New Hohenberg-Kohn theorems

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Presentation of : G., *Hohenberg-Kohn theorems for interactions, spin and temperature*, (arxiv:1906.03191), Journal of Statistical Physics (2019)

Standard Hohenberg-Kohn theorem

$$H^N(v) := \sum_{i=1}^{N} -\Delta_i + \sum_{1\leqslant i<j\leqslant N} w(x_i - x_j) + \sum_{i=1}^{N} v(x_i)$$

Theorem (Standard Hohenberg-Kohn)

Let $p > \max(2d/3, 2)$, let $w, v_1, v_2 \in (L^p + L^\infty)(\mathbb{R}^d)$ such that $H^N(v_1)$ and $H^N(v_2)$ have ground states Ψ_1 and Ψ_2. If

$$\int_{\mathbb{R}^d} (v_1 - v_2)(\rho_{\Psi_1} - \rho_{\Psi_2}) = 0,$$

then $v_1 = v_2 + (E_1 - E_2)/N$.

- The above assumption enhances the v/ρ duality
- Extends to more general v's, and any boundary condition
- The mathematically technical step relies on a **unique continuation property** as Lieb realized. It is proved in (G. 19, arXiv:1901.03207) for Coulomb systems.

Hohenberg-Kohn theorem for interactions

$$H^N(v,w) := \sum_{i=1}^{N} -\Delta_i + \sum_{1\leqslant i<j\leqslant N} w(x_i - x_j) + \sum_{i=1}^{N} v(x_i)$$

Theorem (Hohenberg-Kohn for interactions)

Let $w_1, w_2, v_1, v_2 \in (L^p + L^\infty)(\mathbb{R}^d)$. If there are two ground states Ψ_1 and Ψ_2 of $H^N(v_1, w_1)$ and $H^N(v_2, w_2)$, such that

$$\int_{\mathbb{R}^d} (v_1 - v_2)\left(\rho_{\Psi_1} - \rho_{\Psi_2}\right) + \int_{\mathbb{R}^{2d}} (w_1 - w_2)(x-y)\left(\rho^{(2)}_{\Psi_1} - \rho^{(2)}_{\Psi_2}\right)(x,y)\mathrm{d}x\mathrm{d}y = 0,$$

then $w_1 = w_2 + c$ and $v_1 = v_2 + \frac{E_1 - E_2}{N} - \frac{c(N-1)}{2}$ for some $c \in \mathbb{R}$.

- Siedentop and Müller (81') have a similar statement, but with an incomplete proof
- Pair correlations contain the information of the interaction

Consequence for the Kohn-Sham setting

Corollary

Take potentials $v_1, v_2, w \in (L^p + L^\infty)(\mathbb{R}^d)$*, where* w *is even and not constant, such that* $H^N(v_1, w)$ *and* $H^N(v_2, 0)$ *have ground states* Ψ_1 *and* Ψ_2*. Then* $\rho^{(2)}_{\Psi_1} \neq \rho^{(2)}_{\Psi_2}$*.*

Kohn-Sham effective systems cannot reproduce pair correlations

Interactions and several types of particles

Take N particles of type a and M of type b (bosons or fermions)

$$H^{N,M}(v_{\rm a}, v_{\rm b}, w_{\rm a}, w_{\rm b}, w_{\rm ab}) := \sum_{i=1}^{N}(-\Delta_i + v_{\rm a}(x_i)) + \sum_{k=N+1}^{N+M}(-\alpha\Delta_k + v_{\rm b}(x_k))$$
$$+ \sum_{1 \leqslant i<j \leqslant N} w_{\rm a}(x_i - x_j) + \sum_{N+1 \leqslant k<l \leqslant N+M} w_{\rm b}(x_k - x_l) + \sum_{\substack{1 \leqslant i \leqslant N \\ N+1 \leqslant k \leqslant N+M}} w_{\rm ab}(x_i - x_k)$$

Theorem (Hohenberg-Kohn for different particles)

Let $H^{N,M}(v_{{\rm a},i}, v_{{\rm a},i}, w_{{\rm a},i}, w_{{\rm b},i}, w_{{\rm ab},i})$ have ground states Ψ_i, $i \in \{1,2\}$. If $\rho^{(2)}_{{\rm a},\Psi_1} = \rho^{(2)}_{{\rm a},\Psi_2}$, $\rho^{(2)}_{{\rm b},\Psi_1} = \rho^{(2)}_{{\rm b},\Psi_2}$ and $\rho^{(2)}_{{\rm ab},\Psi_1} = \rho^{(2)}_{{\rm ab},\Psi_2}$, then $v_{\eta,1} - v_{\eta,2}$, $w_{\eta,1} - w_{\eta,2}$, and $w_{{\rm ab},1} - w_{{\rm ab},2}$ are constant (for $\eta \in \{{\rm a},{\rm b}\}$.

Hohenberg-Kohn for interactions is thus very robust

Hohenberg-Kohn for the Zeeman interaction

$$H^N(v,B)=\sum_{i=1}^N\big(-\Delta_i+\sigma_i\cdot B(x_i)+v(x_i)\big)+\sum_{1\leqslant i<j\leqslant N} w(x_i-x_j)$$

Counterexample of the $(v,B)\mapsto(\rho,m)$ injectivity in Capelle and Vignale (2000). But we have a strong constraint on the external fields.

Theorem (Partial Hohenberg-Kohn for Spin DFT)

Take $H^N(v_1,B_1)$ and $H^N(v_2,B_2)$ having ground states Ψ_1 and Ψ_2. If $\int_{\mathbb{R}^3}(v_1-v_2)(\rho_{\Psi_1}-\rho_{\Psi_2})+\int_{\mathbb{R}^3}(B_1-B_2)\cdot(m_{\Psi_1}-m_{\Psi_2})=0$, then

$$|B_1-B_2|\,\chi=\frac{E_1-E_2}{N}+v_2-v_1,$$

where χ is a function taking its values in $\{-1,-1+\frac{2}{N},-1+\frac{4}{N},\ldots,1-\frac{2}{N},1\}$.

If we also assume $v_1=v_2$, $E_1=E_2$ and N odd, then $B_1=B_2$.

Counterexample for Matrix DFT

- For non local potentials G's, we define

$$H^N(G) = \sum_{i=1}^{N} -\Delta_i + \sum_{1 \leqslant i < j \leqslant N} w(x_i - x_j) + \sum_{i=1}^{N} G_i.$$

- It is hence natural to ask whether $G \mapsto \gamma$ is injective. But we can find a large class of counterexamples when $w = 0$.

Counterexample

Take $w = 0$, let G_1 be such that $H^N(G_1)$ has a unique ground state Ψ_1, isolated in the spectrum. We take $G_2 = G_1 + \epsilon |\phi\rangle \langle\phi|$, where ϕ is $\perp$ to the N components of γ_{Ψ_1}. For $\epsilon \geqslant 0$, G_2 and G_1 have the same (unique) ground state.

Open question : prove that it's true or false for $w = |\cdot|^{-1}$.

Warm Hohenberg-Kohn

Theorem (Hohenberg-Kohn at positive temperatures)

$T_1, T_2 > 0$, Γ_1, Γ_2 the grand canonical Gibbs states corresponding respectively to $\mathcal{E}_{v_1,T_1}$ and $\mathcal{E}_{v_2,T_2}$. If

$$-(T_1 - T_2)(S_{\Gamma_1} - S_{\Gamma_2}) + \int_{\mathbb{R}^d} (v_1 - v_2)(\rho_{\Gamma_1} - \rho_{\Gamma_2}) = 0,$$

then $T_1 = T_2$ and $v_1 = v_2$.

- Extends Mermin's (65') $v \mapsto \rho$ injectivity at fixed T
- Works also when we only assume that $T_1, T_2 \geqslant 0$.
- Can be extended to $(T, v, A, w) \mapsto (S, \rho, m, \rho^{(2)})$, for non local $G \mapsto \gamma$, for classical systems, and in the canonical ensemble
- Conjecture : ρ does not contain the information of both T and v.