Effective Hamiltonians in RDMFT and single particle properties

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Outline

1. Foundations of RDMFT
    - Basic concept
    - Minimization
2. Single particle spectrum
    - Derivative discontinuities
    - Extended Koopmans' Theorem
    - Canonical Representation
    - Derivative at half-occupancy
    - Many-body effective-energy theory
3. Effective Hamiltonians
    - with non local effective potential
    - local RDMFT

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RDMFT Foundations

- In RDMFT, the one-body reduced density matrix (1-RDM) is the fundamental variable, $E = E[\gamma]$

$$\gamma(\mathbf{r},\mathbf{r}') = N\int\cdots\int d^3\mathbf{r}_2\cdots d^3\mathbf{r}_N\,\Psi^*(\mathbf{r}',\mathbf{r}_2,\cdots,\mathbf{r}_N)\,\Psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)$$

- Natural orbitals, occupation numbers:

$$\int d^3\mathbf{r}'\,\gamma(\mathbf{r},\mathbf{r}')\,\varphi_i(\mathbf{r}') = n_i\,\varphi_i(\mathbf{r})$$

- Gilbert's Theorem (T. Gilbert Phys. Rev. B **12**, 2111 (1975)):

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

- Every ground-state observable is a functional of the ground-state 1RDM.
- In most approximations $E = E[\{n_i\},\{\varphi_i\}]$

Unitary Transformations of degenerate φ_i

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

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

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- If there are degeneracies in n_i's:
  γ is invariant under transformations in the subspaces of degeneracies, but not E

$$\gamma \longrightarrow \left\{ \begin{array}{lll} \longrightarrow & \{n_i\},\{\varphi_i\} & \longrightarrow \quad E \\ \longrightarrow & \{n_i\},\{\varphi_i\}' & \longrightarrow \quad E' \end{array} \right.$$

- Some exploited functionals are Invariant: Müller, power.

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- Some exploited functionals are Invariant: Müller, power.
- For not invariant functionals we can define

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

RDMFT Foundations

- Total energy

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

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

$$E_{\text{ee}} = E_{\text{H}} + E_{\text{xc}}$$

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

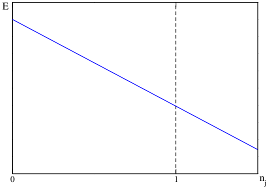
- Exchange-correlation energy: $E_{\text{xc}} = E_{\text{xc}}[\{n_i\},\{\varphi_i\}]$
- E_{xc} does not contain any kinetic energy contributions

Minimization

- We need to minimize $\mathcal{F}$, with respect to n_j and φ_j

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

- Minimization with respect to n_j can have border minima (pinned states)



- At the solution, $\mu = dE/dn_j$, ∀ fractional n_j

Minimization

- Minimization with respect to φ_j is complicated:

$$\frac{\delta E_{\mathrm{tot}}}{\delta \varphi_j^*(r)} = F^{(j)} \varphi_j(r)\,, \quad F^{(j)} \varphi_j(r) = \sum_k \lambda_{jk} \varphi_k(r)$$

- Not a diagonalization problem: Fock-like operator F is index dependent.
- The Lagrangian Matrix λ_{jk} is Hermitian at the extremum.
- Orbital optimization remains a bottleneck for RDMFT.

Scaling of RDMFT

- Scaling depends only on the Hilbert space size M (all orbitals are occupied) and not the number of electrons.
- Nominal scaling M^5.
  For comparison, DFT, HF: M^4; CI, CCSD(T), MP4: M^7
- Orbital minimization can be extremely expensive.
- Iterative schemes have been developed (effective Hamiltonian schemes) but the problem still remains.

Comparison with DFT

- Similarly to DFT, RDMFT is not a variational method.
- The kinetic energy is a known functional of the 1RDM. On the contrary, it is NOT a functional of the density.
- Without the exact kinetic energy functional,DFT resorts on the fictitious Konh-Sham (KS) system to restore the quantum mechanics.
- In RDMFT no there is no KS system.
- In KS-DFT, kinetic energy parts “pollute” the xc energy term.
- In RDMFT, no such terms exist. Easier to create functionals.
- The KS system with a single Slater determinant is difficult to describe non-dynamic correlations.
- Due to the non-idempotency of the 1RDM, RDMFT can describe more naturally non-dynamic correlation.

The price to pay!

- RDMFT is much less efficient than DFT due to:
  - Nominal scaling M^5 vs M^4.
  - In principle, all orbitals are occupied.
  - Extra occupation number optimization.
  - Orbital optimization is inefficient.
- For routine calculations that DFT works well, there is no need to use RDMFT.
- Where can RDMFT be useful? In systems with strong non-dynamic correlations where single Slater description is poor: Molecular dissociation, diradicals, band gaps of semiconductors, insulators and highly correlated periodic systems.

Effective Hamiltonians/Single electron spectrum

- In RDMFT there is no Kohn-Sham scheme.
- Exact KS-DFT $\epsilon_{\mathrm{HOMO}} = IP$; Koopmans' theorem in HF.
- There are attempts to define single particle schemes or effective Hamiltonians with two targets:
  - To obtain effectively natural orbitals (e.g. iterative diagonalization).
  - To provide a useful single electron picture.
- Single particle properties/Effective Hamiltonians
  - Energy derivative discontinuities
  - Extended Koopmans' Theorem
  - Canonical Orbital Representation
  - Energy derivative at half-occupancy
  - Many-body effective-energy theory
  - Effective Hamiltonians with non-local potential
  - Local RDMFT

Derivative discontinuities

- Extend to fractional particle number
- Lagrange multiplier μ is the chemical potential
- $\mu(N)$ is a step function with step at integer N
- The fundamental gap is given as the discontinuity of μ at integer particle number[1]

$$\begin{aligned}\Delta &= I - A \\ &= \lim_{\eta\to 0}\left(\mu(N+\eta) - \mu(N-\eta)\right)\end{aligned}$$

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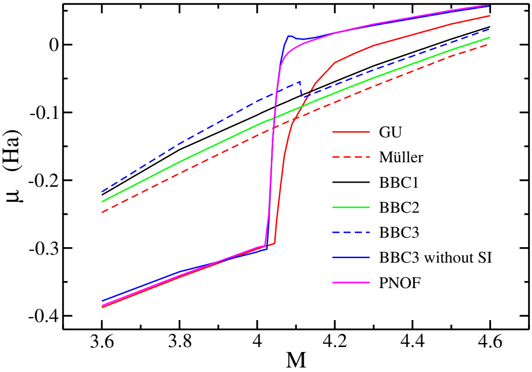
[1] Helbig et al, Europhys. Lett. **77**, 67003 (2007)

Results for LiH



The discontinuity of μ at $N = 4$ electrons for LiH[2]

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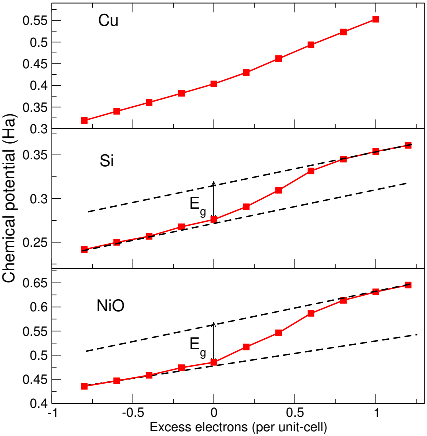
[2] Helbig et al, Phys. Rev. A **79**, 022504 (2009)

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

Discontinuity for solids



$\mu(N)$ for Cu, Si, NiO[3]

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[3] Sharma et al, PRB **78**, 201103R (2008)

Extended Koopmans' Theorem (EKT)

- To obtain the natural orbitals one minimizes:

$$F = E - \sum_{i,j} \lambda_{ij} \left[\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right]$$

- EKT: IPs are given as eigenvalues of

$$\Lambda_{ij} = \frac{\lambda_{ij}}{\sqrt{n_i n_j}}$$

Extended Koopmans' Theorem (EKT)

- Calculation for BBC and GU (He, Be, Ne, LiH, Li_2, HF, N_2)[4]:

Functional	BBC1	BBC2	BBC3	GU
Abs. Rel. Error (%)	6	6	4	4

- Calculation with PNOF1 for 16 molecules[5]:

IP	Error EKT (%)	Error KT/HF (%)
FIPS	3.5	5.6
HIPS	5.5	7.0
All	4.7	6.5

- Calculation for 11 molecules[6]:

System	**Müller**	**GU**	**Power**	**AC3**	**PNOF1**	**BBC3**	**ML**
Δ_{FIP} (%)	12.22	2.47	6.26	2.82	2.99	5.16	5.11
Δ_{HIP} (%)	10.56	5.69	11.80	6.45	5.15	4.21	12.02
Δ (%)	11.43	4.00	8.90	4.55	4.02	4.71	8.40

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[4] Pernal & Cioslowski, CPL **412**, 71 (2005).

[5] Leiva & Piris, J. Mol. Str.: THEOCHEM **770**, 45 (2006).

[6] E. N. Zarkadoula, S. Sharma, et al, PRA **85**, 032504 (2012)

Canonical representation

- To obtain the natural orbitals one minimizes:

$$F = E - \sum_{i,j} \lambda_{ij} \left[\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right]$$

- At the solution, γ: diagonal, λ is Hermitian.
- HF: γ, λ are simultaneously diagonal.
- RDMFT: Two representations[7]:
  - Natural orbitals (eigenvalues of γ)
  - Canonical orbitals (eigenvalues of λ)
- Evaluated for PNOF5:
  - NOs and COs have a different localization behavior
  - IPs from the eigenvalues of λ are close to EKT and experimental values.

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[7] Piris et al, Theor. Chem. Acc. **132**, 1298 (2013)

Derivative at half occupancy

- One particle spectrum associated with the natural orbitals[8]:

$$\epsilon_i = \frac{\partial E}{\partial n_i}\bigg|_{\{n_j, j\neq i\}=\text{optimal}, n_i=1/2}$$

- Resembles the process of adding and removing an electron to/from the i-th orbital if $E(n_i)$ is linear in $0 \leq n_i \leq 1$.
- It was applied to periodic systems, with the Power functional, yielding very good results for strongly correlated TMOs:
  - TMOs are found insulators also in the non-magnetic state[9]

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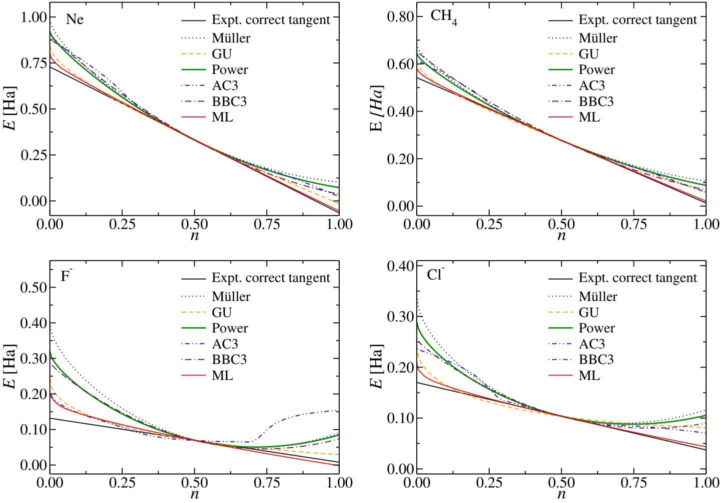
[8] S. Sharma, J. K. Dewhurst, et al, PRL **110**, 116403 (2013)

[9] Y. Shinohara, et al, J. Chem. Theory Comput. **11**, 4895 (2015).

Derivative at half occupancy for finite systems



E. Zarkadoula, et al, PRA **85**, 032504 (2012).

Derivative at half occupancy for finite systems

- Ionization Potentials[10]:

	Müller	**GU**	**Power**	**AC3**	**PNOF1**	**BBC3**	**ML**	**HF/KT**
Δ_{FIP} (%)	12.38	10.91	7.42	4.10	9.19	6.93	2.07	4.43
Δ_{HIP} (%)	7.45	7.29	4.61	8.78	5.04	10.83	6.48	6.43
Δ (%)	10.03	9.19	6.08	6.33	7.21	8.79	4.17	4.45
$\Delta_{\mathrm{FIP}}^{(\mathrm{EKT})}$ (%)	12.22	2.47	6.26	2.82	2.99	5.16	5.11	
$\Delta_{\mathrm{HIP}}^{(\mathrm{EKT})}$ (%)	10.56	5.69	11.80	6.45	5.15	4.21	12.02	
$\Delta^{(\mathrm{EKT})}$ (%)	11.43	4.00	8.90	4.55	4.02	4.71	8.40	

- Electron affinities:

System	**Müller**	**GU**	**Power**	**AC3**	**PNOF1**	**BBC3**	**ML**	**QCI(T)**	**Expt.**
LiH	0	0.192	0	0.219	0.317	0.106	0.264	0.317	0.34
OH	3.157	6.735	3.456	2.626	1.784	3.157	2.441	1.645	1.83
F	5.651	3.297	5.040	3.196	3.552	5.539	4.363	3.241	3.34
Li	0	0.403	0.139	0.275	0.400	0	0.212	0.601	0.62
Cl	3.687	2.190	3.632	3.678	2.660	4.186	3.623	3.430	3.61
CN	1.807	2.328	2.332	4.264	2.470	4.873	4.585	3.627	3.77
C_2	1.044	1.419	1.298	3.386	4.416	4.560	3.722	3.055	3.54
BO	1.243	1.326	1.982	3.252	2.076	3.222	3.252	2.359	2.83
SH	1.386	0.706	1.908	1.968	1.352	2.454	2.168	2.119	2.32
PH	0.304	0	1.200	1.252	0.186	2.192	1.145	2.023	1.00
Δ(%)	63.24	70.81	48.73	21.39	28.63	52.00	21.53	17.28	

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[10] E. Zarkadoula, et al, PRA **85**, 032504 (2012).

Many-body effective-energy theory (MEET)

- Electron removal and addition energies δ_i^R, δ_i^A, are poles of the one-body Green's function.[11]
- Approximations in terms of density matrices:

$$\delta_i^R = h_{ii} + \sum_j V_{ijij} n_j + \frac{1}{n_i} \sum_{jkl} V_{ijkl} \Gamma^{(2)}_{\mathrm{xc},klji}$$

$$\delta_i^A = h_{ii} + \sum_j V_{ijij} n_j - \frac{1}{1-n_i} \left[\sum_j V_{ijji} n_j + \sum_{jkl} V_{ijkl} \Gamma^{(2)}_{\mathrm{xc},klji} \right]$$

- Accurate results for the spectral function for model systems.
- NiO was found insulator in the paramagnetic state.

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[11] S. Di Sabatino, et al, Phys. Rev. B **94**, 155141 (2016).

Effective Hamiltonians with non local potential

- Assume that NOs are eigenvalues of a Hamiltonian:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right]\varphi(r) + \int V_{\text{eff}}(r,r')\,\varphi_i(r')dr' = \epsilon_i\,\varphi_i(r)$$

- Like in OEP: make total energy stationary w.r.t. $V_{\text{eff}}(r,r')$.[12]
- $E = E[\{n_i\},\{\varphi_i\}]$: Use chain rule + perturbation theory for

$$\frac{\delta n_i}{\delta V_{\text{eff}}(r,r')}, \quad \frac{\delta \varphi_i(x)}{\delta V_{\text{eff}}(r,r')}$$

- Optimal, for $i \neq j$

$$(V_{\text{eff}})_{ij} = \frac{1}{n_i - n_j}\int\left[\frac{\delta E_{\text{ee}}}{\delta\varphi_i(r)}\varphi_j(r) - \frac{\delta E_{\text{ee}}}{\delta\varphi_j^\star(r)}\varphi_i^\star(r)\right]dr$$

- Diagonal $(V_{\text{eff}})_{ii}$ not determined !

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[12] K. Pernal, PRL **94**, 233002 (2005).

Effective Hamiltonians with non local potential

- Gilbert's operator:

$$\mathcal{H}(r,r') = \frac{\delta E}{\delta \gamma(r,r')}$$

- Non-diagonal elements: same as varying total energy w.r.t V_{eff}
- Diagonal $(V_{\text{eff}}^{(G)})_{ii} = \frac{\partial E_{\text{ee}}}{\partial n_i}$
- At convergence

$$\mathcal{H}(r,r') = \mu\, \delta(r,r')$$

- The problem of minimization is

$$\left(\mathcal{H}\left[\{n_i\},\{\varphi_i\}\right]\right)_{ij} = \mu\, \delta_{ij}$$

- NOT an eigenvalue problem !
- No spectrum associated with $\mathcal{H}$.

Effective Hamiltonians with non local potential

- Exploring the hermiticity of λ at the solution[13]

$$\lambda_{ki} - \lambda_{ik}^{\star} = (n_i - n_k)\, h_{ki} + g_{ik}^{\star} - g_{kj} = 0$$

$$g_{ik} = \int \frac{\delta E_{\text{ee}}}{\delta \varphi_i(r)} \varphi_k(r)\, dr$$

- A Hermitian matrix that is simultaneously diagonal with γ:

$$F_{ki} = \theta(i-k)\left[\lambda_{ki} - \lambda_{ik}^{\star}\right] + \theta(k-i)\left[\lambda_{ik}^{\star} - \lambda_{ki}\right]$$

- Ansatz for the diagonal elements:
  - Starting: eigenvalues of $(1/2)(\lambda_{ij} + \lambda_{ji}^{*})$
  - Then onwards: eigenvalues of previous iteration
- Scaling down the large off-diagonal elements.
- 50-200 faster than SQP minimization.

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[13] M. Piris, J. M. Ugalde, J. Comp. Chem. **30**, 2078 (2009).

Effective Hamiltonians with non local potential

- Effective non interacting system at finite temperature with the same γ as the interacting at zero temperature[14]

$$E[\gamma] = T[\gamma] + V_{\text{ext}}[\gamma] + W[\gamma]$$

$$\Omega_o[\gamma] = T[\gamma] + V_{\text{ext}}[\gamma] + \mu N[\gamma] - \frac{1}{\beta} S_o[\gamma]$$

- The non-interacting system is constructed such that

$$\frac{\delta \Omega_o[\gamma]}{\delta \gamma} = \frac{\delta E[\gamma]}{\delta \gamma}$$

- Effective potential with non diagonal

$$(V_{\text{eff}})_{ij} = \frac{1}{n_i - n_j} \int \left[\frac{\delta E_{\text{ee}}}{\delta \varphi_i(r)} \varphi_j(r) - \frac{\delta E_{\text{ee}}}{\delta \varphi_j^{\star}(r)} \varphi_i^{\star}(r) \right] dr$$

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[14] T. Baldsiefen, E.K.U. Gross, Comp. Theor. Chem. **1003**, 114 (2013).

Effective Hamiltonians with non local potential

- And diagonal

$$(V_{\text{eff}})_{ii} = \frac{\delta E}{\delta n_i} + \mu + \frac{\sigma_i}{\beta}$$

with

$$\sigma_i = \frac{\partial S_o}{\partial n_i}, \quad S_o = -\sum_i n_i \ln n_i + (1-n_i)\ln(1-n_i)$$

- Temperature $1/\beta$ controls convergence; Also temperature tensor employed.
- Applied to periodic systems; Speeds up minimization considerably.

Local RDMFT

- Minimize RDMFT functionals under the additional constraint that the orbitals are eigenfunctions of a single particle Hamiltonian with a local potential.

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(r) + v_{\text{rep}}(r)\right]\varphi_j(r) = \epsilon_j \varphi_j(r).$$

- Local potential in RDMFT is an approximation: true natural orbitals do not come from a local potential
- Total energy will be higher than full RDMFT.
- Optimization of a local potential: smaller scale problem than orbital optimization.
- Are the obtained single-electron properties reasonable?

Local RDMFT

- Novel framework that bridges RDMFT with OEP-DFT.
- The dependence on V_{rep} is implicit:

$$E = E[\{n_i\}, V_{\text{rep}}(\mathbf{r})]$$

- Optimization can be performed in the OEP fashion.
- For given $\{n_i\}$ we have an ensemble-KS-DFT functional for the ground state.
- The kinetic energy:

$$\sum_i n_i \int d\mathbf{r}\, \varphi_i^*(\mathbf{r}) \left(-\frac{\nabla}{2}\right) \varphi_i(\mathbf{r})$$

- Local-RDMFT: An ensemble DFT scheme with the weights provided by a separate functional minimization.

Local RDMFT

- Instead of $V_{\rm rep}$, we minimize w.r.t. the corresponding repulsive density:

$$\nabla^2 V_{\rm rep}(\mathbf{r}) = -4\pi \rho_{\rm rep}(\mathbf{r})$$

- Two additional constraints:

$$\begin{aligned} \int d\mathbf{r}\; \rho_{\rm rep}(\mathbf{r}) &= N-1, \\ \rho_{\rm rep}(\mathbf{r}) &\geq 0\,. \end{aligned}$$

- The first[15,2] is a necessary condition of the exact KS potential fixing the asymptotic behavior and correcting self interactions.
- The second[16] is sufficient to avoid unphysical solutions.
- The problem reduces to the iterative solution of a linear system.

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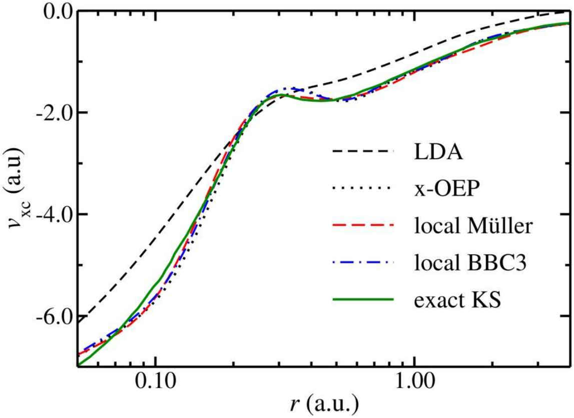
[15] Görling, Phys. Rev. Lett. **83**, 5459 (1999).

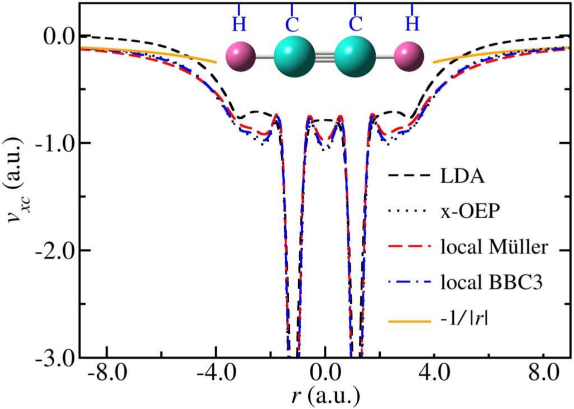
[16] Gidopoulos, NNL, JCP **136** 224109 (2012).

Local potentials for Ne atom



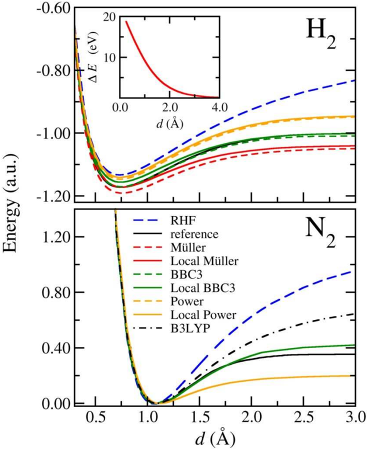
NNL, et al, Phys. Rev. A **90**, 032511 (2014)

Local potentials for C_2H_2 molecule



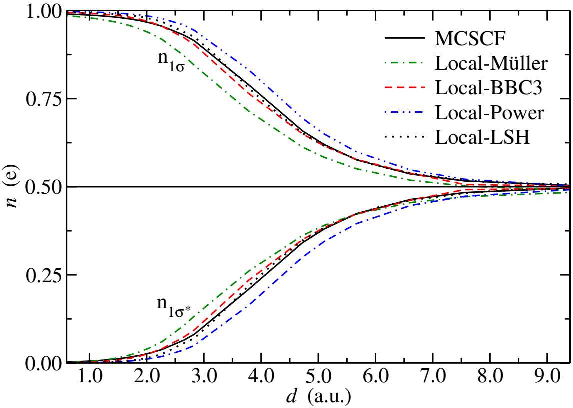
NNL, et al, Phys. Rev. A **90**, 032511 (2014)

H_2, N_2 dissociation



- When a full-RDMFT functional reproduces the correct dissociation of H_2, corresponding local-RDMFT functional does also.

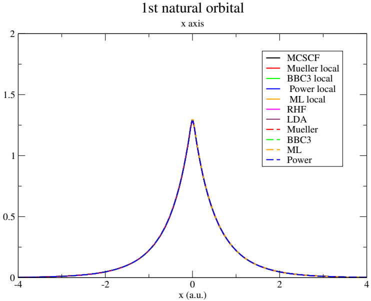
H_2 Occupation numbers



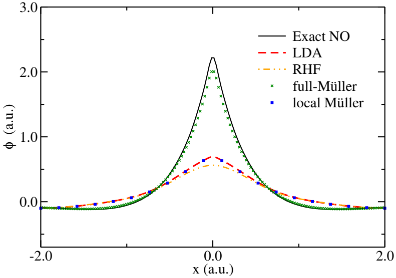
Occupation numbers vs distance for the two mostly occupied orbitals of H_2 obtained with several local-RDMFT functionals (JCP **143**, 054106 (2015)).

Local-RDMFT orbitals, He atom

$1s$



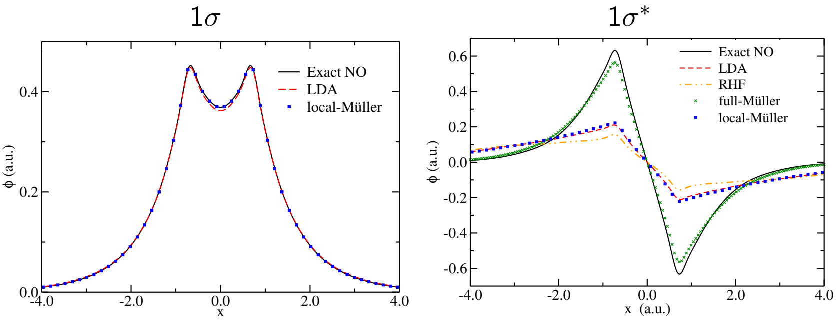
$2s$



- $1s$ strongly occupied orbital is identical in all theories.
- $2s$ local-RDMFT orbital is closer to the corresponding KS orbital than natural orbital.

Theophilou et al, JCP **143**, 054106 (2015)

Local-RDMFT orbitals, H_2



- 1σ orbital is identical in all theories.
- $1\sigma^*$ from local-RDMFT is much closer to KS than to natural orbital.

Theophilou et al, JCP **143**, 054106 (2015)

IP's for small molecules

System		HF Koopmans'	Müller	GU	BBC3	AC3	Power	PNOF1	ML	Expt. IP
He	IP	24.970	24.69	24.87	24.57	24.84	24.84	24.88	25.15	24.59
	E_c	0	0.77	0.75	0.74	0.75	0.68	0.75	0.79	
Be	IP	5.60	9.51	8.46	8.73	8.46	8.58	8.44	8.55	9.32
	E_c	0	0.87	0.89	0.90	0.90	0.91	0.90	0.94	
Ne	IP1	23.01	22.90	21.32	20.92	20.88	21.65	20.91	21.32	21.60
	IP2	52.45	46.52	45.02	44.67	44.59	45.38	44.62	45.04	48.47
	E_c	0	0.75	0.73	0.70	0.72	0.65	0.73	0.84	
H_2	IP	16.17	16.24	16.19	16.15	16.15	16.13	16.18	16.28	15.43
	E_c	0	0.68	0.67	0.62	0.65	0.57	0.65	0.73	
H_2O	IP1	13.73	12.59	12.03	12.35	12.06	12.10	12.12	12.64	12.78
	IP2	15.71	14.21	14.09	14.42	14.16	14.06	14.20	14.75	14.83
	IP3	19.15	17.52	17.57	17.88	17.63	17.45	17.67	18.23	18.72
	E_c	0	0.66	0.61	0.61	0.56	0.53	0.57	0.73	
NH_3	IP1	11.64	11.03	10.52	10.65	10.53	10.74	10.56	10.95	10.80
	IP2	16.93	15.22	15.36	15.48	15.42	15.39	15.45	15.88	16.80
	E_c	0	0.65	0.59	0.59	0.54	0.53	0.55	0.72	
CH_4	IP1	14.82	13.55	13.47	13.72	13.41	13.43	13.54	13.84	13.60,14.40
	IP2	25.65	21.34	21.16	21.52	21.20	21.21	21.32	21.62	23.00
	E_c	0	0.62	0.64	0.55	0.55	0.46	0.55	0.71	

IP's for small molecules (eV)

System		HF Koopmans'	Müller	GU	BBC3	AC3	Power	PNOF1	ML	Expt. IP
C_2H_2	IP1	11.07	11.67	11.01	11.12	11.20	11.46	11.31	11.59	11.49
	IP2	18.47	16.15	15.98	16.25	16.29	16.37	16.39	16.78	16.70
	IP3	20.88	17.88	17.76	18.02	18.07	18.13	18.19	18.52	18.70
	E_c	0	0.72	0.66	0.64	0.64	0.62	0.65	0.79	
C_2H_4	IP1	10.24	10.68	10.43	10.45	10.61	10.47	10.59	10.90	10.68
	IP2	13.76	12.07	12.11	12.41	12.47	12.15	12.61	12.87	12.80
	E_c	0	0.68	0.63	0.55	0.59	0.57	0.60	0.75	
CO_2	IP1	14.74	13.81	13.24	13.67	13.41	13.30	13.89	14.42	13.78
	IP2	19.21903	16.95	16.48	16.93	16.84	16.51	17.16	17.57	18.30
	E_c	0	0.78	0.74	0.69	0.64	0.72	0.73	0.82	
$\Delta_{\rm all}$		7.85	4.06	5.34	4.01	4.73	4.56	4.25	3.11	
$\Delta_{\rm 1st}$		8.57	2.50	4.20	2.98	3.91	3.21	3.52	3.14	

Ionization potentials (in eV) for atoms and small molecules compared to experiment. $\Delta_{\rm all}$, $\Delta_{\rm 1st}$*: average absolute errors for all IPs and for the first IP, respectively.*
$\Delta = 100 \times (1/N) \sum_i |(x_i - x_i^{\rm ref})/x_i^{\rm ref}|$.

Vertical experimental IPs: NIST Chemistry WebBook.

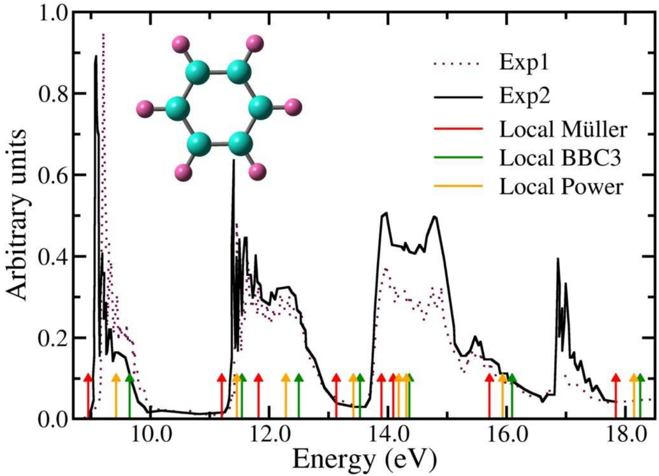
NNL, et al, Phys. Rev. A **90**, 032511 (2014)

IPs for larger molecules (eV)

System	HF Koopmans'	Mueller	BBC3	Power	ML	Exp.
Benzene	9.07(-1.69)	9.65(4.53)	8.95(-3.03)	9.42(2.08)	9.30(0.81)	9.23
Pyridine	9.33(0.78)	9.77(5.51)	8.86(-4.32)	9.62(3.89)	9.55(3.13)	9.26
Naphthalene	7.80(-3.54)	8.26(2.13)	7.54(-6.84)	7.77(-4.01)	7.84(-3.04)	8.09
Phenanthrene	7.62(-3.71)	7.58(-4.17)	6.83(-13.65)	7.03(-11.13)	7.10(-10.24)	7.91
Anthracene	6.91(-6.95)	7.32(-1.48)	6.37(-14.27)	6.74(-9.29)	6.85(-7.81)	7.43
Pyrene	6.97(-6.05)	7.24(-2.43)	6.31(-14.96)	6.63(-10.65)	6.64(-10.51)	7.42
Methane	14.77(8.57)	13.69(0.66)	13.51(-0.66)	13.53(-0.51)	13.93(2.43)	13.60,14.40
Ethane	13.13(9.53)	11.81(-1.50)	12.37(3.17)	12.02(0.25)	12.62(5.25)	11.99
Propane	12.63(9.77)	11.68(1.48)	11.50(-0.09)	11.62(0.96)	12.15(5.56)	11.51
Butane	12.37(11.54)	11.32(2.07)	11.18(0.81)	11.33(2.16)	11.80(6.40)	11.09
Pentane	12.14(11.39)	10.89(-0.09)	10.76(-1.28)	10.05(-7.80)	11.47(5.23)	10.90
Cyclo-Pentane	12.14(10.29)	11.20(1.73)	11.25(2.18)	11.25(2.18)	11.75(6.72)	11.01
Hexane	11.93(17.73)	10.64(5.03)	10.57(4.34)	10.77(6.32)	11.14(9.97)	10.13
Cyclo-Hexane-b	11.52(11.61)	10.72(3.88)	10.86(5.23)	10.72(3.88)	11.16(8.14)	10.32
Cyclo-Hexane-c	11.52(11.62)	10.82(4.84)	10.83(4.94)	10.93(5.91)	11.08(7.36)	10.32
Heptane	11.77(18.50)	10.30(3.73)	10.25(3.22)	10.50(5.74)	10.89(9.67)	9.93
Octane	11.64(18.80)	10.20(4.08)	9.99(1.94)	10.28(4.90)	10.66(8.78)	9.80
Methanol	12.05(9.91)	10.40(-5.11)	9.90(-9.67)	10.39(-5.20)	11.20(2.19)	10.96
Ethanol	11.84(11.28)	10.39(2.35)	9.35(-12.12)	10.24(3.76)	10.97(3.10)	10.64
Propanol	11.83(12.59)	10.17(-3.24)	9.32(-11.32)	10.28(-2.19)	11.00(4.66)	10.51
Azulene	6.99(-5.80)	7.72(4.04)	7.08(-4.58)	7.29(-1.75)	7.27(-2.02)	7.42
Ethylene	11.11(4.03)	10.76(0.75)	10.21(-4.40)	10.39(-2.72)	10.46(-2.06)	10.68
Butadiene	8.66(-4.13)	8.90(-1.44)	8.37(-7.31)	8.77(-2.88)	8.78(-2.77)	9.03
Hexatriene	7.87(-5.20)	8.02(-3.37)	7.27(-12.41)	7.84(-5.54)	7.73(-6.87)	8.30
Octatetraene	7.37(-5.37)	7.46(-4.24)	6.65(-14.63)	7.24(-7.06)	7.17(-7.96)	7.79
Δ	8.81	2.96	6.46	4.51	5.49	
σ	1.04	0.32	0.71	0.48	0.61	

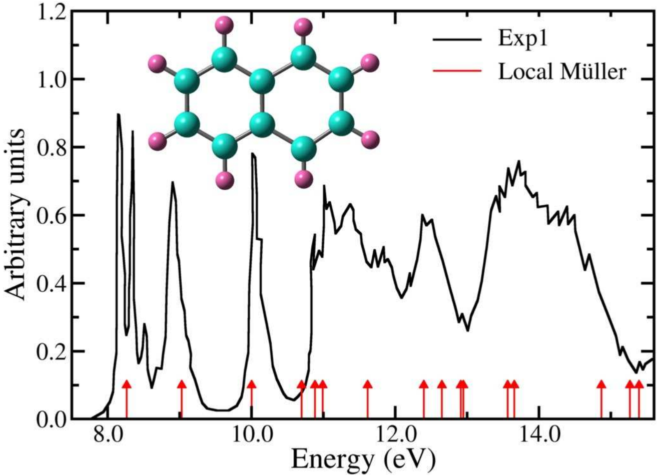
$\Delta = 100 \times (1/N) \sum_i |(x_i - x_i^{\mathrm{ref}})/x_i^{\mathrm{ref}}|$; $\sigma = (1/\sqrt{N})\sqrt{\sum_i (x_i - x_i^{\mathrm{ref}})^2}$ (JCP **141**, 164120 (2014))

Benzene Photoelectron Spectrum



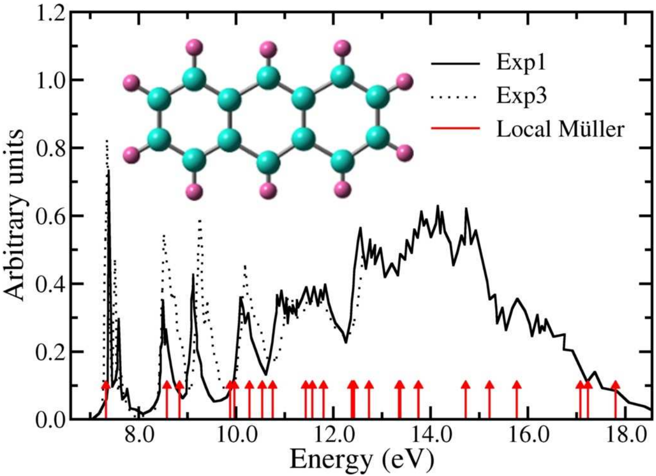
NNL, et al, J. Chem. Phys., **141**, 164120 (2014)

Naphthalene Photoelectron Spectrum



NNL, et al, J. Chem. Phys., **141**, 164120 (2014)

Anthracene Photoelectron Spectrum



NNL, et al, J. Chem. Phys., **141**, 164120 (2014)

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Thank you !

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Ευρωπαϊκή Ένωση
Ευρωπαϊκό Κοινωνικό Ταμείο

ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ
επένδυση στην κοινωνία της γνώσης
ΥΠΟΥΡΓΕΙΟ ΠΑΙΔΕΙΑΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ
ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

ΓΓΕΤ

ΕΣΠΑ
2007-2013
πρόγραμμα για την ανάπτυξη
ΕΥΡΩΠΑΪΚΟ ΚΟΙΝΩΝΙΚΟ ΤΑΜΕΙΟ