Kantorovich dual solution for strictly correlated electrons in atoms and molecules

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Outline

- Introduction
- Strictly correlated electron and optimal transport
- Kantorovich dual formulation for strictly correlated electrons
- Numerical results
- Conclusion

Ground state electronic structure theory

$$H = \underset{\substack{\Big\uparrow \\ \hat{T}}}{-\frac{1}{2}\sum_{i=1}^{N} \Delta_i} \underset{\substack{\Big\uparrow \\ \hat{V}_{ext}}}{- \sum_{\alpha=1}^{M}\sum_{j=1}^{N} \frac{Z_\alpha}{|x_i - R_\alpha|}} \underset{\substack{\Big\uparrow \\ \hat{V}_{ee}}}{+ \frac{1}{2}\sum_{\substack{i,j=1, \\ i\neq j}}^{N} \frac{1}{|x_i - x_j|}}$$

Many body ground state electron energy

$$E = \inf_{\Psi} \langle \Psi | H | \Psi \rangle$$

$\Psi(x_1, \dots, x_N)$ is a 3N dimensional antisymmetric function.

Curse of dimensionality.

Density functional theory

Represent many body ground state energy as universal functional of the marginal distribution (electron density) [Hohenberg-Kohn,1964]

$$\rho(x) = N\int |\Psi(x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N$$

$$E = \inf_{\Psi}\langle\Psi|H|\Psi\rangle = \inf_{\rho}\inf_{\Psi\mapsto\rho}\langle\Psi|\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}|\Psi\rangle$$

$$= \inf_{\rho}\Big(\boxed{\inf_{\Psi\mapsto\rho}\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle} + \int \rho(x) v_{ext}(x)\, dx\Big)$$

$$\equiv \inf_{\rho} F^{HK}[\rho] + \int \rho(x) v_{ext}(x)\, dx$$

$$\hat{V}_{ext}(x_1, \dots, x_N) = \sum_{i=1}^{N} v_{ext}(x_i)$$

Constrained minimization viewpoint [Levy, 1979], [Lieb, 1983]

Kohn-Sham density functional theory

- $F^{HK}[\rho]$ exists but does not have known explicit form.
- Kohn-Sham density functional theory

$$
\begin{aligned}
F^{HK}[\rho] &= \inf_{\Psi\mapsto\rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \\
&= \inf_{\Psi\mapsto\rho} \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|} + E_{xc}[\rho] \\
&\equiv F^{KS}[\rho]
\end{aligned}
$$

- $\inf_{\Psi\mapsto\rho} \langle \Psi | \hat{T} | \Psi \rangle$ corresponds to a non-interacting system. Its minimizer is one single Slater determinant. This is called the Kohn-Sham kinetic energy functional.

Kohn-Sham density functional theory

- Euler-Lagrange equation gives the Kohn-Sham equations [Kohn-Sham, 1965]

$$\left(-\frac{1}{2}\Delta + v_{ext} + \int dx' \, \frac{\rho(x')}{|x - x'|} + \frac{\delta E_{xc}}{\delta\rho}[\rho]\right)\psi_i(x) = \varepsilon_i \psi_i(x)$$

$$\rho(x) = \sum_{i=1}^{N} |\psi_i(x)|^2 , \qquad \int dx \, \psi_i^*(x)\psi_j(x) = \delta_{ij}$$

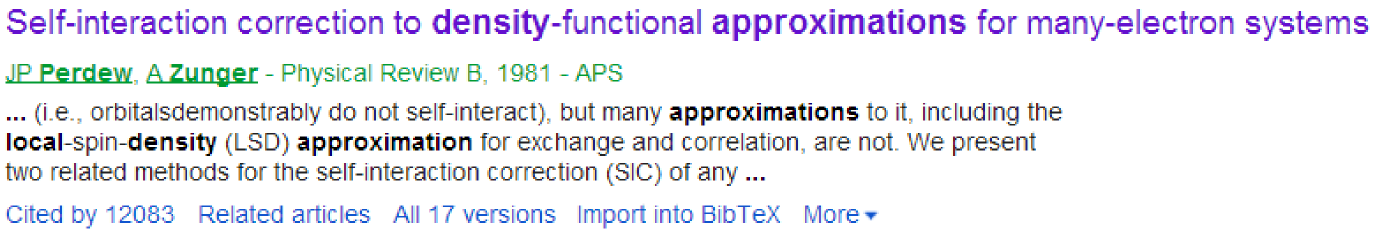
- One always solves eq in R^3 for N electrons (as opposed to eq in R^{3N})

Kohn-Sham density functional theory

- Best balances efficiency and accuracy. Most widely used electronic structure theory for molecules, liquids, solids etc.
- Exchange-correlation energy only takes less than 0.1% of the total energy, but it is this small part of the energy that significantly impacts chemical properties e.g. hydrogen bonding, van der Waals, dissociation etc.

Successful work on exchange-correlation functional is unusually important

- LDA (KS, PZ)



Self-interaction correction to **density**-functional **approximations** for many-electron systems

JP Perdew, A Zunger - Physical Review B, 1981 - APS

... (i.e., orbitalsdemonstrably do not self-interact), but many **approximations** to it, including the **local**-spin-**density** (LSD) **approximation** for exchange and correlation, are not. We present two related methods for the self-interaction correction (SIC) of any **...**

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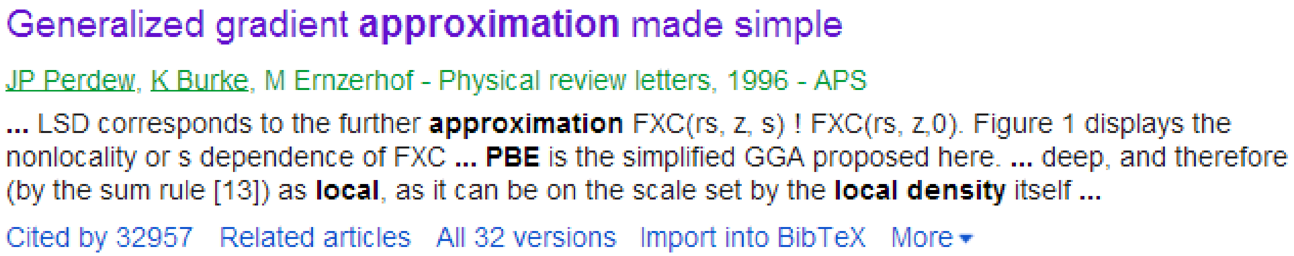
- GGA (PBE)



Generalized gradient **approximation** made simple

JP Perdew, K Burke, M Ernzerhof - Physical review letters, 1996 - APS

... LSD corresponds to the further **approximation** FXC(rs, z, s) ! FXC(rs, z,0). Figure 1 displays the nonlocality or s dependence of FXC **... PBE** is the simplified GGA proposed here. **...** deep, and therefore (by the sum rule [13]) as **local**, as it can be on the scale set by the **local density** itself **...**

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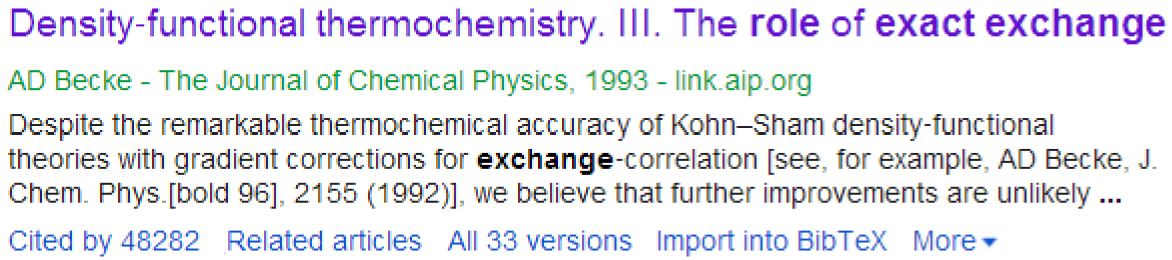
- Hybrid (B3LYP)



Density-functional thermochemistry. III. The **role of exact exchange**

AD Becke - The Journal of Chemical Physics, 1993 - link.aip.org

Despite the remarkable thermochemical accuracy of Kohn–Sham density-functional theories with gradient corrections for **exchange**-correlation [see, for example, AD Becke, J. Chem. Phys.[bold 96], 2155 (1992)], we believe that further improvements are unlikely **...**

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More on exchange-correlation functionals

- Local density approximation (LDA)

$$E_{xc}[\rho] = \int \rho(x)\epsilon_{xc}(\rho(x))\, dx$$

- Generalized gradient approximation (GGA)

$$E_{xc}[\rho] = \int \rho(x)\epsilon_{xc}(\rho(x), \nabla\rho(x))\, dx$$

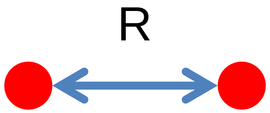
- Hybrid functional (B3LYP implemented in Gaussian package)

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = 0.2E_{\mathrm{x}}^{\mathrm{HF}} + 0.8E_{\mathrm{x}}^{\mathrm{LDA}} + 0.72\Delta E_{\mathrm{x}}^{\mathrm{B88}} + 0.81E_{\mathrm{c}}^{\mathrm{LYP}} + 0.19E_{\mathrm{c}}^{\mathrm{VWN}}$$

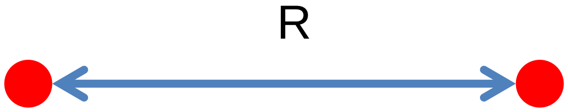
- More extreme: M11-L functional (48 fitting parameters, [Peverati-Truhlar, 2011]). Machine learning (10^6 parameters [Burke et al. 2012])

Current status of designing functional

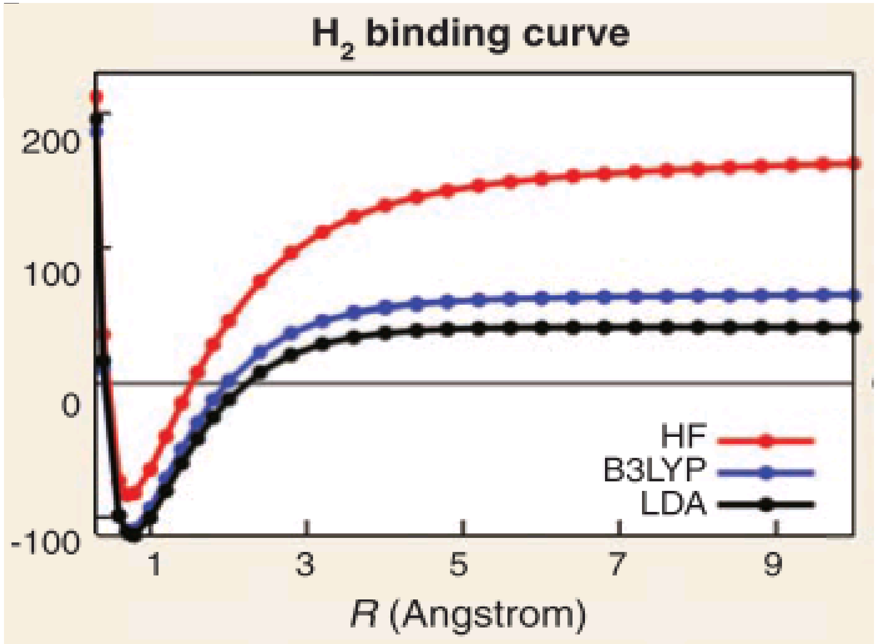
Surprisingly simple system, fail for all DFT functionals: H_2 dissociation



Equilibrium bond length



Dissociation limit



[Cohen, Mori-Sanchez, Yang, Science 2008]

Similar failure process: [Lee-Handy, 1993], [Andersson-Roos, 1994], many others

Strictly correlated electron state

- Hohenberg-Kohn functional

$$
\begin{aligned}
&F^{HK}[\rho] = \inf_{\Psi \mapsto \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \\
&\approx \inf_{\Psi \mapsto \rho} \langle \Psi | \hat{T} | \Psi \rangle + \inf_{\Psi \mapsto \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle \\
&\equiv T_s[\rho] + V_{ee}^{SCE}[\rho] \\
&\equiv F^{KS-SCE}[\rho]
\end{aligned}
$$

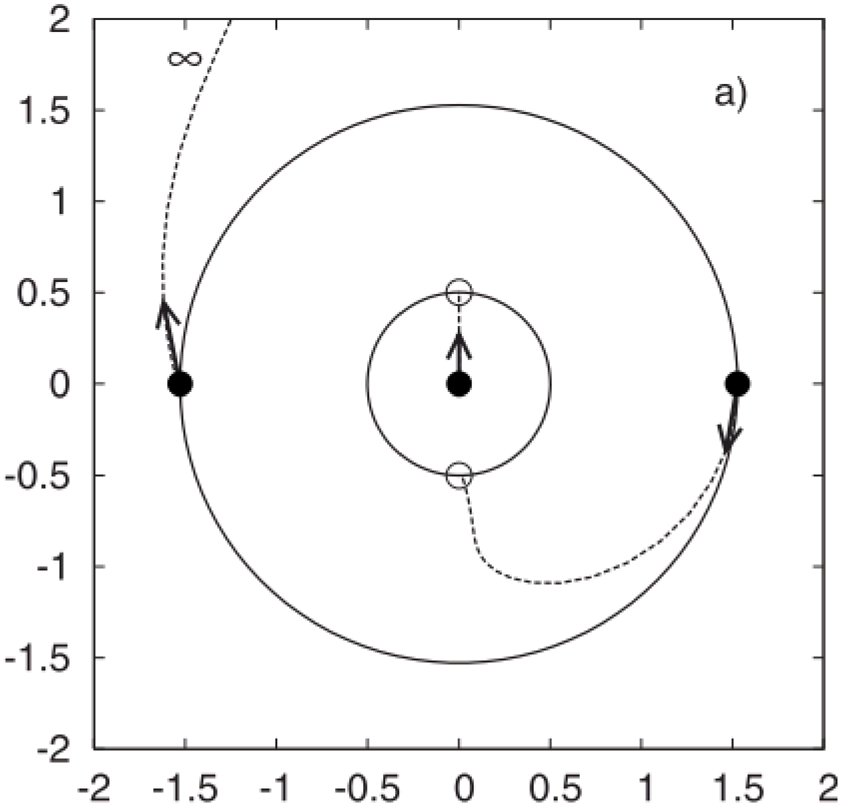
Strictly correlated electron state

- Hohenberg-Kohn functional

$$\begin{aligned} F^{HK}[\rho] &= \inf_{\Psi\mapsto\rho}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle \\ &\approx \inf_{\Psi\mapsto\rho}\langle\Psi|\hat{T}|\Psi\rangle + \boxed{\inf_{\Psi\mapsto\rho}\langle\Psi|\hat{V}_{ee}|\Psi\rangle} \\ &\equiv T_s[\rho] + V_{ee}^{SCE}[\rho] \\ &\equiv F^{KS-SCE}[\rho] \end{aligned}$$

- The minimizer $\Psi[\rho]$ corresponding to $V_{ee}^{SCE}[\rho]$ is referred to as the “strictly correlated electron state” (SCE) [Seidl-Perdew-Levy, 1999]

Strictly correlated nature



The positions of electrons in the SCE state for Li atom.
[Seidl- Gori-Giorgi - Savin, 2007]

Properties of the SCE functional

- Complementary to the KS functional

- Fully non-local

- More natural in the dissociation limit

- Motivated from the adiabatic connection formula for the exact exchange-correlation functional [Langreth-Perdew, 1975], [Gunnarsson-Lundqvist, 1976]

- [Liu-Burke, JCP 2009]

  In any event, the advent of SC calculations opens up a whole new alternative approach to DFT calculations of electronic structure, and only experience can show how and when this will prove more fruitful than the traditional KS scheme.

SCE formulation

$$\hat{V}_{ee}(x_1, \dots, x_N) = \sum_{i<j} c(x_i, x_j), \qquad c(x, y) = \frac{1}{|x-y|}$$

$$V_{ee}^{SCE}[\rho] = \inf_{\Psi \mapsto \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

$$= \inf_{\Psi \mapsto \rho} \int \hat{V}_{ee}(x_1, \dots, x_N) |\Psi(x_1, \dots, x_N)|^2 \, dx_1 dx_2 \cdots dx_N$$

Or equivalently

$$\inf_{P} \int \hat{V}_{ee}(x_1, \dots, x_N) P(x_1, \dots, x_N) \, dx_1 dx_2 \cdots dx_N$$

$$s.t. \int P(x, \dots, x_N) dx_2 \cdots dx_N = \frac{\rho(x)}{N}$$

$$P(x_1, \dots, x_N) = P\left(x_{\Pi(1)}, \dots, x_{\Pi(N)}\right)$$

$$P(x_1, \dots, x_N) \geq 0$$

Π: Permutation

This is an N-body optimal transport problem with Coulomb cost function (after relaxation due to Kantorovich).

Remarks on SCE formulation

- SCE does not distinguish between bosonic (symmetric) and fermionic (antisymmetric) wavefunctions.

- Optimal transport usually studied with $|x-y|$ or $|x-y|^2$ cost functions. These are attractive cost functions. In SCE, the Coulomb cost function is repulsive and singular, which leads to qualitatively different behavior.

- Rigorous theory for Coulomb cost with $N=2$ [Cotar-Friesecke-Kluppelberg, 2013]

Remarks on SCE formulation

- The N-body SCE problem can be solved exactly by a 2-body problem. Define the pair density matrix:

$$\rho_2(x,y) = \int P(x,y,x_3,\dots,x_N)\, dx_3 \cdots dx_N$$

SCE becomes

$$\inf_{\rho_2} \binom{N}{2} \int c(x,y)\, \rho_2(x,y) dx dy$$

$$s.t. \int \rho_2(x,y) dy = \frac{\rho(x)}{N}$$

$$P \mapsto \rho_2$$

- $P \mapsto \rho_2$: Any admissible ρ_2 must be the marginal distribution of some P. This is called N representability of the pair density matrix.

Remarks on SCE formulation

- Neglecting the N-representability leads to energy that is too low [Coleman, 1963]

$$\inf_{\rho_2} \binom{N}{2} \int c(x,y)\, \rho_2(x,y) dx dy$$

$$s.t. \int \rho_2(x,y) dy = \frac{\rho(x)}{N}$$

$$\rho_2(x,y) = \rho_2(y,x), \qquad \rho_2(x,y) \geq 0$$

- Systematic condition and approximation of the N-representability [Friesecke-Mendl-Pass-Cotar-Kluppelberg, 2013], [Mazziotti 2012]

- Here we consider solving the N-body optimal transport problem directly.

Monge formulation

- Introduce ansartz

$$P(x_1, \dots, x_N) = \frac{\rho(x_1)}{N} \delta(x_2 - T_2(x_1)) \cdots \delta(x_N - T_N(x_1))$$

- The optimal P is a very singular function in the 3N-dimensional space.

- $T_i : R^3 \to R^3$ are called the optimal maps, or co-motion functions. They satisfy the mass conservation condition

$$\int_A \rho = \int_{T_i(A)} \rho \,, \qquad \mathrm{i} \geq 2$$

- Rigorous justification for $N = 2$ [Cotar-Friesecke-Kluppelberg, 2013]

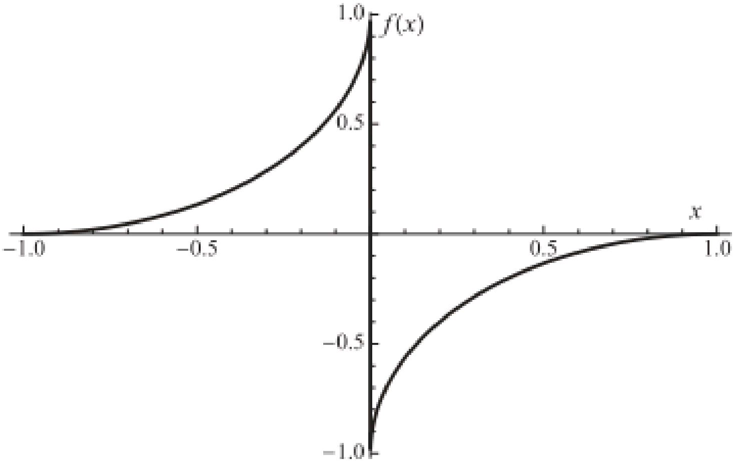
Problem of Monge formulation

- The mass conservation condition is difficult to implement numerically.

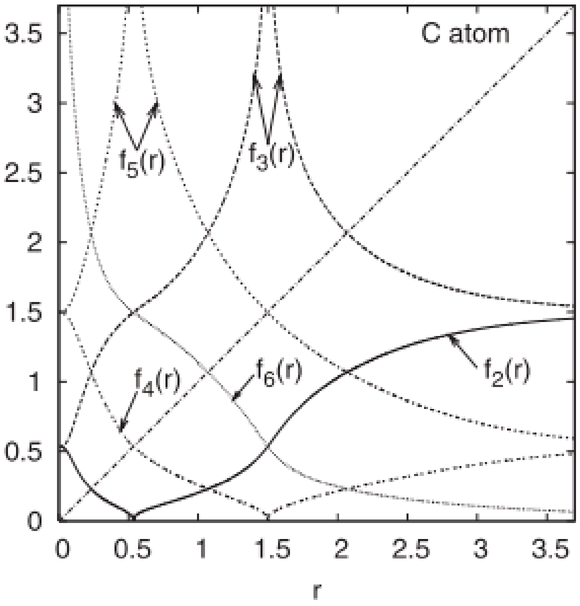
- Each optimal maps is again singular in general. The singularity is rooted in the repulsive nature of the Coulomb cost function. The location of singularity is so far not systematically predictable for general systems.

- With the help of semi-analytic method, Monge formulation can be solved for spherical-symmetric atoms, and strictly 1D systems, but so far no more.

Problem of Monge formulation



Co-motion function for a 1D atom with N=2
[Buttazzo-Pascale - Gori-Giorgi, 2012]



Radial co-motion functions for Carbon
[Seidl- Gori-Giorgi - Savin, 2007]

Linear programming viewpoint

- Consider

$$\inf_P \int \hat{V}_{ee}(x_1, \dots, x_N) P(x_1, \dots, x_N)\, dx_1 dx_2 \cdots dx_N$$

$$s.t. \int P(x, \dots, x_N) dx_2 \cdots dx_N = \frac{\rho(x)}{N}$$

$$P(x_1, \dots, x_N) = P\left(x_{\Pi(1)}, \dots, x_{\Pi(N)}\right)$$

$$P(x_1, \dots, x_N) \geq 0$$

- Assume we discretize R^3 into M points, then $P(x_1, \dots, x_N)$ are discretized into M^N variables. This is a linear programming problem for these M^N variables.

Kantorovich dual formulation

- Duality for linear programming [Dantzig-von Neumann 1947]

$$
\begin{array}{rl}
\max\limits_{x} & c^T x \\
\text{s.t.} & Ax \leq b \\
 & x \geq 0
\end{array}
\quad \Longleftrightarrow \quad
\begin{array}{rl}
\min\limits_{y} & b^T y \\
\text{s.t.} & A^T y \geq c \\
 & y \geq 0
\end{array}
$$

Kantorovich dual formulation

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$$\begin{aligned}\max_x \; & c^T x \\ \text{s.t.}\; & Ax \leq b \\ & x \geq 0\end{aligned} \quad \Longleftrightarrow \quad \begin{aligned}\min_y \; & b^T y \\ \text{s.t.}\; & A^T y \geq c \\ & y \geq 0\end{aligned}$$

$$\inf_P \int \hat{V}_{ee}(x_1, \dots, x_N) P(x_1, \dots, x_N)\, dx_1 dx_2 \cdots dx_N$$

$$s.t. \int P(x, \dots, x_N) dx_2 \cdots dx_N = \frac{\rho(x)}{N}$$

$$\int P(x_1, x, \dots, x_N) dx_1 dx_3 \cdots dx_N = \frac{\rho(x)}{N}$$

$$\dots$$

$$\int P(x_1 \dots, x_{N-1}, x) dx_1 \cdots dx_{N-1} = \frac{\rho(x)}{N}$$

$$P(x_1, \dots, x_N) \geq 0$$

Kantorovich dual formulation

- Duality for linear programming [Dantzig-von Neumann 1947]

$$\begin{aligned}&\max_{x} c^T x\\ &\text{s.t.}\, Ax \leq b\\ &\qquad x \geq 0\end{aligned} \quad \Longleftrightarrow \quad \begin{aligned}&\min_{y} b^T y\\ &\text{s.t.}\, A^T y \geq c\\ &\qquad y \geq 0\end{aligned}$$

$$\begin{aligned}&\sup_{\{u_i(x)\}} \sum_{i=1}^{N} \frac{1}{N} \int dx\, u_i(x)\rho(x)\\ &s.t. \textstyle\sum_{i=1}^{N} u_i(x_i) \leq \hat{V}_{ee}(x_1, \dots, x_N)\end{aligned} \quad \Longleftrightarrow \quad \begin{aligned}&\inf_{P} \int \hat{V}_{ee}(x_1, \dots, x_N) P(x_1, \dots, x_N)\, dx_1 dx_2 \cdots dx_N\\ &s.t. \int P(x, \dots, x_N) dx_2 \cdots dx_N = \frac{\rho(x)}{N}\\ &\int P(x_1, x, \dots, x_N) dx_1 dx_3 \cdots dx_N = \frac{\rho(x)}{N}\\ &\dots\\ &\int P(x_1 \dots, x_{N-1}, x) dx_1 \cdots dx_{N-1} = \frac{\rho(x)}{N}\\ &P(x_1, \dots, x_N) \geq 0\end{aligned}$$

Kantorovich dual formulation

- Define the Kantorovich potential

$$u(x) = \frac{1}{N}\sum_{i=1}^{N} u_i(x)$$

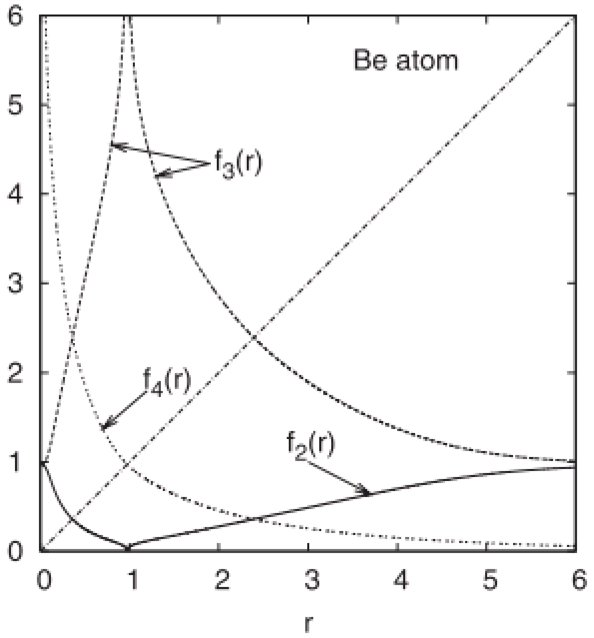
and use symmetry, we have the Kantorovich dual formulation for SCE

$$\sup_u \int dx\, u(x)\rho(x)$$

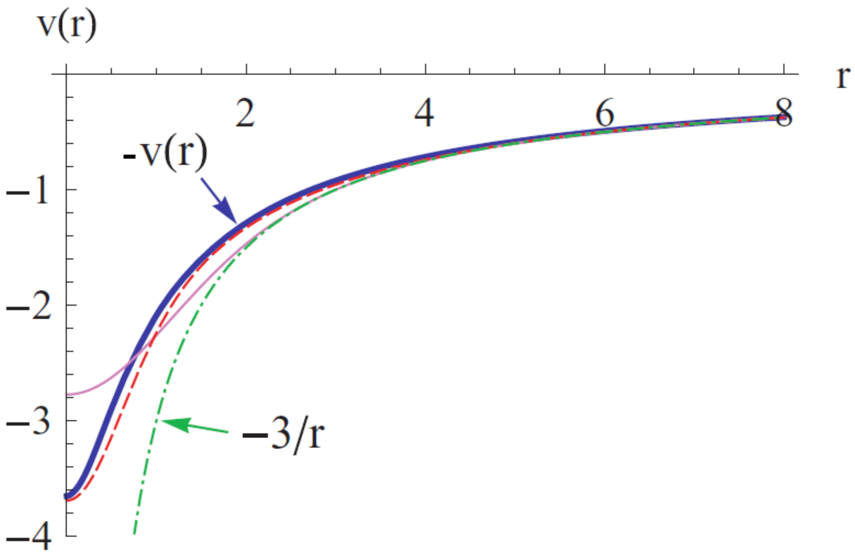
$$s.t. \sum_{i=1}^{N} u(x_i) \leq \hat{V}_{ee}(x_1, \ldots, x_N)$$

- Dual formulation for SCE introduced by [Buttazzo-Pascale - Gori-Giorgi, 2012]. More rigorous treatment of Monge-Kantorovich duality but for quadratic cost e.g. [Gangbo-Swiech, 1998].

Kantorovich potential is more regular



co-motion functions, Be atom
[Seidl- Gori-Giorgi - Savin, 2007]



Kantorovich dual potential, Be atom

Problem of Kantorovich formulation

- $\sum_{i=1}^{N} u(x_i) \leq \hat{V}_{ee}(x_1, \dots, x_N)$ should be satisfied $\forall x_1, \dots, x_N$:
  M^N number of constraints

Problem of Kantorovich formulation

- $\sum_{i=1}^{N} u(x_i) \leq \hat{V}_{ee}(x_1, \ldots, x_N)$ should be satisfied $\forall x_1, \ldots, x_N$: M^N number of constraints

Monge	Kantorovich dual
Solve for $N-1$ optimal maps $R^3 \rightarrow R^3$	Solve for one Kantorovich potential $R^3 \rightarrow R$
Mass conservation condition	M^N number of constraints
Optimal maps are singular	Kantorovich potential is (conjectured to be) more regular
Rely on semi-analytical formula	May work for general systems such as atoms and molecules
(So far) only for spherical symmetric atoms and strictly 1D systems	No work done yet

Problem of Kantorovich formulation

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[Mendl-LL, PRB 2013]

Reformulation

- Consider isolated molecule. Define

$$u(x) = v(x) + C$$

C is a constant chosen so that asymptotically [Buttazzo-Pascale - Gori-Giorgi, 2012]

$$v(x) \to \frac{N-1}{|x|}, \qquad |x| \to \infty$$

- Define

$$g[v] = \inf_{\{r_i\}} \hat{V}_{ee}(x_1, \dots, x_N) - \sum_{i=1}^{N} v(x_i)$$

Then

$$V_{ee}^{SCE}[\rho] = \sup_{v,C} \int dx\, v(x)\rho(x) + NC$$

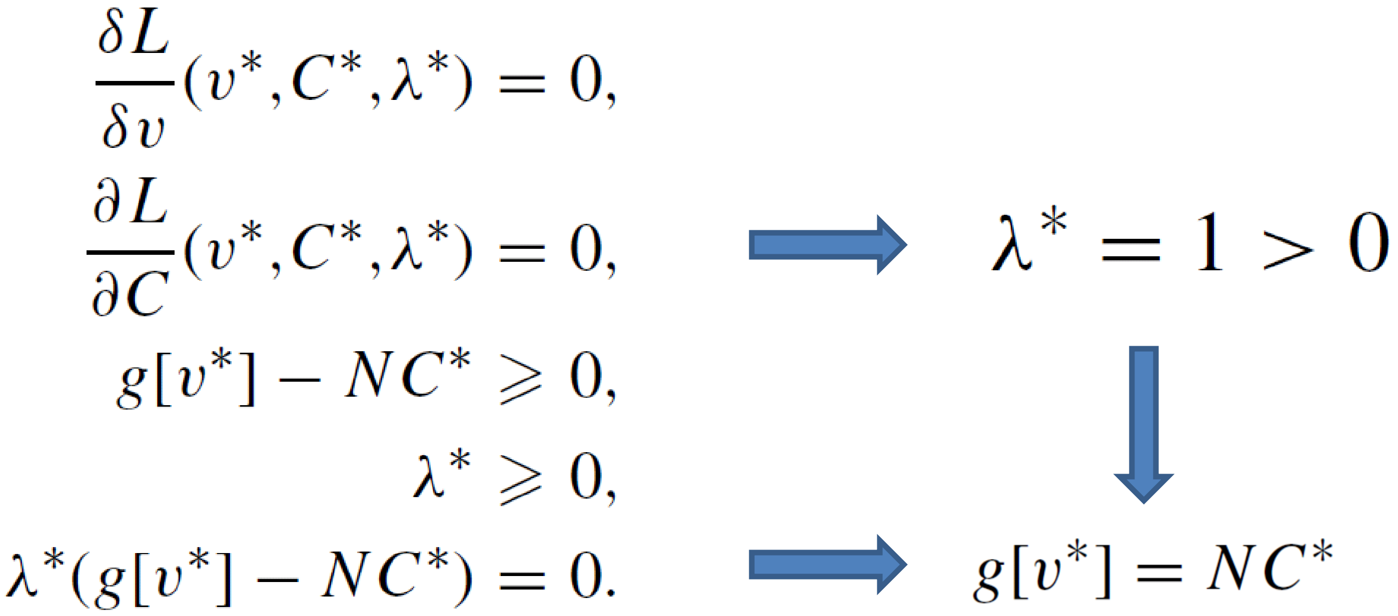
$$s.t.\ g[v] \geq NC$$

Reformulation

- Define

$$L[v, C, \lambda] = -\int v(x)\rho(x)dx - NC - \lambda(g[v] - NC)$$

The Karush-Kuhn-Tucker (KKT) condition states that



$$\begin{aligned} \frac{\delta L}{\delta v}(v^*, C^*, \lambda^*) &= 0, \\ \frac{\partial L}{\partial C}(v^*, C^*, \lambda^*) &= 0, \\ g[v^*] - NC^* &\geqslant 0, \\ \lambda^* &\geqslant 0, \\ \lambda^*(g[v^*] - NC^*) &= 0. \end{aligned}$$

$$\frac{\partial L}{\partial C}(v^*, C^*, \lambda^*) = 0 \Longrightarrow \lambda^* = 1 > 0$$

$$\lambda^* = 1 > 0 \Big\Downarrow \quad \lambda^*(g[v^*] - NC^*) = 0 \Longrightarrow g[v^*] = NC^*$$

Nested optimization problem

- Nested unconstrained optimization problem. Addressing M^N number of constraints by optimization

$$V_{ee}^{SCE}[\rho] = \sup_{v} \int dx\, v(x)\rho(x) + g[v]$$

- $v(x)$ decays slowly in the real space

$$v(x) \to \frac{N-1}{|x|}, \qquad |x| \to \infty$$

Introduce pseudocharge

$$v(x) = \int \frac{m(y)}{|x-y|} dy$$

$$\int m(x)dx = N - 1$$

Then $m(x)$ should decay rapidly can be represented on a small computational domain.

Problem of the nested optimization approach

- Now we run into the “no-free-lunch theorem”…

Problem of the nested optimization approach

- Now we run into the “no-free-lunch theorem”…

- The difficulty due to singularity of the optimal maps and the mass conservation condition must still exist in the Kantorovich dual formulation.

- In the nested optimization formulation, the difficulty is that

$$\frac{\delta g[v]}{\delta v} \text{ or } \frac{\delta g[m]}{\delta m}$$

is not computable through the Hellman-Feynman type formula.

Computing the derivative

- Consider

$$f(x) = \min_{y} g(x, y)$$

If for each x there is a unique $y^*(x)$ as the minimizer and $y^*(x)$ is smooth, then using chain rule

$$f'(x) = g_x\big(x, y^*(x)\big) + \cancel{g_y\big(x, y^*(x)\big)}\big(y^*(x)\big)' = g_x\big(x, y^*(x)\big)$$

- However, it can be shown that $g[v]$ has at least M minimizers at the optimal v^* which makes the above argument invalid.

Computing the derivative

- Even if cost is not an issue, finite difference scheme is also difficult.

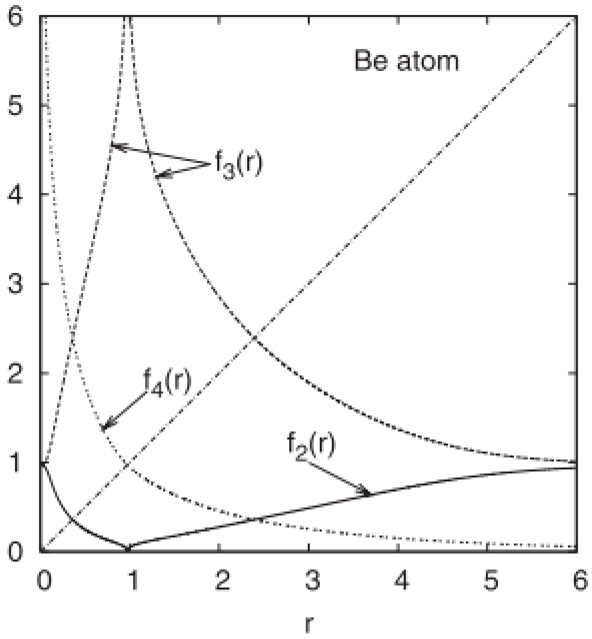
- In practice we compute the derivative for the outer iteration using derivative-free optimization schemes [e.g. Nelder-Mead 1965]

- Derivative-free optimization only allows to use a very small number of degrees of freedom, which is the major drawback of this work.

- Represent the pseudocharge $m(x)$ by a few basis functions such as Gaussians.

Beryllium atom

- Spherically symmetric system.
- Converged electron density obtained from configuration-interaction calculation.
- Semi-analytic form for co-motion functions.



[Seidl- Gori-Giorgi - Savin, 2007]

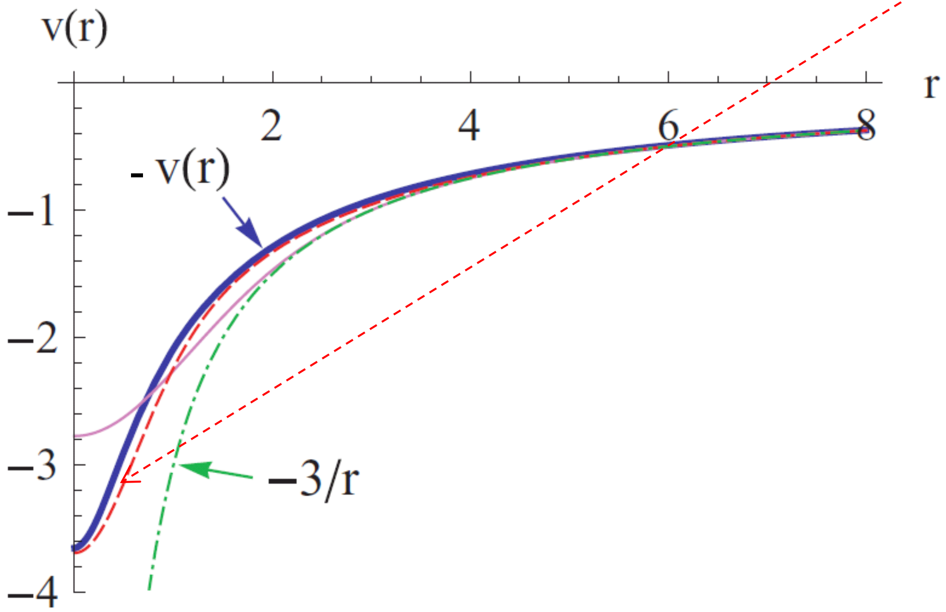
Beryllium atom

One Gaussian

$$m(\mathbf{r};\sigma) = \frac{N-1}{(2\pi\sigma^2)^{3/2}}\, e^{-\frac{\mathbf{r}^2}{2\sigma^2}}$$

Two Gaussians

$$m(\mathbf{r}) = (N-1)\left(\cos^2(\vartheta)\frac{e^{-\frac{\mathbf{r}^2}{2\sigma_1^2}}}{\left(2\pi\sigma_1^2\right)^{3/2}} + \sin^2(\vartheta)\frac{e^{-\frac{\mathbf{r}^2}{2\sigma_2^2}}}{\left(2\pi\sigma_2^2\right)^{3/2}}\right)$$

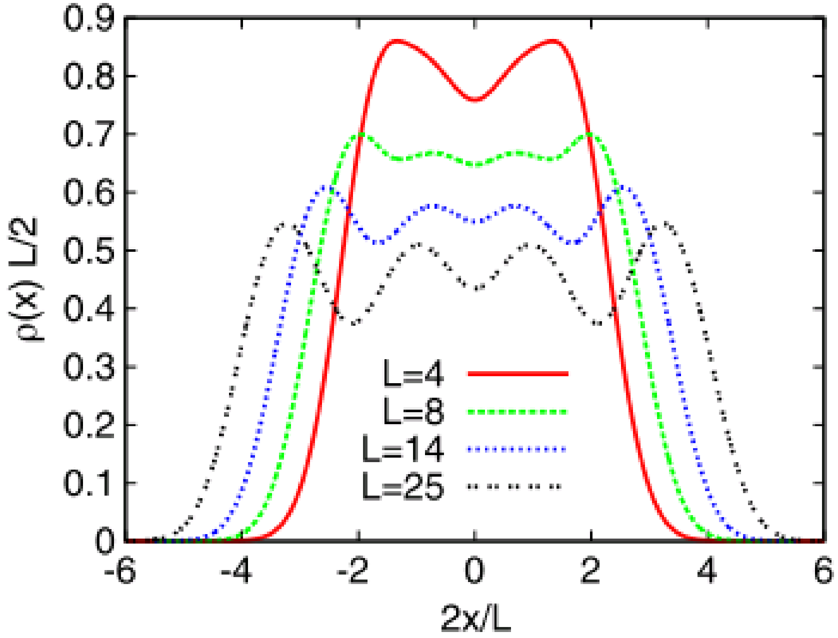


Gaussians for $m(x)$	1	2
Error of $V_{ee}^{SCE}[\rho]$	20.3%	1.6%

1D quantum wire

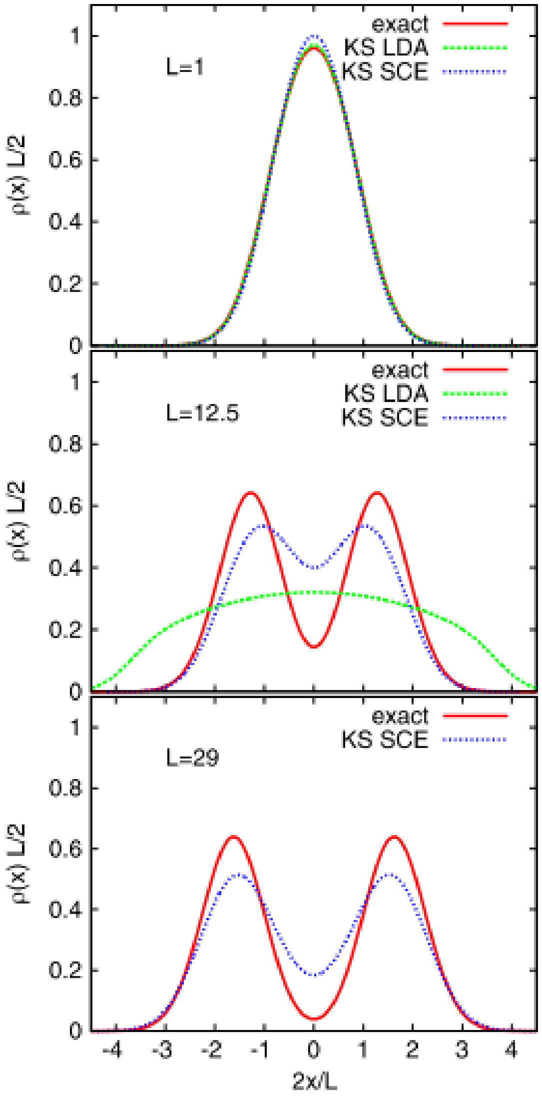
$$H = -\frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2}{\partial x_i^2} + \sum_{i=1}^{N}\sum_{j>i}^{N} w_b(x_i - x_j) + \sum_{i=1}^{N} v_{\text{ext}}(x_i).$$

$$w_b(x) = \frac{\sqrt{\pi}}{2b}\exp\left(\frac{|x|^2}{4b^2}\right)\text{erfc}\left(\frac{|x|}{2b}\right) \qquad v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2 \qquad L \equiv 2\omega^{-1/2}$$



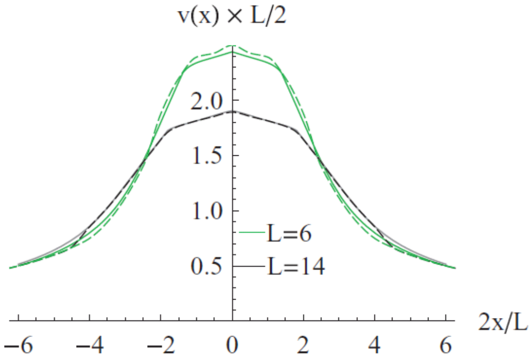
4 electrons
[Malet- Gori-Giorgi, 2013]

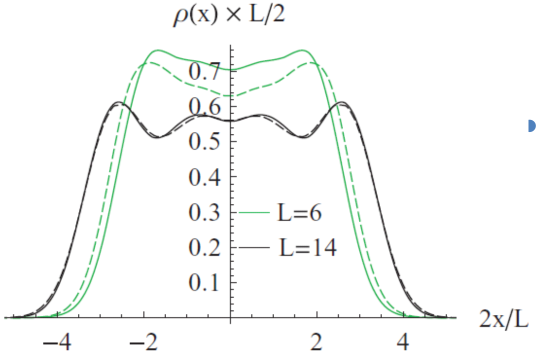
Comparing SCE with LDA



- [Malet- Gori-Giorgi, 2013]
- N=2
- LDA systematically fails in the dissociation limit as L increases, while SCE at least qualitatively predicts the correct behavior.

1D quantum wire



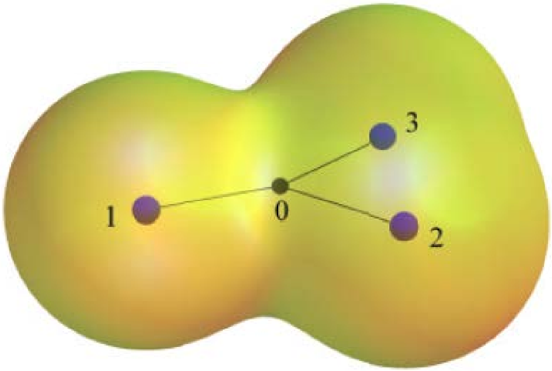


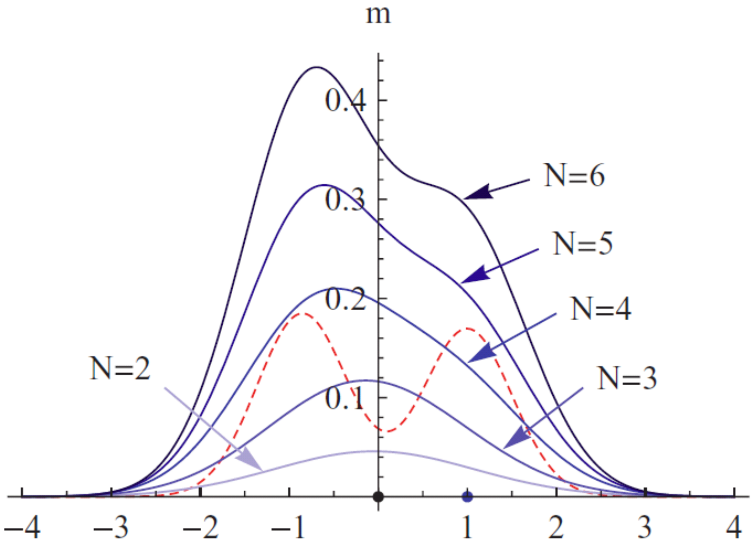
L	6	14
“exact” V_{ee}^{SCE}	1.025	0.3408
dual-K V_{ee}^{SCE}	0.9394	0.3381
relative error	8.4%	0.8%

- KS-SCE, with self-consistent iteration.
- Periodic boundary condition, v represented by ~ 10 Fourier modes.
- Qualitatively correct with the co-motion function formulation.
- Strong correlation (L=12) is even easier than weak correlation (L=6)
- Sensitive to initial guess.

Model trimer

Pseudocharge: three Gaussians with distance R to 0, and variance σ.





N	2	3	4	5	6
V_{ee}^{SCE}	0.1973	0.4617	0.7584	1.0711	1.3959
σ	1.1073	0.9804	0.8313	0.7741	0.7315
R	0.2260	0.5322	0.8538	0.9062	0.9417

Conclusion

- Systematic failure of existing DFT functional for strongly correlated systems, such as H_2 in the dissociation limit.
- Strictly correlated electron (SCE). The key obstacle is a general and reliable algorithm that allows the computation of SCE functional for general systems.
- Optimal transport problem with Coulomb cost. Monge formulation and Kantorovich dual formulation. The Kantorovich dual formulation may work better for general systems.
- Nested optimization approach as a first step for solving this optimal transport problem in the Kantorovich dual formulation.
- Derivative-free optimization is a major drawback.

Future work and open questions

- Allow the computation of the derivative $\frac{\delta g[m]}{\delta m}$.
- Computing the H_2 dissociation limit in the KS-SCE formulation using a set of basis functions (such as Gaussians).
- Monge-Kantorovich duality for optimal transport problem with Coulomb cost. $N > 2$.
- Regularity of the Kantorovich potential.

Thank you for your attention!