Strictly-Correlated Electrons systems and their dissociation at infinity

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Ground-state energy problem

Quantum many-body problem:

- N fermions/bosons in $\mathbb{R}^d$ $\rightsquigarrow$ Anti/symmetric wavefunction $\Psi \in L^2(\mathbb{R}^{dN})$
- $w(x-y)$ symmetric two-body interaction potential — *e.g.* $w_s(x) = |x|^{-s}$ for $s > 0$
- $V : \mathbb{R}^d \to \mathbb{R}$ external potential

$$H_V(N) := -\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} V(x_i) + \sum_{1 \le i < j \le N} w(x_i - x_j)$$

Ground-state energy problem:

$$E_N(V) := \inf \left\{ \langle \Psi, H_N(V)\Psi \rangle_{L^2} \quad : \quad \Psi \in L^2(\mathbb{R}^{dN}) \text{ with } \|\Psi\|_{L^2} = 1 \right\}$$

☹ Very high-dimensional problem when $N \gg 1$: infeasible !

Density Functional Theory

- Wavefunction $\Psi \in L^2(\mathbb{R}^{dN})$ has one-particle density $\rho_\Psi \in L^1(\mathbb{R}^d)$

$$\rho_\Psi(x) := N \int_{\mathbb{R}^{d(N-1)}} |\Psi|^2(x, x_2, \dots, x_N) \mathrm{d}x_2 \dots, \mathrm{d}x_N$$

- Two-step minimisation : split *infimum* into two *infima*

$$E_N(V) = \inf_{\|\Psi\|_{L^2}=1} \{\cdots\} = \inf_{\substack{\rho \geq 0 \\ \int_{\mathbb{R}^d} \rho = N + \dots}} \inf_{\substack{\|\Psi\|_{L^2}=1 \\ \rho_\Psi = \rho}} \{\cdots\} = \inf_{\substack{\rho \geq 0 \\ \int_{\mathbb{R}^d} \rho = N + \dots}} \left\{ F_\hbar(\rho) + \int_{\mathbb{R}^d} V\rho \right\}$$

where $F_\hbar(\rho)$ is Levy–Lieb functional:

$$F_\hbar(\rho) = \inf_{\substack{\|\Psi\|_{L^2}=1 \\ \rho_\Psi = \rho}} \left\{ \frac{\hbar^2}{2} \int_{\mathbb{R}^{dN}} |\nabla \Psi|^2 + \int_{\mathbb{R}^{dN}} \sum_{1 \leq i < j \leq N} w(x_i - x_j) |\Psi|^2 \right\}$$

☻ Variational problem on $L^1(\mathbb{R}^d)$: does not depend on N !

Universal Functionals in Density Functional Theory, Lewin, Lieb & Seiringer '19

Approximate functionals for $F_\hbar(\rho)$

☹ Unknown $F_\hbar(\rho)$: use approximate functionals !

Kohn-Sham (KS) : Leading order = kinetic energy [Kohn–Sham, '84]

$$F_\hbar(\rho) = \inf_{\substack{\|\Psi\|_{L^2}=1 \\ \rho_\Psi=\rho}} \left\{ \frac{\hbar^2}{2} \int_{(\mathbb{R}^d)^N} |\nabla\Psi|^2 \right\} \quad + \quad \textit{corr. terms for interactions}.$$

= non-interacting systems of bosons/fermions

Strictly–Correlated Electrons (SCE) : Leading order = interactions [Seidl, Perdew & Levy '99]

$$F_\hbar(\rho) = \inf_{\substack{\|\Psi\|_{L^2}=1 \\ \rho_\Psi=\rho}} \left\{ \int_{(\mathbb{R}^d)^N} \sum_{1\le i<j\le N} w(x_i - x_j)|\Psi|^2 \right\} \quad + \quad \textit{corr. terms for kinetic energy}$$

= only interactions, no kinetic energy = classical problem

Density functionals based on the mathematical structure of the Strong-interaction limit of DFT, Vuckovic et al. '23

The Strong-Interaction Limit of Density Functional Theory, Friesecke, Gori-Giorgi & Gerolin '23

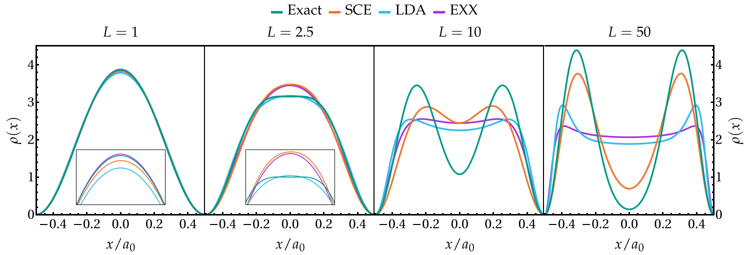
Strictly–Correlated Electrons [See *e.g.* Seidl & Gori–Giorgi's research group]

- Exact approximation in strong-correlation regime $\hbar \to 0$

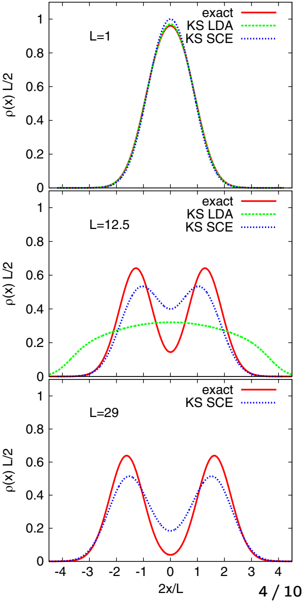
[Cotar, Friesecke & Klüppelberg '13 & '18, Bindini & De Pascale '17, Lewin '18]

- In practice, used in corrections terms for Kohn–Sham (KS–SCE)

Mott insulator [Marie *et al.* PRR '22] :



Quantum 1D wire [Malet & Gori–Giorgi PRL '12] ⟶



Multimarginal Optimal Transport & SCE [Buttazzo, De Pascale & Gori-Giorgi '12] & [Cotar, Friesecke & Klüppelberg '13]

- Minimizing $\mathbb{P} \neq |\Psi|^2$ to SCE is (generically) a singular measure:

$$F_{SCE}(\rho) := \min_{\substack{\mathbb{P} \in \mathscr{P}_{sym}(\mathbb{R}^{dN}) \\ \mathbb{P} \mapsto \rho}} \left\{ \int_{\mathbb{R}^{dN}} \sum_{1 \le i < j \le N} w(x_i - x_j) \mathrm{d}\mathbb{P}(x_1, \ldots, x_N) \right\}$$

➔ Multimarginal OT problem : N marginals and cost of transportation is interaction energy

What is OT ? Given two probability measures $\mu, \nu \in \mathscr{P}(\mathbb{R}^d)$ and a function $c : \mathbb{R}^d \times \mathbb{R}^d \to \mathbb{R}_+$ such that $c(x,y)$ is the cost of transporting an infinitesimal mass from x to y, the Kantorovich formulation of OT reads

$$OT(\mu, \nu) := \inf_{\pi \in \Pi(\mu,\nu)} \left\{ \int_{\mathbb{R}^d \times \mathbb{R}^d} c(x,y) \mathrm{d}\pi(x,y) \right\}$$

where $\Pi(\mu, \nu)$ is the set of $\pi \in \mathscr{P}(\mathbb{R}^d \times \mathbb{R}^d)$ such that the first (resp. second) marginal of π is μ (resp. ν).
Under the weak assumption that c is l.s.c., a minimising π^* always exists (*idem* for several marginals)

Optimal transport for applied mathematicans, Santambrogio '15

Optimal transportation theory with repulsive costs, Di Marino, Gerolin & Nenna '17

Kantorovich duality & SCE [Buttazo, Champion & De Pascale '17, Colombo, Di Marino & Stra '18]

Kantorovich duality The OT is equivalent to the following maximisation problem

$$OT(\mu,\nu) = \sup_{\phi,\psi \in C^0} \left\{ \int_{\mathbb{R}^d} \phi\mu + \int_{\mathbb{R}^d} \psi\nu + E(\phi,\psi) \right\} \quad \text{where } E(\phi,\psi) := \inf_{x,y} \{c(x,y) - \phi(x) - \psi(y)\}$$

Under some assumptions on c (and the marginals), a minimising pair (ψ,ϕ) exists, so-called **Kantorovich potential**. If the marginals are the same $\mu = \nu$, one can always suppose that $\psi = \phi$.

- **Application to SCE** : For all density ρ, there exists an external potential $v_{SCE} : \mathbb{R}^d \to \mathbb{R}$:

$$v_{SCE} \in \arg\max_{v} \left\{ E_N(v) - \int_{\mathbb{R}^d} v\rho \right\}, \qquad E_N(v) := \inf \left\{ \sum_{1 \le i < j \le N} w(x_i - x_j) + \sum_{i=1}^{N} v(x_i) \right\}$$

- Effective potential v_{SCE} gives rise to ground-state density ρ:

$$\sum_{1 \le i < j \le N} w(x_i - x_j) + \sum_{i=1}^{N} v_{SCE}(x_i) = E_N(v_{SCE}) \quad \text{on the support of minimising } \mathbb{P}$$

Ionisation conjecture for SCE

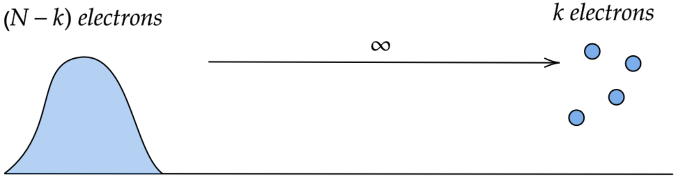
- Density $\rho \in L^1(\mathbb{R}^d)$ with $\rho > 0$ almost everywhere
- By definition of OT, we can send one electron to infinity:

$$\text{If } \mathbb{P} \in \mathscr{P}_{sym}(\mathbb{R}^{dN}) \text{ minimises } F_{SCE}(\rho) \rightsquigarrow \mathbb{P}(x_i \to \infty) > 0 \text{ for any } i \in \{1, \dots, N\}$$

❓ ***How many particles $k \leq N$ can we freely dissociate at infinity ?***

- Reminiscent of ionisation conjecture in quantum physics, conjectured[1] to be $k = 1$:

« *An atom with atomic number Z can bind at most $Z + 1$ electrons* »



[1] *The Strong-Interaction Limit of Density Functional Theory*, Friesecke, Gori-Giorgi & Gerolin '23

Ionisation conjecture for SCE (for *e.g* Coulomb-like interaction $w(x-y)=|x-y|^{-s}$)

Theorem (Ionisation conj. for SCE) [L, '22]

For all particle density $\rho \in L^1$ with $\overline{\{\rho > 0\}}$ unbounded, we have $k=1$. More precisely, if $\mathbb{P} \in \mathscr{P}_{sym}(\mathbb{R}^{dN})$ minimises $F_{SCE}(\rho)$, then it holds that

$$\mathbb{P}(x_i \to \infty, x_j \to \infty) = 0, \qquad \forall i \neq j \in \{1, \dots, N\}.$$

- Proof relies on *c*-cyclical monotonicity of optimal transport plans in OT
- Known $N=2$ with radial ρ & for all N in $d=1$ [Pass, '13] & [Colombo, De Pascale & Di Marino '15]

Corollary (Asymptotics of v_{SCE}) [L, '22]

For all particle density $\rho \in L^1$ with $\int_{\mathbb{R}^d} \rho = N$ and $\overline{\{\rho > 0\}}$ unbounded and connected, the following asymptotic holds:

$$v_{SCE}(x) \sim -(N-1)w(x) + o(w(x)) \qquad x \to \infty$$

- Somehow « exceptional » potential binding one additional electron.

Proof when $N = 2$ for Coulomb interaction $w(x-y) = |x-y|^{-1}$

- Let $\mathbb{P} \in \mathscr{P}(\mathbb{R}^{dN})$ be a minimiser for $F_{SCE}(\rho)$.
By c-cyclical monotonicity, for any $(x_1, x_2), (y_1, y_2) \in \mathrm{Supp}(\mathbb{P})$:

$$\frac{1}{|x_1 - x_2|} + \frac{1}{|y_1 - y_2|} \leq \frac{1}{|x_1 - y_1|} + \frac{1}{|x_2 - y_2|}$$

If it is possible to find $y_1, y_2 \to \infty$, we would obtain the contradiction $0 < \frac{1}{|x_1 - x_2|} \leq 0$ □

- By definition of v_{SCE} as the effective potential which forces the system into ρ:

$$\nabla v_{SCE}(x_1) = -\nabla_{x_1} |x_1 - x_2|^{-1}, \quad (x_1, x_2) \in \mathrm{Supp}(\mathbb{P})$$

and letting x_1 runs to infinity, we obtain the asymptotic (on ∇v_{SCE}) since x_2 remains in a compact set. □

Conclusion

- SCE is a DFT method that performs well for strongly-correlated systems
- It amounts to a peculiar multimarginal optimal transport problem

☻ We can then appeal to tools from OT: existence of v_{SCE} & « ionisation conjecture »

Lots of remaining questions...

- Shape of minimisers $\mathbb{P}$ to $F_{SCE}(\rho)$: ***Does there exist a map*** $T : \mathbb{R}^d \times \mathbb{R}^d$ ***such that***

$$\mathbb{P}(x_1,\dots,x_N) = \rho(x_1) \otimes \delta_{T(x_1)}(x_2) \otimes \cdots \otimes \delta_{T^{(N-1)}(x_1)}(x_N)$$

is a minimiser for $F_{SCE}(\rho)$ ***?*** Far from being understood...

- Efficient numerical methods to solve the OT problem ?