Functionals from the strong-coupling limit of DFT: promises and challenges

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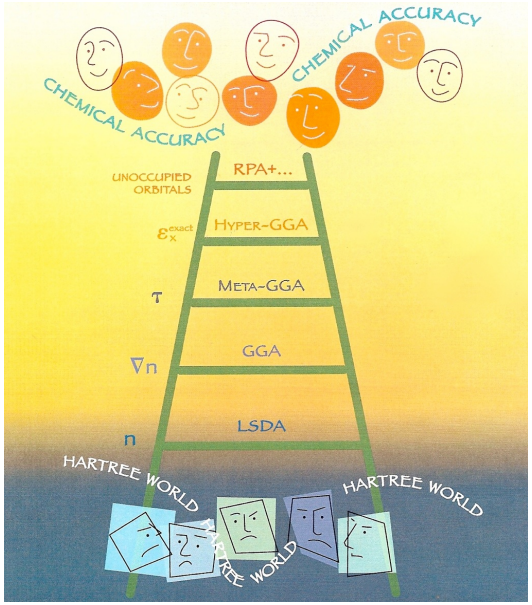
Existing approximations (hundreds...)

	functional	year	cites	like	neutral	hate	empty	points
Primera Divisió								
1	PBE	1996	24231	75	45	7	44	263
2	PBE0	1996	3754	70	40	11	50	239
3	B3LYP	1994	25488	66	36	32	37	202
4	PW91	1992	9582	45	43	11	72	167
5	BP86	1988	909	38	45	10	78	149
6	B97-D	2006	85	28	50	11	82	123
7	B3LYP-D	2006	56	29	50	21	71	116
8	M06-2X	2008	389	41	25	33	72	115
9	BLYP	1988	1347	28	48	18	77	114
10	revPBE	1998	561	25	44	11	91	108
11	CAM-B3LYP	2004	1033	23	45	11	92	103
12	B2PLYP	2006	428	21	44	12	94	95
13	B3PW91	1993	1218	21	45	14	91	94
14	SSB-D							
15	TPSSh							
16	M06-L							
17	B3LYP*							
18	PWPB95-D$_3$							
19	revTPSS-D							
20	revTPSS							
Segona Divisió								
1	LDA	1980	11795	42	34	24	71	136
2	ωB97X-D	2008	402	41	26	13	91	136
3	HSE	2003	875	31	28	10	102	111
4	M06	2008	636	24	33	28	86	77
5	OLYP	2001	101	16	34	14	107	68
6	LC-wPBE	2006	312	15	34	14	108	65
7	LC-PBE	2007	95	11	34	14	112	53
8	SAOP	2000	77	9	33	8	121	52
9	PW6B95	2005	19	11	33	15	112	51
10	LB94	1994	35	9	32	10	120	49
11	RPBE	1999	1796	9	38	16	108	49
12	mPW1K	2000	774	7	38	16	110	43
13	M05-2X	2006	945	15	32	35	89	42
14	optB88-vdW	2010	75	11	11	5	144	39
15	APBE	2011	13	4	36	9	122	39
16	BHandH	1993	57	8	35	22	106	37
17	DSD-BLYP	2010	25	7	29	13	122	37
18	M05	2005	243	10	36	33	92	33
19	VSXC	1998	43	3	34	18	116	25
20	τ-HCTH	2002	158	3	30	17	121	22
21	X3LYP	2004	79	5	31	25	110	21
22	XLYP	2004	4	0	29	25	117	4

Different structure/ingredients from the strong coupling limit

Density functionals polls
Swart, Bickelhaupt & Duran

they all use the same "ingredients" combined in many different ways, with parameters, etc.



Broken symmetry and strong correlation

- Broken symmetry solutions can mimic strong correlation (not always!)
- Often better energies, but wrong characterizations of several properties (e.g. magnetism)
- Potential energy surfaces with kinks/discontinuous
- Huge literature: controversial, wrong interpretation, etc...
- Crucial for: transition metals, Mott insulators, bond breaking, nanostructures,...

Strong coupling limit (SCE) of DFT

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

HK functional

$$T_s[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} | \Psi \rangle$$

KS kinetic energy

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

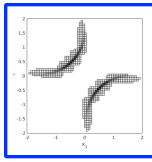
SCE functional

"strictly correlated electrons"

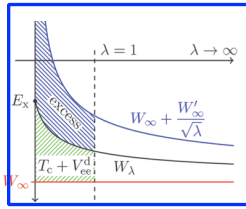
Hartree + xc functional tends asymptotically to SCE in the low-density or strong-coupling limit

Cotar, Friesecke, & Kluppelberg, Comm. Pure Appl. Math. 66, 548 (2013)

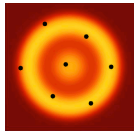
Studying and using the SCE functional



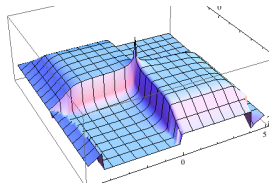
optimal transport theory: algorithms, exact results



xc functionals: approximations, scaling local interpolation, spin



low-dimensional physics: electrons, cold atoms..



time-dependent: adiabatic SCE kernel, quantum transport

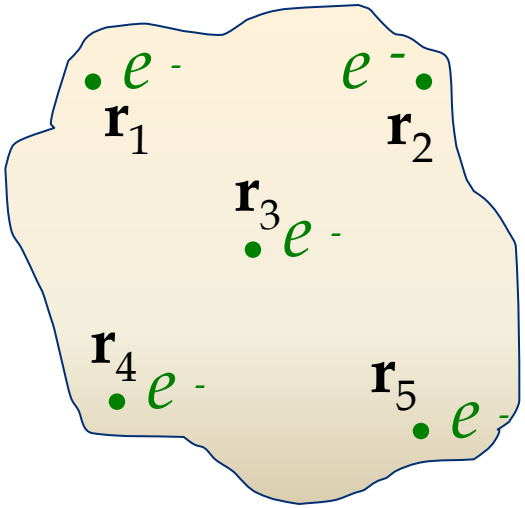
$$\Lambda[\rho] \equiv \max_{\Psi \to \rho} \lambda[\Psi]$$

Lieb-Oxford bound

What is the structure of the SCE functional?

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

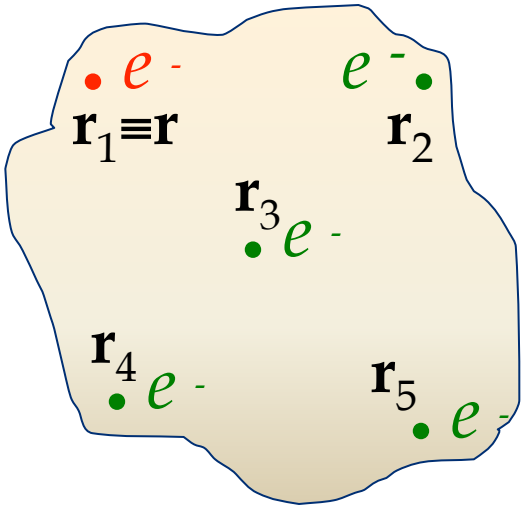
The strictly-correlated electrons functional



Minimize e-e repulsion in a given density

- ***N*** **classical charges, equilibrium positions** $\mathbf{r}_i$

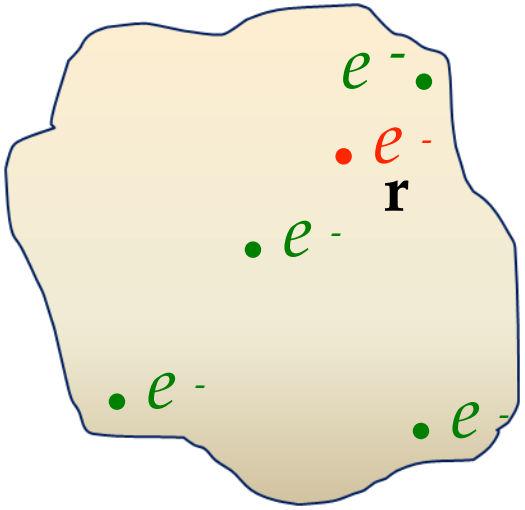
The strictly-correlated electrons functional



Minimize e-e repulsion in a given density

- ***N*** **classical charges, equilibrium positions** $\mathbf{r}_i$
- **Take one (e.g. #1) as reference**

The strictly-correlated electrons functional



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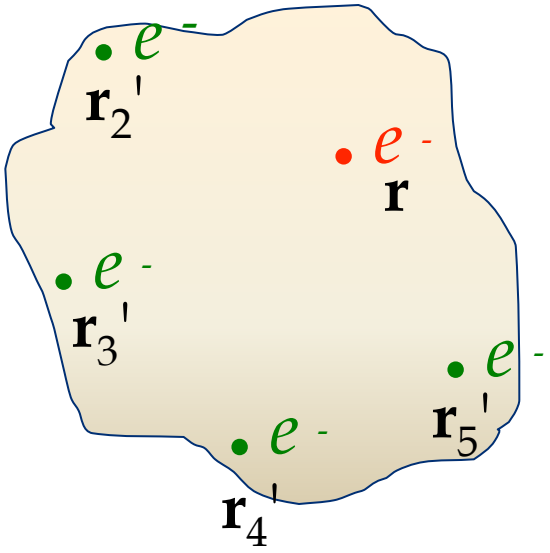

Minimize e-e repulsion in a given density

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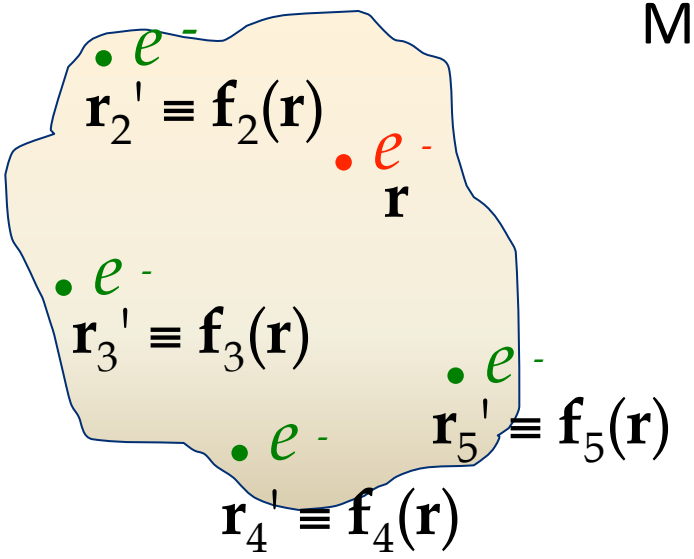
The strictly-correlated electrons functional

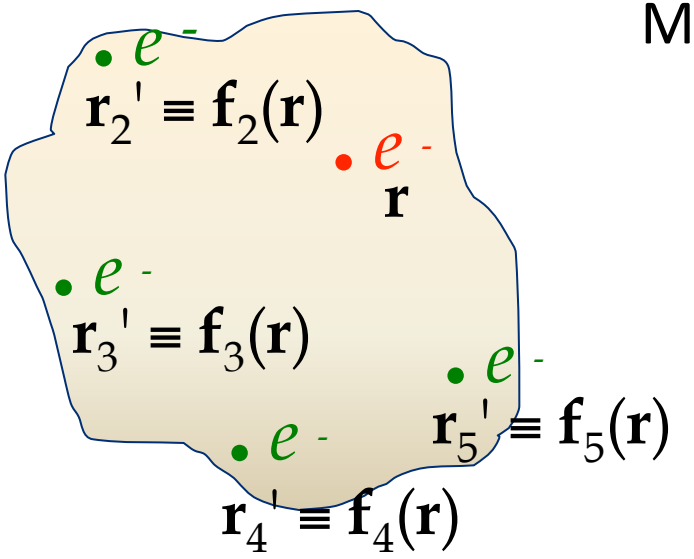


$\mathbf{f}_i(\mathbf{r})$: co-motion functions

Minimize e-e repulsion in a given density

- N classical charges, equilibrium positions $\mathbf{r}_i$
- Take one (e.g. #1) as reference
- The position of the other N-1 charges become a function of $\mathbf{r}$: $\mathbf{r}_i \equiv \mathbf{f}_i(\mathbf{r})$

The strictly-correlated electrons functional



Minimize e-e repulsion in a given density

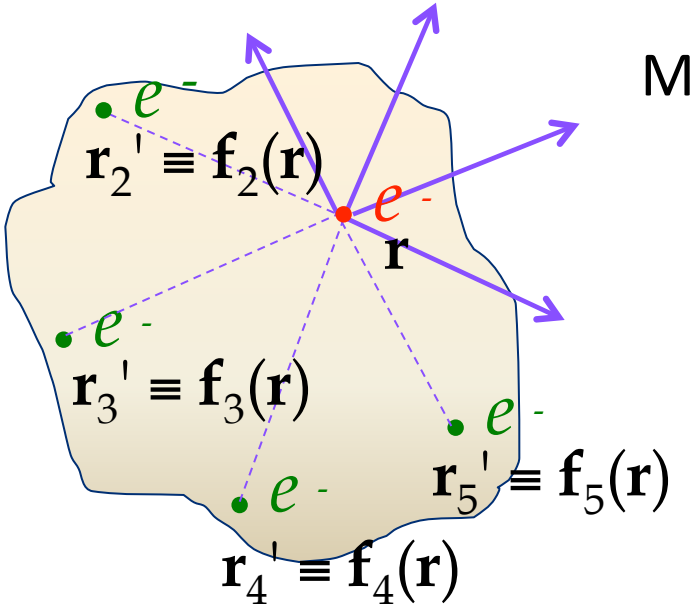
- **For a given smooth density $\rho(\mathbf{r})$:**

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

$\mathbf{f}_i(\mathbf{r})$: co-motion functions

$$\text{Prob}\left(\begin{array}{c}\text{find electron } 1\\ \text{at position } \mathbf{r}\end{array}\right) = \text{Prob}\left(\begin{array}{c}\text{find electron } i\\ \text{at position } \mathbf{f}_i(\mathbf{r})\end{array}\right)$$

The strictly-correlated electrons functional



Minimize e-e repulsion in a given density

- **For a given smooth density $\rho(\mathbf{r})$:**

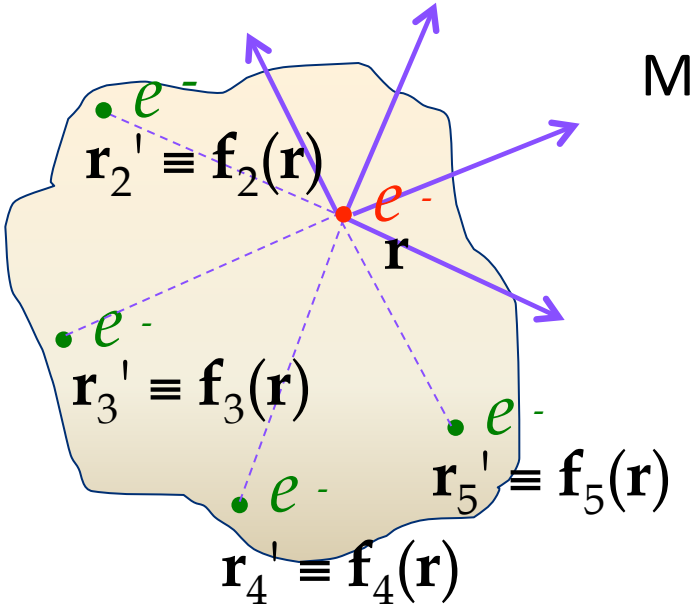
$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

$$\mathbf{F}_{\mathrm{Coul}}(\mathbf{r}) = \sum_{\mathbf{i}=\mathbf{2}}^{\mathbf{N}} \frac{\mathbf{r} - \mathbf{f}_\mathbf{i}[\rho](\mathbf{r})}{|\mathbf{r} - \mathbf{f}_\mathbf{i}[\rho](\mathbf{r})|^3}$$

$\mathbf{f}_i(\mathbf{r})$: co-motion functions

The total Coulomb force acting on the electron at position r becomes a function of only r itself

The strictly-correlated electrons functional



Minimize e-e repulsion in a given density

- **For a given smooth density $\rho(\mathbf{r})$:**

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

- **A local one-body potential can be defined:**

$$-\nabla v_{\mathrm{SCE}}[\rho](\mathbf{r}) = \mathbf{F}_{\mathrm{Coul}}(\mathbf{r}) = \sum_{\mathbf{i}=\mathbf{2}}^{\mathbf{N}} \frac{\mathbf{r} - \mathbf{f_i}[\rho](\mathbf{r})}{|\mathbf{r} - \mathbf{f_i}[\rho](\mathbf{r})|^{\mathbf{3}}}$$

$\mathbf{f}_i(\mathbf{r})$: co-motion functions

The total Coulomb force acting on the electron at position r becomes a function of only r itself

SCE functional ("wave function")

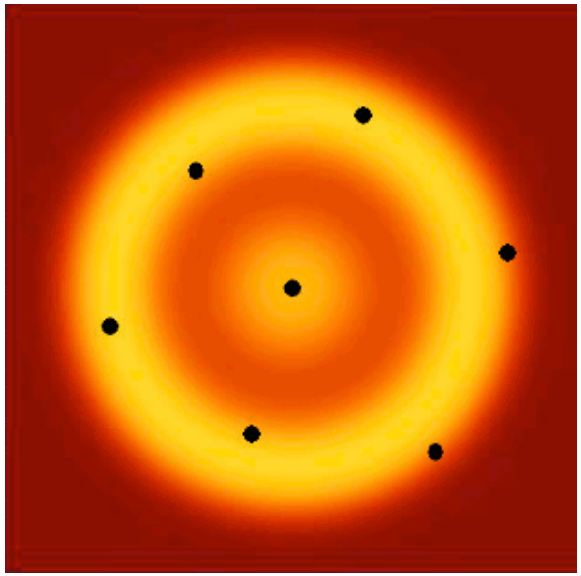
$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

$$|\Psi_{\mathrm{SCE}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 = \frac{1}{N!} \sum_{\mathcal{P}} \int d\mathbf{s} \frac{\rho(\mathbf{s})}{N} \delta(\mathbf{r}_1 - \mathbf{f}_{\mathcal{P}(1)}(\mathbf{s})) \delta(\mathbf{r}_2 - \mathbf{f}_{\mathcal{P}(2)}(\mathbf{s})) \ldots \delta(\mathbf{r}_N - \mathbf{f}_{\mathcal{P}(N)}(\mathbf{s}))$$

the wavefunction collapses to a 3D subspace of the full 3N-dimensional configuration space

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

$$\begin{aligned}
\mathbf{f}_1(\mathbf{r}) &\equiv \mathbf{r}, \\
\mathbf{f}_2(\mathbf{r}) &\equiv \mathbf{f}(\mathbf{r}), \\
\mathbf{f}_3(\mathbf{r}) &= \mathbf{f}(\mathbf{f}(\mathbf{r})), \\
\mathbf{f}_4(\mathbf{r}) &= \mathbf{f}(\mathbf{f}(\mathbf{f}(\mathbf{r}))), \\
&\vdots \\
\underbrace{\mathbf{f}(\mathbf{f}(\ldots\mathbf{f}(\mathbf{f}(\mathbf{r}))))}_{N \text{ times}} &= \mathbf{r}.
\end{aligned}$$



Seidl, PRA 60, 4387 (1999)

*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*

*Malet & Gori-Giorgi, PRL **109** 246402 (2012)*

*Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB **87** 115146 (2013)*

SCE functional and functional derivative

$$V_{ee}^{\mathrm{SCE}}[\rho] = \int d\mathbf{r} \frac{\rho(\mathbf{r})}{N} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|}$$

$$= \frac{1}{2} \int \rho(\mathbf{r}) \sum_{i=2}^{N} \frac{1}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|}$$

$$\frac{\delta V_{ee}^{\mathrm{SCE}}[\rho]}{\delta \rho(\mathbf{r})} = v_{\mathrm{SCE}}(\mathbf{r})$$

$$\nabla v_{\mathrm{SCE}}(\mathbf{r}) = -\sum_{i=2}^{N} \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

shortcut to the functional derivative

*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*

*Malet & Gori-Giorgi, PRL **109** 246402 (2012)*

*Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB **87** 115146 (2013)*

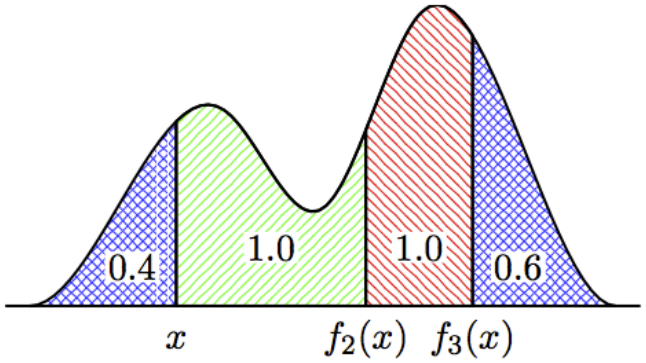
SCE functional: rigorous results

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

equivalent to an optimal transport (or mass transportation theory) problem with Coulomb cost

- *Buttazzo, De Pascale, & Gori-Giorgi, Phys. Rev. A. 85, 062502 (2012)*
- *Cotar, Friesecke, & Kluppelberg, Comm. Pure Appl. Math. 66, 548 (2013)*
- *Pass, Nonlinearity 26, 2731 (2013)*
- *Mendl & Lin, Phys. Rev. B 87, 125106 (2013)*
- *Chen, Friesecke, & Mendl, J. Chem. Theory Comput 10, 4360 (2014)*
- *Colombo, De Pascale, Di Marino, Can. J. Math. 67, 350 (2015)*
- *Benamou, Carlier, Cuturi, Nenna, L.; Peyré, arXiv:1412.5154*
- *Benamou, Carlier, Nenna, arXiv:1505.01136v2*
- *Friesecke, Mendl, Pass, Cotar & Kluppelberg, J. Chem. Phys. 139, 164109 (2013)*
- *De Pascale, arXiv:1503.07063*
- *Colombo & Stra, arXiv:1507.08522*

1D case is transparent (and as cheap as LDA)



$$N_e(x) = \int_{-\infty}^{x} \rho(x')\,dx'$$

$$a_k = N_e^{-1}(k)$$

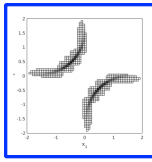
$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + i - 1] & x \le a_{N+1-i} \\ N_e^{-1}[N_e(x) + i - 1 - N] & x > a_{N+1-i}, \end{cases}$$

Written on simple physical considerations: *M. Seidl, PRA **60**, 4387 (1999)*

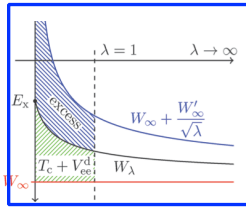
Rigorous Proof: *M. Colombo, L. De Pascale, S. Di Marino, Can. J. Math. 67, 350 (2015)*

KS SCE applied to 1D physics: *Malet & Gori-Giorgi, PRL 109 246402 (2012);*
Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB 87 115146 (2013)

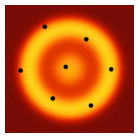
Studying and using the SCE functional



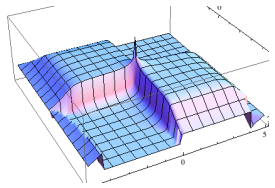
optimal transport theory: algorithms, exact results



xc functionals: approximations, scaling local interpolation, spin



low-dimensional physics: electrons, cold atoms..



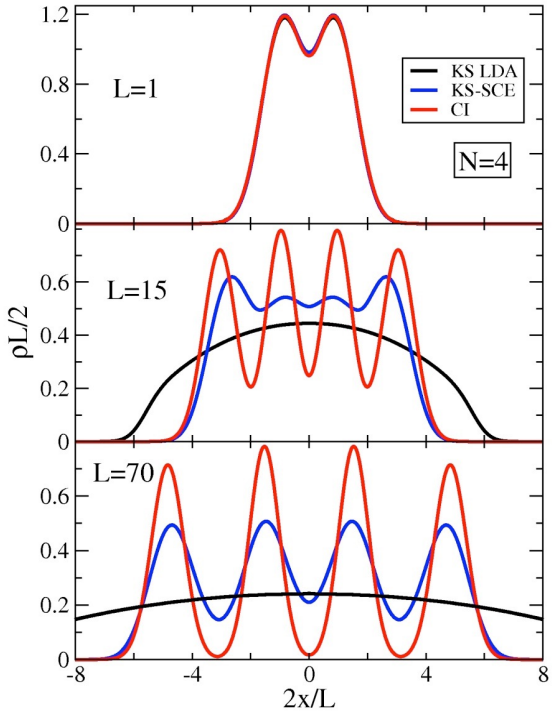
time-dependent: adiabatic SCE kernel, quantum transport

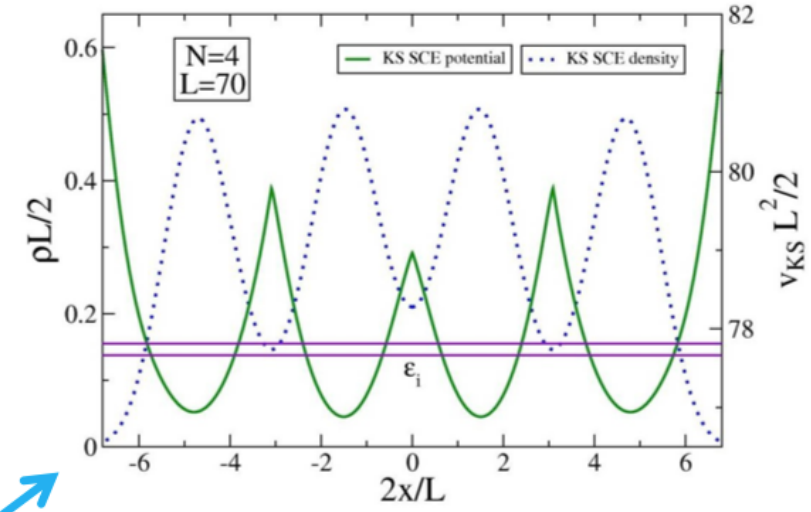
$$\Lambda[\rho] \equiv \max_{\Psi \to \rho} \lambda[\Psi]$$

Lieb-Oxford bound

KS SCE in 1D: $2k_F$ - $4k_F$ crossover without magnetic order

1D harmonic confinement: $v_{\rm ext}(x) = \frac{1}{2}\omega^2 x^2 \quad \omega = \frac{4}{L^2}$ *L*: effective length





Previous attempts include self-interaction corrections (SIC) and GGA:

S. H. Abedinpour, M. Polini, G. Xianlong, and M. P. Tosi, Eur. Phys. J. B 56, 127 (2007)

D. Vieira and K. Capelle, J. Chem. Theory Comput. 6, 3319 (2010)

D. Vieira, Phys. Rev. B 86, 075132 (2012)

Spherically symmetric systems

ansatz: 1D solution for the radial part + relative angles minimization

*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*

not always the lowest solution (it depends on the density)

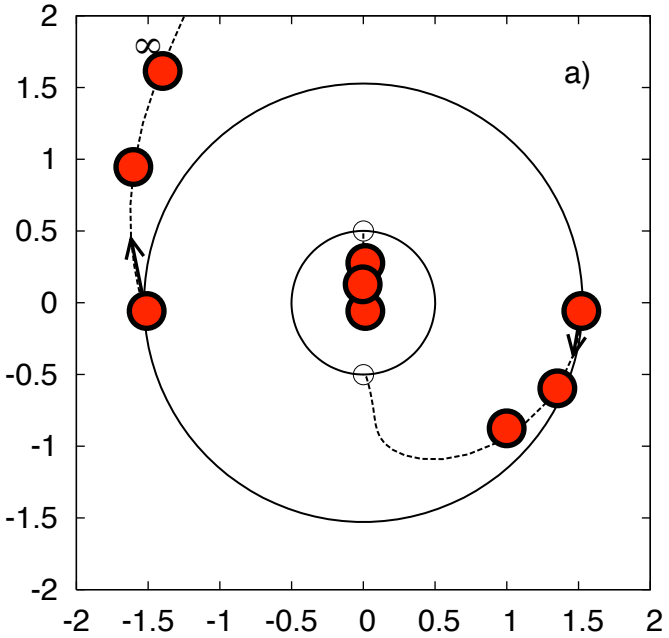
Colombo & Stra, arXiv:1507.08522

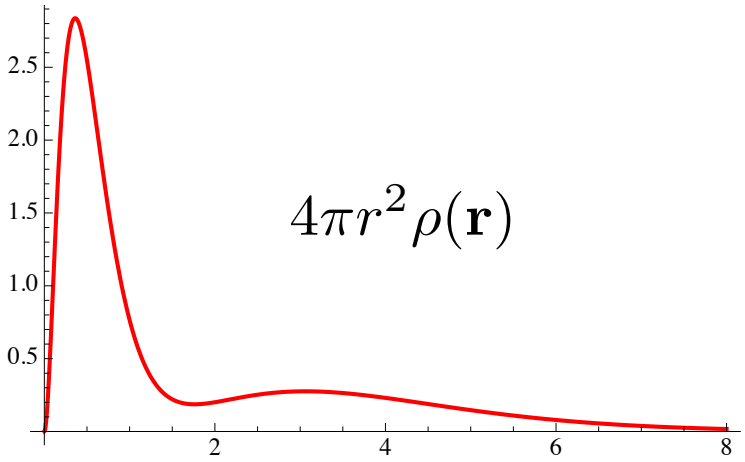
however, the 1D-like solution is very close to the true minimum, and the potential computed from it is the functional derivative of the 1D-like SCE functional

Seidl, Di Marino, Gerolin, Nenna, Giesbertz & Gori-Giorgi, in preparation

$$\nabla v_{\mathrm{SCE}}(\mathbf{r}) = -\sum_{i=2}^{N} \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

Example: solution for the Li atom density



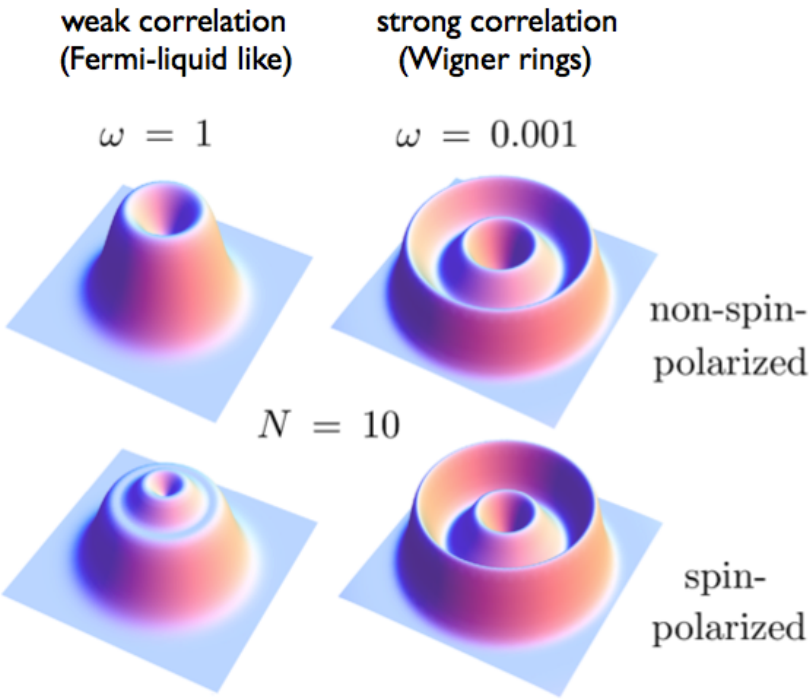


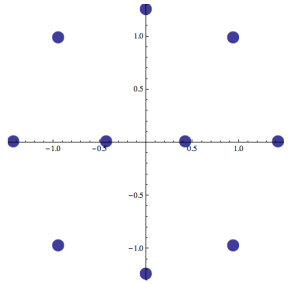
Maximum possible angular and radial correlation in a given density

Spherically symmetric systems: applications

Example: Electrons confined in semiconductor heterostructures

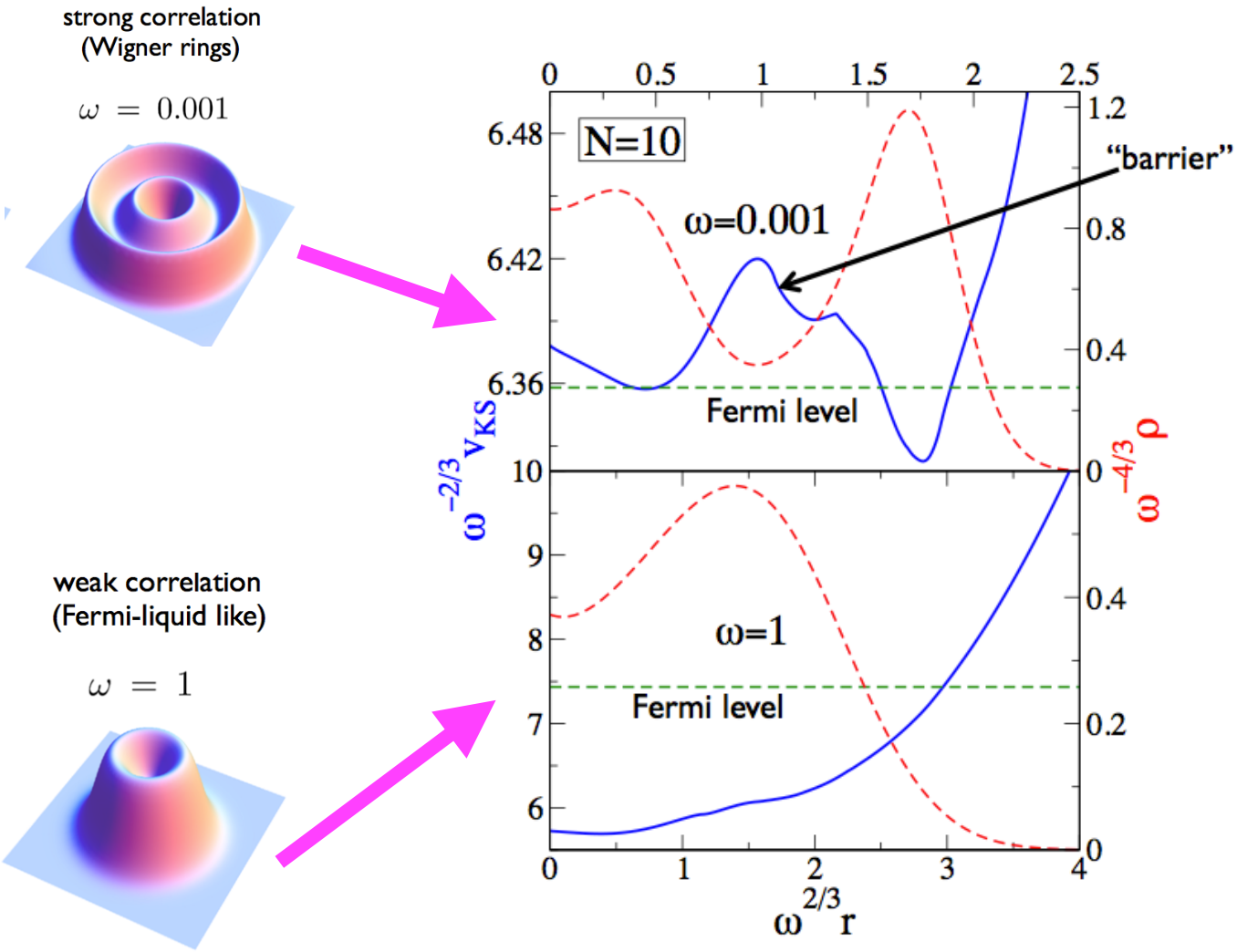
Self-consistent KS densities with the SCE functional





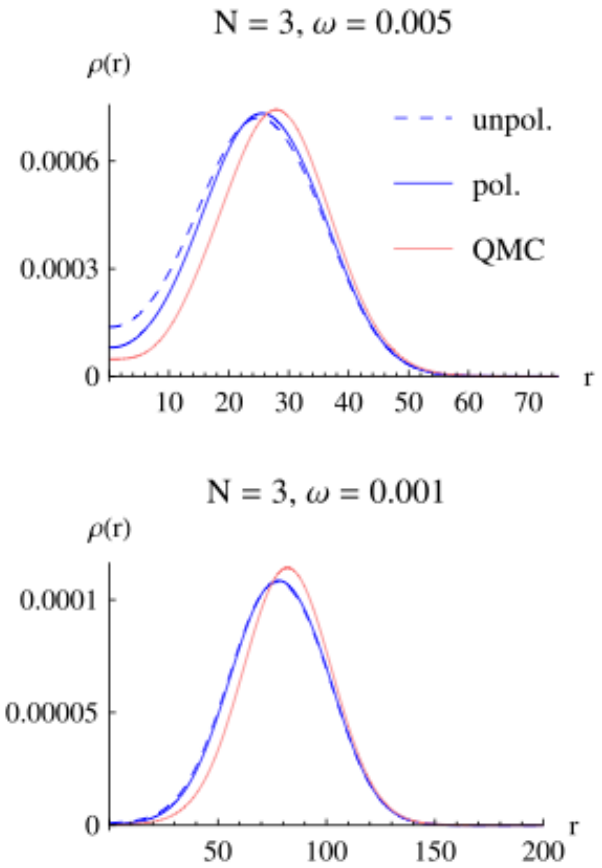
*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

Classically forbidden regions & strong correlation



*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

Accuracy of KS SCE for low-density



energy accuracy
of ~ 1 mH* (~4%)

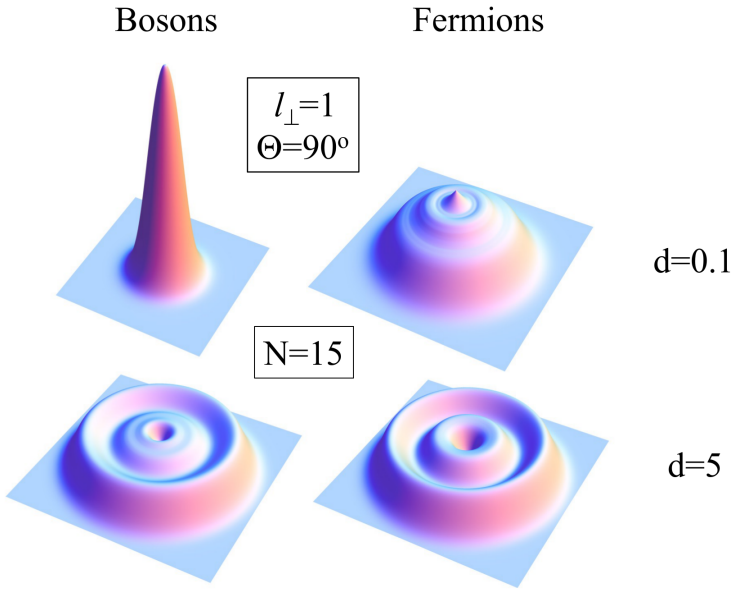
QMC: *D. Guclu and C.J. Umrigar*

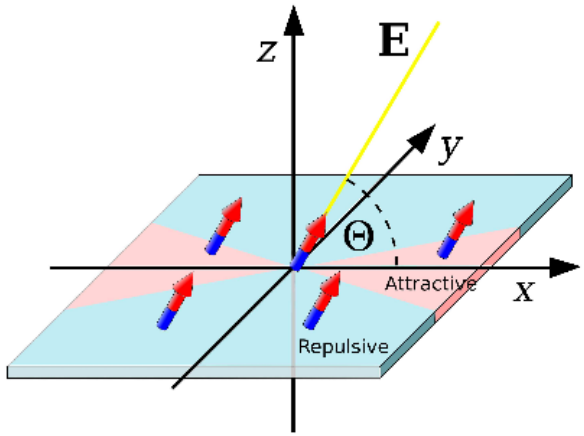
*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

Ultracold dipolar quantum gases

Bosons and fermions: change the kinetic energy functional

Easy to treat tunable interactions with the SCP functional



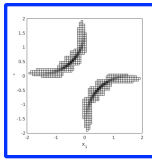


$$V_{\rm int}^{\rm SCP}[n] = \frac{1}{2}\int d\mathbf{r} n(\mathbf{r}) \sum_{i=2}^{N} v_{\rm int}(\mathbf{r} - \mathbf{f}_i(\mathbf{r}))$$

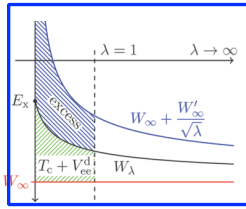
$$\nabla v_{\rm SCP}([n];\mathbf{r}) = \sum_{i=2}^{N} \nabla v_{\rm int}(\mathbf{r} - \mathbf{f}_i(\mathbf{r}))$$

*Malet, Mirtschink, Mendl, Bjerlin, Karabulut, Reimann & PG-G, PRL **115**, 033006 (2015)*

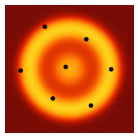
Studying and using the SCE functional



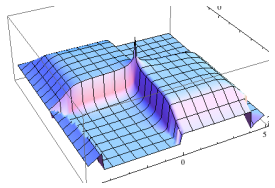
optimal transport theory: algorithms, exact results



xc functionals: approximations, scaling local interpolation, spin



low-dimensional physics: electrons, cold atoms..



time-dependent: adiabatic SCE kernel, quantum transport

$$\Lambda[\rho] \equiv \max_{\Psi \to \rho} \lambda[\Psi]$$

Lieb-Oxford bound

Lieb-Oxford bound

$$W[\Psi] \equiv \langle \Psi | \hat{V}_{ee} | \Psi \rangle - U[\rho_\Psi]$$

$$U[\rho] = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$W[\Psi]$ is bounded from below by its density $\rho_\Psi(\mathbf{r})$

$$W[\Psi] \geq -C_3 \int d^3r \, \rho_\Psi(\mathbf{r})^{4/3}$$

the minimum $C_3 > 0$ that makes the inequality true for all wave functions is not known

a rigorous upper bound for C_3 is known:

$C_3 \leq 1.6358$ *Lieb & Oxford, IJQC 19, 427 (1981); Chan & Handy, PRA 59, 3075 (1999)*

it was believed that a lower bound for C_3 was given by the total energy of the Wigner crystal

$C_3 \geq 1.444$ not rigorous! *Lewin & Lieb, PRA 91, 022507 (2015)*

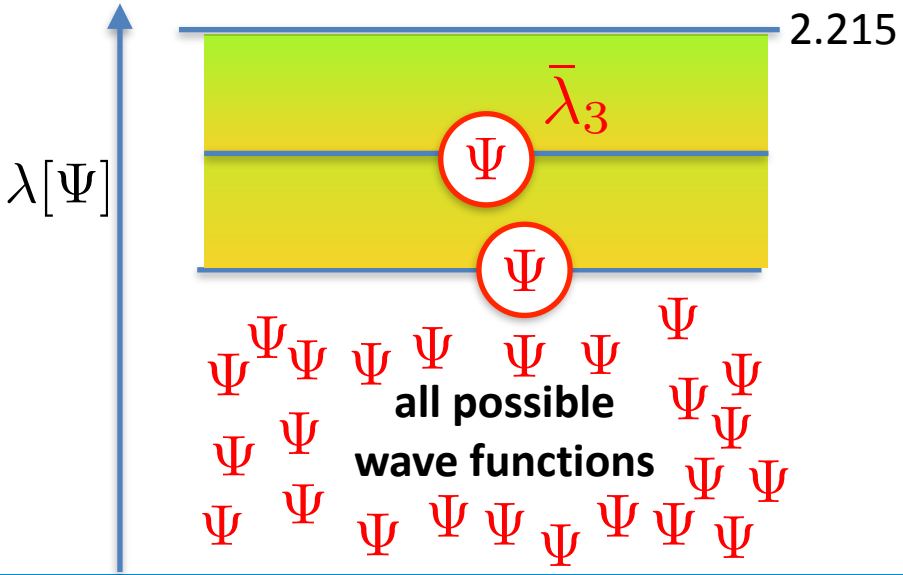
Lieb-Oxford bound in terms of LDA exchange

$$\lambda[\Psi] \equiv \frac{W[\Psi]}{E_{\mathrm{x}}^{\mathrm{LDA}}[\rho_\Psi]}$$

$$E_x^{\mathrm{LDA}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r\ \rho(\mathbf{r})^{4/3}$$

$$\lambda[\Psi] \leq \bar{\lambda}_3 \qquad\qquad \bar{\lambda}_3 = \frac{C_3}{\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}}$$

$\bar{\lambda}_3 \leq 2.215$ *Lieb & Oxford, IJQC 19, 427 (1981); Chan & Handy, PRA 59, 3075 (1999)*



SCE wave functions are the most challenging for the bound: very efficient way to improve the lower bound

Lower bounds from SCE

for any given density, we use the wave function that maximally challenges the bound

$$\Lambda[\rho] \equiv \max_{\Psi\to\rho} \frac{\langle\Psi|\hat{V}_{ee}|\Psi\rangle - U[\rho]}{E_x^{LDA}[\rho]} = \frac{V_{ee}^{SCE}[\rho] - U[\rho]}{E_x^{LDA}[\rho]}$$

$$\lambda[\Psi] = \frac{W[\Psi]}{E_x^{LDA}[\rho_\Psi]}$$ is a wave function functional

$\Lambda[\rho]$ is a density functional

we can search over density instead than wave functions

we can also look at the bound for a given number of particles N

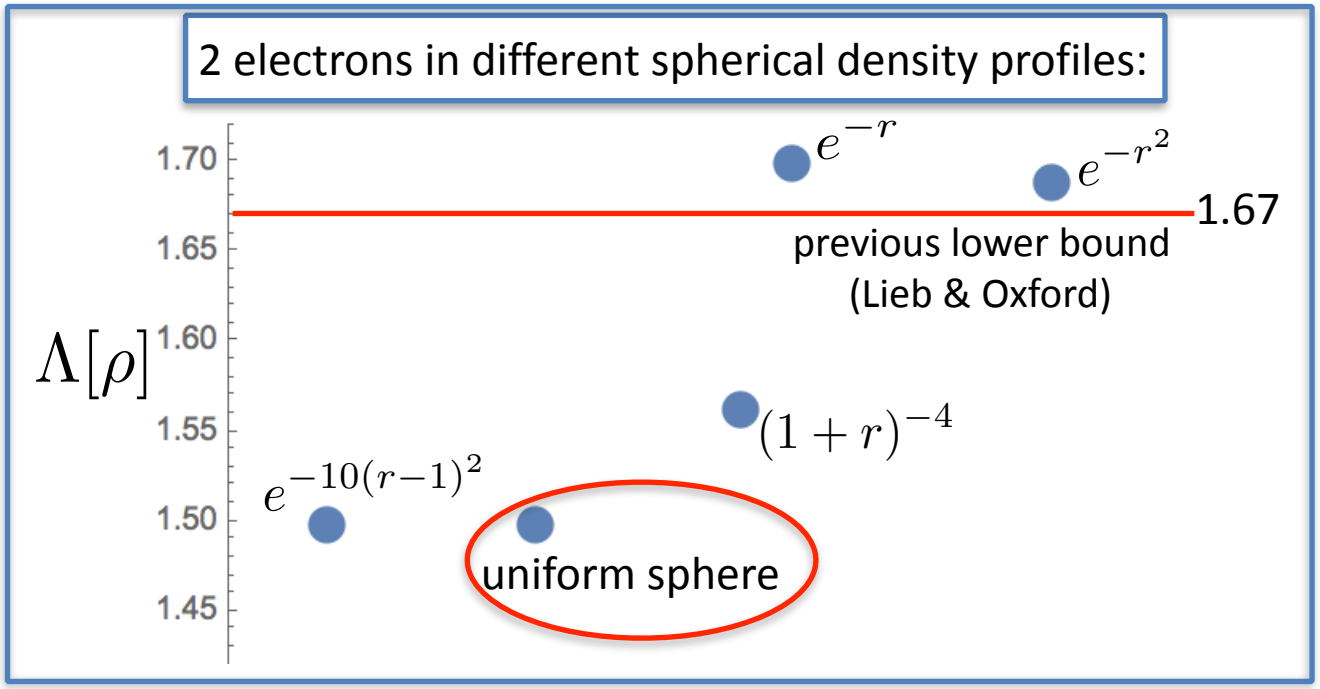
$$\bar{\lambda}_3(N) = \sup_{\Psi\to N} \lambda[\Psi] \qquad \bar{\lambda}_3(N) \le \bar{\lambda}_3(N+1)$$

$$\lim_{N\to\infty} \bar{\lambda}_3(N) = \bar{\lambda}_3$$

Lieb & Oxford, IJQC 19, 427 (1981)

The bound for $N = 2$

Useful for metaGGA functionals (e.g. SCAN) *Sun, Ruzsinszky & Perdew, PRL 115, 036402 (2015)*

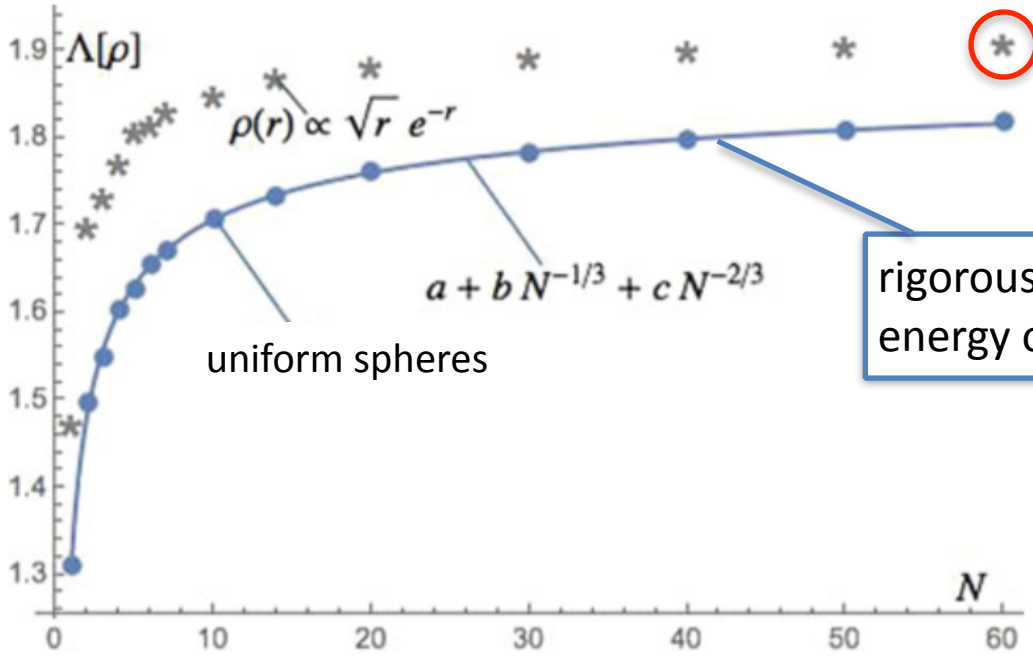


maximising, we find the new lower bound: $\bar{\lambda}_3(2) \geq 1.701052$

a uniform density profile is not the most challenging!

Seidl, Vuckovic & Gori-Giorgi, Mol. Phys., published online (Savin special issue)

The bound for general *N*



1.91175

highest value ever found

uniform spheres

rigorous way to obtain the indirect energy of low-density uniform gas

$$a = 1.918$$

$$1.91175 \leq \bar{\lambda}_3 \leq 2.215$$

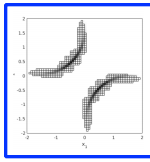
$$1.4119 \leq C_3 \leq 1.6358$$

rigorous bounds

for finite N a uniform density is not the most challenging!

Seidl, Vuckovic & Gori-Giorgi, Mol. Phys., published online (Savin special issue)

Studying and using the SCE functional



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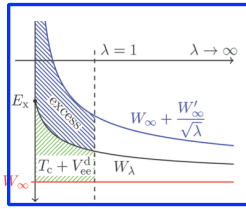

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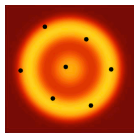

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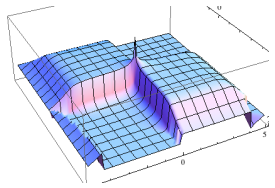


time-dependent: adiabatic SCE kernel, quantum transport

$$\Lambda[\rho] \equiv \max_{\Psi \to \rho} \lambda[\Psi]$$

Lieb-Oxford bound

General 3D geometry: algorithms from optimal transport

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

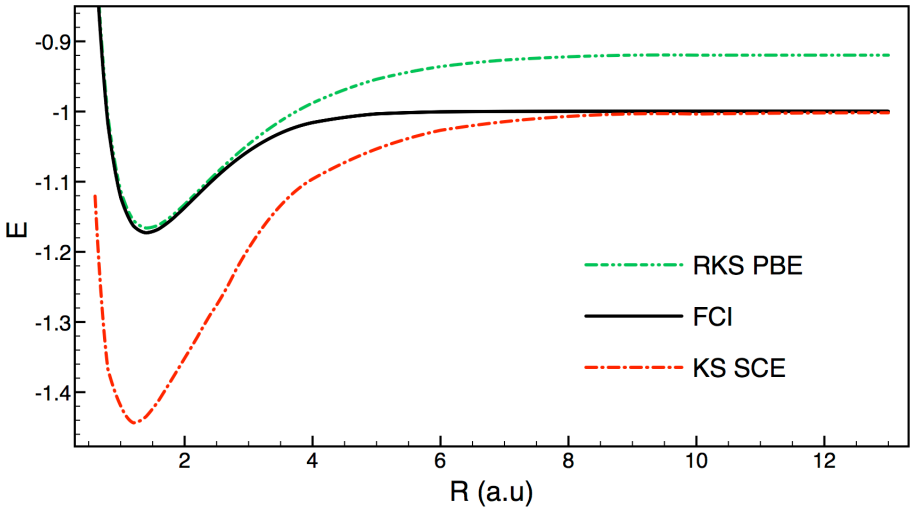
Kantorovich dual formulation (linear programming algorithm)

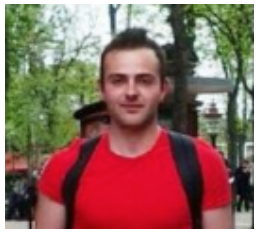
- *Buttazzo, De Pascale, & Gori-Giorgi, Phys. Rev. A. 85, 062502 (2012)*
- *De Pascale, arXiv:1503.07063*
- *Mendl & Lin, Phys. Rev. B 87, 125106 (2013)*

Entropic regularization algorithm

- *Benamou, Carlier, Nenna, arXiv:1505.01136v2*

H_2 molecule (SCE from Kantorovich formulation)





Stefan Vuckovic

-KS SCE dissociates correctly
-horrible at equilibrium and beyond
-higher order terms improve the results

$$F[\rho] = T_s[\rho] + V_{ee}^{\mathrm{SCE}}[\rho] + \boxed{T_c[\rho] + V_{ee}^{d}[\rho]} \geq 0$$

approximated

Vuckovic, Wagner, Mirtschink & Gori-Giorgi, JCTC 11, 3153 (2015)

Approximations to SCE

The SCE non-locality is too extreme

Density Functionals for Coulomb Systems

ELLIOTT H. LIEB

Departments of Mathematics and Physics, Princeton University, P.O.B. 708, Princeton, New Jersey 08544, U.S.A.

exist. Any reader who is devoted to abstract density functional theory, in the spirit of Sec. 3 or (5.8), should try to guess a plausible form for $\tilde{I}(\rho)$. (Proving it is another matter.) It will quickly be seen that $\tilde{I}(\rho)$ must be extremely complicated, and to say that it is "nonlocal" is an understatement. To see this,

however, local, semi-local will not capture self-consistently the right physics

A simple approximation with (some) non locality

$$\int_{\Omega(\mathbf{r})} \rho(\mathbf{r}')d\mathbf{r}' = 1$$

in each point of space, define a radius such that the density integrates to 1 (spherically)

Lucas Wagner

use it to approximate the SCE exchange-correlation hole:

$$w_\infty(\mathbf{r}) = -\frac{1}{2}\int_{\Omega(\mathbf{r})} d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

local interpolation between weak (exchange) and strong correlation

see also recent work by H. Bahman, M. Ernzerhof, J. Precechtelova, M. Kaupp,...

*Wagner & PG-G, PRA **90**, 052512 (2014)*

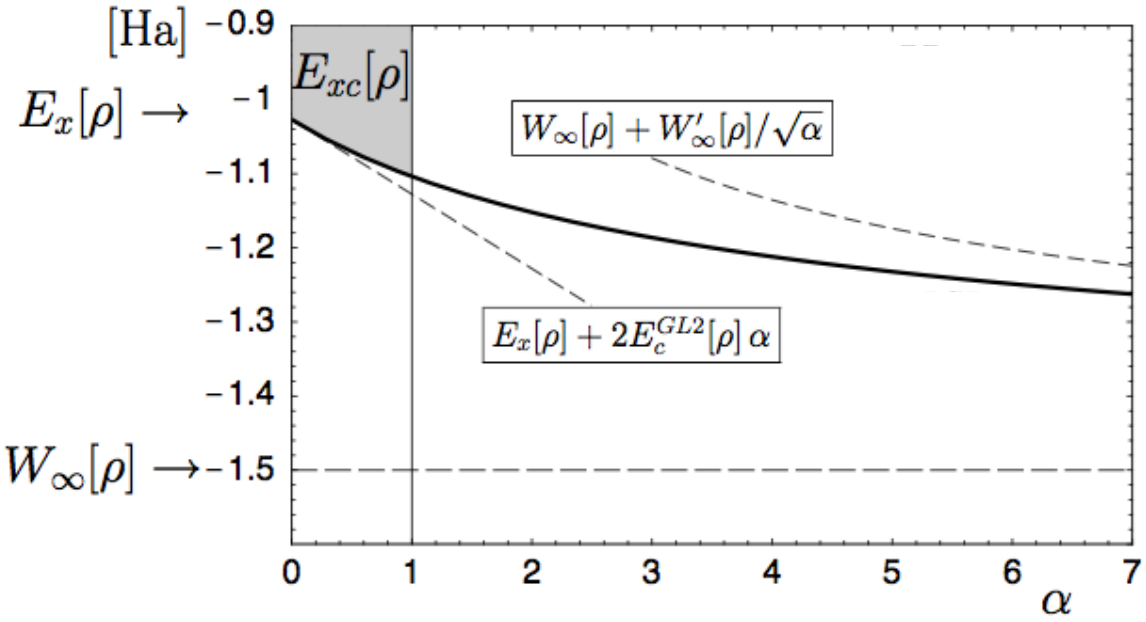
Construction of exchange-correlation functionals through interpolation between the non-interacting and the strong-correlation limit

Yongxi Zhou,[1] Hilke Bahmann,[2] and Matthias Ernzerhof[1,a)]
[1]*Département de Chimie, Université de Montréal, C.P. 6128, Succursale A, Montréal, Québec H3C 3J7, Canada*
[2]*Department of Chemistry, Technische Universität Berlin, Strasse des 17 Juni, Berlin, Germany*

(Received 12 March 2015; accepted 7 September 2015; published online 23 September 2015)

Drawing on the adiabatic connection of density functional theory, exchange-correlation functionals of Kohn-Sham density functional theory are constructed which interpolate between the extreme limits of the electron-electron interaction strength. The first limit is the non-interacting one, where there is only exchange. The second limit is the strong correlated one, characterized as the minimum of the electron-electron repulsion energy. The exchange-correlation energy in the strong-correlation limit is approximated through a model for the exchange-correlation hole that is referred to as nonlocal-radius model [L. O. Wagner and P. Gori-Giorgi, Phys. Rev. A **90**, 052512 (2014)]. Using the non-interacting and strong-correlated extremes, various interpolation schemes are presented that yield new approximations to the adiabatic connection and thus to the exchange-correlation energy. Some of them rely on empiricism while others do not. Several of the proposed approximations yield the exact exchange-correlation energy for one-electron systems where local and semi-local approximations often fail badly. Other proposed approximations generalize existing global hybrids by using a fraction of the exchange-correlation energy in the strong-correlation limit to replace an equal fraction of the semi-local approximation to the exchange-correlation energy in the strong-correlation limit. The performance of the proposed approximations is evaluated for molecular atomization energies, total atomic energies, and ionization potentials.

Global interpolations



$$\alpha = \lambda$$

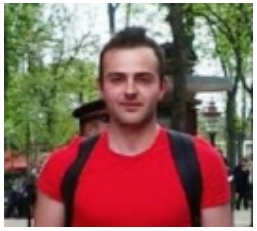
not size consistent

M. Seidl, J.P. Perdew, M. Levy PRA 59, 51 (1999)
Seidl, Perdew & Kurth, Phys. Rev. Lett. 84, 5070 (2000)

Local interpolations along the adiabatic connection

Global interpolations violate size consistency: turn to local interpolation

$$E_{xc}[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r})\, \epsilon_{xc}(\mathbf{r})$$



Stefan Vuckovic

$$\epsilon_{xc}(\mathbf{r}) = \int_0^1 w_\lambda(\mathbf{r}) d\lambda$$

Tom Irons
Andy Teale

All the ingredients should be in the same “gauge”

The xc hole potential gauge

$$\epsilon_{xc}(\mathbf{r}) = \int_0^1 w_\lambda(\mathbf{r}) d\lambda \qquad E_{xc}[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r})\, \epsilon_{xc}(\mathbf{r})$$

$$P_2^\lambda(\mathbf{r},\mathbf{r}') = N(N-1) \sum_{\sigma_1,\ldots,\sigma_N} \int |\Psi_\lambda(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, \mathbf{r}_3\sigma_3, \ldots, \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_3 \ldots d\mathbf{r}_N$$

$$h_{xc}^\lambda(\mathbf{r},\mathbf{r}') = \frac{P_2^\lambda(\mathbf{r},\mathbf{r}')}{\rho(\mathbf{r})} - \rho(\mathbf{r}') \qquad w_\lambda(\mathbf{r}) = \frac{1}{2}\int \frac{h_{xc}^\lambda(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$w_\lambda(|\mathbf{r}| \to \infty) \sim -\frac{1}{2|\mathbf{r}|} \qquad \epsilon_{xc}(|\mathbf{r}| \to \infty) \sim -\frac{1}{2|\mathbf{r}|}$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\rho(\mathbf{r})} \sim -\frac{1}{|\mathbf{r}|} \qquad w_{\lambda\to 0}(\mathbf{r}) \to \epsilon_x(\mathbf{r})$$

The SCE xc energy density in the xc hole potential gauge

$$|\psi(\mathbf{r}_1,...,\mathbf{r}_N)|^2 = \frac{1}{N!}\sum_P \int d\mathbf{s}\ \frac{\rho(\mathbf{s})}{N}\delta(\mathbf{r}_1 - \mathbf{f}_{P(1)}(\mathbf{s}))...\delta(\mathbf{r}_N - \mathbf{f}_{P(N)}(\mathbf{s}))$$

$$P_2^{\mathrm{SCE}}(\mathbf{r},\mathbf{r}') = \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \int d\mathbf{s}\frac{\rho(\mathbf{s})}{N}\delta(\mathbf{r} - \mathbf{f}_i(\mathbf{s}))\delta(\mathbf{r}' - \mathbf{f}_j(\mathbf{s}))$$

$$w_\infty(\mathbf{r}) = \frac{1}{2}\sum_{k=2}^{N}\frac{1}{|\mathbf{r} - \mathbf{f}_k(\mathbf{r})|} - \frac{1}{2}v_H(\mathbf{r})$$

$$w_\lambda(|\mathbf{r}| \to \infty) \sim -\frac{1}{2|\mathbf{r}|}$$

xc SCE satisfies both

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\rho(\mathbf{r})} \sim -\frac{1}{|\mathbf{r}|}$$

$$\nabla(v_{xc}^{\mathrm{SCE}}(\mathbf{r}) + v_H(\mathbf{r})) = -\sum_{i=2}^{N}\frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

Mirtschink, Seidl, PG-G, JCTC 8, 3097 (2012)

How to get a local slope (in the right gauge)?

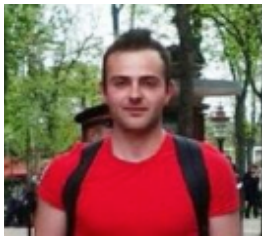
First step: compute the exact slope for small systems

A. Teale

$$F_\lambda[\rho] = \sup_v \left(E_\lambda[v] - \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r}\right)$$

- Use WFT approaches to compute $E[v]$ and input the physical density ρ for all λ

local interpolation using exact ingredients...



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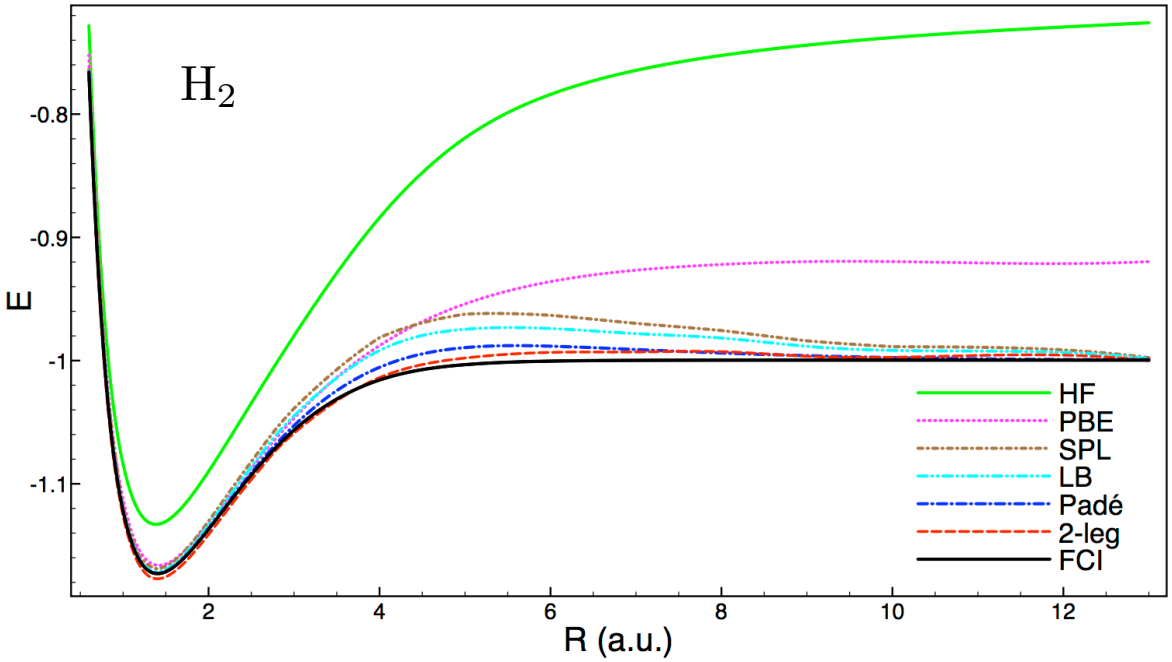
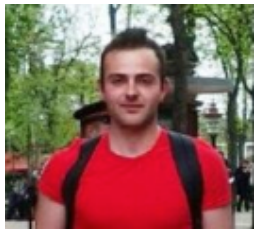
Interpolating locally using exact ingredients



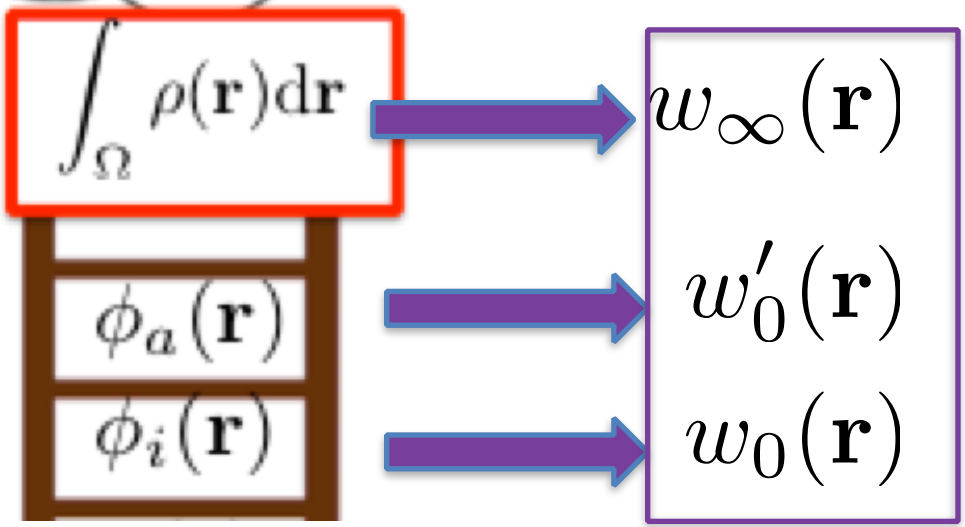


Stefan Vuckovic

$$E_{\mathrm{xc}}[\rho] = \int_0^1 \int \rho(\mathbf{r}) w_{\mathrm{xc},\lambda}(\mathbf{r})\, \mathrm{d}\mathbf{r}\, \mathrm{d}\lambda,$$

Vuckovic, Irons, Savin, Teale & Gori-Giorgi, JCTC submitted

Heaven of Chemical Accurancy



Where?

Non-local radius approximation (**NLR**) available in **Gaussian, Turbomole**

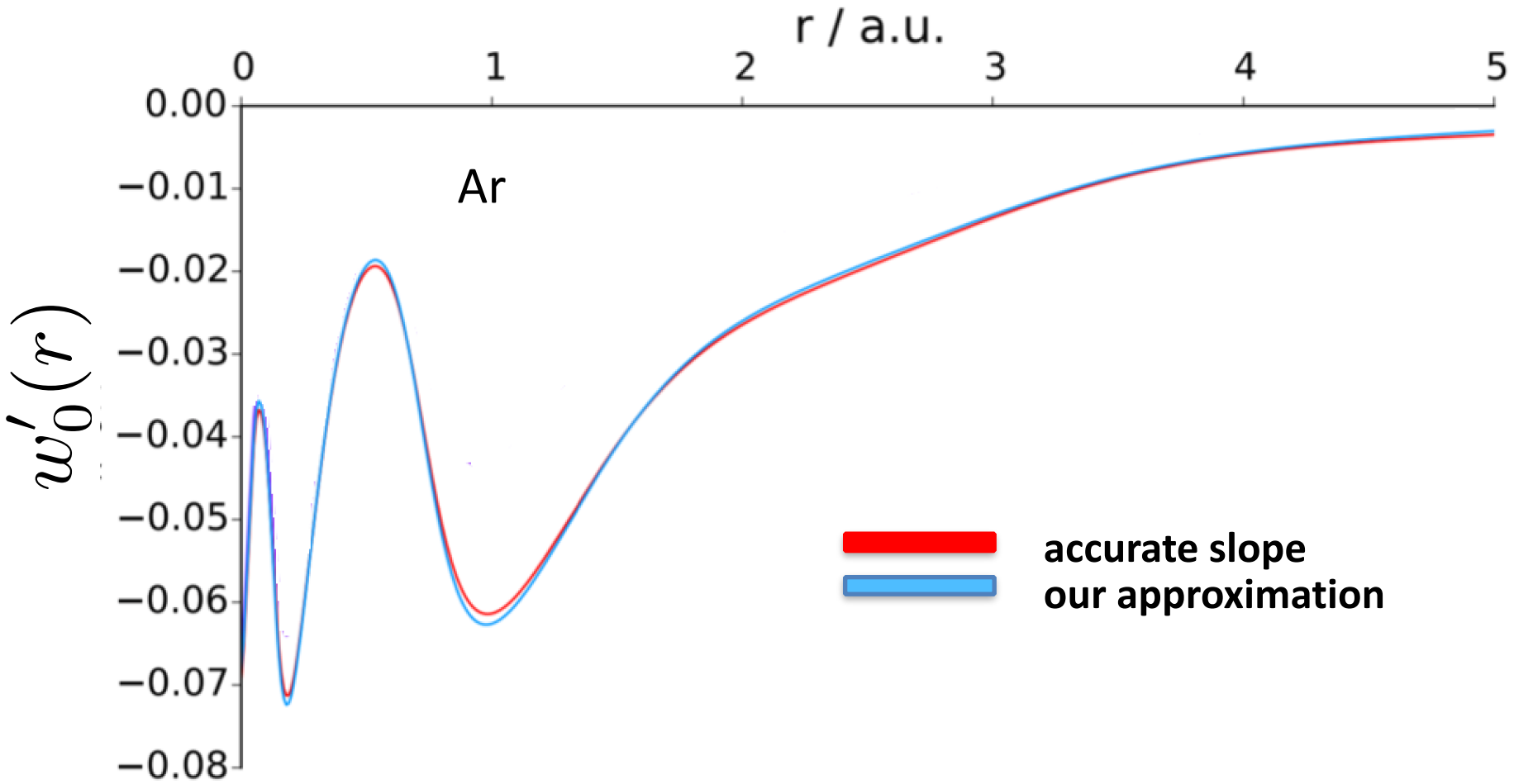
We derived it in terms of KS orbitals arxiv: 1602.05434

Efficient implementation in **Turbomole**

All in the XC hole gauge!

The local slope

$$E_c^{\mathrm{GL2}} \approx E_c^{\mathrm{MP2}}$$



The accurate and approximate local slopes (computed with LDA orbitals) for the argon atom

Courtesy of Andrew Teale and Tom Irons

SCE adiabatic kernel for one-dimensional systems

Giovanna Lani
Simone Di Marino
Augusto Gerolin
Robert van Leeuwen

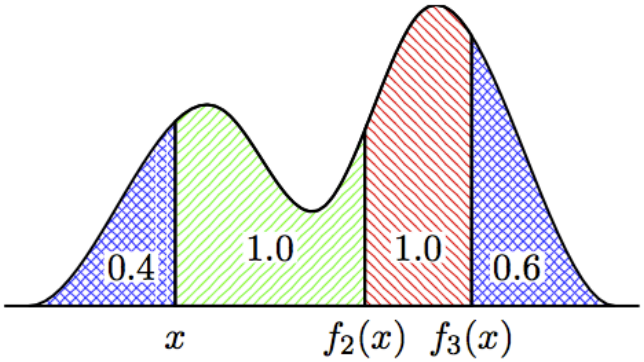
$$\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];\mathbf{r},\mathbf{r}') = \frac{\delta^2 V_{ee}^{\mathrm{SCE}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}$$

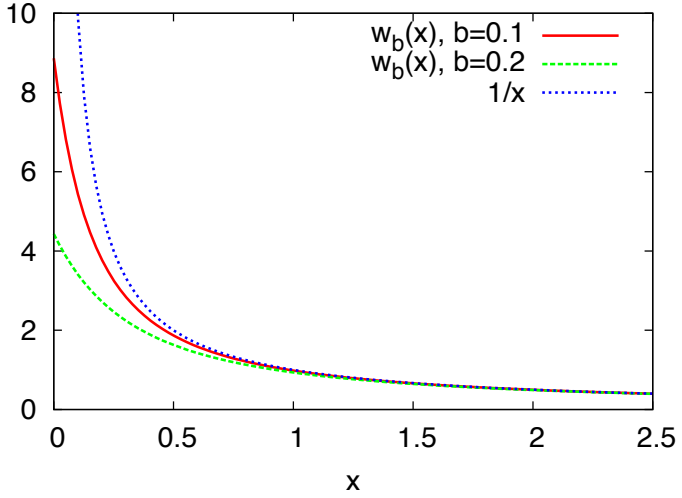
Giovanna Lani

N.B.: $\rho(\mathbf{r}) \to n(\mathbf{r})$ density

1D hamiltonians

$$H_{1D} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\frac{\partial^2}{\partial x_i^2} + \sum_{i=1}^{N}\sum_{j>i}^{N} w_b(|x_i - x_j|) + \sum_{i=1}^{N} v_{\rm ext}(x_i)$$





$$v_{\rm Hxc}^{\rm SCE}([n];x) = -\sum_{i=2}^{N}\int_{x}^{\infty} w'(|\,y - f_i([n];y)|) \times {\rm sgn}(\,y - f_i([n];y))\,{\rm d}y.$$

$$\mathcal{F}_{\rm Hxc}^{\rm SCE}([n];x,x') = \frac{\delta v_{\rm Hxc}^{\rm SCE}([n];x)}{\delta n(x')}$$

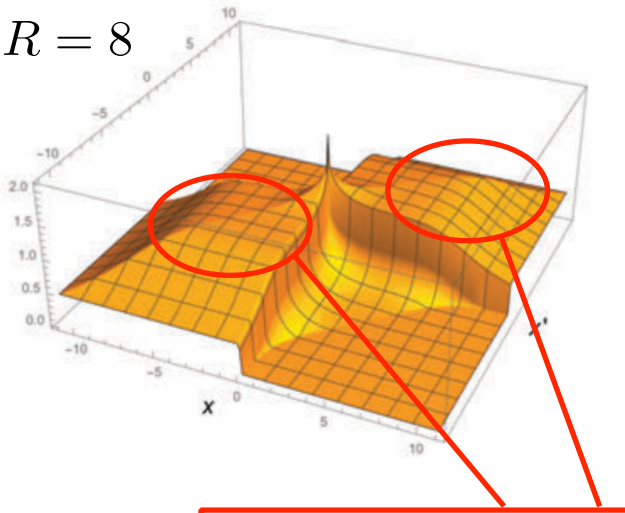
we can analyse the kernel analytically

1D SCE kernel

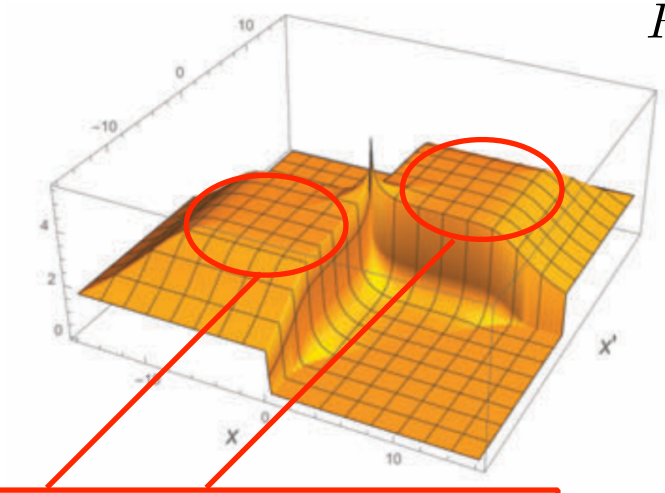
$$\mathcal{F}_{\rm Hxc}^{\rm SCE}([n];x,x') = \sum_{i=2}^{N} \int_x^{\infty} \frac{w''(|y - f_i([n];y)|)}{n(f_i([n];y))} \left[\theta(y-x') - \theta(f_i([n];y) - x')\right] dy$$

example: model homonuclear dissociation $n(x) = \frac{a}{2}\left(\mathrm{e}^{-a\left|x-\frac{R}{2}\right|} + \mathrm{e}^{-a\left|x+\frac{R}{2}\right|}\right)$

$R = 8$



$R = 12$



plateau regions around each atom of size $\approx R \times R$

plateau height:

$$\approx \frac{1}{n(0)(R - 1/a)^2}$$

density in the midbond: the height diverges as R increases

Analysis of the divergence

$$^1\Sigma_g \rightarrow {}^1\Sigma_u$$ excitation to the lowest singlet state in H_2

Gritsenko, van Gisbergen, Gorling & Baerends, J. Chem. Phys., 113, 8478 (2000)
Giesbertz & Baerends Chem. Phys. Lett., 461, 338 (2008)

$$(\epsilon_u - \epsilon_g) \int dx \int dx' \sigma_g(x)\sigma_u(x)\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x')\sigma_g(x')\sigma_u(x')$$

goes to zero
as R gets larger

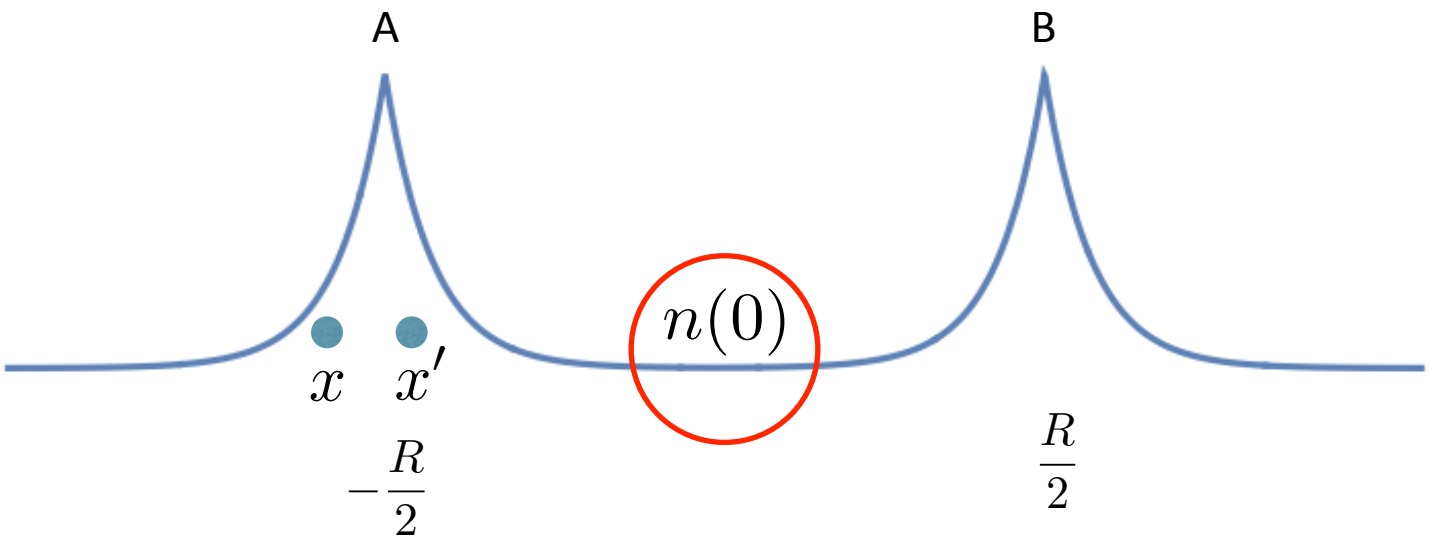
$$\int \mathrm{d}x \int \mathrm{d}x' |\phi_{\mathrm{A}}(x)|^2 \mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x')|\phi_{\mathrm{A}}(x')|^2 \approx \frac{1}{n(0)(R-1/a)^2}.$$

the divergence appears in the atomic regions, due to the presence of another distant atom (highly non-local dependence on the density)

Analysis of the divergence

$$\int dx \int dx' |\phi_A(x)|^2 \mathcal{F}_{Hxc}^{SCE}([n]; x, x') |\phi_A(x')|^2 \approx \frac{1}{n(0)(R - 1/a)^2}.$$

the divergence appears in the atomic regions, due to the presence of another distant atom (highly non-local dependence on the density)



Lani, Di Marino, Gerolin, van Leeuwen & Gori-Giorgi, PCCP, published online (Baerends special issue)

Challenges/Perspectives

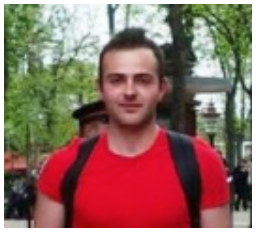
- SCE limit “too far”: kinetic correlation needed

Sara Giarrusso

- inclusion of spin: a natural framework to import lattice results to the continuum

Juri Grossi

- local interpolations along the adiabatic connection



Stefan Vuckovic

Derk Kooi

- insight to construct new xc kernel for TD DFT

Klaas Giesbertz

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MARIE CURIE ACTIONS

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Thank you for your attention!