

Differentiable but Exact Formulation of Density-Functional Theory

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Formal and Practical Aspects of Electronic Structure Simulations with Density Functional Theory

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Hohenberg–Kohn variation principle

- ▶ In DFT, the ground-state energy for a given **potential** v and **electron number** N is given by

$$E(v) = \min_{\rho \rightarrow N} (F(\rho) + (v|\rho)) \quad \text{Hohenberg–Kohn (HK) variation principle}$$

where ρ is the density and where

$$F(\rho) = \min_{\Psi \mapsto \rho} \langle \Psi | T + W | \Psi \rangle \quad \text{Levy constrained-search density functional}$$

$$(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \quad \text{interaction of density with external potential}$$

- ▶ The solution of the HK minimisation problem is given by the **Euler–Lagrange equation**

$$\frac{\delta F(\rho)}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) - \mu \quad \text{Euler–Lagrange equation with chemical potential } \mu$$

- ▶ clearly, an underlying assumption is that F is **differentiable**
 - ▶ however, F is **everywhere discontinuous** and therefore **nondifferentiable**
- ▶ Outline:
 - ▶ nondifferentiability of the universal density functional in DFT
 - ▶ Moreau–Yosida regularisation of DFT with differentiable density functional
 - ▶ consequences for Kohn–Sham theory
- ▶ S. Kvaal, U. Ekström, A. Teale, and T. Helgaker, JCP **140**, 18A518 (2014)

Discontinuity of universal density functional

- ▶ For a **one-electron system**, the universal density functional has a simple explicit form:

$$F(\rho) = \frac{1}{2} \int |\nabla \rho^{1/2}(\mathbf{r})|^2 d\mathbf{r} \quad \leftarrow \text{one-electron kinetic energy}$$

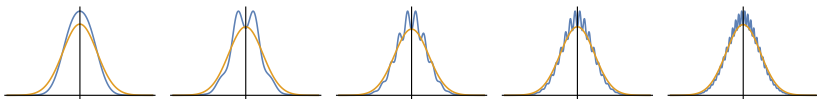
- ▶ A one-electron **Gaussian density** of unit exponent has a finite kinetic energy:

$$\rho(\mathbf{r}) = \pi^{-3/2} \exp(-r^2), \quad F(\rho) = 3/4$$

- ▶ Let $\{\rho_n\}$ be a sequence that approaches ρ in the norm,

$$\lim_{n \rightarrow +\infty} \|\rho - \rho_n\|_\rho = 0,$$

while developing increasingly **rapid oscillations** of increasingly **small amplitude**:



- ▶ The kinetic energy $F(\rho_n)$ is driven **arbitrarily high** in the sequence and F is not continuous:

$$\lim_n F(\rho_n) = +\infty \neq F\left(\lim_n \rho_n\right) = 3/4$$

- ▶ The universal density functional is everywhere **discontinuous** and hence **nondifferentiable**

- ▶ P. E. Lammert, *Int. J. Quantum Chem.* **107**, 1943 (2007)

Lieb variation principle

- ▶ The nondifferentiability of F makes it **awkward** to work with
 - ▶ we shall develop a more regular DFT with a differentiable density functional
 - ▶ we must first examine the relationship between E and F more carefully
- ▶ Lieb showed that the energy and density functional are symmetrically related:

$$F(\rho) = \sup_v (E(v) - (v|\rho)) \quad \text{the Lieb variation principle (1983)}$$

$$E(v) = \inf_\rho (F(\rho) + (v|\rho)) \quad \text{the Hohenberg–Kohn variation principle (1964)}$$

- ▶ These are alternative attempts at sharpening the same inequality into an equality

$$E(v) \leq F(\rho) + (v|\rho) \iff F(\rho) \geq E(v) - (v|\rho)$$

- ▶ In the language of convex analysis, E and F are said to be **conjugate functions**

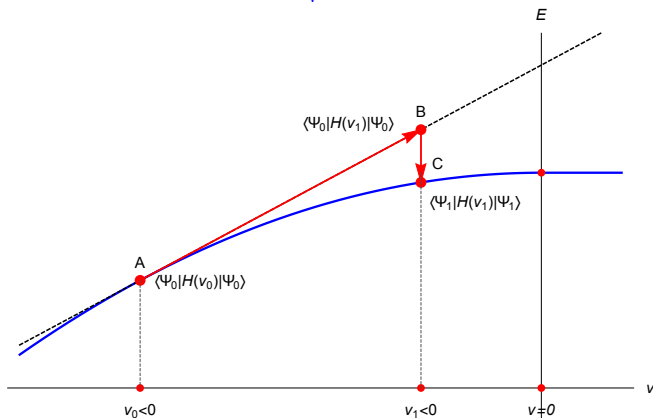
$$E(\text{concave and semi-cont.}) \iff F(\text{convex and semi-cont.})$$

- ▶ such **conjugate functions** contain the same information, represented in different manners
- ▶ each property of one function is exactly reflected in some property of its conjugate function
- ▶ Being a conjugate function, F is automatically **convex** and **semi-continuous**
 - ▶ however, F is **not continuous** even though E is continuous
 - ▶ for this, even more is required of E
- ▶ **Our strategy**: to modify E so that F becomes continuous and differentiable

Concavity of the ground-state energy

- ▶ The ground-state energy is **concave** in the external potential

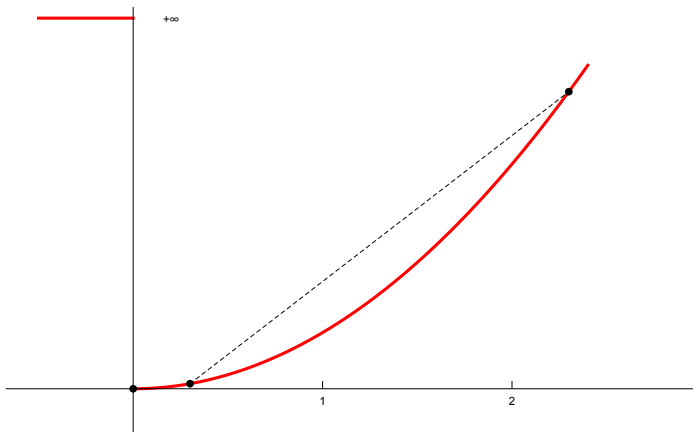
$$E(v) = \min_{\Psi} \langle \Psi | H(v) | \Psi \rangle$$



- ▶ The concavity of $E(v)$ may be understood in the following two-step manner:
 - 1 from A to B, the energy increases linearly since $H(v)$ is linear in v and Ψ_0 is fixed
 - 2 from B to C, the energy decreases as the wave function relaxes to the ground state Ψ_1

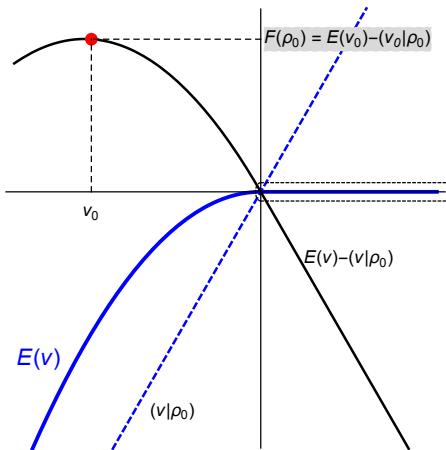
Convexity of the universal density functional

- ▶ Being conjugate to E , the density functional F is **convex** and **lower semi-continuous**
 - ▶ **convexity** ensures that all local minima are global in the HK variation principle
 - ▶ **lower semi-continuity** allows functions to jump down but not up as limits are taken
- ▶ However, F is **neither continuous nor differentiable**

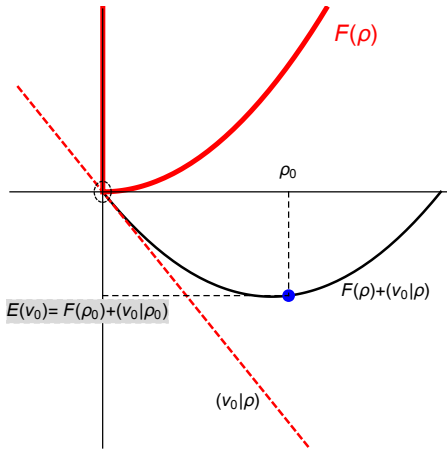


Hohenberg–Kohn and Lieb variation principles

$$F(\rho) = \max_v (E(v) - (v|\rho))$$

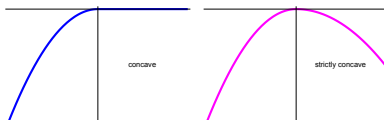


$$E(v) = \min_\rho (F(\rho) + (v|\rho))$$



Moreau–Yosida regularisation of DFT

- ▶ The ground-state energy $E(v)$ is **concave but not strictly concave**



- ▶ We obtain a **strictly concave** energy E_γ by subtracting a term proportional to $\|v\|^2$:

$$E_\gamma(v) = E(v) - \frac{1}{2}\gamma\|v\|^2, \quad \gamma > 0$$

- ▶ such strict concavity is sufficient to guarantee continuity of its conjugate function
- ▶ caveat: v must be square integrable (Coulomb potential in a box)
- ▶ We now introduce the **density functional** F_γ in the usual manner, as the conjugate to E_γ :

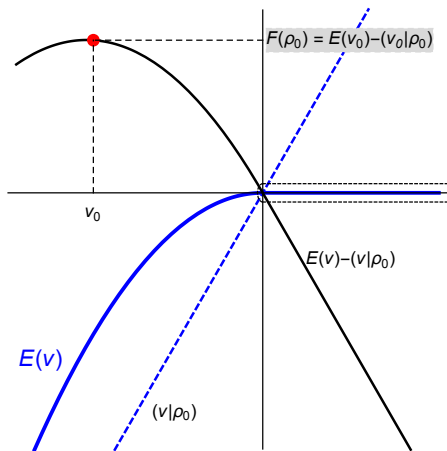
$$F_\gamma(\rho) = \max_v (E_\gamma(v) - (v|\rho)) \quad \text{Lieb variation principle}$$

$$E_\gamma(v) = \min_\rho (F_\gamma(\rho) + (v|\rho)) \quad \text{Hohenberg–Kohn variation principle}$$

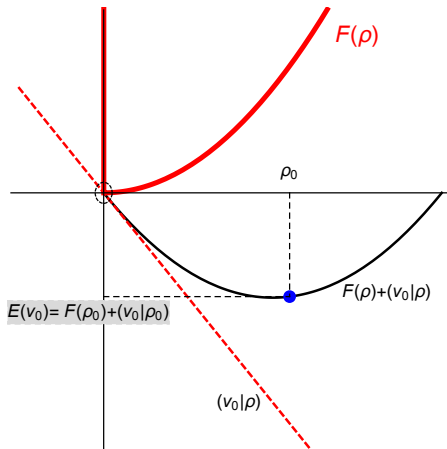
- ▶ unlike F , the new density functional F_γ is **continuous and differentiable**
- ▶ This procedure is known as **Moreau–Yosida (MY) regularisation**
 - ▶ a standard technique in convex optimisation

Unregularised DFT

$$F(\rho) = \max_v (E(v) - (v|\rho))$$

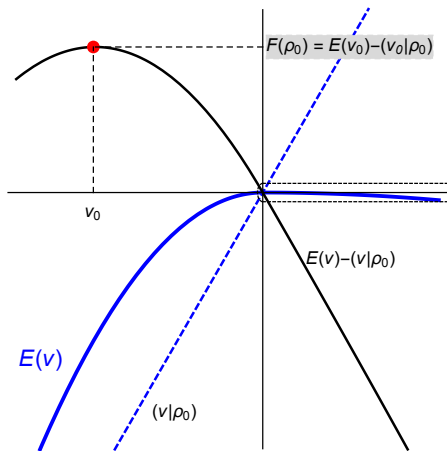


$$E(v) = \min_\rho (F(\rho) + (v|\rho))$$

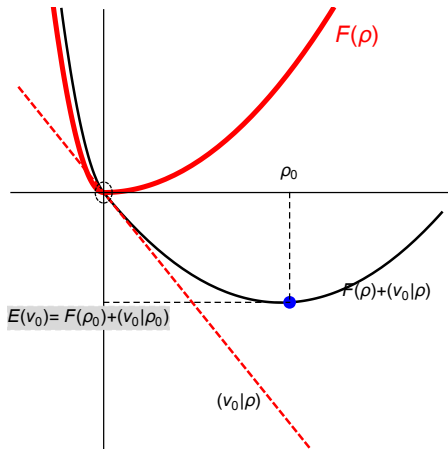


Moreau–Yosida regularised DFT

$$F_\gamma(\rho) = \max_v (E_\gamma(v) - (v|\rho))$$



$$E_\gamma(v) = \min_\rho (F_\gamma(\rho) + (v|\rho))$$

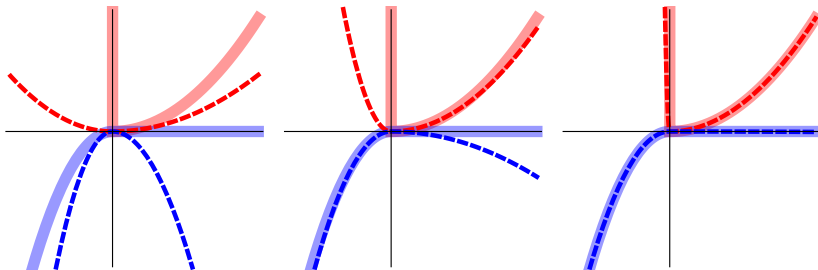


Moreau envelope F_γ of F

- ▶ The **regularised density functional** F_γ is known as the **Moreau envelope** of F
 - ▶ it is an everywhere **finite, continuous and differentiable** approximation to F
 - ▶ it is a lower bound to F but has the **same minimum**
 - ▶ it approaches F pointwise from below as $\gamma \rightarrow 0$

$$F_\gamma(\rho) = \min_{\tilde{\rho}} \left(F(\tilde{\rho}) + \frac{1}{2\gamma} \|\tilde{\rho} - \rho\|^2 \right)$$

- ▶ **Moreau–Yosida regularisation** with **large** γ (left), **medium** γ (middle), and **small** γ (right):
 - ▶ **BLUE curves**: strictly concave E_γ (dashed) tends to E from below
 - ▶ **RED curves**: differentiable F_γ (dashed) tends to F from below



Hohenberg–Kohn variation principle in MY DFT

$$E_\gamma(v) = \min_\rho (F_\gamma(\rho) + (v|\rho))$$

Euler–Lagrange equation

- ▶ The Euler–Lagrange equation is now **well defined**:

$$\frac{\delta F_\gamma(\rho)}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) - \mu$$

- ▶ Its solution ρ_v^γ yields the **modified energy** E_γ and therefore also the **true energy** E :

$$E_\gamma(v) = F_\gamma(\rho_v^\gamma) + (\rho_v^\gamma|v) = E(v) - \frac{1}{2}\gamma\|v\|^2$$

- ▶ More solutions exist when degeneracies are present

Quasi-densities

- ▶ The solution ρ_v^γ is related to the **true ground-state density** ρ_v in a simple manner:

$$\rho_v^\gamma = \rho_v - \gamma v \quad \leftarrow \quad \text{'depot'} = \text{density} - \text{potential}$$

- ▶ Densities in MY DFT are not physical densities but **pseudo-densities** or **quasi-densities**
 - ▶ they may be negative and need not integrate to the correct number of electrons
 - ▶ however, they may always be decomposed in the above manner

MY regularised Kohn–Sham theory

- ▶ KS theory assumes a **noninteracting system with the same density as the physical system**
 - ▶ this assumption is unfounded: the noninteracting representability problem
- ▶ In Moreau–Yosida DFT, the two systems share the **same quasi-density**:

- 1 the **interacting** Euler–Lagrange equation determines the quasi-density ρ_v^γ :

$$\frac{\delta F_\gamma(\rho_v^\gamma)}{\rho_v^\gamma(\mathbf{r})} = -v(\mathbf{r}) - \mu \quad \text{interacting system with differentiable } F_\gamma$$

- 2 the **noninteracting** Euler–Lagrange equation determines the Kohn–Sham potential v_s^γ :

$$\frac{\delta (T_s)_\gamma(\rho_v^\gamma)}{\rho_v^\gamma(\mathbf{r})} = -v_s^\gamma(\mathbf{r}) - \mu_s \quad \text{noninteracting system with differentiable } (T_s)_\gamma$$

- ▶ A **regularised Kohn–Sham potential** v_s^γ exists for each external potential v :
 - ▶ same quasi-density but different physical densities:

$$\rho_v = \rho_v^\gamma + \gamma v \quad \text{interacting density and potential}$$

$$\rho_s^\gamma = \rho_v^\gamma + \gamma v_s^\gamma \quad \text{noninteracting density and potential}$$

- ▶ the physical densities differ by an amount proportional to γ

Different regularisation metrics

- ▶ It is possible to work with more general MY regularisations:

$$E_\gamma(v) = E(v) - \frac{1}{2}\gamma\langle v|M|v\rangle$$

- ▶ Two choices of metric: $M = I$ (**overlap**) and $M = T$ (**kinetic**)

$$\langle v|I|v\rangle = \int |v(\mathbf{r})|^2 d\mathbf{r} = \|v\|^2$$

$$\langle v|T|v\rangle = \int |\nabla v(\mathbf{r})|^2 d\mathbf{r} = \|\nabla v\|^2$$

- ▶ The kinetic metric favours **smooth potentials** in the Lieb variation principle:

$$\begin{aligned} F_\gamma(\rho) &= \max_v (E_\gamma(v) - (v|\rho)) \\ &= \max_v (E(v) - (v|\rho) - \frac{1}{2}\gamma\|\nabla v\|^2) \end{aligned}$$

- ▶ related to the OEP regularisation of **Heaton–Burgess, Bulat and Yang** (2007)

Conclusions

- ▶ **Universal density functional** of DFT is an exceedingly complicated function of the density
 - ▶ it is discontinuous and nondifferentiable
 - ▶ ill-defined Euler–Lagrange equations and Kohn–Sham representability problem
- ▶ **Moreau–Yosida regularisation** gives a regular but exact DFT
 - ▶ we can build arbitrarily accurate differentiable universal density functionals
 - ▶ well-defined Euler–Lagrange equations and no Kohn–Sham representability problem
- ▶ **Publication:**
 - ▶ S. Kvaal, U. Ekström, A. Teale, and T. Helgaker, JCP **140**, 18A518 (2014)
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