Density functional theory in magnetic fields

U. E. Ekström†, T. Helgaker†, S. Kvaal†, E. Sagvolden†, E. Tellgren†, A. M. Teale†‡

†Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, Norway
‡School of Chemistry, University of Nottingham, Nottingham, UK

Kathmandu 2012 Workshop on Theoretical Chemistry
Atoms, molecules and solids: models and concepts

Radisson Hotel, Kathmandu, Nepal, April 30–May 4, 2012
Consider the ground-state energy with interaction strength $\lambda$:

$$E_\lambda[v] = \inf_{\psi} \langle \psi | T + \sum_i v(r_i) + \lambda W | \psi \rangle$$

the Rayleigh–Ritz variation principle

We may summarize density-functional theory in two variation principles:

$$E_\lambda[v] = \inf_\rho \left( F_\lambda[\rho] + (v|\rho) \right)$$

the Hohenberg–Kohn variation principle (1964)

$$F_\lambda[\rho] = \sup_v (E_\lambda[v] - (v|\rho))$$

the Lieb variation principle (1983)

these are alternative attempts at sharpening the same inequality into an equality

$$F_\lambda[\rho] \geq E_\lambda[v] - (v|\rho) \iff E_\lambda[v] \leq F_\lambda[\rho] + (v|\rho)$$

Fenchel’s inequality

The Hohenberg–Kohn variation principle underlies all applications of DFT in chemistry

its success hinges on the accurate modelling of $F_\lambda[\rho]$

The Lieb variation principle provides a tool for studying $F_\lambda[\rho]$ numerically

we have implemented the Lieb variation principle at various levels ab initio theory

accurate numerical studies of $F_\lambda[\rho]$ are a guide to insight

our motivation is to benchmark approximate $F_\lambda[\rho]$ and to help develop new ones

Previous work:

studies by Colonna and Savin (1999) for few-electron atoms

work by Wu and Yang (2003) on Lieb maximizations
Conjugate functionals $E[v] \leftrightarrow F[\rho]$

- The ground-state energy $E[v]$ is **concave** in $v$ by the Rayleigh–Ritz variation principle
  - it can therefore be exactly represented by its **convex conjugate** $F[\rho]$: $E[v] \leftrightarrow F[\rho]$

- Both variation principles represent a **Legendre–Fenchel transformation**
  - the essential point is the concavity of $E[v]$ rather than the details of the Schrödinger equation
  - roughly speaking, the derivatives of $E[v]$ are $F[\rho]$ are inverse functions
  - the density functional $F[\rho]$ is more complicated than $E[v]$
We will first consider the Lieb maximization:

$$F_\lambda[\rho] = \sup_\nu (E_\lambda[\nu] - (\nu|\rho))$$

- optimization techniques and regularization

We will next consider the adiabatic connection

- the exchange–correlation functional
- adiabatic-connection curves

Finally, we consider DFT in magnetic fields

- the choice of variables: CDFT, BDFT
- BDFT adiabatic-connection curves
For a given density $\rho(r)$ and level of theory $E_\lambda[v]$, we wish to calculate

$$F_\lambda[\rho] = \max_v (E_\lambda[v] - (v | \rho))$$

The potential is parameterized as suggested by Wu and Yang 2003:

$$v_c(r) = v_{\text{ext}}(r) + (1 - \lambda)v_{\text{ref}}(r) + \sum_t c_t g_t(r)$$

- the physical, external potential $v_{\text{ext}}(r)$
- the Fermi–Amaldi reference potential to ensure correct asymptotic behaviour
- an expansion in Gaussians $g_t(r)$ with coefficients $c_t$

The maximization may be carried out by Newton-type methods:

- because of concavity, all maxima are global maxima
- 5–10 iterations with the exact Hessian to gradient norm $10^{-6}$
- 10–15 iterations with an approximate noninteracting Hessian
- Hessian regularized by a singular-value decomposition with cutoff $10^{-6}$
- possible (unphysical) oscillations in the potential do not affect $F_\lambda[\rho]$

Convergence is mostly unproblematic but difficulties may arise

- from a (near) piecewise linearity in $c_t$
- from a poor description of $E_\lambda[v_c]$ for large $c_t$ (typically for $\lambda \approx 0$)

All code is implemented in DALTON for HF, MP2, CCD, CCSD, and CCSD(T)
The bundle method for near piecewise linear functions

- The goal function contains alternating regions of small and large curvature

- The cutting-plane method minimizes linearized functions (supporting hyperplanes)
  ![Graph showing linearized functions with cutting planes](image)

- The bundle method combines Newton's method (Hessian information) with cutting planes

---

Helgaker et al. (CTCC, University of Oslo)

Kathmandu 2012 Workshop
Moreau–Yosida regularization I

- The density functional is **unbounded** for non-$N$-representable densities

$$F_\lambda[\rho] = \sup_v (E_\lambda[v] - (v|\rho)) = \sup_v (\langle \psi_v | T + \lambda W | \psi_v \rangle + (v|\rho_v - \rho))$$

  - $\rho_v = \rho$ yields a maximum but this may be impossible to satisfy in a small orbital basis
  - maximization may then give a too large potential $v$ and a too high $F_\lambda[\rho]

- This may be avoided by adding a **penalty function** to the ground-state energy:

$$E_\lambda^{\mu}[v] = E_\lambda[v] - \frac{\mu}{2} \|v\|^2 \quad \leftarrow \text{penalty for large potentials}$$

- It gives a bounded **regularized universal density functional**:

$$F_\lambda^{\mu}[\rho] = \sup_v (E_\lambda^{\mu}[v] - (v|\rho))$$

  where the **Moreau envelope** of the density functional is given by

$$F_\lambda^{\mu}[\rho] = \inf_n \left( F_\lambda[n] + \frac{1}{2\mu} \|\rho - n\|^2_* \right) \quad \leftarrow \text{infimal convolution}$$

  - the intrinsic energy of the most favourable nearby density $n$ rather than that of $\rho$
  - $F_\lambda^{\mu}[\rho]$ is bounded and differentiable, with the same minimum as $F_\lambda[\rho]$

- The **regularization norms** are related by convex conjugation:

$$\|v\|^2 = \langle v|M|v \rangle \quad \leftrightarrow \quad \|\rho\|_*^2 = \langle \rho|M^{-1}\rho \rangle \quad \leftarrow \text{convex conjugation}$$

  - different choices of $\mu$ and $M$ give different regularizations
Moreau–Yosida regularization II

Moreau envelope (g = 0.1, 0.02, 0.001)
Moreau–Yosida regularization of energy and density functional:

\[ E_\lambda^\mu[v] = E_\lambda[v] - \frac{\mu}{2} \langle v|M|v \rangle \quad \leftarrow \text{extrinsic energy with damped potential} \]

\[ F_\lambda^\mu[\rho] = \inf_{\Delta \rho} \left( F_\lambda[\rho + \Delta \rho] + \frac{1}{2\mu} \langle \Delta \rho|M^{-1}|\Delta \rho \rangle \right) \quad \leftarrow \text{intrinsic energy of favoured nearby density} \]

- Two choices of metric: \( M = I \) (overlap) and \( M = T \) (kinetic)
  - the kinetic metric gives the regularization of Heaton–Burgess, Bulat and Yang (2007)
    \[ \langle v|T|v \rangle = \int |\nabla v(r)|^2 \, dr \quad \leftarrow \text{small for smooth } v \]
    \[ \langle \Delta \rho|T^{-1}|\Delta \rho \rangle = \int \int \Delta \rho(r_1)r_1^{-1}\Delta \rho(r_2) \, dr_1 \, dr_2 \quad \leftarrow \text{small for oscillatory } \Delta \rho \]
  - \( v \) becomes smoother as density oscillations are removed

- More generally, Moreau–Yosida regularization sets up a regularized DFT

- Exact DFT:
  - \( F_\lambda[\rho] \) is convex, unbounded, everywhere discontinuous and not everywhere (sub)differentiable
  - not all densities are \( v \)-representable or even \( N \)-representable

- Moreau–Yosida DFT:
  - \( F_\lambda^\mu[\rho] \) with is convex, bounded, everywhere continuous and differentiable for \( \mu > 0 \)
  - all densities are \( N \)-representable and even \( v \)-representable
  - reminiscent of Lammert’s coarse-grained DFT (2010)
MY regularization for the neon atom with $\mu = 10^{-18}$

aug-cc-pVTZ orbital basis; 35s even-tempered potential basis

Helgaker et al. (CTCC, University of Oslo)
MY regularization for the neon atom with $\mu = 10^{-9}$

aug-cc-pVTZ orbital basis; 35s even-tempered potential basis

Helgaker et al. (CTCC, University of Oslo)
MY regularization for the neon atom with $\mu = 10^{-5}$

aug-cc-pVTZ orbital basis; 35s even-tempered potential basis
We introduce Kohn–Sham theory by expanding about $\lambda = 0$:

$$F_\lambda[\rho] = F_0[\rho] + \lambda F'_0[\rho] + E_{c,\lambda}[\rho] = T_s[\rho] + \lambda(J[\rho] - K[\rho]) + E_{c,\lambda}[\rho]$$

The correlation energy is the only term that depends on $\lambda$ in a nontrivial manner:

$$E'_{c,\lambda}[\rho] = F'_\lambda[\rho] - F'_0[\rho] = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - \langle \Psi_0 | V_{ee} | \Psi_0 \rangle = W_\lambda[\rho]$$ ← AC integrand

The correlation energy obtained by integration over the AC integrand:

$$E_c[\rho] = \int_0^1 W_\lambda[\rho] \, d\lambda$$

CCSD and CCSD(T) AC curves for the water molecule:
H$_2$ dissociation: from dynamical to static correlation

- Near equilibrium, correlation is predominantly dynamic
  - nearly linear curve since correlation is dominated by doubles ($\lambda^2$ in PT)
- Towards dissociation, static correlation becomes important
  - increased curvature from higher-order contributions in PT
- At dissociation, correlation is fully static
  - wave function adjusts immediately for $\lambda \neq 0$ (degenerate PT)
  - first-order degenerate PT yields constant curve for $\lambda > 0$
A two-parameter model for the H$_2$ molecule

- From a two-level CI model, we obtain the ground-state energy
  \[ E_{\text{CI}}(\lambda) = \frac{1}{2} \Delta E - \frac{1}{2} \sqrt{\Delta E^2 + 4g^2 \lambda^2}, \quad \Delta E = h + g \lambda \]

- Differentiation gives a two-parameter model for the AC integrand
  - good least-square fits (full lines) and fits to initial gradient and end point (dashed lines)

- Only the initial slope (GL2) and the end point (perhaps at $\lambda = \infty$) are needed
The BLYP functional treats correlation as dynamical at all bond distances:
- it was designed for spin-unrestricted theory but is used here in a spin-restricted manner;
- it hence ignores static correlation.
The improved BLYP performance arises from an overestimation of exchange. Error cancellation between exchange and correlation reduces total error to about one third.
Molecules in magnetic fields

- A magnetic field $B$ modifies the kinetic-energy operator:

$$\mathbf{H}(B) = \mathbf{T}(B) + W + \sum_i \mathbf{v}(r_i), \quad \mathbf{T}(B) = \frac{1}{2} \sum_i (\mathbf{\sigma} \cdot \mathbf{\pi}_i)^2$$

where $\mathbf{\sigma}$ are the Pauli spin matrices and $\mathbf{\pi}_i$ the kinetic-momentum operator:

$$\mathbf{\pi}_i = -i\nabla_i + A(r_i), \quad A = \frac{1}{2} B \times (\mathbf{r} - \mathbf{O})$$

- We have recently developed the London code for molecular calculations in strong fields
  - complex wave functions and London atomic orbitals
  - Hartree–Fock, FCI and Kohn–Sham models

- Our calculations have revealed many interesting features:
  - transition from paramagnetism to diamagnetism for all molecules at a critical $B_c$
  - molecular bonding of triplet $\mathbf{H}_2$ and singlet $\mathbf{He}_2$ in strong fields

What can we learn about the exchange–correlation functional in magnetic fields?

Helgaker et al. (CTCC, University of Oslo)
BDFT: magnetic-field DFT

- The simplest approach is to set up a separate DFT for each \( B \):
  \[
  E_0[v, B] = \inf_\rho (F[\rho, B] + (v|\rho))
  \]
- magnetic-field DFT (BDFT) (Grayce & Harris 1994)
- The density functional now depends on the density and on the field strength
  \[
  F[\rho, B] = \min_{\Psi \rightarrow \rho} \langle \Psi | T_\pi (B) + W | \Psi \rangle = T_s[\rho, B] + J[\rho] + E_{xc}[\rho, B]
  \]
- the noninteracting magnetic response is exactly taken care of by \( T_s[\rho, B] \)
- AC correlation curves of \( H_2 \) in a perpendicular magnetic field
  - \( E_{xc}[\rho, B] \) differs from \( E_{xc}[\rho] \) only at stretched geometries
  - an earlier onset of static correlation in strong magnetic fields
CDFT: current DFT

- Alternatively, we can build DFT with \((\rho, j)\) as variables, conjugate to \((v, A)\).

- The current consists of paramagnetic and diamagnetic parts:
  \[
  j = j_p + j_d = j_p + \rho A,
  \quad j_p = -i \frac{1}{2} \psi^\dagger(r) \nabla \psi(r) + \text{c.c.}
  \]

- Nota bene: different physical systems may share the same ground-state wave function:
  \[(\rho, j) \leftrightarrow (v, A) \rightarrow (\rho, j_p) \leftrightarrow \Psi \leftarrow \text{up to convex combinations and gauge transformations}\]

- We may now set up current DFT (CDFT):
  \[
  E_0[v, A] = \inf_{\rho, j_p} \left( F[\rho, j_p] + (v + \frac{1}{2} A^2 | \rho) + (A | j_p) \right)
  \]
  \[
  = \inf_{\rho, j} \left( F[\rho, j_p] + (v - \frac{1}{2} A^2 | \rho) + (A | j) \right)
  \]
  - the universal density functional depends on \(\rho\) and \(j_p\):
    \[
    F[\rho, j_p] = \min_{\Psi \mapsto \rho, j_p} \langle \Psi | T + W | \Psi \rangle
    \]
  - A Lieb variation principle can be set up to calculate \(F[\rho, j_p]\).
    - Ayers and Fuentealba (2009)
A Kohn–Sham decomposition of the CDFT functional yields (Vignale and Rasolt):

\[
F[\rho, j_p] = T_s[\rho, j_p] + J[\rho] + E_{xc}[\rho, \nu], \quad \nu(r) = \nabla \times \frac{j_p(r)}{\rho(r)} \leftarrow \text{vorticity}
\]

- all gauge dependence is located in the kinetic energy in the usual manner
- the exchange and correlation functionals are separately gauge invariant
- they depend on the vorticity rather than the paramagnetic current


\[
E_{xc}[\rho, j_p] = E_{xc}^0[\rho] + \int \frac{m_e k_F(r)}{24\pi^2} \left( \frac{\chi_L}{\chi_L^0} - 1 \right)(r) \nu(r) \, dr
\]

- several parametrizations of the diamagnetic susceptibility ratio \( \chi_L/\chi_L^0 \) are available

We have completed a KS-CDFT implementation to the LONDON program
- pilot VRG calculations are being carried out . . .
We have discussed Lieb’s theory of DFT
- ground-state energy and universal density functional related by conjugation

We have discussed Lieb maximizations
- Moreau–Yosida regularization of energy and density functional

We have discussed the adabatic connection
- ab-initio adiabatic-connection curves for benchmarking and modelling

We have discussed DFT in magnetic fields
- B-dependent (BDFT) and current-dependent (CDFT) density functionals

This work was supported by
- Norwegian Research Council
- European Research Council