Differentiable but Exact Formulation of Density-Functional Theory

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

$$E(v) = \min_{\rho \rightarrow N} (F(\rho) + (v|\rho))$$

Hohenberg–Kohn (HK) variation principle

where $\rho$ is the density and where

$$F(\rho) = \min_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle$$

Levy constrained-search density functional

$$(v|\rho) = \int v(r) \rho(r) \, dr$$

interaction of density with external potential

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

$$\frac{\delta F(\rho)}{\delta \rho(r)} = -v(r) - \mu$$

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

Discontinuity of universal density functional

- For a one-electron system, the universal density functional has a simple explicit form:
  \[ F(\rho) = \frac{1}{2} \int |\nabla \rho^{1/2}(r)|^2 \, dr \]
  one-electron kinetic energy

- A one-electron Gaussian density of unit exponent has a finite kinetic energy:
  \[ \rho(r) = \pi^{-3/2} \exp(-r^2), \quad F(\rho) = \frac{3}{4} \]

- Let \( \{\rho_n\} \) be a sequence that approaches \( \rho \) in the norm,
  \[ \lim_{n \to +\infty} \| \rho - \rho_n \|_p = 0, \]
  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:
  \[ \lim_{n} F(\rho_n) = +\infty \neq F(\lim_{n} \rho_n) = \frac{3}{4} \]

- The universal density functional is everywhere discontinuous and hence nondifferentiable
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 concavity of the energy $E(v)$ follows from two circumstances:
- the linearity of $H(v)$ changes the energy linearly from $v_0$ to $v_1$ for fixed $\Psi_0$
- the variation principle lowers the energy from $\Psi_0$ to $\Psi_1$ for fixed $v_1$

There are two cases to consider: **strict concavity** (left) and **nonstrict concavity** (right)

$$[H(v_0), H(v_1)] \neq 0 \Rightarrow \Psi_1 \neq \Psi_0 \Rightarrow \rho_1 \neq \rho_0 \text{ strict concavity}$$

$$[H(v_0), H(v_1)] = 0 \Rightarrow \Psi_1 = \Psi_0 \Rightarrow \rho_1 = \rho_0 \text{ non-strict concavity}$$

- note: the density is given by the derivative of the blue curve

We have **strict concavity and different densities** except if $v_1 - v_0 = c$ is a scalar
- the Hohenberg–Kohn theorem: the density determines the potential up to a constant
- with vector potentials, non-strict concavity occurs more generally
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

\[ F(\rho) = \max_v \left( E(v) - (v|\rho) \right) \]

\[ E(v) = \min_\rho \left( F(\rho) + (v|\rho) \right) \]
Moreau–Yosida regularisation of DFT

- The ground-state energy $E(\nu)$ is **concave but not strictly concave**

- We obtain a **strictly concave** energy $E_\gamma$ by subtracting a term proportional to $\|\nu\|^2$:

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

  - such strict concavity is sufficient to guarantee continuity of its conjugate function
  - caveat: $\nu$ must be square integrable (Coulomb potential in a box)

- We now introduce the **density functional** $F_\gamma$ in the usual manner, as the conjugate to $E_\gamma$:

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

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

  - unlike $F$, the new density functional $F_\gamma$ is **continuous and differentiable**

- This procedure is known as **Moreau–Yosida (MY) regularisation**

  - a standard technique in convex optimisation
Unregularised DFT

\[ F(\rho) = \max_{\nu} \left( E(\nu) - (\nu|\rho) \right) \]

\[ E(\nu) = \min_{\rho} \left( F(\rho) + (\nu|\rho) \right) \]

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Moreau–Yosida regularised DFT

\[ F_\gamma(\rho) = \max_v \left( E_\gamma(v) - (v|\rho) \right) \]

\[ E_\gamma(v) = \min_\rho \left( F_\gamma(\rho) + (v|\rho) \right) \]
Moreau envelope $F_\gamma$ of universal density functional $F$

- We have defined $F_\gamma$ as the conjugate of $E_\gamma$ by the Lieb variation principle:

$$F_\gamma(\rho_0) \overset{\text{def}}{=} \sup_v (E_\gamma(v) - (v|\rho_0))$$

- We may express $F_\gamma$ explicitly in terms of the original density functional $F$ as

$$F_\gamma(\rho_0) = \min_{\rho} \left( F(\rho) + \frac{1}{2\gamma} \| \rho - \rho_0 \|^2 \right) \quad \leftarrow \text{Moreau envelope } F_\gamma \text{ of } F$$

  - for each $\rho_0$, we minimise $F(\rho)$ with a penalty term $\| \rho - \rho_0 \|^2 / 2\gamma$
Moreau envelope $F_\gamma$ of $F$

- The regularised density functional $F_\gamma$ 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 $\gamma \to 0$

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

- Moreau–Yosida regularisation with large $\gamma$ (left), medium $\gamma$ (middle), and small $\gamma$ (right):
  - BLUE curves: strictly concave $E_\gamma$ (dashed) tends to non-strictly concave $E$ from below
  - RED curves: differentiable $F_\gamma$ (dashed) tends to non-differentiable $F$ from below
Moreau envelope illustration
Hohenberg–Kohn variation principle in MY DFT

\[ E_\gamma(\nu) = \min_\rho \left( F_\gamma(\rho) + (\nu|\rho) \right) \]

Euler–Lagrange equation

- The Euler–Lagrange equation is now well defined:

\[ \frac{\delta F_\gamma(\rho)}{\delta \rho(r)} = -\nu(r) - \mu \]

- Its solution \( \rho_\gamma \) yields the modified energy \( E_\gamma \) and therefore also the true energy \( E \):

\[ E_\gamma(\nu) = F_\gamma(\rho_\gamma) + (\rho_\gamma|\nu) = E(\nu) - \frac{1}{2} \gamma \|\nu\|^2 \]

- More solutions exist when degeneracies are present

Quasi-densities

- The solution \( \rho_\gamma \) is related to the true ground-state density \( \rho_\nu \) in a simple manner:

\[ \rho_\gamma = \rho_\nu - \gamma \nu \quad \text{‘depot’ = density – potential} \]

- 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 $\rho^\gamma_v$:

\[
\frac{\delta F^\gamma_v}{\rho^\gamma_v(r)} = -v(r) - \mu \quad \text{interacting system with differentiable } F^\gamma
\]

  2. the **noninteracting** Euler–Lagrange equation determines the Kohn–Sham potential $v^\gamma_s$:

\[
\frac{\delta (T^\gamma_s)}{\rho^\gamma_v(r)} = -v^\gamma_s(r) - \mu_s \quad \text{noninteracting system with differentiable } (T^\gamma_s)
\]

- A **regularised Kohn–Sham potential $v^\gamma_s$** exists for each external potential $v$:
  - same quasi-density but different physical densities:

\[
\rho_v = \rho^\gamma_v + \gamma v \quad \text{interacting density and potential}
\]
\[
\rho^\gamma_s = \rho^\gamma_v + \gamma v^\gamma_s \quad \text{noninteracting density and potential}
\]
  - the physical densities differ by an amount proportional to $\gamma$
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)

\[ \langle v | I | v \rangle = \int |v(r)|^2 \, dr = \|v\|^2 \]
\[ \langle v | T | v \rangle = \int |\nabla v(r)|^2 \, dr = \|\nabla v\|^2 \]

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

\[ F_\gamma(\rho) = \max_v \left( E_\gamma(v) - \langle v | \rho \rangle \right) \]
\[ = \max_v \left( E(v) - \langle v | \rho \rangle - \frac{1}{2} \gamma \|\nabla v\|^2 \right) \]

- 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

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