# Optimal transport with Coulomb cost: theory and applications to electronic structure of atoms & molecules (lecture 2)

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(Young European Probabilists)

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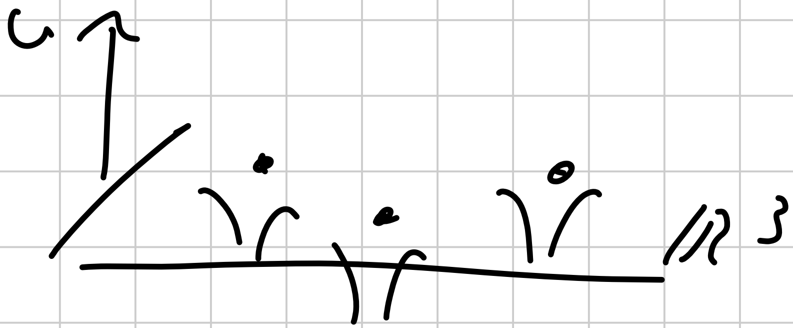
# 4. Precise connection QM → OT

**QM** QM ground state energy of $N$ electrons in external potential $v$ ( $v$ molecule-dep., $v(x) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|x-R_\alpha|}$ )




$E_0$ = lowest e-value of

$$H_{el} = \underbrace{\sum_{i=1}^{N} -\frac{\hbar^2}{2}\Delta_{x_i} + \sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|}}_{\text{universal } =: H_{el}^{univ}} + \underbrace{\sum_{i=1}^{N} v(x_i)}_{\text{molecule-dep.}}$$

$H_{el}$ selfadj on $L^2_{anti}(\mathbb{R}^{3N})$

$$\psi(x_1,\dots,x_i,\dots,x_j,\dots,x_N) = -\psi(x_1,\dots,x_j,\dots,x_i,\dots,x_N)$$

$$E_0 = \min_{\|\psi\|_{L^2}=1} \langle \psi, H_{el}\psi\rangle_{L^2}$$

<u>Hohenberg-Kohn theorem (1964)</u> (Fix $N$.)

$\exists$ universal (ie, molecule-indep.) fctnal $F^{HK}$ of the single-particle density $\rho$ s.t. $\forall v$

$$E_0 = \min_{\rho} \left( F^{HK}[\rho] + N \int_{\mathbb{R}^3} v(x)\rho(x)\,dx \right)$$

(min over $\rho : \mathbb{R}^3 \to \mathbb{R}$, $\rho \geq 0$, $\int \rho = 1$)

<u>Pf</u> 1. Non-universal part of $\langle \psi, H_{el}\psi\rangle$ dep. only on

$$\rho_\psi(x_1) := \int_{\mathbb{R}^{3N-3}} |\psi(x_1,x_2,\dots,x_N)|^2\, dx_2 \dots dx_N :$$

$$\langle \Psi, \sum_i v(x_i)\, \Psi \rangle = \int \sum_i v(x_i)\, |\Psi(x_1, \dots, x_N)|^2 \, dx_1 \dots dx_N$$
$$= N \int v(x)\, \rho_\Psi(x)\, dx$$

2. Partition min: first over $\Psi \to \rho$, then over $\rho$

$$E_0 = \inf_\Psi \left( \langle \Psi, H_{el}^{univ} \Psi \rangle + N \int \rho_\Psi(x)\, v(x)\, dx \right)$$
$$= \inf_\rho \Big( \underbrace{\inf_{\Psi \to \rho} \langle \Psi, H_{el}^{univ} \Psi \rangle}_{=: F^{HK}[\rho]} + N \int \rho \cdot v \Big)$$

M. Levy
E. Lieb

Universality of correlations. $\exists$ universal map $\rho(x_1) \to \rho_2(x_1, x_2)$ which gives the exact pair density of any $N$-electron ground state $\Psi(x_1, \dots, x_N)$ as a fctnal of its one-body density.

Pf Fix $\rho$.

$\Psi_* :=$ minimizer of $\langle \Psi, H_{el}^{univ} \Psi \rangle$ s/to $\Psi \to \rho$

$\rho_2 :=$ pair density of $\Psi_*$

$$\rho_2(x_1, x_2) = \int_{\mathbb{R}^{3N-6}} |\Psi(x_1, x_2, x_3, \ldots, x_N)|^2 \, dx_3 \ldots dx_N$$

$$\left[\text{Rk}: \ \langle \Psi, \sum_{i<j} \frac{1}{|x_i - x_j|} \Psi \rangle = \binom{N}{2} \int_{\mathbb{R}^6} \rho_2(x,y) \frac{1}{|x-y|} \, dx \, dy \right]$$

Thm (Cotar, GF, Klüppelberg)

(a)
$$F_\hbar^{HK}[\rho] = \min_{\substack{\Psi \in H^1_{anti}(\mathbb{R}^{3N}) \\ \Psi \to \rho}} \langle \Psi, \left(-\frac{\hbar^2}{2}\Delta + \sum_{i<j} \frac{1}{|x_i - x_j|}\right) \Psi \rangle$$

$$\xrightarrow[\hbar \to 0]{} \min_{\substack{\gamma \in \mathcal{P}_{sym}(\mathbb{R}^{3N}) \\ \gamma \to \rho}} \int \sum_{i<j} \frac{1}{|x_i - x_j|} \, d\gamma =: V^{SCE}[\rho]$$

(b) $\Psi_\hbar$ minimizes $\underset{(\text{subsequence})}{\Longrightarrow}$ $|\Psi_\hbar|^2 \xrightarrow[\hbar \to 0]{*} \gamma$ optimal plan.

- Limit pb up to passage to prob. measures: (physics lit.) Seidl 1999, Seidl, Gori-Giorgi, Savin 2007
- Difficulty: show lim (1st inf) $\not>$ 2nd inf
  (any $\psi$ with $|\psi|^2 = \gamma^{opt}$ has $\psi \notin H^1$, $\psi \notin L^2$, and hence cannot be used as a trial fctn in the 1st inf; but smoothing destroys the marginal constraint)

**Lemma** (Smoothing under marginal constraint)

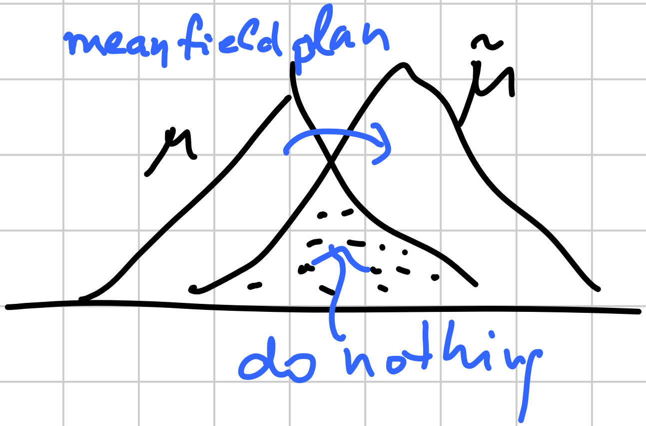
$$\mu, \nu \in \mathcal{P}(\mathbb{R}^d) \cap W^{1,1}(\mathbb{R}^d) \Rightarrow \{\gamma \in W^{1,1}(\mathbb{R}^{2d}) \mid \gamma \rightrightarrows \mu, \nu\}$$

$\sqrt{\mu}, \sqrt{\nu}$ $\quad W^{1,2}$ $\quad \sqrt{\gamma} \in W^{1,2}$

weak* dense in

$$\{\gamma \in \mathcal{P}(\mathbb{R}^{2d}) \mid \gamma \rightrightarrows \mu, \nu\}$$

Pf

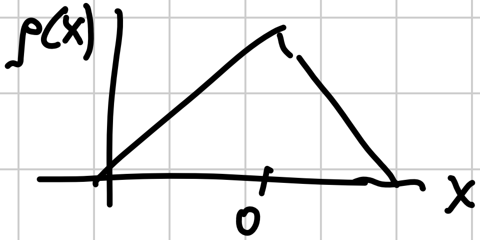



$$\tilde{\gamma} := (G \otimes G) * \gamma \rightrightarrows \begin{array}{l} \tilde{\mu} = G * \mu \\ \tilde{\nu} = G * \nu \end{array}$$

smoothed plan w/ wrong marginals (e.g. $G$ Gaussian)

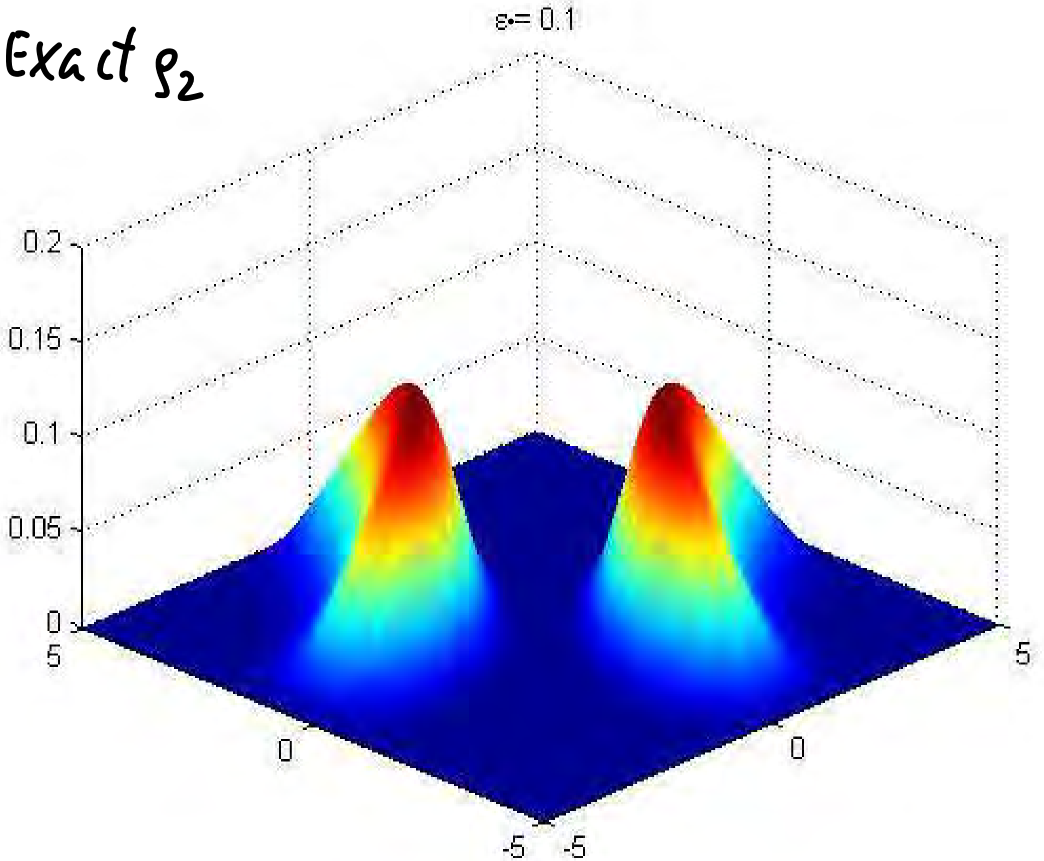
$$\gamma_{smooth} = \gamma_{\mu \to \tilde{\mu}} \circ \tilde{\gamma} \circ \gamma_{\tilde{\nu} \to \nu}$$

Ex. (The universal map $\rho \to \rho_2$)

1), 

, Huajie Chen / GF

Exact $\rho_2$




Optimal transport prediction