Kohn-Sham Density Functional Theory in the Framework of "Strictly Correlated Electrons"

(joint work with Lin Lin, Huajie Chen, Gero Friesecke, Francesc Malet and Paola Gori-Giorgi)

Christian B. Mendl

Technische Universität München (TUM)

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Wigner crystallization at low electron density

Homogeneous electron gas will "crystallize" and form a lattice for low densities, predicted by Wigner 1934. Somewhat counter-intuitively, the low density limit corresponds to strong correlation: denote the average distance between electrons by a:

$$\text{kinetic energy}: E_{\mathrm{kin}} \sim \frac{p^2}{2m} \sim \frac{\hbar^2}{2ma^2}$$

$$\text{potential energy}: V_{\mathrm{ee}} \sim \frac{e^2}{a}$$

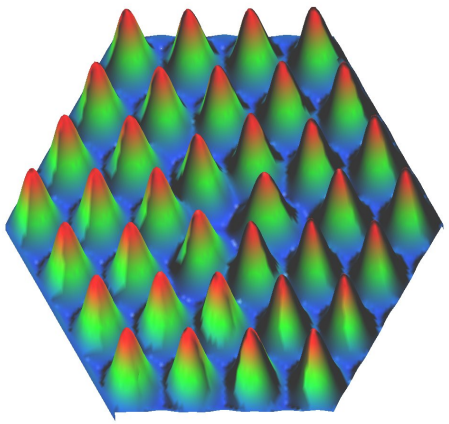


Figure: Wigner crystal (image by John Trail)

Thus for large a, potential energy (Coulomb repulsion) dominates!

DFT for strictly correlated electrons (SCE)

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. 1999a,b, 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

Connection with "optimal transport"

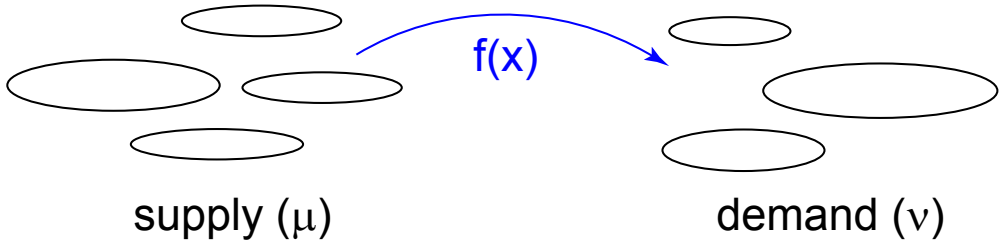


Figure: transport plan f from "supply" to "demand"

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

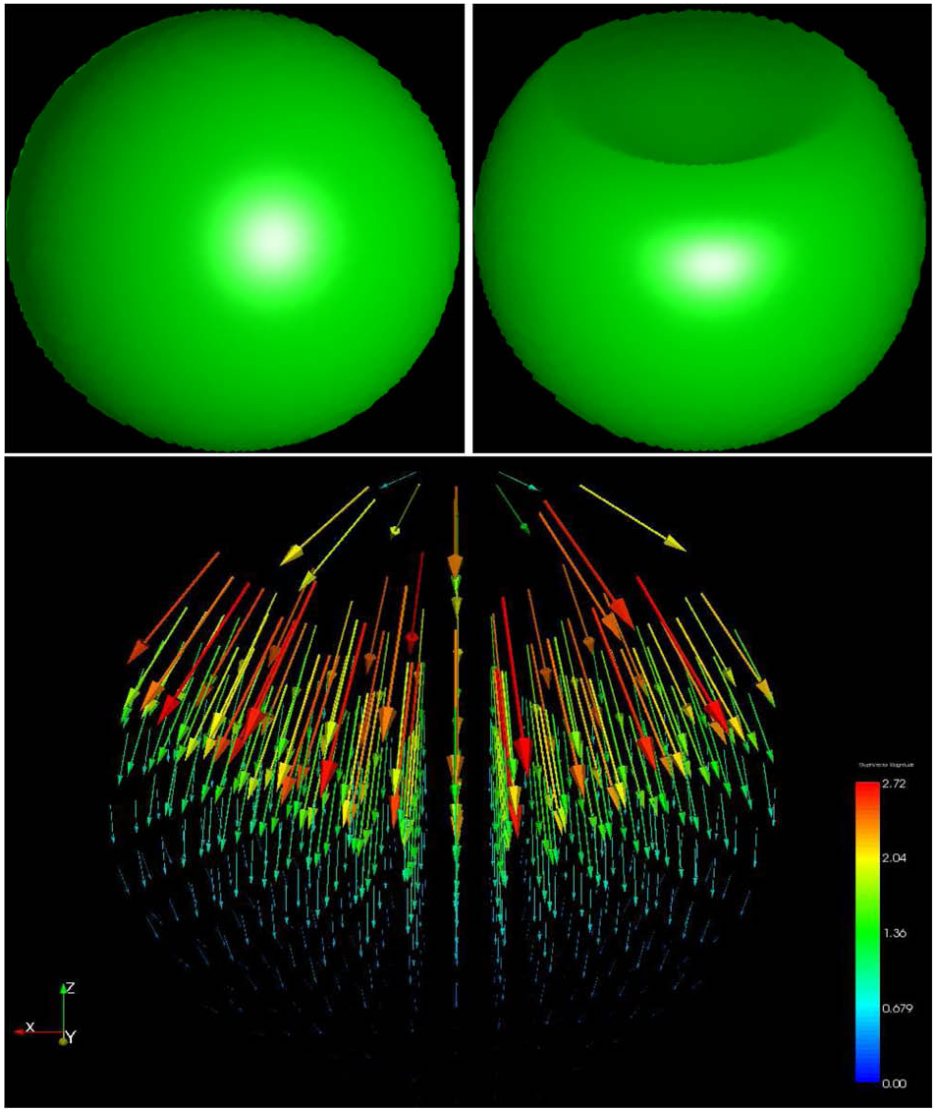


Figure: Sphere mapped to its deformed counterpart (Rehman et al. 2009)

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 $N = 2$:

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

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. 1999a,b, 2007), corresponding 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* $\rho(\mathbf{f}_i(\mathbf{r})) \, |\det \nabla \mathbf{f}_i(\mathbf{r})| = \rho(\mathbf{r})$, and

$$\mathbf{f}_1(\mathbf{r}) := \mathbf{r}, \quad \mathbf{f}_2(\mathbf{r}) := \mathbf{f}(\mathbf{r}), \quad \mathbf{f}_3(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{r})), \quad \mathbf{f}_4(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{f}(\mathbf{r}))),$$
$$\cdots \quad \underbrace{\mathbf{f}(\mathbf{f}(\ldots \mathbf{f}(\mathbf{f}(\mathbf{r}))))}_{N \text{ times}} = \mathbf{r}$$

due to indistinguishability of the electrons

Application: Wigner localization in 2D quantum dots

(C. B. Mendl, F. Malet and P. Gori-Giorgi PRB 2014)
N electrons in two dimensions, laterally confined by a parabolic potential, described by Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} m \omega^2 r_i^2 \right) + e^2 \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

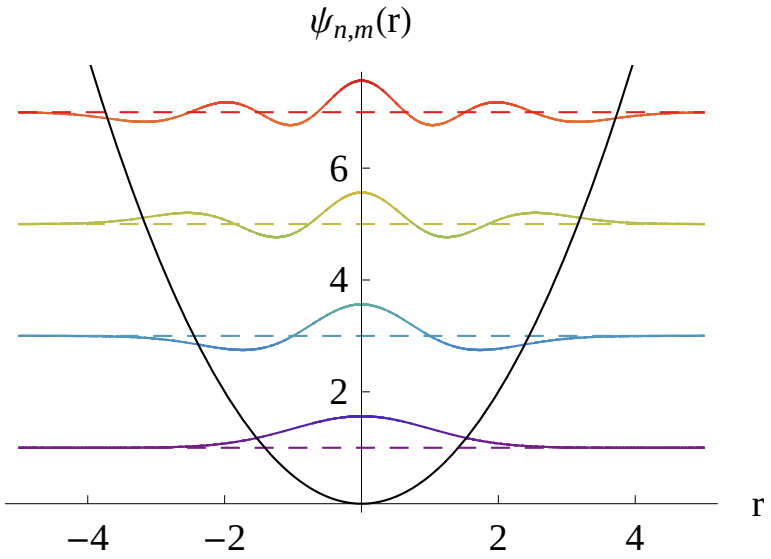


Figure: Single-electron eigenstates for $\omega = 1$

Wigner localization in 2D quantum dots

Standard spin-restricted Kohn-Sham equations

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

with $v_{\mathrm{KS}}[\rho](\mathbf{r})$ the Kohn-Sham potential. Here, approximate

$$v_{\mathrm{KS}}(\mathbf{r}) \simeq v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{SCE}}(\mathbf{r})$$

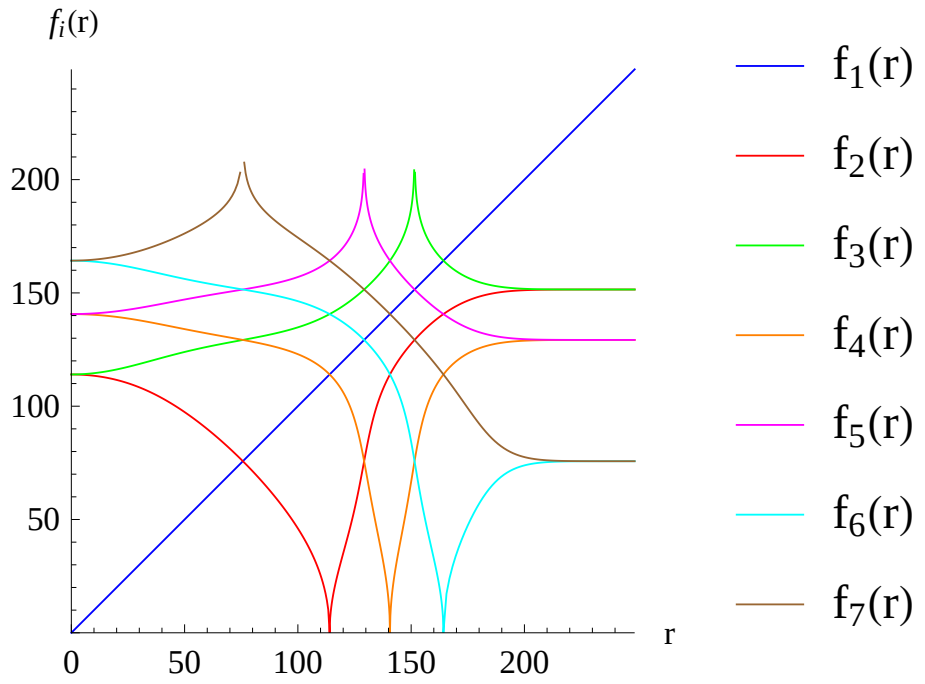
with $v_{\mathrm{ext}}(\mathbf{r}) = \frac{1}{2} m \omega^2 r^2$ the external potential and $v_{\mathrm{SCE}}(\mathbf{r})$ the one-body local potential corresponding to the Coulomb repulsion from the other electrons:

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

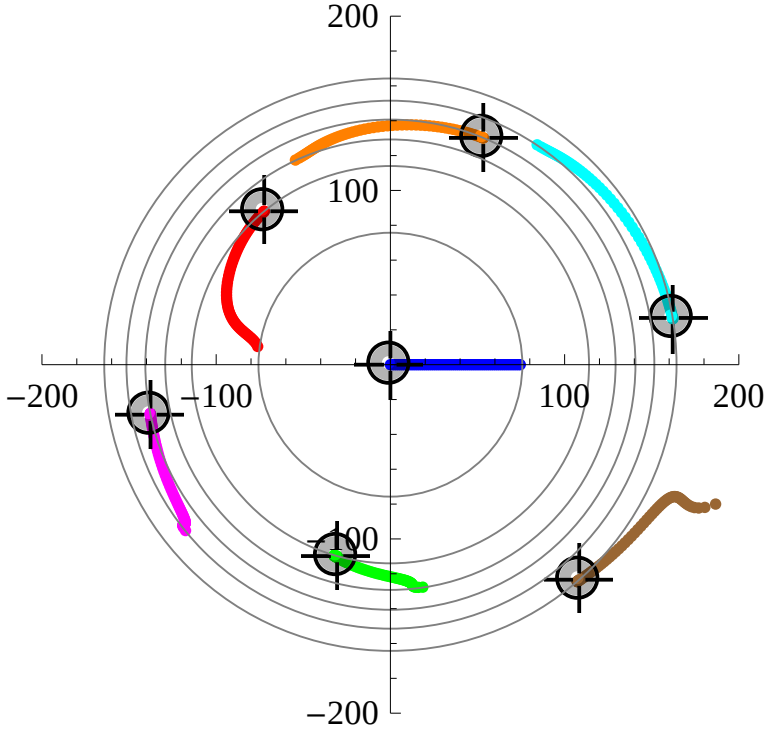
It holds that $v_{\mathrm{SCE}}[\rho](\mathbf{r}) = \frac{\delta V_{\mathrm{ee}}^{\mathrm{SCE}}[\rho]}{\delta \rho(\mathbf{r})}$.

Wigner localization in quantum dots: co-motion functions

For *circularly* symmetric systems, can separate co-motion functions into radial and an angular part! Semi-analytic formulas for radial part, simplifies calculation considerably.



(a) radial components



(b) trajectories

Figure: Co-motion functions $\mathbf{f}_i(\mathbf{r}) = (f_i(r), \theta_i(r))$ for the unpolarized quantum dot with $N = 7$ and $\omega = 0.001$

Wigner localization in quantum dots: co-motion functions

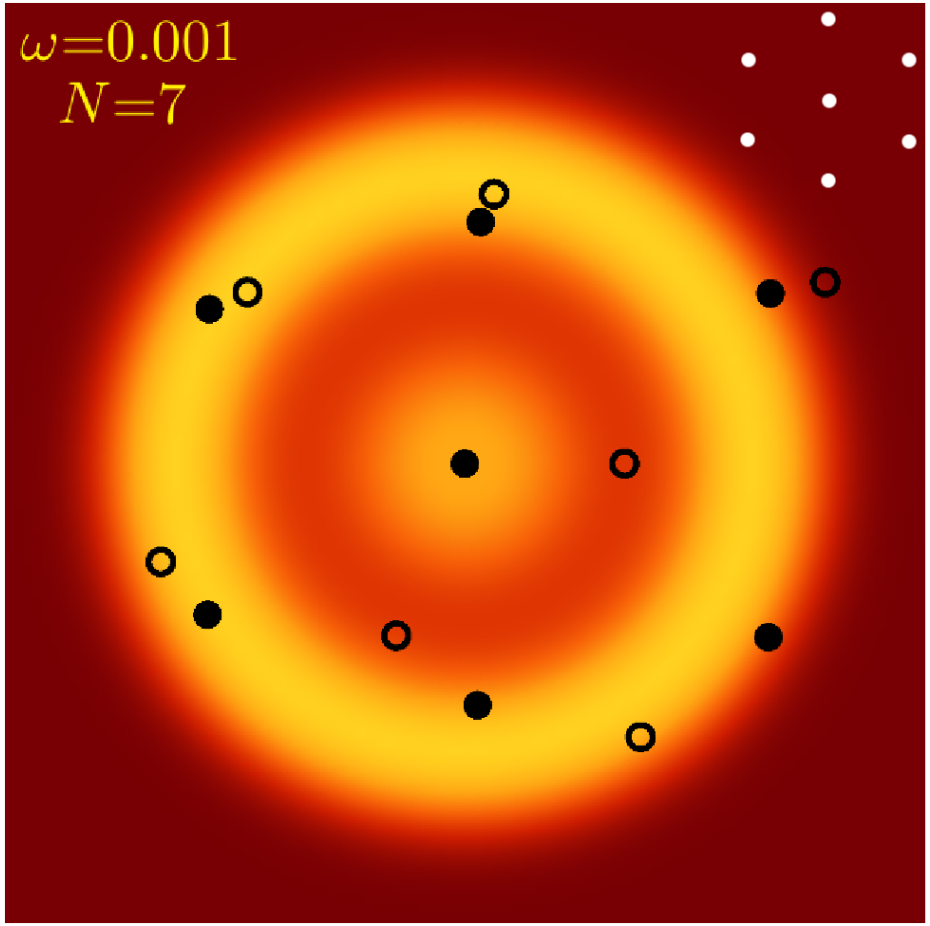
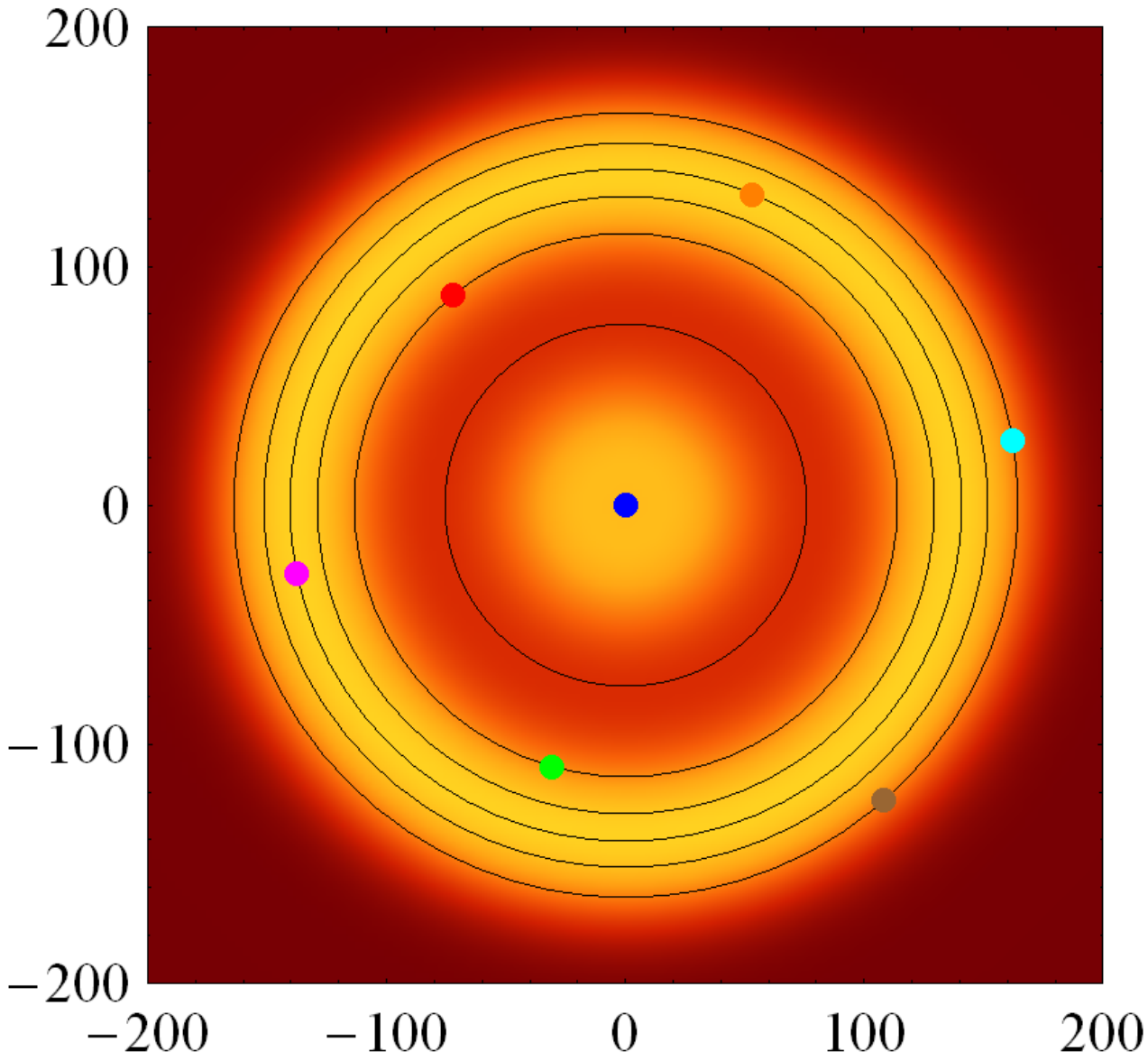


Figure: Co-motion functions $\mathbf{f}_i(\mathbf{r}) = (f_i(r), \theta_i(r))$ for two different positions of the "first" electron, corresponding to the unpolarized dot with $N = 7$ and $\omega = 0.001$

Wigner localization in quantum dots: co-motion functions



Wigner localization in 2D quantum dots: density

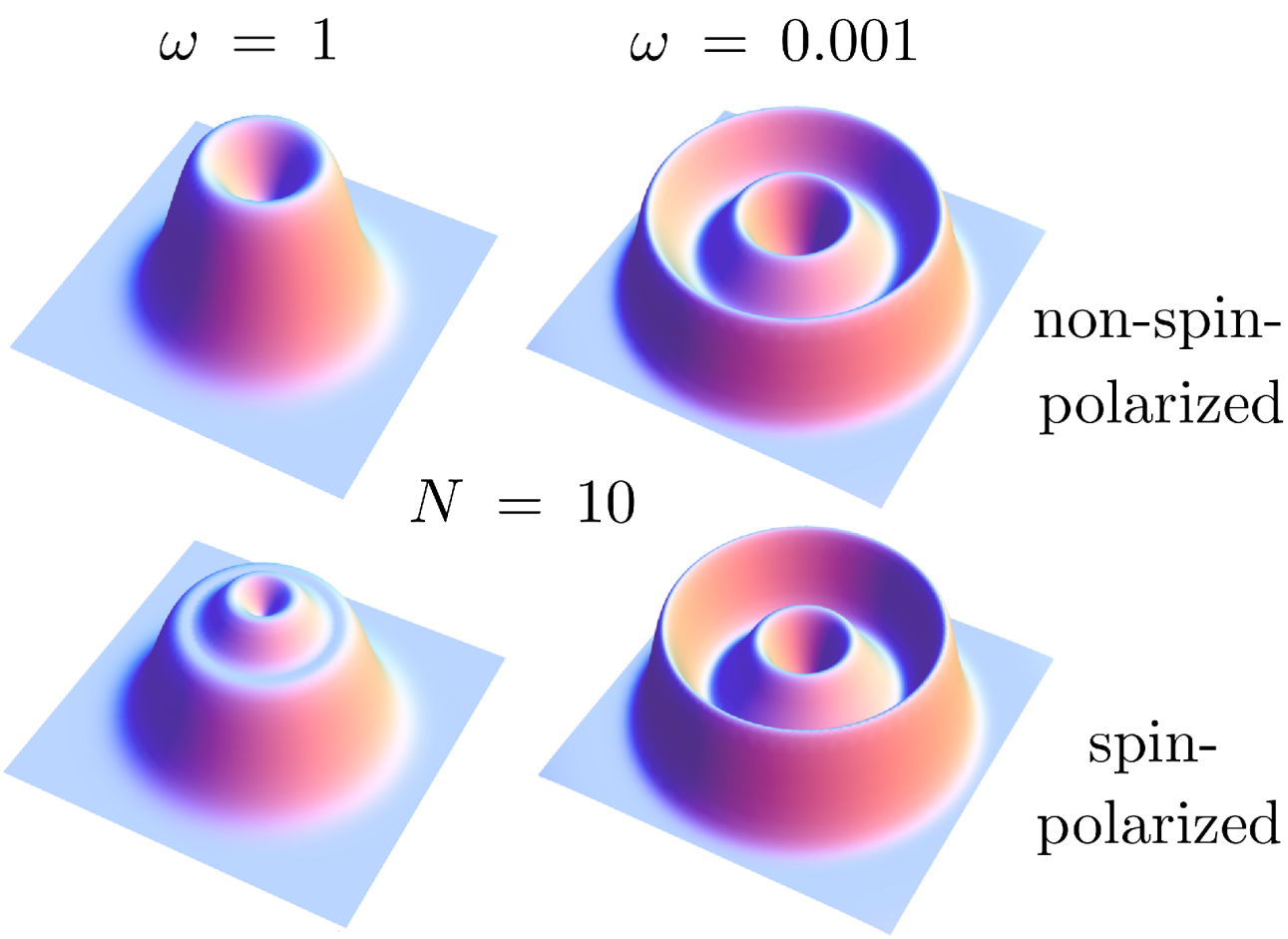


Figure: Electronic density $\rho(r)$ for a quantum dot with $N = 10$ electrons, for $\omega = 1$ and $\omega = 0.001$

Kantorovich dual formulation of optimal transport

Kantorovich dual formulation of optimal transport

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:

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

$\rightsquigarrow$ 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

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

Example: Beryllium atom

Results using the dual formulation:

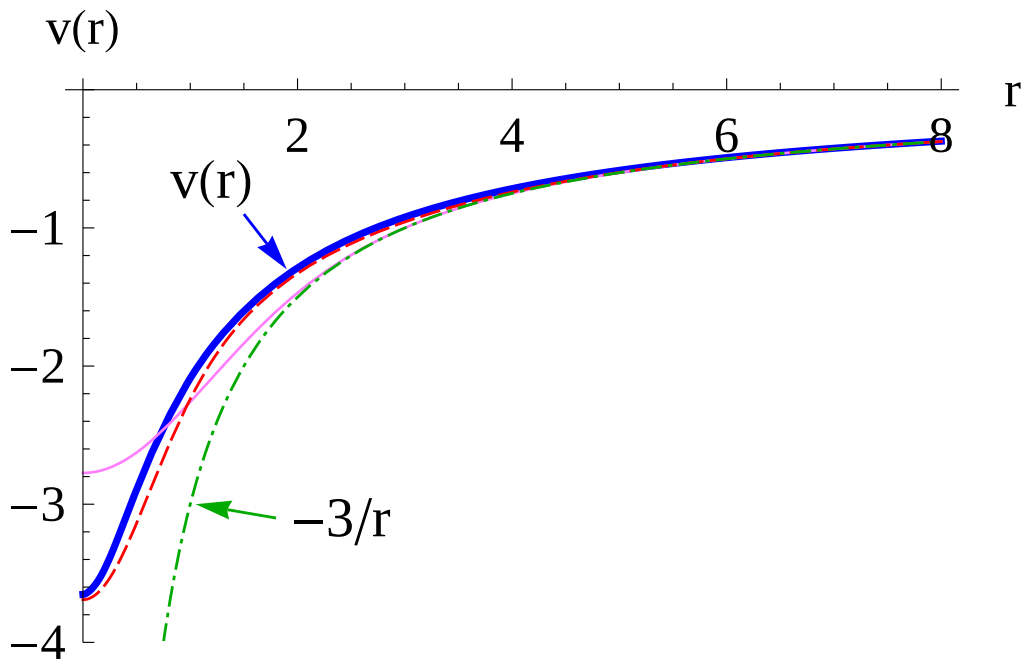
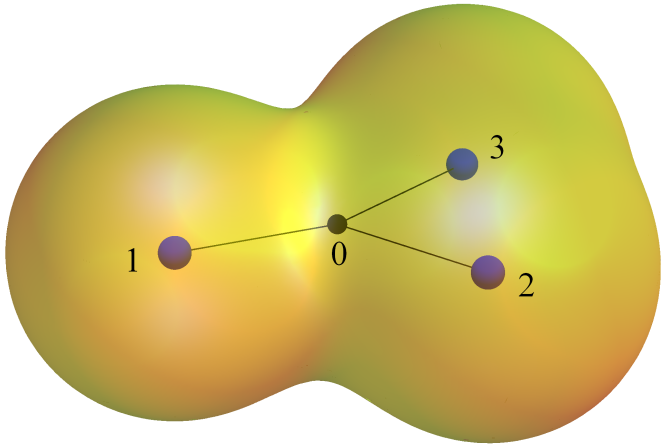
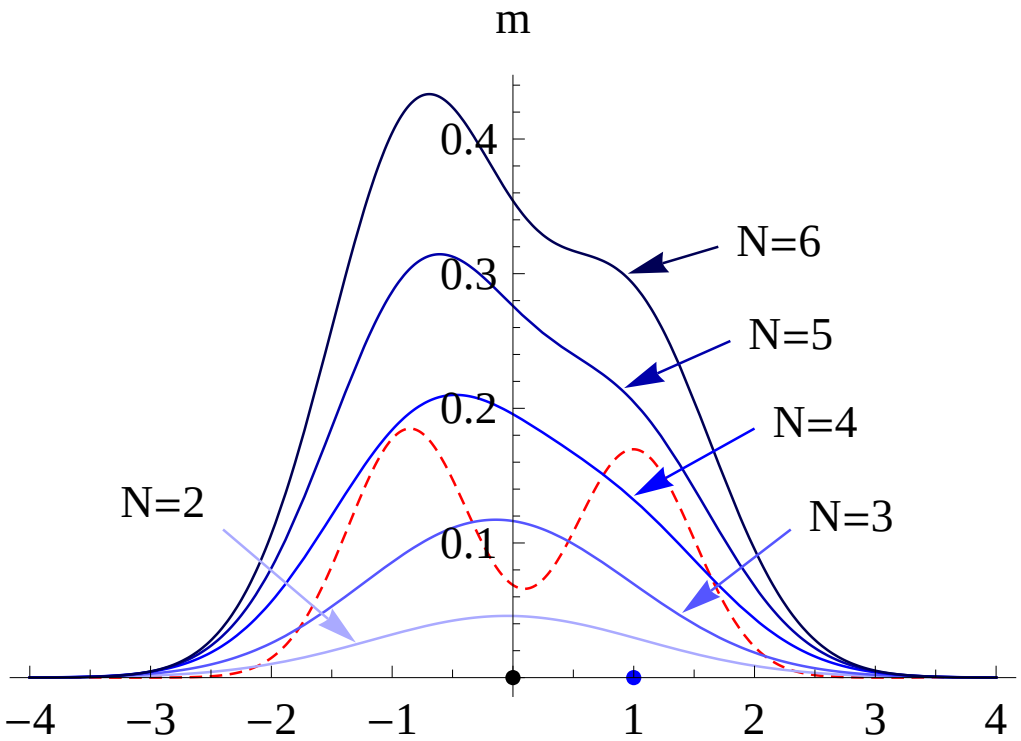


Figure: Kantorovich potential $v(\mathbf{r})$: co-motion formulation (thick blue solid line), Kantorovich dual formulation with the pseudocharge $m(\mathbf{r})$ parametrized by a single Gaussian (thin magenta solid line) and by the sum of two Gaussians (red dashed line). The green dot-dashed line shows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

Example: 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).

Outlook: co-motion functions using finite elements

(joint work in progress with H. Chen and G. Friesecke)
Finite elements $e_1, \cdots, e_n$, with barycenters $\mathbf{c}_k$ and electron mass $\rho_k = \int_{e_k} \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$. Approximate the co-motion function by

$$\mathbf{f}(\mathbf{c}_k) = \sum_{1 \le l \le n} \mathbf{c}_l \frac{x_{kl}}{\rho_l}.$$

x_{kl} represents the electron mass transported from $\mathbf{c}_k$ to $\mathbf{c}_l$.
$\rightsquigarrow$ linear programming problem

$$\min_{x} \sum_{1 \le k,l \le n} \frac{x_{kl}}{|\mathbf{r}_k - \mathbf{r}_l|}$$

$$\text{s.t.} \sum_{1 \le k \le n} x_{kl} = \rho_k, \quad l = 1, \cdots, n$$

$$\sum_{1 \le l \le n} x_{kl} = \rho_l, \quad k = 1, \cdots, n$$

$$x_{kl} \ge 0$$

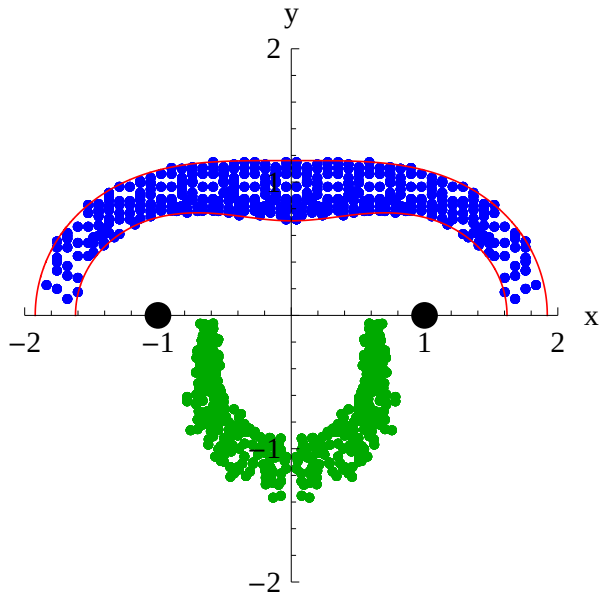


Figure: OT map example for H_2 molecule

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