Scaling limits of density functional theory: cross-over from mean field theory to optimal transport

Gero Friesecke

TU Munich

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Organizers: Luigi Ambrosio, Bob Jerrard, Felix Otto, Mary Pugh, Robert Seiringer

joint work with H.Chen (TUM), C.Cotar (University College London), C.Klüppelberg (TUM), B.Pass (Alberta)

C.Cotar, G.F., C.Klüppelberg, CPAM 66, 548-599, 2013
G.F., Ch.Mendl, B.Pass, C.C, C.K., J.Chem.Phys. 139, 164109, 2013
C.C., G.F., B.Pass, arXiv 1307.6540, 2013
H.Chen, G.F., on arXiv soon, 2014

Density functional theory

Dirac 1929 Chemically specific behaviour of atoms and molecules captured, "in principle", by quantum mechanics.

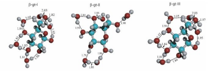
Emission/absorption spectra, binding energies, equilibrium geometries, interatomic forces,...

Catch Curse of dimension. Schrödinger eq. is for N- electron wavefunction $\Psi : (\mathbb{R}^3 \times \mathbb{Z}_2)^N to \mathbb{C}$. H_2O, N=10, PDE in $\mathbb{R}^{30}$, 10 gridpts each direction, 10^{30} gridpts.

Hohenberg, Kohn, Sham 1964/65 Replace Schröd.eq. by closed eq./var.principle for the one-point (or marginal) density $\rho : \mathbb{R}^3 \to \mathbb{R}$,

$$\rho(x_1) = N \sum_{s_1,..,s_N \in \mathbb{Z}_2} \int_{\mathbb{R}^{3(N-1)}} |\Psi(x_1, s_1, .., x_N, s_N)|^2 dx_2 \cdots dx_N.$$

– Nobel Prize 1998 for W.Kohn
– Routinely used in phys., chem., materials, molecular biology; huge non-math.literature (Ex.: Momany, Carbohyd. Res. 2005)



– Theory: ∃ 'exact' fctnal; practice: clever semi-empirical fctnals: LDA, B3LYP, PBE,...
– accuracy not so high; some failures; fctnals not systematically derivable/improvable

This talk Behaviour of 'exact' functional in scaling limits

Example: Original semi-empirical Kohn-Sham functional

- N-electron molecule, nuclear charges $Z_1, .., Z_M > 0$, nuclear positions $R_1, .., R_M \in \mathbb{R}^3$
- potential exerted by nuclei on electrons:
  $v(x) = -\sum_{\alpha=1}^{M} Z_\alpha |x - R_\alpha|^{-1}$
- Ground state energy:

$$E_0^{KS} = \min_\rho \quad \Big(\quad T^{KS}[\rho] + \frac{1}{2}\int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|} dx\, dy$$
$$- \quad \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int_{\mathbb{R}^3} \rho^{4/3} + \int v\,\rho \quad \Big)$$

where

$$T^{KS}[\rho] = \min\{\sum_{i=1}^{N} \frac{1}{2}\int_{\mathbb{R}^3} |\nabla\psi|^2 \, : \, \sum_i |\psi_i(x)|^2 = \rho(x), \, \langle\psi_i, \psi_j\rangle = \delta_{ij}, \, \psi_i \in H^1(\mathbb{R}^3; \mathbb{C}^2)\}$$

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Where do all these terms come from ...(???)...

'Exact' DFT according to Levy/Lieb

- Start from quantum Hamiltonian of N-electron system:

$$H_{e\ell} = \sum_{i=1}^{N}(-\frac{1}{2}\Delta_{x_i}) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} + \sum_{i=1}^{N} v(x_i)$$

(typically, $v(x_i) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|x_i - R\alpha|}$ potential exerted onto electrons by atomic nuclei)

- Ground state energy:

$$E_0 = \min_{\Psi\in\mathcal{A}_N} \left\langle \Psi, H_{e\ell}\Psi \right\rangle_{L^2}$$

where

$$\mathcal{A}_N = \{\Psi \in H^1((\mathbb{R}^3 \times \mathbb{Z}_2)^N; \mathbb{C}) \,:\, \Psi \text{ antisymmetric}, \ ||\Psi||_{L^2} = 1\}$$

'Exact' DFT according to Levy/Lieb, ctd.

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Hohenberg-Kohn-Theorem (1964) For each fixed N, there exists a universal (i.e., molecule-independent) functional F^{HK} of the single-particle density ρ such that for any external potential v, the exact QM ground state en. satisfies

$$E_0 = \min_{\rho \in \mathcal{R}_N} \Big(F^{HK}[\rho] + \int_{\mathbb{R}^3} v(x)\rho(x)\, dx \Big),$$

where $\mathcal{R}_N = \{\rho \in L^1(\mathbb{R}^3) \,:\, \rho \geq 0, \int \rho = N, \sqrt{\rho} \in H^1(\mathbb{R}^3)\}$.

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Proof 1. The non-universal part of the energy only depends on ρ_Ψ:

$$\langle \Psi, \sum_i v(x_i)\Psi \rangle = \int \sum_i v(x_i)|\Psi(x_1, .., x_N)|^2 = \int_{\mathbb{R}^3} v(x)\, \rho_\Psi(x)\, dx.$$

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2. Partition the min over Ψ into a double min, first over Ψ subject to fixed ρ, then over ρ: letting $H^{univ}_{e\ell} := -\frac{\hbar^2}{2}\Delta + \sum_{i<j} \frac{1}{|x_i - x_j|}$,

$$\begin{aligned} E_0 &= \inf_\Psi \Big(\langle \Psi, H^{univ}_{e\ell} \Psi \rangle + \int v(r)\, \rho_\Psi(r)\, dr \Big) \\ &= \inf_\rho \underbrace{\inf_{\Psi \mapsto \rho} \Big(\langle \Psi, H^{univ}_{e\ell} \Psi \rangle \Big)}_{=: F^{HK}[\rho]} + \int v(r)\, \rho(r)\, dr. \end{aligned}$$

Universal map $\rho \to \rho_2$ from densities to pair densities

Corollary of the HK theorem There exists a universal (i.e., molecule-independent) map from single-particle densities $\rho(x_1)$ to pair densities $\rho_2(x_1, x_2)$ which gives the exact pair density of any N-electron molecular ground state $\Psi(x_1, s_1, .., x_N, s_N)$ in terms of its single-particle density.

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Proof $\Psi_* :=$ minimizer of $\langle \Psi, H_{e\ell}^{univ} \Psi \rangle$ subject to marginal constraint $\Psi \mapsto \rho$

$\rho_2 :=$ pair density of minimizer, i.e.
$\rho_2(x_1, x_2) = \sum_{s_1,..,s_N} \int |\Psi_*(x_1, s_1, .., x_N, s_N)|^2 dx_3..dx_N$

(Analogously, $\int ...dx_{k+1}..dx_N$ gives universal k-pt. density)

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ρ_2 may be nonunique since GS may be degenerate. Hence map multi-valued.

Map highly nontrivial and not comp'ly feasible – still uses high-dim. wavefunctions.

Pair density gives exact interaction energy

$\langle \Psi_*, \sum\limits_{i<j} \frac{1}{|x_i - x_j|} \Psi_* \rangle = \int_{\mathbb{R}^6} \frac{\rho_2(x,y)}{|x-y|} dx\, dy$

Comp'ly feasible interaction en. fctnals $\approx$ approximate the map

Thinking about the pair density in an elementary way

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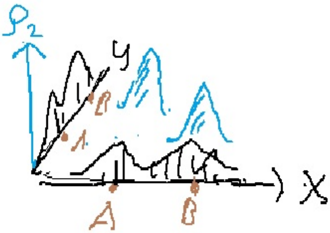
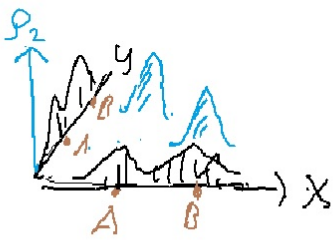


Thinking about the pair density in an elementary way

Non-interacting particles

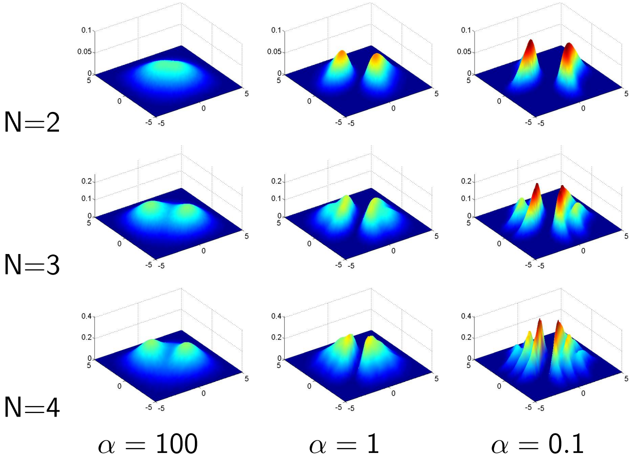


Repulsive interactions

What does the map $\rho \mapsto \rho_2$ look like?

Simulations by Huajie Chen/G.F., to appear

Ex.: 1D, N electrons, ρ simple 'lump', scaling parameter $\alpha > 0$
$\rho(x) = \alpha \frac{N}{2L}(1 + \cos(\alpha \frac{\pi}{2L} x)), \; x \in [-\alpha L, \alpha L]$



Density scaling

For any given density $\rho \in L^1(\mathbb{R}^d)$, let $\rho_\alpha(x) := \alpha^d \rho(\alpha x)$, $\alpha > 0$

$F^{HK}[\rho] = \alpha F^{HK}_\alpha[\rho]$ (simple computation)

$$F^{HK}_\alpha[\rho] = \min_{\Psi \in H^1,\, \Psi \mapsto \rho} \langle \Psi, (-\tfrac{\alpha}{2}\Delta + \textstyle\sum_{i<j} \frac{1}{|x_i - x_j|})\Psi \rangle_{L^2}$$

For dilute systems ($\alpha << 1$), 'semiclassical' behaviour

Scaling limit 1: $\alpha \to 0$

In limit $\alpha \to 0$, exact DFT turns into optimal transport.

Theorem (Cotar/GF/Klüppelberg, CPAM 2013)

$$F^{HK}[\rho] = \min_{\Psi \in H^1, \Psi \mapsto \rho} \left(\langle \Psi, (-\frac{\alpha}{2}\Delta + \sum_{i<j} \frac{1}{|x_i - x_j|})\Psi \rangle_{L^2} \right)$$

$$\underset{\alpha \to 0}{\to} \min_{\gamma \in \mathcal{P}_{\mathcal{N}}, \gamma \mapsto \rho} \int_{\mathbb{R}^{3N}} \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} d\gamma(x_1, .., x_N) =: F^{OT}[\rho]$$

where $\mathcal{P}_N$ is the set of symmetric probability measures on $\mathbb{R}^{3N}$.

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- Difficulty (regularity issue): Any Ψ with $|\Psi|^2 = \gamma$=optimal plan of OT pb. has $\Psi \notin H^1$, $\Psi \notin L^2$, $T[\Psi] = +\infty$, and hence cannot be used as trial state in var. principle for F^{HK}. Smoothing the optimal OT plan doesn't work either, since this destroys the marginal constraint.

More on rigorous passage DFT to OT

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Non-DFT counterex.

(Cotar/GF/Kl. 2014, inspired by Mania 1934, Lavrentiev 1927)

$J[u] = \int_0^1 (u(x)^3 - x)^2 u'(x)^6 dx$, $u(0) = 0$, $u(1) = 1$

$\lim_{\alpha\to 0} \min_u (\frac{\alpha}{2} \int_0^1 (u')^2 + J[u]) \geq \frac{1}{2}(\frac{7}{8})^2 (\frac{3}{10})^5$
$\min_u J[u] = 0$ (minimizer: $u = x^{1/3}$) "Lavrentiev gap"

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Similarity to semiclassical limit of HK functional:
minimizers of the limit problem have infinite kinetic energy, and are hence not admissible trial functions when the semiclassical parameter is nonzero.

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Similarity to semiclassical limit of HK functional: minimizers of the limit problem have infinite kinetic energy, and are hence not admissible trial functions when the semiclassical parameter is nonzero.

Proof that the DFT problem does not have a "Lavrentiev gap": Take a minimizer of the limit pb. Smooth it by convolution with a Gaussian. This has finite kinetic energy, and nearly the same interaction energy, but the wrong one-body density (the latter is also smoothed). Now construct a nonlinear projection which restores the correct one-body density without loss of regularity.

Behaviour of limit pb

Multi-marginal OT problem, all marginals equal, cost decreases with distance

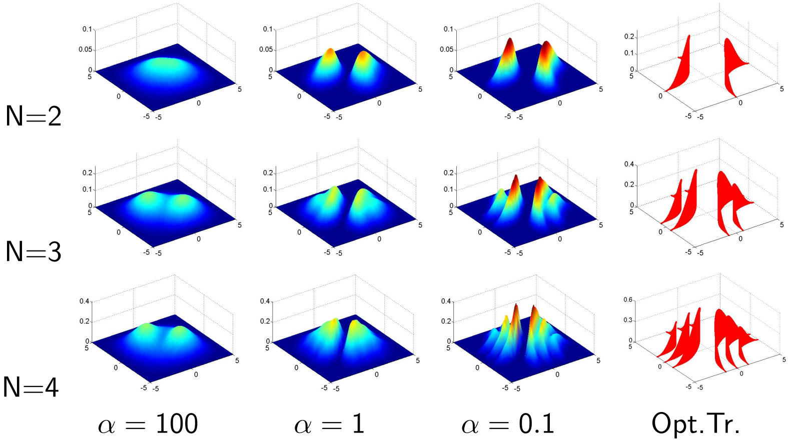
$\min_{\gamma\in\mathcal{P}_{\mathcal{N}},\gamma\mapsto\rho}\int_{\mathbb{R}^{Nd}}\sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|}d\gamma(x_1,..,x_N)$

- For N=2, unique minimizer, of 'Monge' form $\gamma(x,y)=\rho(x)\delta_{T(x)}(y)$ (Cotar, G.F., Klueppelberg, arXiv 2011, CPAM 2013, adapting Gangbo-McCann; different proof via Kantorovich duality: Buttazzo, DePascale, Gori-Giorgi 2012)
- For N¿2, non-Monge minimizers possible (B.Pass 2013)
- For N¿2, existence of Monge minimizers open
- For N arbitrary but d=1, unique symmetric minimizer, of symmetrized Monge form (Colombo, DePascale, DiMarino, preprint 2013)

$$\gamma(x_1,..,x_N) = \text{symmetrization of } \rho(x_1)\delta_{T_2}(x_1)(x_2)\cdots\delta_{T_N(x_1)}(x_N)$$

Comparison exact DFT – optimal transport

Huajie Chen, G.F., on arXiv soon



Scaling limit 2: $\alpha \to \infty$

Conjecture (highly non-rigorous):
The limiting kinetic energy functional is the Kohn-Sham kinetic energy functional. The limiting pair density always is the pair density of some Slater determinant. The Slater determinant consists of lowest eigenstates of the one-body operator whose potential is the functional derivative of $\delta F^{HK}[\rho]/\delta\rho$. Warning: rigorously, F^{HK} not even known to be continuous!

Theorem (Huajie Chen, G.F., soon on arXiv) For the homogeneous electron gas with periodic bc's in one dimension, the limit of the pair density as $\alpha \to \infty$ is unique, and given, say for N divisible by 4, by that of the (spin-polarized) Slater determinant

$$|-(\frac{N}{4}-1)\uparrow, -(\frac{N}{4}-1)\downarrow, ..., (\frac{N}{4}-1)\uparrow, (\frac{N}{4}-1)\downarrow, -\frac{N}{4}\uparrow, \frac{N}{4}\uparrow\rangle,$$

where $|k\rangle(x) := \frac{1}{\sqrt{2L}} e^{ik(\pi/L)x}$.

Optically indistinguishable from exact ρ_2 for $\alpha = 100$.

Scaling limit 3: $\alpha \to 0$, then $N \to \infty$

Minimize

$$C_\infty[\gamma] := \lim_{N\to\infty} \binom{N}{2}^{-1} \sum_{1\le i<j\le N} c(x_i, x_j) d\gamma(x_1, x_2, ...) \text{ (cost per particle pair)}$$

over prob.measures $\gamma \in \mathcal{P}_{sym}((\mathbb{R}^d)^\infty)$ s/to $\gamma \mapsto \mu \in \mathcal{P}(\mathbb{R}^d)$.

Questions: Behaviour of C_∞. Relation to C_N.

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Theorem 1 (Cotar, G.F., Pass, arXiv 2013): Suppose $c(x,y) = \ell(x-y)$, ℓ has positive Fourier trf. Then

$$\gamma_{opt} = \mu \otimes \mu \otimes \cdots$$

is the unique minimizer.

Proof that infinite-body minimizer = indep.meas. (strategy)

Consider arbitrary $\gamma \in \mathcal{P}_{sym}((\mathbb{R}^d)^\infty)$, $\gamma \mapsto \mu_2 \mapsto \mu$.

Re-write cost $C[\gamma]$ using 3 ingredients

- **DeFinetti-Hewitt-Savage theorem**: for each $\gamma \in \mathcal{P}_{sym}((\mathbb{R}^d)^\infty)$ there exists a unique $\nu \in \mathcal{P}(\mathcal{P}(\mathbb{R}^d))$ s.th.

$$\gamma = \int_{\mathcal{P}(\mathbb{R}^d)} Q^{\otimes\infty} d\nu(Q).$$

  Note that this implies $\mu_2 = \int_{\mathcal{P}(\mathbb{R}^d)} Q \otimes Q \, d\nu(Q)$.
- **Fourier calculus**: use $\widehat{Q}(z) := \int e^{-iz\cdot x} dQ(x)$ Fourier trf.
- **elementary probabilistic error splitting**

Proof that infinite-body minimizer = indep.meas. (details)

$$
\begin{aligned}
C_\infty[\gamma] &= \int_{(\mathbb{R}^d)^\infty} c(x_1,x_2)\,d\gamma(x_1,x_2,\ldots) = \int_{\mathbb{R}^{2d}} c(x,y)\,d\mu_2(x,y) \\
&= \int_{\mathcal{P}(\mathbb{R}^d)} \underbrace{\int_{\mathbb{R}^{2d}} \ell(x-y)dQ(x)dQ(y)}_{=\int_{\mathbb{R}^d}\widehat{\ell}(z)|\widehat{Q}(z)|^2dz \text{ (by Fourier calc.)}} \; d\nu(Q) \text{ (by deFinetti)} \\
&= (2\pi)^{-d}\int_{\mathbb{R}^d}\widehat{\ell}(z)\int_{\mathcal{P}(\mathbb{R}^d)}|\widehat{Q}(z)|^2 d\nu(Q)\,dz \;\; \text{(by Fubini).}
\end{aligned}
$$

Analogously

$$
C_\infty[\mu\otimes\mu\otimes\ldots] = (2\pi)^{-d}\int_{\mathbb{R}^d}\widehat{\ell}(z)\left|\int_{\mathcal{P}(\mathbb{R}^d)}\widehat{Q}(z)d\nu(Q)\right|^2 dz.
$$

Subtracting both expressions yields

$$
C_\infty[\gamma] - C_\infty[\mu\otimes\mu\otimes\ldots] = (2\pi)^{-d}\int_{\mathbb{R}^d}\underbrace{\widehat{\ell}(z)}_{>0}\;\underbrace{var_{\nu(dQ)}\widehat{Q}(z)}_{=0 \text{ iff } \nu=\delta_{Q_0}=\delta_\mu}\,dz
$$

Argument rigorous up to justifying Fourier calculus steps for costs that are not bounded and continuous; for that see our paper. Note that one must allow general probability measures Q.

Scaling limit 3: $\alpha \to 0$ then $N \to \infty$, ctd

Behaviour of energy:

Theorem 2 (Cotar, G.F., Pass) For costs with positive Fourier trf., including $c(x,y) = |x-y|^{-1}$, and any $\rho \geq 0$, $\int \rho = 1$, $\sqrt{\rho} \in H^1(\mathbb{R}^3)$,

$$\lim_{N\to\infty} \lim_{\alpha\to 0} \frac{F_\alpha^{HK}[N\rho]}{\binom{N}{2}} = J[\rho],$$

with the mean field cost

$$J[\rho] = \int c(x,y)\rho(x)\rho(y)\, dx\, dy.$$

Proofidea

Normalized 1-body and 2-body marginals:

$$\begin{aligned} p_1(x_1) &= \int_{\mathbb{R}^{3(N-1)}} p_N(x_1,..,x_N)dx_2..dx_N \\ p_2(x_1,x_2) &= \int_{\mathbb{R}^{3(N-2)}} p_N(x_1,..,x_N)dx_3..dx_N \end{aligned}$$

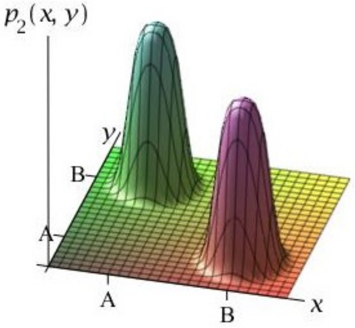
Notation: $p_N \mapsto p_1$, $p_N \mapsto p_2$, etc.

Def. A probability measure p_2 on $\mathbb{R}^6$ is said to be *N*-density-representable, $N \geq 2$, if there exists a symmetric probability measure p_N on $\mathbb{R}^{3N}$ such that $p_N \mapsto p_2$, and infinite-density-representable if there exists a symm. p_∞ on $(\mathbb{R}^3)^\infty$ s.th. $p_\infty \mapsto p_2$.

N-body and infinite-body problem can be reformulated as min. over N-repr. resp. infinitely repr. μ_2

Diaconis/Freedman: for any N-representable μ_2, there exists a nearby infinitely representable $\tilde{\mu}_2$, which has the same one-point marginal.

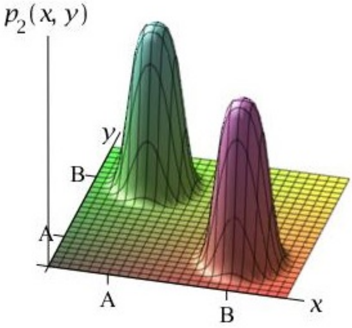
Example of a pair density which is not 3-representable



Violates the necessary condition of GF et al that for any partition of $\mathbb{R}^3$ into two subsets $\mathcal{A}$ and $\mathcal{B}$,

$$\int_{\mathcal{A}\times\mathcal{B}} p_2 + \int_{\mathcal{B}\times\mathcal{A}} p_2 \leq 2\Big(\int_{\mathcal{A}\times\mathcal{A}} p_2 + \int_{\mathcal{B}\times\mathcal{B}} p_2\Big)$$

Example of a pair density which is not 3-representable



Violates the necessary condition of GF et al that for any partition of $\mathbb{R}^3$ into two subsets $\mathcal{A}$ and $\mathcal{B}$,

$$\int_{\mathcal{A}\times\mathcal{B}} p_2 + \int_{\mathcal{B}\times\mathcal{A}} p_2 \leq 2(\int_{\mathcal{A}\times\mathcal{A}} p_2 + \int_{\mathcal{B}\times\mathcal{B}} p_2)$$

Physically: weight of 'neutral' configurations can at most be twice as big as weight of 'ionic' configurations.

Summary

In the fixed-N, inhomogeneous dilute limit, electron correlations converge to (strongly N-dependent) extreme correlations governed by optimal transport.

In the fixed-N, inhomogeneous concentrated limit, electron correlations reduce to certain Hund's rule exchange correlations.

In the large-N, inhomogeneous concentrated limit, independence emerges.

http://www-m7.ma.tum.de

Thanks for attention!