d^3r_{p+1}..d^3r_N\,\Psi^*(\mathbf{r}'_1,..\mathbf{r}'_p,\mathbf{r}_{p+1}..\mathbf{r}_N)\,\Psi(\mathbf{r}_1,..\mathbf{r}_N)$$

Density matrices

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$$\Gamma^{(N)}(\mathbf{r}_1, \mathbf{r}_2..\mathbf{r}_N; \mathbf{r}'_1, \mathbf{r}'_2..\mathbf{r}'_N) = \Psi^*(\mathbf{r}'_1, \mathbf{r}'_2..\mathbf{r}'_N)\,\Psi(\mathbf{r}_1, \mathbf{r}_2..\mathbf{r}_N)$$

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- Recurrence relation

$$\Gamma^{(p-1)}(\mathbf{r}_1, ..\mathbf{r}_{p-1}; \mathbf{r}'_1, ..\mathbf{r}'_{p-1}) = \frac{p}{N-p+1} \int d^3r_p\, \Gamma^{(p)}(\mathbf{r}_1, ..\mathbf{r}_p; \mathbf{r}'_1, ..\mathbf{r}'_{p-1}, \mathbf{r}_p)$$

Total energy

- One-body density matrix

$$\Gamma^{(1)}(\mathbf{r};\mathbf{r}') = \frac{2}{N-1}\int d^3r_2\,\Gamma^{(2)}(\mathbf{r},\mathbf{r}_2;\mathbf{r}',\mathbf{r}_2) =: \gamma(\mathbf{r};\mathbf{r}')$$

Total energy

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$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{int}}$$

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- Total energy

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{int}}$$

$$E_{\text{kin}} = \int d^3r\,d^3r'\,\delta(\mathbf{r}-\mathbf{r}')\left(-\frac{\nabla^2}{2}\right)\gamma(\mathbf{r};\mathbf{r}')$$

Total energy

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- Total energy

$$E_{\rm tot} = E_{\rm kin} + E_{\rm ext} + E_{\rm int}$$

$$E_{\rm ext} = \int d^3r\, v_{\rm ext}(\mathbf{r})\,\gamma(\mathbf{r};\mathbf{r})$$

Total energy

- One-body density matrix

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- Total energy

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{int}}$$

$$E_{\text{int}} = \int d^3r\, d^3r' \frac{\Gamma^{(2)}(\mathbf{r},\mathbf{r}';\mathbf{r},\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|}$$

Total energy

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- Total energy

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{int}}$$

  is a functional of $\Gamma^{(2)}$

- Why don't we minimize the total energy with respect to $\Gamma^{(2)}$?

N-representability

- Remember

$$\Gamma^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) = \frac{N(N-1)}{2}\int d^3r_3..d^3r_N\Psi^*(\mathbf{r}'_1,\mathbf{r}'_2,\mathbf{r}_3..\mathbf{r}_N)\Psi(\mathbf{r}_1..\mathbf{r}_N)$$

  with an antisymmetric, normalized wave function Ψ

- For $\Gamma^{(2)}$ only several necessary N-representability conditions are known[1]
- Not sufficient leading to too small total energies in the minimization

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[1] JCP **128**, 164113 (2008)

N-representability

- For γ the N-representability conditions are known and quite simple
- Diagonalization of γ

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

Occupation numbers: $0 \leq n_j \leq 1$, $\sum_j n_j = N$
Natural orbitals:

$$\int d^3r \, \varphi_j(\mathbf{r}) \, \varphi_k^*(\mathbf{r}) = \delta_{jk}$$

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- Choice between knowing the functional dependence and knowing the N-representability conditions

RDMFT Foundations

- Gilbert's Theorem:[2] Every ground-state observable is a functional of the ground-state one-body reduced density matrix

$$\gamma_{gs}(\mathbf{r};\mathbf{r}') \overset{1-1}{\longleftrightarrow} \Psi_{gs}(\mathbf{r}_1,\mathbf{r}_2 ... \mathbf{r}_N)$$

- No 1-1 correspondence to external potential as in DFT
- Idempotency: for non-interacting particles $n_j = 0, 1$, no Kohn-Sham system

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

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- Total energy

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{H}} + E_{\text{xc}}$$

Exchange-correlation energy does not contain any kinetic energy contributions

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

Müller type functionals

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

- Hartree-Fock: $f(n_j, n_k) = n_j n_k$
- Müller functional[3]: $f(n_j, n_k) = \sqrt{n_j n_k}$
- Goedecker-Umrigar[4]: $f(n_j, n_k) = \sqrt{n_j n_k}(1-\delta_{jk}) + n_j^2\delta_{jk}$

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[3] A. Müller, Phys. Lett. A **105**, 446 (1984); M. A. Buijse, E. J. Baerends, Mol. Phys. **100**, 401 (2002)

[4] S. Goedecker, C. J. Umrigar, Phys. Rev. Lett. **81**, 866 (1998).

Müller type functionals

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

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- BBC1[4]:

$$f(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases}$$

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[4] O. Gritsenko, K. Pernal, E.J. Baerends, J. Chem. Phys. **122**, 204102 (2005)

Müller type functionals

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

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- BBC2[4]:

$$f(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ n_j n_k & j \neq k \text{ both strongly occupied} \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases}$$

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- BBC3[4]:

$$f(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ n_j n_k & \begin{cases} j \neq k \text{ both strongly occupied} \\ j(k) \text{ anti}-\text{bonding }, k(j) \text{ not bonding} \end{cases} \\ n_j^2 & j = k \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases}$$

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[4] O. Gritsenko, K. Pernal, E.J. Baerends, J. Chem. Phys. **122**, 204102 (2005)

Müller type functionals

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- BBC1, BBC2, and BBC3
- PNOF0: Cummulant expansion; BBC1 with removal of $j = k$ terms PNOF: additional term to avoid pinned states; PNOF1-5 [5]

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[5] Piris, Int. J. Quant. Chem. **106**, 1093 (2006); Piris, et al, JCP **134**, 164102 (2011)

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- BBC1, BBC2, and BBC3
- PNOF0: BBC1 with removal of $j = k$ terms
- AC3: Similar to BBC3 with C2,C3 corrections analytic[6]

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[6] Rohr, et al, JCP **129**, 164105 (2008).

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- BBC1, BBC2, and BBC3
- PNOF0: BBC1 with removal of $j = k$ terms
- AC3: Similar to BBC3 with C2,C3 corrections analytic
- ML: Pade approximation for f, fit for a set of molecules[7]

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[7] Marques, Lathiotakis, PRA **77**, 032509 (2008).

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- ML: Pade approximation for f, fit for a set of molecules.
- Power Functional[8]: $f(n_j, n_k) = (n_j n_k)^{\alpha}$

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[8] S. Sharma et al, PRB, **78**, 201103(R) (2008).

Müller type functionals

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

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- ML: Pade approximation for f, fit for a set of molecules
- Power Functional: $f(n_j, n_k) = (n_j n_k)^{\alpha}$
- Range separated hybrid GGA-Müller functional[10]

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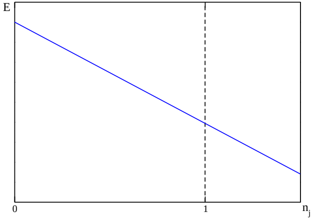
[10] D.R. Rohr, J. Toulouse, K. Pernal, PRA, **82**, 052502 (2010).

Minimization

- Minimize

$$F = E_{\text{tot}} - \mu \left(\sum_{j=1}^{\infty} n_j - N \right) - \sum_{j,k=1}^{\infty} \epsilon_{jk} \left(\int d^3r \varphi_j^*(\mathbf{r}) \varphi_k(\mathbf{r}) - \delta_{jk} \right)$$

- Minimize with respect to n_j and φ_j
- Minimization with respect to n_j can have border minima



Minimization

- Minimize

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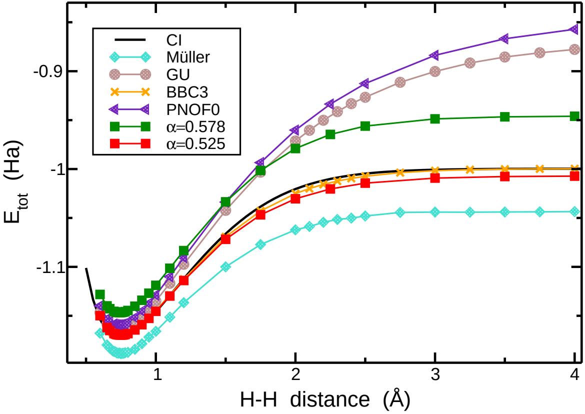
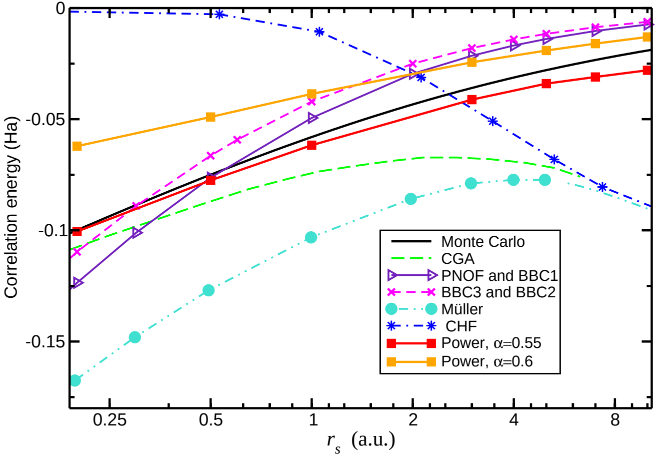
- Minimize with respect to n_j and φ_j
- Minimization with respect to n_j can have border minima
- Minimization with respect to φ_j is complicated; not a diagonalization problem.

H_2 dissociation



PRA **79**, 040501(R) (2009)

Homogeneous Electron Gas



PRB **75**, 195120 (2007); PRA **79**, 040501(R) (2009)

Benchmark for finite systems

- Benchmark for 150 molecules and radicals (G2/97 test set)[11]
- 6-31G* basis set, Comparison with CCSD(T)

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[11] JCP **128**, 184103 (2008)

Benchmark for finite systems

- Benchmark for 150 molecules and radicals (G2/97 test set)[11]
- 6-31G* basis set, Comparison with CCSD(T)

Method	$\bar{\Delta}$	$\Delta_{\max}$	$\bar{\delta}$	$\delta_{\max}$	$\bar{\delta}_e$
Müller	0.55	1.23 (C_2Cl_4)	135.7%	438.3% (Na_2)	0.0193
GU	0.26	0.79 (C_2Cl_4)	51.63%	114.2% (Si_2)	0.0072
BBC1	0.29	0.75 (C_2Cl_4)	69.91%	159.1% (Na_2)	0.0098
BBC2	0.18	0.50 (C_2Cl_4)	45.02%	125.0% (Na_2)	0.0058
BBC3	0.068	0.27 ($SiCl_4$)	18.37%	50.8% (SiH_2)	0.0017
PNOF	0.102	0.42 ($SiCl_4$)	20.84%	59.1% ($SiCl_4$)	0.0021
PNOF0	0.072	0.32 ($SiCl_4$)	17.11%	46.0% (Cl_2)	0.0015
ML(cl. shell)	0.059	0.18 (pyridine)	11.02%	35.7% (Na_2)	0.0015
MP2	0.040	0.074 (C_2Cl_4)	11.86%	35.7% (Li_2)	0.0015
B3LYP	0.75	2.72 ($SiCl_4$)	305.0%	2803.7% (Li_2)	0.022

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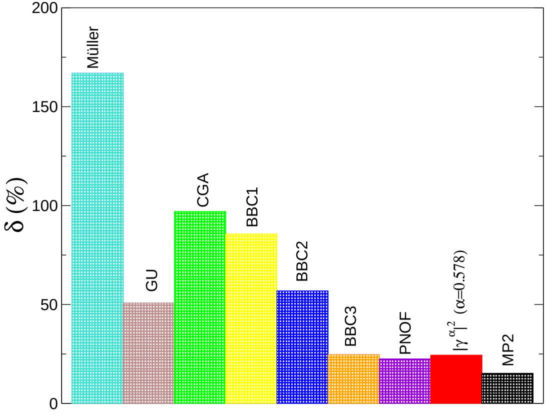
[11] JCP **128**, 184103 (2008)

E_c for finite systems



Error in correlation energy (reference CCSD(T))

PRA **79**, 040501(R) (2009)

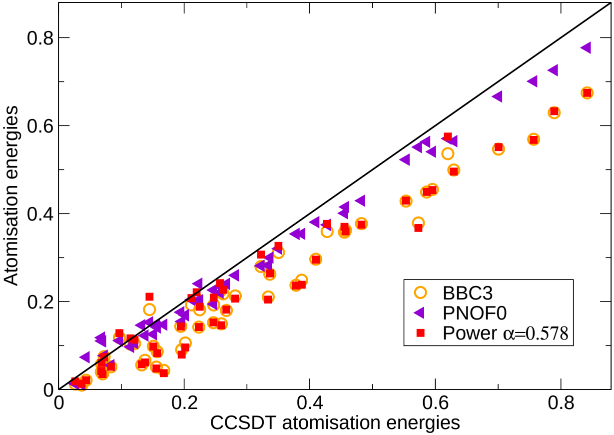
Atomization energies

	set 1		set 2	
	$\bar{\delta}$ (%)	$\delta_{\max}$ (%)	$\bar{\delta}$ (%)	$\delta_{\max}$ (%)
R(O)HF	42.4	195 (F_2)	53.8	233(F_2)
Mueller	32.7	138 (Na_2)	40.6	130(Na_2)
GU	43.7	239 (ClF_3)	50.4	180(F_2)
BBC1	31.0	107 (ClF_3)	34.8	75(O_2)
BBC2	26.9	142 (ClO)	40.1	142(F_2)
BBC3	18.0	117 (Li_2)	25.6	103(Li_2)
PNOF	25.5	161 (ClF_3)	30.4	127(F_2)
PNOF0	17.5	76 (Li_2)	23.9	73(Cl_2)
MP2	6.24	34 (Na_2)	7.94	35(Na_2)
B3LYP	11.7	40 (BeH)	12.1	38(F_2)

set 1: G2/97 test set, 6-31G*-basis

set 2: subset of 50 molecules, cc-pVDZ-basis

Atomization energies



PRA **79**, 040501(R) (2009)

Fundamental gap

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$$\gamma^M = (1-\omega)\gamma^N + \omega\gamma^{N+1}, \quad \omega = M - N$$

- The domain of γ that can be written as ensembles is identical to those satisfying:

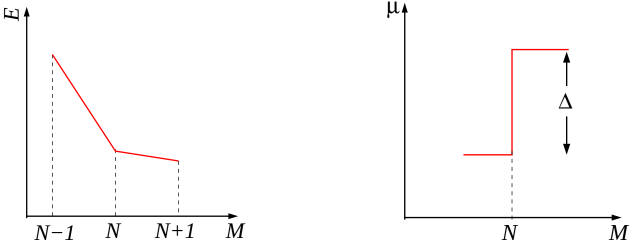
$$\sum_i n_i = M, \quad 0 \leq n_i \leq 1$$

- We can find the optimal γ^M by minimizing E under the above condition.

Fundamental gap

$$F = E_{\rm tot} - \mu(M)\left(\sum_{j=1}^{\infty} n_j - M\right) - \sum_{j,k=1}^{\infty} \epsilon_{jk}\left(\int d^3r\,\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r}) - \delta_{jk}\right)$$

- μ is the chemical potential, dE/dM.[12]
- In the exact theory, $\mu(M)$ is discontinuous and the gap equals its discontinuity



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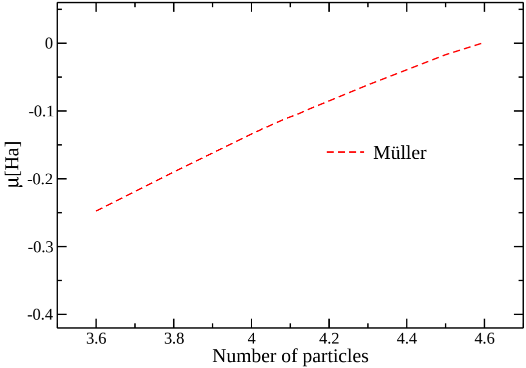
[12] Europhys. Lett. **77**, 67003 (2007)

Results for LiH



The discontinuity of μ at $N = 4$ electrons for LiH[13]

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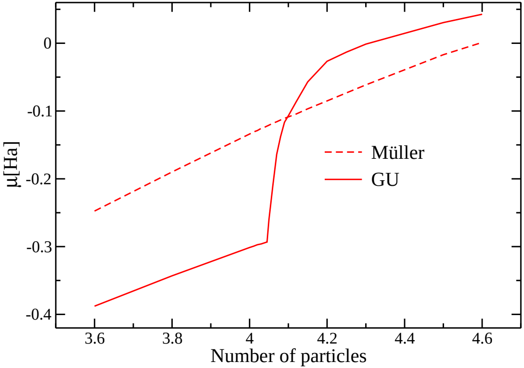

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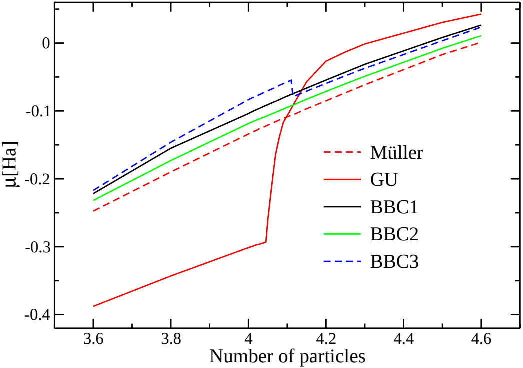

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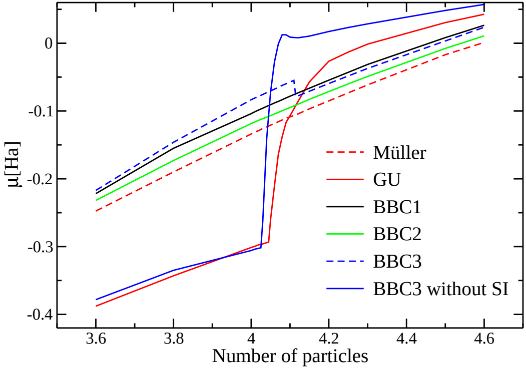

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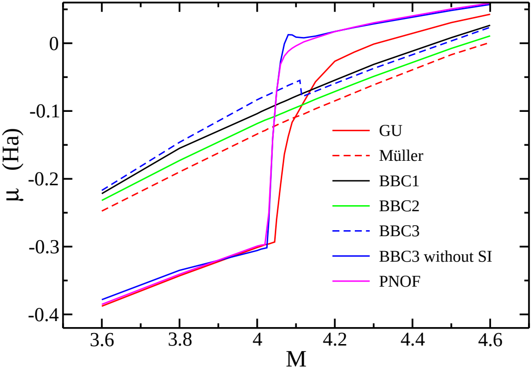

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[13] Europhys. Lett., **77**, 67003 (2007)

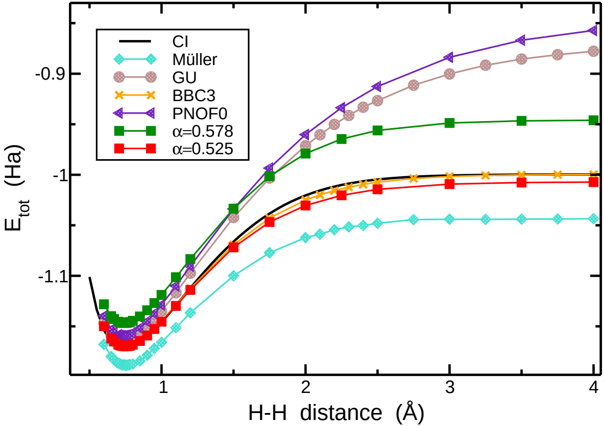
Fundamental gap

System	RDMFT	RDMFT	Other	Experiment
	$\mu(M)$ step	$I - A$	theoretical	
Li	0.177	0.202	0.175	0.175
Na	0.175	0.198	0.169	0.169
F	0.538	0.549		0.514
LiH	0.269, 0.293	0.271	0.286	0.271

Application to solids

- RDMFT is implemented in the Elk code.
- Very promising results for fundamental gaps of semiconductors/insulators.
- Strongly correlated materials - Transition metal oxides.

Why functionals fail for H_2 dissociation?



Unitary Transformations of degenerate ϕ_i

- Explicit functionals of $\{n_i\}$, $\{\phi_i\}$:

$$E[\{n_i\},\{\phi_i\}] \overset{?}{=} E[\gamma]$$

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$$\gamma \longrightarrow \begin{array}{cccc} \longrightarrow & \{n_i\},\{\phi_i\} & \longrightarrow & E \\ \longrightarrow & \{n_i\},\{\phi_i\}' & \longrightarrow & E' \end{array}$$

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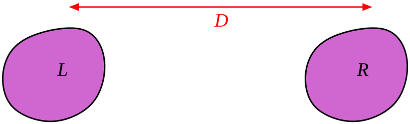
- True functionals of γ: Invariant under unitary transformations (Müller, power).
- For not invariant functionals we can define

$$E[\gamma] = \min_{\{\phi_i\}\to\gamma} \{E[\{n_i\},\{\phi_i\}]\}$$

Unitary Transformations of degenerate ϕ_i

- Two degenerate orbitals $\phi_j^L(\mathbf{r})$, $\phi_j^R(\mathbf{r})$ located far apart



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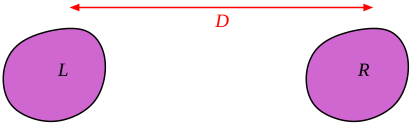


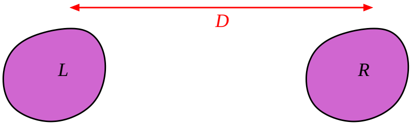
- Delocalization Unitary Transformation (DUT):

$$\begin{aligned}\tilde{\phi}_j^L(\mathbf{r}) &= \sqrt{1-\xi_j}\;\phi_j^L(\mathbf{r}) + \sqrt{\xi_j}\;\phi_j^R(\mathbf{r})\,,\\ \tilde{\phi}_j^R(\mathbf{r}) &= -\sqrt{\xi_j}\;\phi_j^L(\mathbf{r}) + \sqrt{1-\xi_j}\;\phi_j^R(\mathbf{r})\,,\end{aligned}$$

where $0 \leq \xi_j \leq 1/2$ is the delocalization parameter:

- ⋆ $\xi_j = 0$: Localized natural orbitals.
- ⋆ $\xi_j = 1/2$: Fully delocalized natural orbitals.

Unitary Transformations of degenerate ϕ_i



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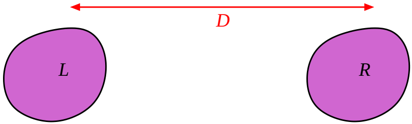

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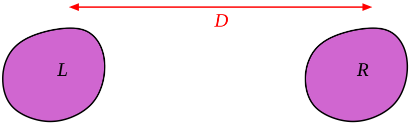

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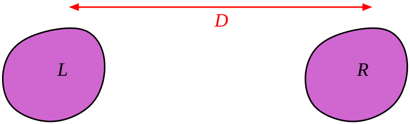

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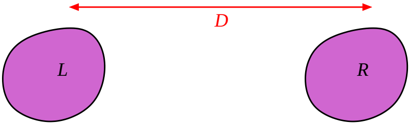

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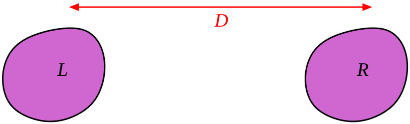

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- Cases 1,2: size consistent;Case 3: size inconsistent

Unitary Transformations of degenerate ϕ_i

Functional	**He**		**Ne**	
	$-E_{\rm cor}$ (Ha)	Δ (%)	$-E_{\rm cor}$ (Ha)	Δ (%)
Müller	0.0481	0.0	0.3848	0.0
GU	0.0333	-17.3	0.2940	-12.57
BBC1	0.0409	0.0	0.3203	0.0
BBC2	0.0409	0.0	0.3052	0.0
BBC3	0.0373	4.02	0.2715	0.495
PNOF	0.0294	-16.8	0.2572	-12.01
PNOF0	0.0294	-7.48	0.2534	-3.68
ML	0.0418	0.0	0.3253	0.0
BBC++	0.0403	0.0	0.2645	0.0
Power	0.0116	0.0	0.1127	0.0
AC3	0.0323	0.0	0.2715	0.0

JCP, **132**, 084105 (2010).

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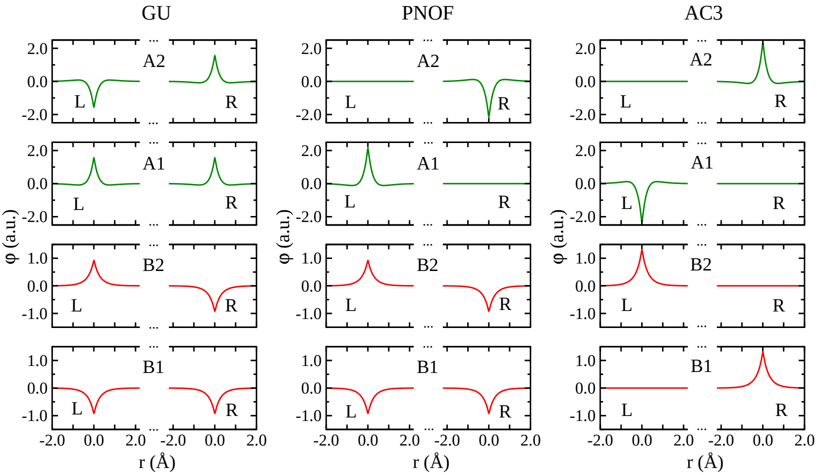

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- The domain of the ensembles satisfying Eq. 1 is identical to those satisfying

$$\sum_i n_i^{\uparrow} = N/2 + s, \quad \sum_i n_i^{\downarrow} = N/2 - s, \quad 0 \leq n_i^{\uparrow(\downarrow)} \leq 1$$

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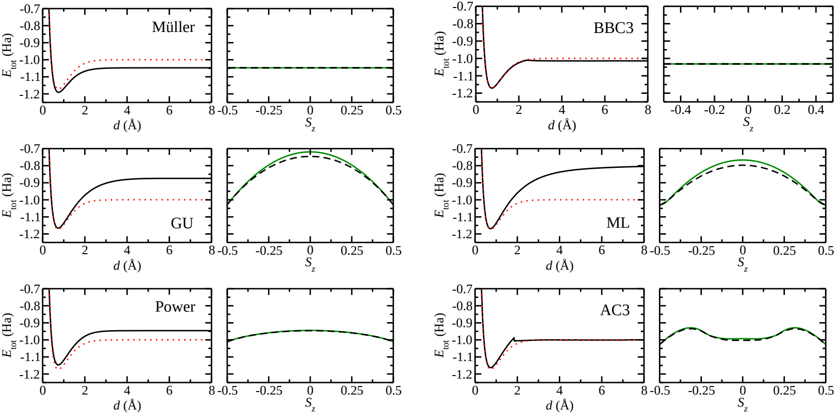
- Alternatively we can build the ensemble using the optimal $\gamma^{1/2}$, $\gamma^{-1/2}$.
- Spin constancy error: $2(E(s=0) - E(s=1/2)$
- If the aforementioned size inconsistency is not present:

  Dissociation error = Spin constancy error

Spin constancy



Left panels: H_2 dissociation (black: RDMFT, red dotted: MRDCI).

Right pannels: $E(s)$ (dotted: minimization, green: ensemble).

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- Successful application to total and atomization energies of molecules
- RDMFT functionals reproduce energy derivative discontinuities: fundamental gap
- Gaps for solids (including Mott insulators) are well reproduced