Kohn-Sham density functional theory for strong-interacting systems

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Outline

• The exact strong-interacting limit (SCE) of DFT as an approximation for the exchange-correlation energy

• Self-consistent KS SCE results for model quantum wires and quantum dots

• Generalization to open systems with fluctuating particle number

• Chemistry

• Monge-Kantorovich formulation of the SCE functional
Example: two electrons (singlet) in 1D harmonic confinement

\[ v_{\text{ext}}(x) = \frac{1}{2} \omega^2 x^2 \]

\[ \omega = \frac{4}{L^2} \]

\( L \): effective length

Weak correlation (small \( L \))

Strong correlation (large \( L \))
Kohn-Sham potential:

“Bump” in the exact KS potential: localization


The “bump” is missing in the KS LDA potential: delocalized density
Stretched bond, e.g. \( \text{H}_2 \) molecule

Stretched bond, e.g. H$_2$ molecule

exact KS potential localizes more: “bump” in the midpoint

Unrestricted KS & strong correlation...

- Like UHF, UKS can mimic strong correlation (not always!)
- Often better energies, but wrong characterizations of several properties
- Formally not well founded
- Huge literature: controversial, wrong interpretation, etc...
- Crucial for: transition metals, Mott insulators, bond breaking, nanostructures,...
Exchange-correlation from the strong-interaction limit of DFT:

The “bumps” in the KS potential from the right physics (no spin/spatial-symmetry breaking)
Kohn-Sham DFT:

\[ F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \to \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho] \]
Kohn-Sham DFT:

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\[ T_S[\rho] \]

(known) (unknown)
Hohenberg-Kohn functional

Kohn-Sham DFT:

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

Kohn-Sham equations:

\[ \left(-\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](r)\right) \phi_i(r) = \varepsilon_i \phi_i(r) \]

\[ v_{\text{KS}}[\rho] = v_{\text{ext}}[\rho] + v_{\text{Hartree}}[\rho] + v_{\text{xc}}[\rho] \]

\[ \rho(r) = \sum_i |\phi_i(r)|^2 \]
Hohenberg-Kohn functional

Kohn-Sham DFT:

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Our approach:

\[ \approx \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle + \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle \]
Hohenberg-Kohn functional

Kohn-Sham DFT:

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\[ T_s[\rho] \quad V_{ee}^{\text{SCE}}[\rho] \]

Strictly-correlated-electrons (SCE) DFT:

- M. Seidl, PRA 60, 4387 (1999)

e-e interaction energy of system with zero kinetic energy and density \( \rho \) (SCE reference system)
Hohenberg-Kohn functional

Kohn-Sham DFT:

\[
F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \min_{\Psi \to \rho} \langle \Psi | \hat{T} | \Psi \rangle + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]
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Our approach:

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\]

\[
V_{ee}^{\text{SCE}}[\rho]
\]

\[
v_{\text{SCE}}[\rho] \simeq v_{\text{Hartree}}[\rho] + v_{\text{xc}}[\rho]
\]

\[
 \left( -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})
\]

\[
v_{\text{KS}}[\rho] = v_{\text{ext}}[\rho] + v_{\text{SCE}}[\rho]
\]

\[
v_{\text{SCE}}[\rho] = \frac{\delta V_{ee}^{\text{SCE}}[\rho]}{\delta \rho}
\]
Strictly-interacting-electrons (SCE) DFT

The SCE reference system:

- For a given smooth density $\rho(r)$:
  \[ \rho(f_i(r))df_i(r) = \rho(r)dr \quad (1) \]

- A local one-body potential can be defined:
  \[ -\nabla v_{SCE}[\rho](r) = F_{\text{Coul}}(r) = \sum_{i=2}^{N} \frac{r - f_i[\rho](r)}{|r - f_i[\rho](r)|^3} \quad (2) \]

KS-SCE approach:

1. Integrate (1) to obtain the co-motion functions $f_i(r)$
2. Integrate (2) to obtain the potential $v_{SCE}(r)$
3. Approximate the $H_{xc}$ potential of KS DFT with $v_{SCE}(r)$

\[ v_{SCE}[\rho] \simeq v_{\text{Hartree}}[\rho] + v_{xc}[\rho] \]
\[
\rho(f_i(r)) df_i(r) = \rho(r) dr
\]

\[
f_1(r) \equiv r, \quad f_2(r) \equiv f(r), \quad f_3(r) = f(f(r)), \quad f_4(r) = f(f(f(r))), \ldots \text{ with } f(f(\ldots f(f(r)))) = r \text{ } N \text{ times}
\]

\[
V_{ee}^{\text{SCE}}[\rho] = \int dr \frac{\rho(r)}{N} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{|f_i(r) - f_j(r)|}
\]

\[
\frac{\delta V_{ee}^{\text{SCE}}[\rho]}{\delta \rho(r)} = v_{\text{SCE}}(r)
\]
\[
\rho(f_i(r)) \, df_i(r) = \rho(r) \, dr
\]

\(f_1(r) \equiv r, \ f_2(r) \equiv f(r), \ f_3(r) = f(f(r)), \ f_4(r) = f(f(f(r))), \ldots \) with \(f(f(\ldots f(f(r))) = r\) \(N\) times

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\]

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

\[
\nabla v_{\text{SCE}}(r) = \sum_{i=2}^{N} \frac{r - f_i(r)}{|r - f_i(r)|^3}
\]

shortcut to the functional derivative

\(F.\ Malet.\ et\ al.,\ PRB\ 87\ 115146\ (2013)\)
The self-consistent KS SCE total energy is a rigorous lower bound to the exact energy.
The self-consistent KS SCE total energy is a rigorous lower bound to the exact energy.

The proof is trivial (minimum of a sum is always larger than the sum of the minima; self-consistency lowers the energy).
First tests: quasi 1D systems

\[ V_\perp(y, z) = \frac{1}{2} m \omega_\perp^2 (y^2 + z^2) \]

\[ b^2 = \frac{\hbar}{2m \omega_\perp} \]

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

\[ w_b(x) = \frac{\sqrt{\pi}}{2} \frac{e_x^2}{b} e^{x^2/4b^2} \text{erfc} \left( \frac{x}{2b} \right) \]

Bednarek et al. PRB 68, 045328 (2003)

LDA: Casula, Sorella & Senatore PRB 74, 245427 (2006)
Electrons confined in (quasi) 1D

Co-motion functions:

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

\[ N_e(x) = \int_{-\infty}^{x} \rho(x') \, dx' \quad a_k = N_e^{-1}(k) \]

\[ v'_{\text{SCE}}[\rho](x) = -\sum_{i=2}^{N} w'_b(|x - f_i(x)|) \text{sgn}(x - f_i(x)) \]

Applications to 1D systems

1D harmonic confinement: \( v_{\text{ext}}(x) = \frac{1}{2} \omega^2 x^2 \) \( \omega = \frac{4}{L^2} \). \( L \): effective length

- Qualitatively good results in both the weak and strong correlation regimes

*F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet et al., PRB 87 115146 (2013)*
Applications to 1D systems

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

- Qualitatively good results in both the weak and strong correlation regimes
- Tends to the exact result in the very strongly-interacting limit

_F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet et al., PRB 87 115146 (2013)_
Applications to 1D systems

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

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Applications to 1D systems

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F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet. et al., PRB 87 115146 (2013)
KS SCE is the first KS DFT approach able to capture the density peak splitting in quasi 1D without introducing magnetic order.

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


## Total Energies

<table>
<thead>
<tr>
<th>$N$</th>
<th>$L$</th>
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CI matrix $10^5$ - $10^6$

*F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet et al., PRB 87 115146 (2013)*
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CI matrix $10^5 - 10^6$

KS SCE is a rigorous lower bound to the exact ground-state energy

*F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet. et al., PRB 87 115146 (2013)*
Ionization potentials from minus HOMO

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F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet. et al., PRB 87 115146 (2013)
Generalization to open systems: The Derivative Discontinuity at integer particle numbers
What exact spin-restricted KS should do

\[ \Delta_{xc} = I - A \]

[Diagram showing energy levels for N-electron open and closed shell systems]
What exact spin-restricted KS should do

What approximate functionals do (UKS)

\[ \Delta_{xc} = I - A \]

Vydrov, Scuseria & Perdew, JCP 126, 154109 (2007)
SCE for fractional particle numbers

\[ \int_{f_i(x)}^{f_{i+1}(x)} \rho(y) dy = 1 \]
\[ \int_{f_i(x)}^{f_{i+1}(x)} \rho(y) \, dy = 1 \]
co-motion functions for \( N + \eta \) electrons

\[
f_i(x) = \begin{cases} 
N_e^{-1}[N_e(x) + 2i] & x < a_{N-2i+\eta} \\
N_e^{-1}[|N_e(x) - 2(N + 1 - i)|] & x > a_{N+2-2i-\eta} \\
\infty & \text{otherwise},
\end{cases}
\]

get the SCE potential by integrating

\[
v'_\text{SCE}[\rho](x) = - \sum_{i=2}^{N} w'_b(|x - f_i(x)|)\text{sgn}(x - f_i(x))
\]

with boundary condition

\[
v_{\text{SCE}}[\rho](x \to \infty) = 0
\]
Self-consistent KS HOMO eigenvalue

quasi 1D

Self-consistent KS HOMO eigenvalue

Applications to 1D systems

1D harmonic confinement:

\[ v_{\text{ext}}(x) = \frac{1}{2} \omega^2 x^2 \quad \omega = \frac{4}{L^2} \quad \text{L: effective length} \]

- KS-SCE allows to treat large strongly-correlated quasi 1D systems (vs CI, limited to 6-8 particles, QMC and DMRG ~ 100 electrons).

- Computational time similar to KS LDA calculations

- Applications in Physics (model semiconductor quantum wires; nanotransport, quantum computation, ...)

F. Malet and P. Gori-Giorgi, PRL 109 246402 (2012); F. Malet et al., PRB 87 115146 (2013)
Electrons confined in two dimensions

\[ \hat{H} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{\omega^2}{2} \sum_{i=1}^{N} r_i^2 \]

Self-consistent KS SCE density

\[ N = 6 \quad \omega = 0.005 \]

C. B. Mendl (Munich Technical University)
F. Malet
What about Chemistry?
1D as a test lab for 3D chemistry

Reference electronic structure calculations in one dimension†

Lucas O. Wagner,* E. M. Stoudenmire,‡ Kieron Burke* and Steven R. White*

Received 24th December 2011, Accepted 1st May 2012
DOI: 10.1039/c2cp24118h

THE JOURNAL OF CHEMICAL PHYSICS 131, 224105 (2009)

Exact Kohn–Sham potential of strongly correlated finite systems

N. Helbig,† I. V. Tokatly,‡ and A. Rubio†

Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, San Sebastián E-20018, Spain

Physical Review A 83, 032503 (2011)

Density functional theory beyond the linear regime: Validating an adiabatic local density approximation

N. Helbig, J. I. Fuks, M. Casula, M. J. Verstraete, M. A. L. Marques, I. V. Tokatly, and A. Rubio

\[ w_s(x) = \frac{1}{\sqrt{x^2 + a^2}} \]
Applications to 1D systems

1D model for $H_2$:

![Graph showing total energies for different models](image-url)
Negative ions (3D)

\[ N = 2 \quad v_{\text{ext}}(\mathbf{r}) = -\frac{Z}{r} \]

\[ Z \rightarrow Z_{\text{crit}} \approx 0.9110289 \quad \text{the system loses 1 electron} \]

accurate results
(C. Umrigar & J. Morgan)
Negative ions (3D)

\[ N = 2 \quad v_{\text{ext}}(r) = -\frac{Z}{r} \]

\[ Z \rightarrow Z_{\text{crit}} \approx 0.9110289 \quad \text{the system looses 1 electron} \]

KS SCE self-consistent: \[ Z_{\text{crit}} \approx 0.73 \]
Negative ions (3D)

\[ N = 2 \quad \nu_{\text{ext}}(\mathbf{r}) = -\frac{Z}{r} \]

\[ Z \rightarrow Z_{\text{crit}} \approx 0.9110289 \quad \text{the system looses 1 electron} \]

KS SCE + local correction (self-consistent):

\[ Z_{\text{crit}} \approx 0.94 \]

A. Mirtschink
How to treat general 3D systems?

Monge-Kantorovich formulation


*see also talk by Gero Friesecke!*
Optimal transport formulation

(Monge-Kantorovich)

\[ \int \rho_1(r) \, dr = \int \rho_2(r) \, dr \]

\begin{align*}
\text{cost function (work necessary to move a unit mass)} \\
c(r_1, r_2) &= |r_2 - r_1|
\end{align*}
Optimal transport formulation
(Monge-Kantorovich)

\[ \int \rho_1(r) \, dr = \int \rho_2(r) \, dr \]

cost function (work necessary to move a unit mass)
\[ c(r_1, r_2) = |r_2 - r_1| \]

minimize total cost  \( \Rightarrow \)  \( \min \int c(r, f(r))\rho_1(r) \, dr \)

optimal map
\[
\min_P \left\{ \int c(x_1, \ldots, x_N) P(dx_1, \ldots dx_N) : \pi_j^P = \frac{\rho}{N} \text{ for } j = 1, \ldots, N \right\}
\]

\[
c(x_1, \ldots, x_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|x_i - x_j|}
\]
\[
\begin{aligned}
\min_{\mathcal{P}} \left\{ \int c(x_1, \ldots, x_N) \mathcal{P}(dx_1, \ldots dx_N) : \pi_j^\# \mathcal{P} = \frac{\rho}{N} \text{ for } j = 1, \ldots, N \right\} \\
\end{aligned}
\]

\[
c(x_1, \ldots, x_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|x_i - x_j|}
\]

here: the further, the better!
Things you can prove from Optimal Transport

- Existence of \( P(r_1, r_2, \ldots, r_N) = |\Psi_{SCE}(r_1, r_2, \ldots r_N)|^2 \)
- \( v_{SCE}(r) \) exists and it is bounded (Kantorovich potential)
- Not possible (so far) to prove general existence of \( f_i(r) \)
- Dual Kantorovich problem

**Dual Kantorovich problem**

\[ V_{SCE}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle \]

\[ V_{SCE}[\rho] = \max_u \left\{ \int \rho(\mathbf{r}) u(\mathbf{r}) d\mathbf{r} : \sum_{i=1}^N u(\mathbf{r}_i) \leq \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\} \]

\[ \nu_{SCE}(\mathbf{r}) = u(\mathbf{r}) + C \]

**Kantorovich potential**

Kantorovich formulation: key to treat the 3D case?

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Kantorovich dual solution for strictly correlated electrons in atoms and molecules

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The many-body Coulomb repulsive energy of strictly correlated electrons provides direct information on the exact Hohenberg-Kohn exchange-correlation functional in the strong interaction limit. Until now the treatment of strictly correlated electrons has been based on the calculation of comotion functions with the help of semianalytic formulations. This procedure is system-specific and has been limited to spherically symmetric atoms and strictly one-dimensional systems. We develop a nested optimization method which solves the Kantorovich dual problem directly, and thus facilitates a general treatment of strictly correlated electrons for systems including atoms and small molecules.
Conclusions and outlook

- Strongly-interacting limit of DFT: approximations for the xc functional able to describe strong correlation within the restricted KS scheme (no artificial symmetry breaking)

- One can treat strongly-correlated quasi 1D systems with large electron numbers

Perspectives:

- Improve the algorithms for 2D and 3D systems
- Corrections to the KS SCE functional:
  \[ F[\rho] = T_s[\rho] + V_{ee}^{SCE}[\rho] + T_c[\rho] + V_{ee}^d[\rho] \]
- Inclusion of spin states
- Approximate SCE forms for new non-local functionals
- Nanotransport
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Thank you for your attention!