Optimal transport limit of the Hohenberg-Kohn functional: Kantorovich dual solution and reduced density models

(joint work with Lin Lin, Gero Friesecke, Paola Gori-Giorgi, Codina Cotar, Brendan Pass, Claudia Klüppelberg)

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Hohenberg-Kohn for strictly correlated systems

Hohenberg-Kohn:

$$E[\rho] = F[\rho] + \int v_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

with $F[\rho]$ an universal functional of the density:

$$F[\rho] = \min_{\Psi \mapsto \rho} \left\langle \Psi \middle| \hat{T} + \hat{V}_{\mathrm{ee}} \middle| \Psi \right\rangle .$$

Standard Kohn-Sham: treat $\hat{V}_{\mathrm{ee}}$ as perturbation, leads to Kohn-Sham noninteracting system.
Here: neglect $\hat{T}$ and minimize (Seidl et al. 1999b,a, 2007)

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] := \min_{\Psi \mapsto \rho} \left\langle \Psi \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi \right\rangle , \quad \hat{V}_{\mathrm{ee}} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} .$$

$\rightsquigarrow$ "classical" electrostatic problem.

Why "optimal transport"?

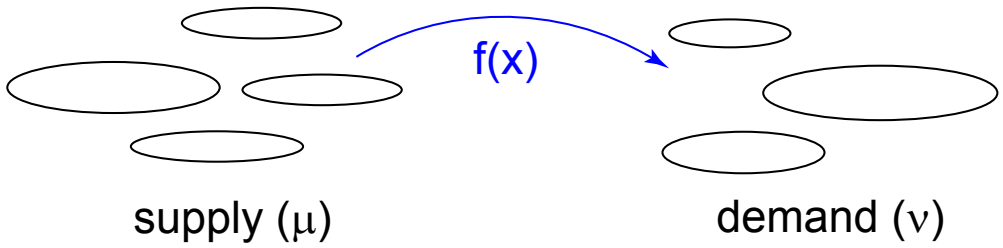


Figure: transport plan f from "supply" to "demand"

Original formulation (Monge 1781): given two probability measures μ, ν and fixed $\alpha \in \{1, 2\}$, optimize

$$\inf_{f\#\mu=\nu} \int_\Omega |x - f(x)|^\alpha \, \mathrm{d}\mu(x)$$

over transport maps f which "push μ forward to ν", i.e.,

$$|\det \nabla f(x)| \; \nu(f(x)) = \mu(x)$$

under certain regularity assumptions.

Optimal transport visualization

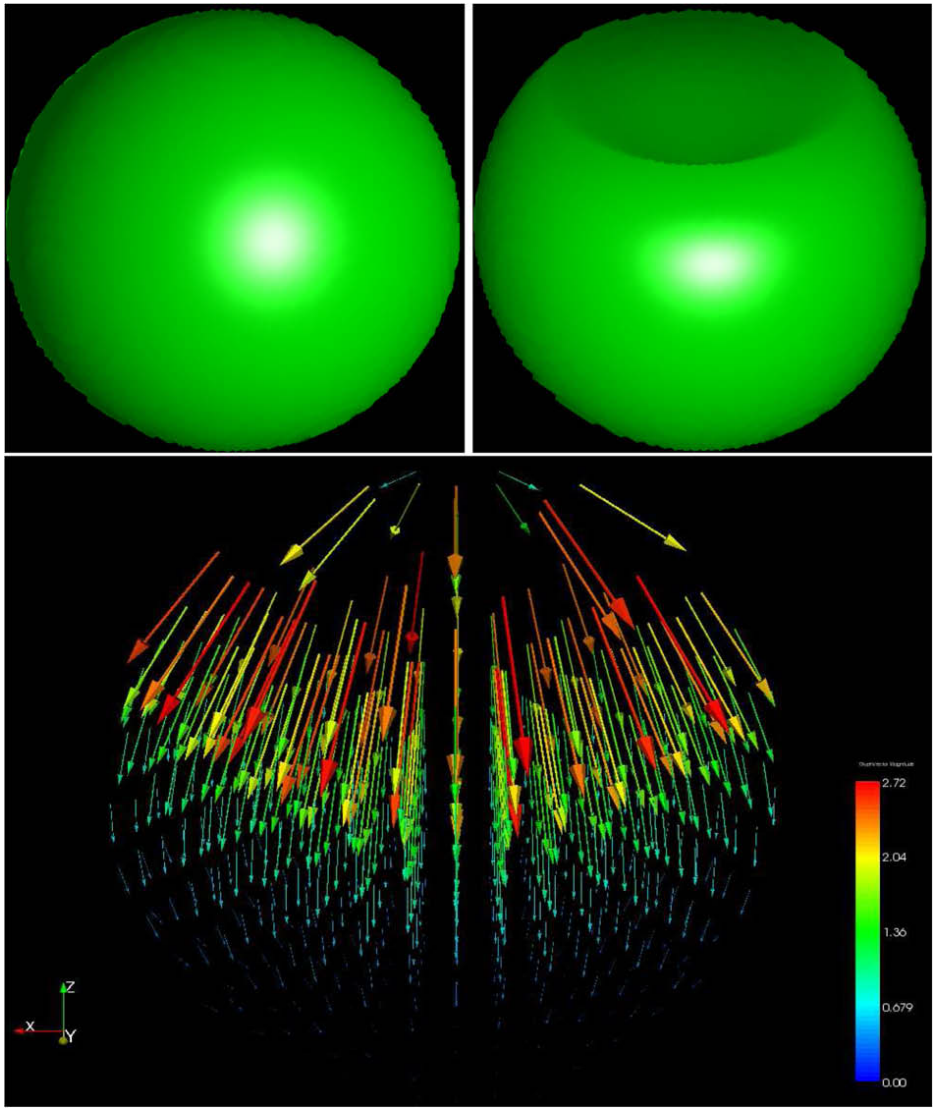


Figure: Sphere mapped to its deformed counterpart (Rehman et al. 2009)

Kantorovich formulation of optimal transport

Formulation by Monge 1781:

$$\inf_{f\#\mu=\nu} \int_\Omega |x - f(x)|^\alpha \, \mathrm{d}\mu(x)$$

Kantorovich formulation (Kantorovich 1940, 1942):

$$\inf_{\gamma\in\Gamma(\mu,\nu)} \int\int |x - y|^\alpha \, \mathrm{d}\gamma(x, y)$$

with $\Gamma(\mu, \nu)$ the set of all joint probability measures.
Quantum mechanics setting: *Coulomb* cost function $\frac{1}{|x-y|}$, i.e., $\alpha = -1$. Compare with $V_{\mathrm{ee}}^{\mathrm{SCE}}$ for $N = 2$:

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \min_{\Psi\mapsto\rho} \sum_{\sigma_1,\sigma_2} \int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2)|^2 \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2.$$

Optimal transport with Coulomb cost

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \left\langle \Psi \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi \right\rangle, \quad \hat{V}_{\mathrm{ee}} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Co-motion formulation (Seidl et al. 1999b,a, 2007) (corresponds to Monge's original version):

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

with *co-motion functions* $\mathbf{f}_i : \mathbb{R}^3 \to \mathbb{R}^3$ satisfying the *mass conservation constraint* $\rho(\mathbf{f}_i(\mathbf{r})) \, |\det \nabla \mathbf{f}_i(\mathbf{r})| = \rho(\mathbf{r})$.

Example: beryllium atom

Co-motion functions $\mathbf{f}_i(\mathbf{r})$ for the beryllium atom (Seidl et al. 2007), numerically feasible for spherically symmetric problems:

$$f_2(r) = \begin{cases} N_e^{-1}(2 - N_e(r)) & r \leq a_2 \\ N_e^{-1}(N_e(r) - 2) & r > a_2 \end{cases}$$

$$f_3(r) = \begin{cases} N_e^{-1}(2 + N_e(r)) & r \leq a_2 \\ N_e^{-1}(6 - N_e(r)) & r > a_2 \end{cases}$$

$$f_4(r) = N_e^{-1}(4 - N_e(r))$$

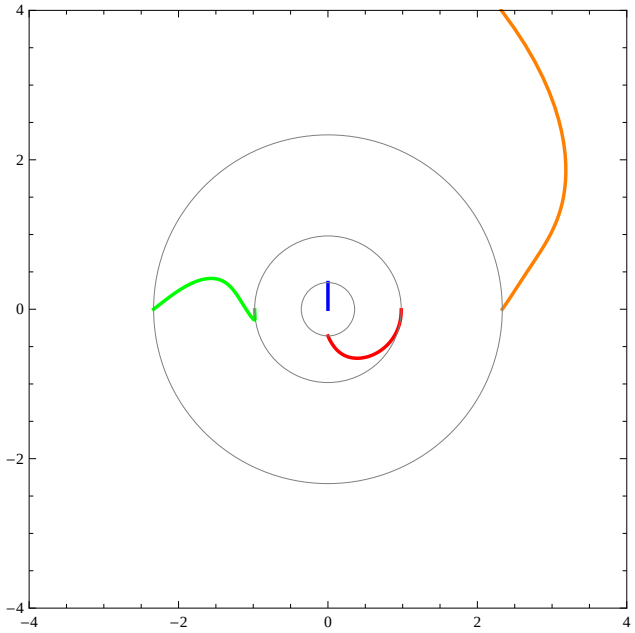
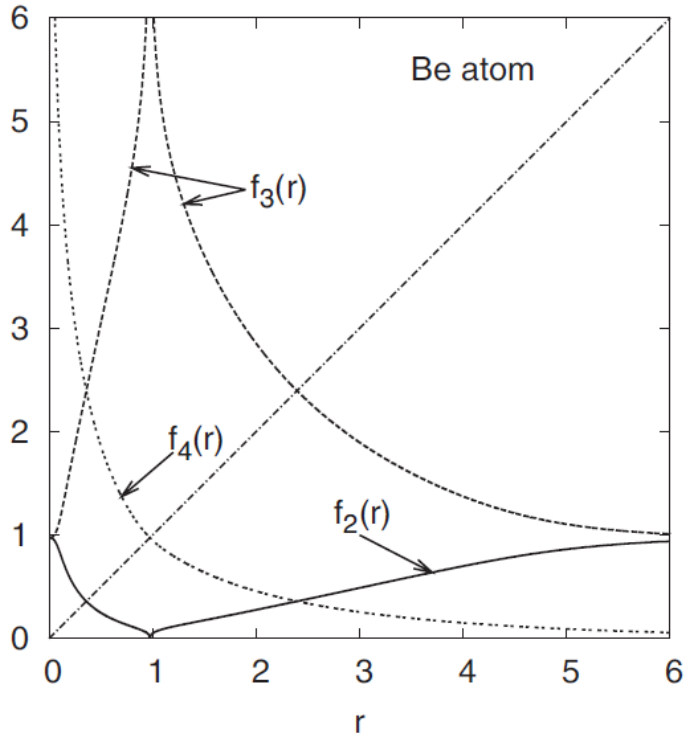


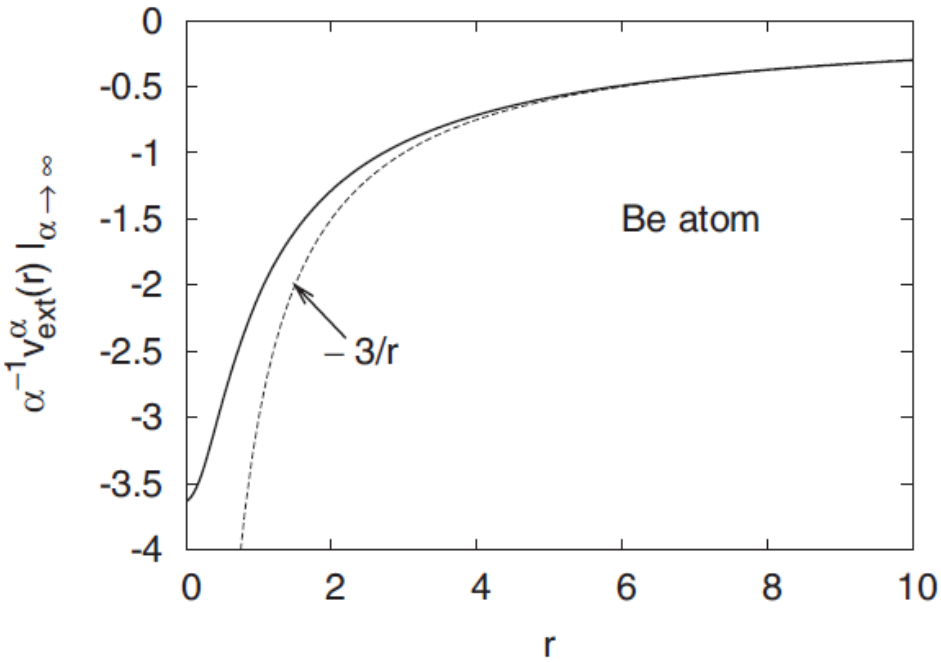
Figure: co-motion $\mathbf{f}_i(\mathbf{r})$

Beryllium atom (cont.)

Seidl et al. (2007)



(a) co-motion $f_i(r)$



(b) potential $v(r)$

Figure: Co-motion functions and potential for the beryllium atom

Kantorovich dual formulation of OT

Difficulty of comotion functions $\mathbf{f}_i$: until now numerically feasible only for spherically symmetric problems or 1D systems.
Alternative: *Kantorovich dual formulation* (Buttazzo et al. 2012; Cotar et al. 2013):

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \max_u \int u(\mathbf{s})\rho(\mathbf{s})\,\mathrm{d}\mathbf{s},$$
$$\text{s.t.} \sum_{i=1}^{N} u(\mathbf{r}_i) \leq \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad \forall \{\mathbf{r}_i\}_{i=1}^{N}$$

Long-range asymptotic behavior:

$$u(\mathbf{r}) = v(\mathbf{r}) + C, \quad v(\mathbf{r}) \sim \frac{N-1}{|\mathbf{r}|} \quad \text{as} \quad |\mathbf{r}| \to \infty$$

This talk: practical numerical method to solve the dual formulation.

Solving the Kantorovich dual formulation

(Mendl and Lin 2013) Introduce a functional $g[v]$ of $v(\mathbf{r})$ by

$$g[v] = \min_{\{\mathbf{r}_i\}} E_{\mathrm{pot}}(\mathbf{r}_1, \ldots, \mathbf{r}_N), \quad \text{with}$$

$$E_{\mathrm{pot}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} v(\mathbf{r}_i),$$

where the minimization is performed over all possible choices of the positions of the N electrons. The Kantorovich dual problem can then be written as

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \max_{v,C} \left(\int v(\mathbf{s})\rho(\mathbf{s})\,\mathrm{d}\mathbf{s} + NC \right),$$
$$\text{s.t. } g[v] \geq NC,$$

using the normalization condition $\int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} = N$.

Solving the Kantorovich dual formulation (cont.)

Constrained optimization problem

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \max_{v,C} \left(\int v(\mathbf{s})\rho(\mathbf{s})\,\mathrm{d}\mathbf{s} + NC \right),$$
$$\text{s.t. } g[v] \geq NC,$$

can be converted to a nested unconstrained optimization problem by eliminating the parameter C, resulting in

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \max_{v} \left(\int v(\mathbf{s})\rho(\mathbf{s})\,\mathrm{d}\mathbf{s} + g[v] \right).$$

Remark: $\frac{\delta g[v]}{\delta v}(\mathbf{r})$ cannot be analytically computed for the exact Kantorovich dual potential $v(\mathbf{r})$.

Solving the Kantorovich dual formulation: pseudocharge

For numerical efficiency, want "small" computational domain (similar to density $\rho(\mathbf{r})$).
Idea: preserve asymptotic behavior of $v(\mathbf{r})$ by introducing a *pseudocharge* $m(\mathbf{r})$ associated to $v(\mathbf{r})$:

$$v(\mathbf{r}) = \int \frac{m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}'.$$

The asymptotic behavior $v(\mathbf{r}) \sim \frac{N-1}{|\mathbf{r}|}$ translates to the constraint

$$\int m(\mathbf{r}) \, \mathrm{d}\mathbf{r} = N - 1.$$

Beryllium atom (dual formulation)

Simple *Ansatz*: parametrize the pseudocharge $m(\mathbf{r})$ by a single Gaussian function:

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

Corresponding Kantorovich potential:

$$v(\mathbf{r};\sigma) = \int \frac{m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}' = \frac{N-1}{|\mathbf{r}|}\,\mathrm{erf}\left(\frac{|\mathbf{r}|}{\sqrt{2}\,\sigma}\right)$$

Relative error of $V_{\mathrm{ee}}^{\mathrm{SCE}}$: 20.3%

Beryllium atom (dual formulation)

Next idea: parameterize the pseudocharge m by a sum of two concentric Gaussian functions:

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

The relative error of $V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho]$ is significantly reduced to 1.6%!

Beryllium atom (dual formulation)

Results using the dual formulation:

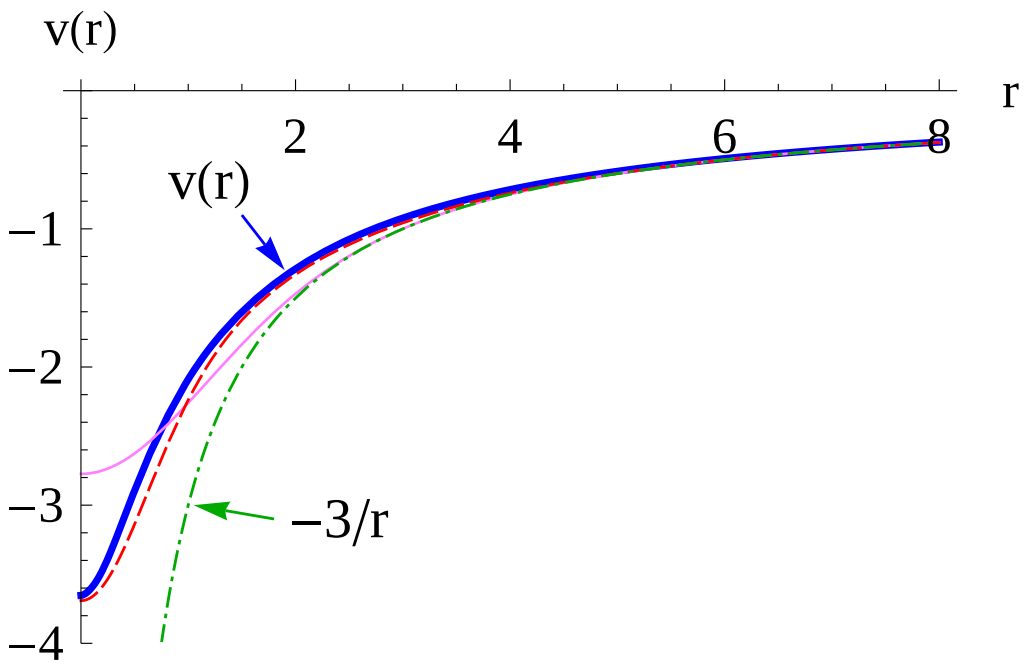


Figure: Kantorovich potential $v(\mathbf{r})$: co-motion formulation (thick blue solid line), Kantorovich dual formulation with the pseudocharge $m(\mathbf{r})$ parametrized by a single Gaussian (thin magenta solid line) and by the sum of two Gaussians (red dashed line). The green dot-dashed line shows the asymptotic expansion.

Quantum wire

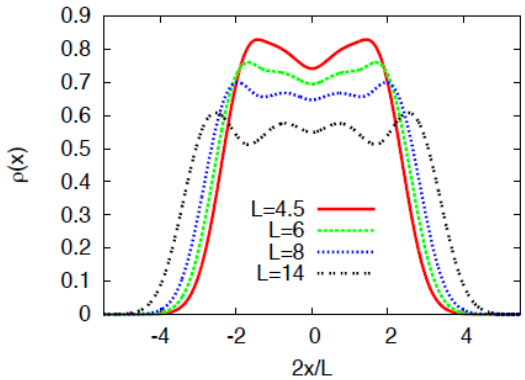
Model problem studied by Malet and Gori-Giorgi (2012).
$N = 4$ electrons, Hamiltonian

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

where $v_{\mathrm{ext}}(x) = \frac{1}{2}\omega^2 x^2$ is a confining potential and

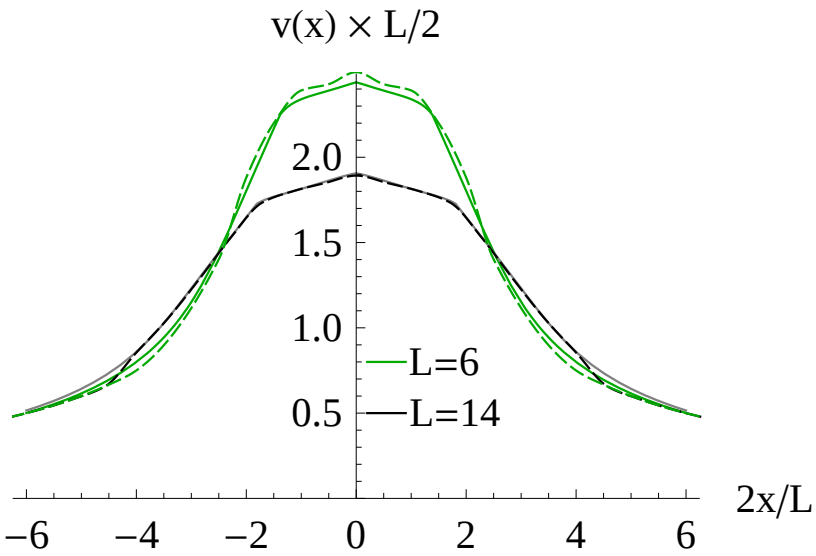
$$w_b(x) = \frac{\sqrt{\pi}}{2\,b}\exp\left(\frac{x^2}{4\,b^2}\right)\mathrm{erfc}\left(\frac{|x|}{2\,b}\right)$$

is the effective Coulomb interaction.

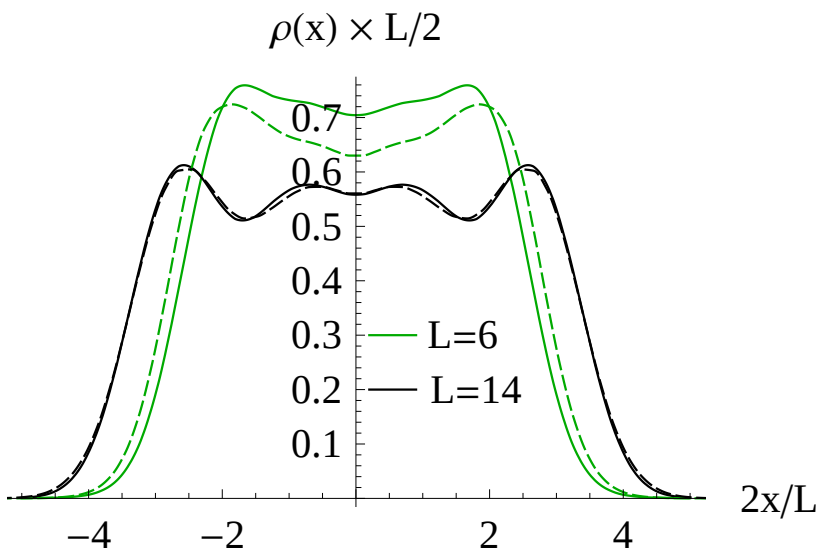


Quantum wire (dual formulation)

- SCF iteration, both for co-motion formulation and Kantorovich dual formulation
- comparison of results:



(a) potential $v(x)$



(b) density $\rho(x)$

Figure: dual formulation (dashed lines) compared to co-motion formulation (reference, solid lines)

Quantum wire (dual formulation)

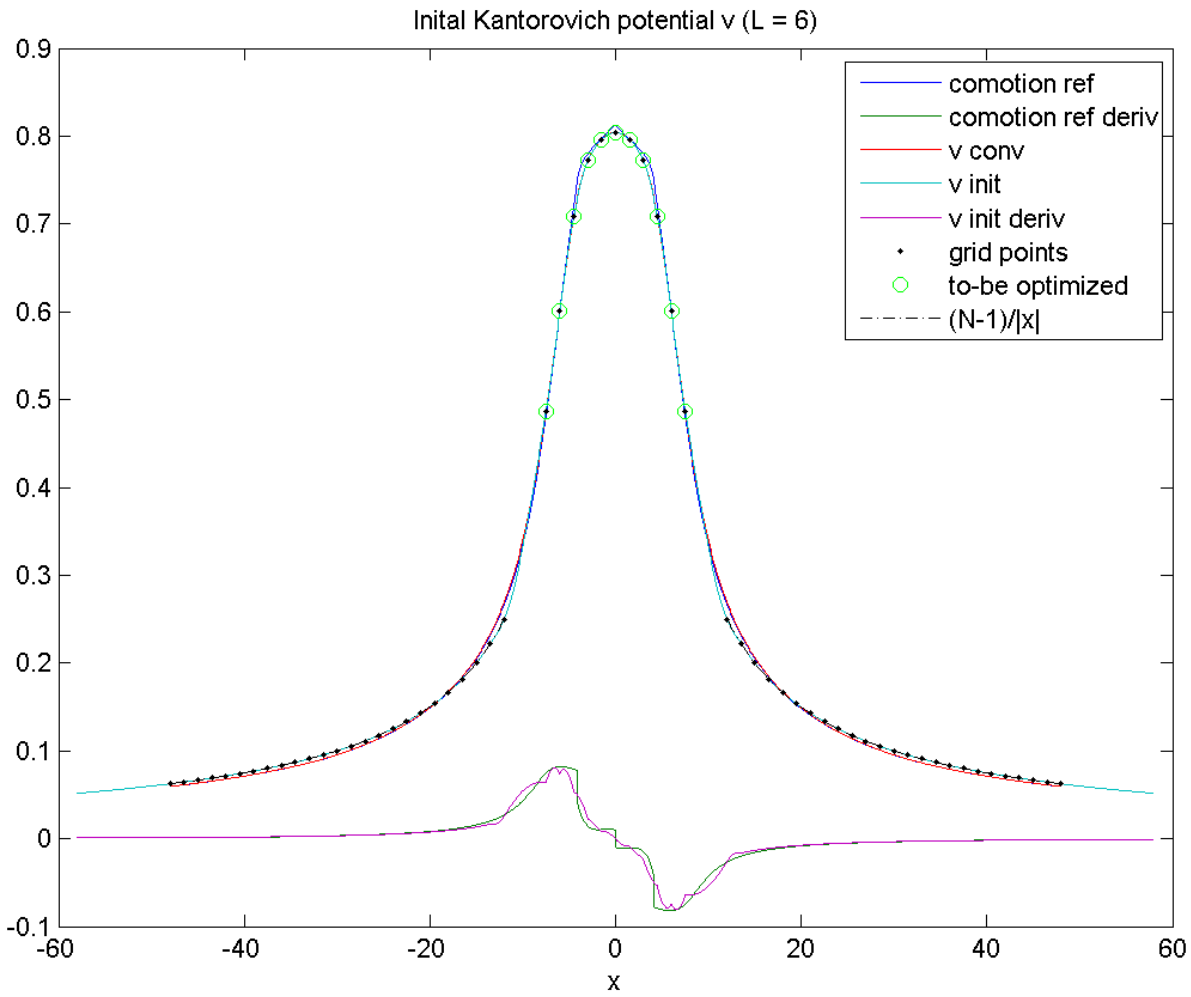
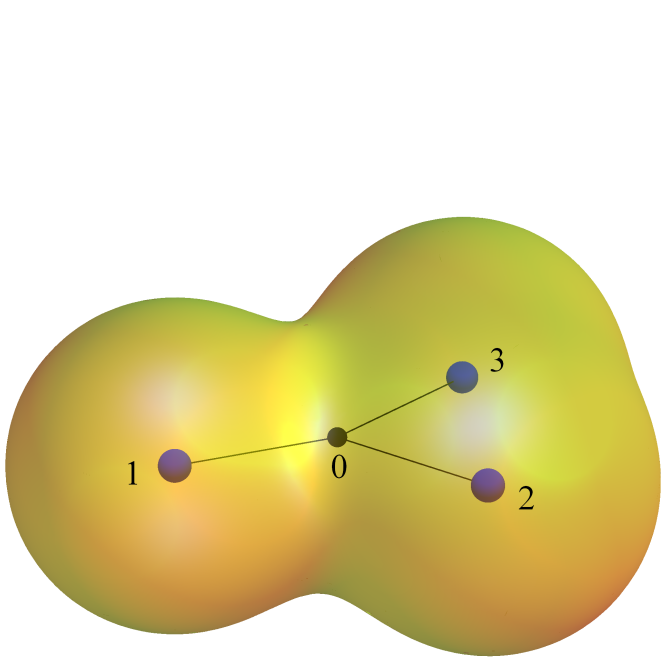
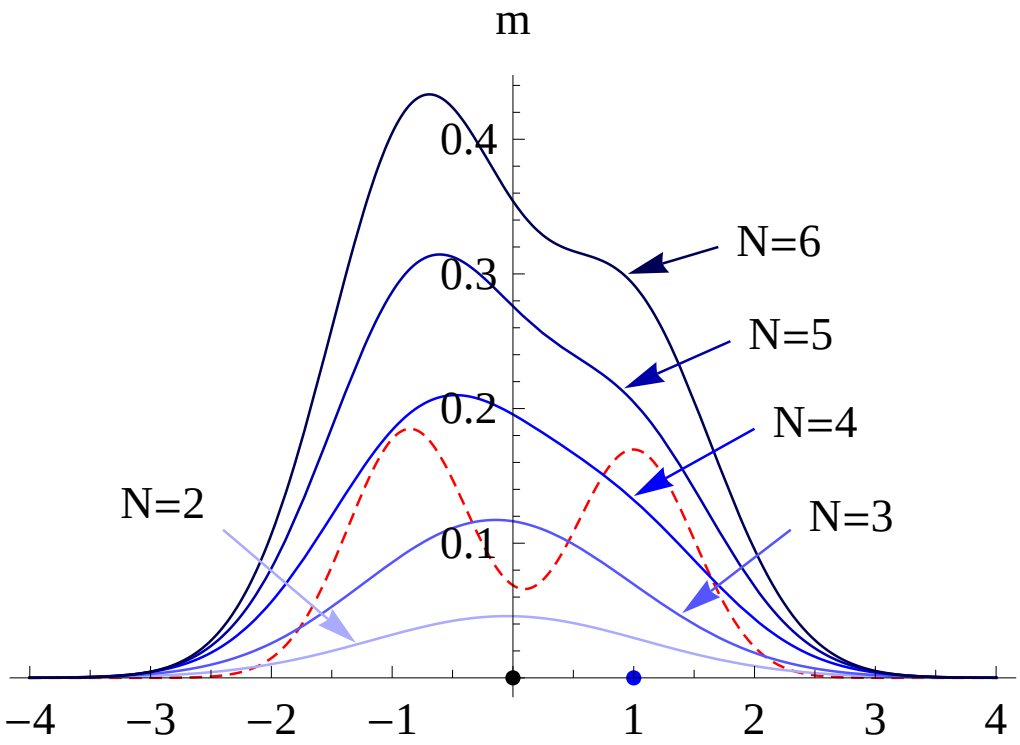


Figure: Parametrization of the dual potential v

Trimer molecule in 3D



(a) density $\rho(\mathbf{r})$



(b) pseudocharge $m(\mathbf{r})$

Figure: (a) isosurface of the electron density $\rho(\mathbf{r})$. (b) Optimized pseudocharge m of the trimer molecule (solid blue) and density $\rho(\mathbf{r})$ as in (a) (dashed red), plotted along the line connecting 1 and 0 in (a).

Reduced density models

Reduction to probability densities

First observation (implicit in Seidl et al. (1999b, 2007)):

$$\left\langle \Psi \left| \hat{V}_{\mathrm{ee}} \right| \Psi \right\rangle = \sum_{\sigma_1,\ldots,\sigma_N} \int \cdots \int \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times |\Psi(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N)|^2 \, \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N$$

only depends on the N-particle density ρ_N obtained by "tracing out" the spin variables:

$$\rho_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{\sigma_1,\ldots,\sigma_N} |\Psi(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N)|^2 .$$

Thus, antisymmetry of the fermionic Ψ translates to symmetry of $\rho_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ under $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$. Taking the "mathematical closure" leads to symmetric probability densities on $\mathbb{R}^{3N}$, i.e.,

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \min_{\rho_N \mapsto \rho,\, \rho_N \in \mathcal{P}_N^{\mathrm{sym}}} \int_{\mathbb{R}^{3N}} V_{\mathrm{ee}} \, \rho_N .$$

Two-body density formulation

Second observation (well known in the physics literature): since $\hat{V}_{\mathrm{ee}}$ is a two-body operator, its expectation value only depends on the two-body reduced density p_2 (ρ_2 rescaled by $\binom{N}{2}$):

$$\int \cdots \int_{\mathbb{R}^{3N}} V_{\mathrm{ee}}\, \rho_N = \binom{N}{2} \int \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, p_2(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2$$

with

$$p_2(\mathbf{r}_1, \mathbf{r}_2) = \int \cdots \int \rho_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_3 \cdots \mathrm{d}\mathbf{r}_N. \qquad (1)$$

This leads to

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \min_{\substack{p_2 \mapsto \rho/N, \\ p_2\ N\text{-density rep.}}} \binom{N}{2} \int \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, p_2(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2,$$

N-density representability meaning that (1) holds for a $\rho_N \in \mathcal{P}_N^{\mathrm{sym}}$.

k-density representability approximation

Observation: if p_2 is N-density representable, then it is also k-density representable for $k < N$ (follows by tracing out $\mathbf{r}_{k+1}, \ldots, \mathbf{r}_N$ from ρ_N). Thus N-density representability becomes more stringent as N increases.
(Friesecke et al. 2013) For $k = 2, 3, \ldots$, define

$$V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho] = \min_{\substack{p_2 \\ p_2 \mapsto \rho/N, \\ k\text{-density-rep.}}} \binom{N}{2} \int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, p_2(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2$$

(take k-body correlations into account) $\rightsquigarrow$ natural hierarchy of approximations:

$$\begin{array}{ccccccc} V_{\mathrm{ee}}^{\mathrm{SCE},2}[\rho] & & \leq & \ldots & V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho] & \leq & \ldots \quad V_{\mathrm{ee}}^{\mathrm{SCE},N}[\rho] \\ \| & & & & & & \| \\ \min_{p_2 \mapsto \rho/N} \int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, p_2 & & & & & & V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] \end{array}$$

Results for ab initio densities for small atoms

$V_{\mathrm{ee}}^{\mathrm{SCE},k}$ of an N-electron system can be obtained by simulating a fictitious k-electron system:

$$V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho] = \frac{\binom{N}{2}}{\binom{k}{2}} V_{\mathrm{ee}}^{\mathrm{SCE}}\left[\tfrac{k}{N}\rho\right].$$

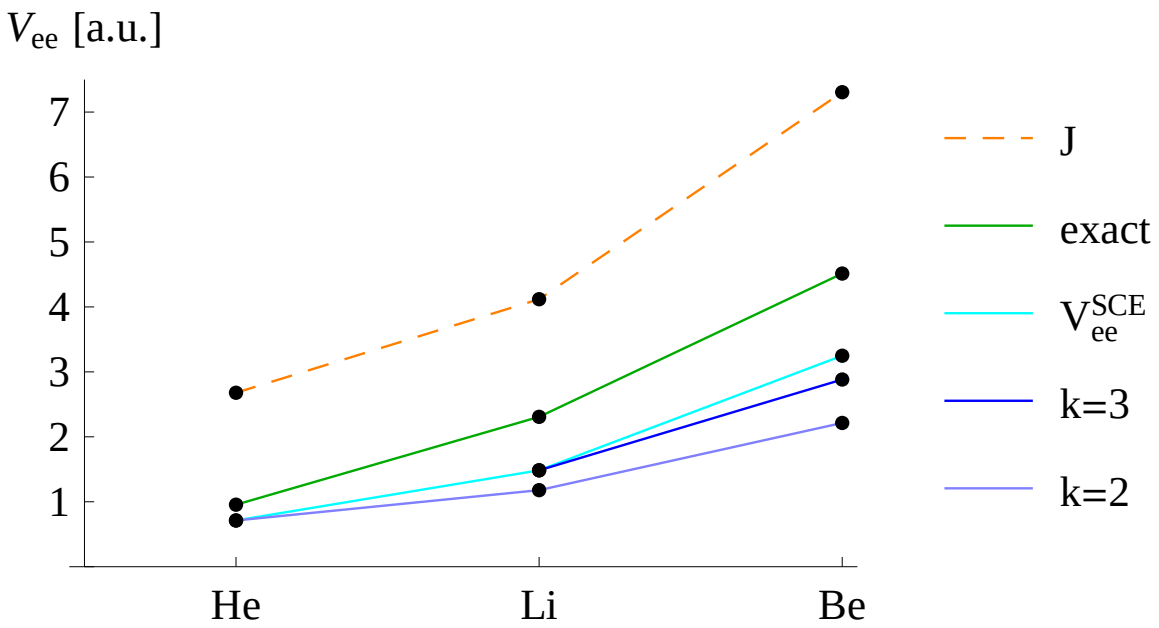


Figure: $V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho]$ (blue) in comparison to the true $V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho]$ (cyan)

Self-consistent Kohn-Sham using $V_{\mathrm{ee}}^{\mathrm{SCE},k}$ for atoms

Energy functional

$$E[\rho] = T_{\mathrm{KS}}[\rho] + V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho] + \int v_{\mathrm{ext}}(\mathbf{r})\,\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

with T_{KS} the Kohn-Sham kinetic energy functional and v_{ext} the external nuclear potential, i.e., $E_{\mathrm{xc}} = V_{\mathrm{ee}}^{\mathrm{SCE},k} - J$.
$\rightsquigarrow$ single-particle Hamiltonian:

$$H[\rho] = -\frac{1}{2}\Delta - \frac{Z}{|\mathbf{r}|} + u[\rho],$$

where $u[\rho] = v[\rho] + C$ is the Kantorovich dual potential. Using

$$\nabla v[\rho](\mathbf{r}) = -\sum_{i=2}^{N} \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}, \qquad \lim_{|\mathbf{r}|\to\infty} v[\rho](\mathbf{r}) = 0$$

to calculate $v[\rho](\mathbf{r})$ as in Seidl et al. (2007).

Self-consistent Kohn-Sham using $V_{\mathrm{ee}}^{\mathrm{SCE},k}$ results

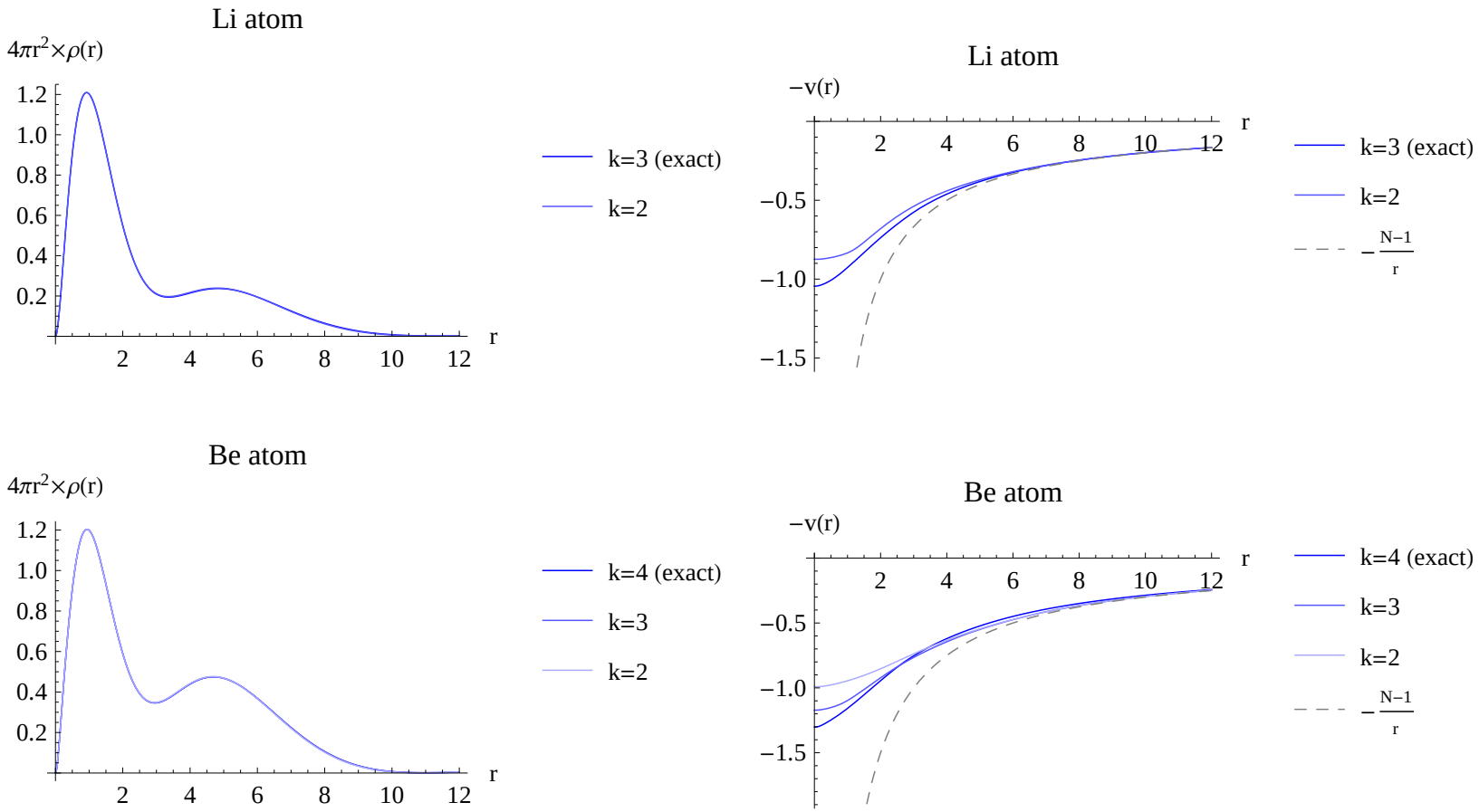


Figure: Self-consistent density and shifted Kantorovich potential $v[\rho]$ (rescaled by $\frac{N-1}{k-1}$) corresponding to $V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho]$.

Summary and conclusions

- Optimal transport with Coulomb cost

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

converted to dual formulation problem

$$V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho] = \max_{v} \left(\int v(\mathbf{s})\rho(\mathbf{s})\,\mathrm{d}\mathbf{s} + g[v] \right),$$

$$g[v] = \min_{\{\mathbf{r}_i\}} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} v(\mathbf{r}_i)$$

- Advantage: applicable to more general systems (without spherical symmetry)

Summary and conclusions (cont.)

- k-density representability approximation

$$V_{\mathrm{ee}}^{\mathrm{SCE},k}[\rho] = \min_{\substack{p_2 \mapsto \rho/N, \\ p_2 \ k\text{-density-rep.}}} \binom{N}{2} \int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} p_2(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2$$

$$= \frac{\binom{N}{2}}{\binom{k}{2}} V_{\mathrm{ee}}^{\mathrm{SCE}}\left[\tfrac{k}{N}\rho\right]$$

- Low-order approximation already captures a large part of the correlations (for the systems considered here)
- Long-term goal: design exchange-correlation functionals based on the SCE limit for strongly correlated systems

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