

# Current-Density-Functional Theory in a Convex Treatment

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Workshop on Quantum Theory: Foundations and Extensions of Density-Functional Theory

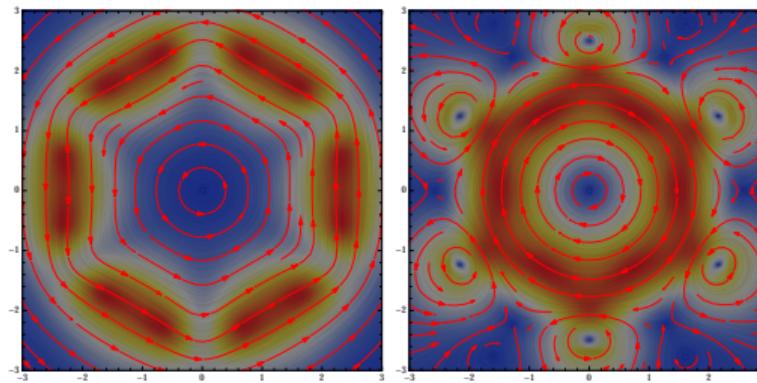
The OsloMet Quantum Hub  
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# Density-Functional Theory (DFT) in a magnetic field

- ▶ In standard DFT, everything depends on the density  $\rho$  and universal density functional  $F$ :

$$E(v) = \inf_{\rho} (F(\rho) + (v|\rho))$$

- ▶ the density  $\rho$  interacts with the external scalar potential  $v$  as  $(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$
- ▶ In an external magnetic field  $\mathbf{B} = \nabla \times \mathbf{A}$ , currents are induced in the electronic system
  - ▶ density and current density in benzene above (left) and in (right) the plane in a perpendicular field



- ▶ Our main question: how do we modify DFT to calculate the ground-state energy  $E(v, \mathbf{A})$ ?
  - ▶ in particular, what role do the induced currents play?

# Overview

- ▶ DFT without a magnetic field
  - ▶ emphasis on Lieb's convex theory
- ▶ DFT in a magnetic field
  - ▶ generalization of Lieb's convex theory to molecules in a magnetic field
  - ▶ magnetic-field density-functional theory (BDFT)
  - ▶ current-density functional theory (CDFT)
- ▶ Kohn–Sham theory in a magnetic field
  - ▶ Kohn–Sham decomposition and equations
  - ▶ exchange–correlation functional
- ▶ Molecules in a strong magnetic field studied by DFT
  - ▶ chemical bonding and molecular structure

# Hohenberg–Kohn theorem and variation principle

- ▶ The Hohenberg–Kohn theorem (1964) for ground-state densities:

*'Thus  $v(\mathbf{r})$  is (to within a constant) a unique functional of  $\rho(\mathbf{r})$ ; since, in turn,  $v(\mathbf{r})$  fixes  $H(v)$  we see that the full many-body ground state is a unique functional of  $\rho(\mathbf{r})$ .'*

$$\rho \mapsto v_\rho \mapsto \Psi_\rho \quad \text{Hohenberg–Kohn mapping for } v\text{-representable densities}$$

- ▶ the proof is elementary (apart from some subtleties) but perhaps difficult to grasp intuitively
- ▶ For a  $v$ -representable density  $\rho \mapsto v_\rho$ , the Hohenberg–Kohn functional is defined as

$$F_{HK}(\rho) = E(v_\rho) - (v_\rho | \rho)$$

where we have introduced the short-hand notation

$$(v_\rho | \rho) = \int v_\rho(\mathbf{r}) \rho(\mathbf{r}) \, d\mathbf{r}$$

- ▶ The Hohenberg–Kohn variation principle (1964) now follows by some simple arguments:

$$E(v) = \min_\rho (F_{HK}(\rho) + (v | \rho))$$

- ▶ The representability problem: the sets of density and potentials are unknown
  - ▶ we have no optimality conditions except by the HK mapping  $\rho \mapsto v_\rho$

# Levy–Lieb constrained-search functional

- The  $v$ -representability problem was solved with the Levy–Lieb constrained-search functional:

$$F_{\text{LL}}(\rho) = \min_{\Psi \mapsto \rho} \langle \Psi | T + W | \Psi \rangle$$

- well defined for all nonnegative densities with a finite von Weizsäcker kinetic energy (i.e., a known set)
- We may now search over all such  $N$ -representable densities in the Hohenberg–Kohn variation principle:

$$E(v) = \inf_{\rho \in \mathcal{I}_N} (F_{\text{LL}}(\rho) + (v|\rho))$$

- if  $v$  does not support a ground state, then  $E(v)$  is well defined as a greatest lower bound
- Regarding the optimality conditions, Levy writes (1979):

*'One can now confidently use existing Euler equations without being concerned about whether or not the functions in the immediate neighbourhood of the optimum functions are  $v$ -representable.'*

$$\frac{\delta F_{\text{LL}}(\rho)}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) + c, \quad c \in \mathbb{R}$$

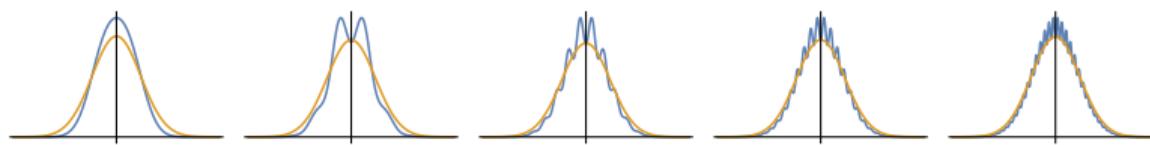
- the Euler equations provide the desired HK mapping—but is  $F_{\text{LL}}$  differentiable?

# Discontinuity of universal density functional

- ▶ For a one-electron system, a Gaussian density of unit exponent has a finite kinetic energy:

$$\rho(\mathbf{r}) = \pi^{-3/2} \exp(-r^2), \quad F(\rho) = \frac{1}{2} \int |\nabla \rho^{1/2}(\mathbf{r})|^2 d\mathbf{r} = 3/4$$

- ▶ Let  $\{\rho_n\}$  approach  $\rho$  in the norm, while developing increasingly rapid oscillations of increasingly small amplitude:



- ▶ The kinetic energy  $F(\rho_n)$  is driven arbitrarily high in the sequence, while  $F(\rho)$  is finite:

$$\lim_n F(\rho_n) = +\infty \gg F\left(\lim_n \rho_n\right) = 3/4 \quad \leftarrow \quad F \text{ is everywhere discontinuous (Lammert 2007)}$$

- ▶ However, universal density functional  $F$  is lower semi-continuous

- ▶ a continuous function cannot jump – neither up nor down – as we move away from a point
- ▶ a lower semi-continuous function can jump up – but not down – as we move away from a point

# Lieb's formulation of DFT

- ▶ Elliot Lieb laid the foundation for rigorous DFT in IJQC 24, 243 (1983)

## Density Functionals for Coulomb Systems

ELLIOTT H. LIEB

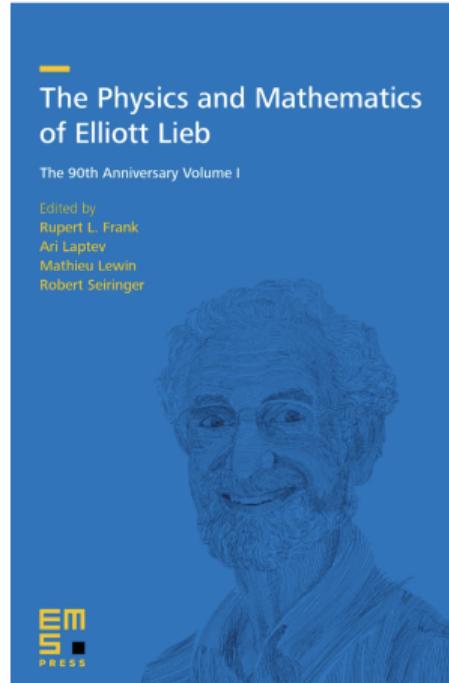
*Departments of Mathematics and Physics, Princeton University, P.O.B. 708, Princeton,  
New Jersey 08544, U.S.A.*

- ▶ Not easily accessible to most quantum chemists
- ▶ Andy Teale and I wrote [Lieb variation principle in density-functional theory](#) for [The Elliot Lieb 90th Anniversary Volume](#) (2022)

*Dear Professors Helgaker and Teale*

*I just found your beautiful paper in the 90 volume published by EMS and I thank you for it. It makes me feel that my old work is still relevant, even if not universally so. As you say, the presentation is informal, which is exactly what is needed. This brings great clarity to the subject.*

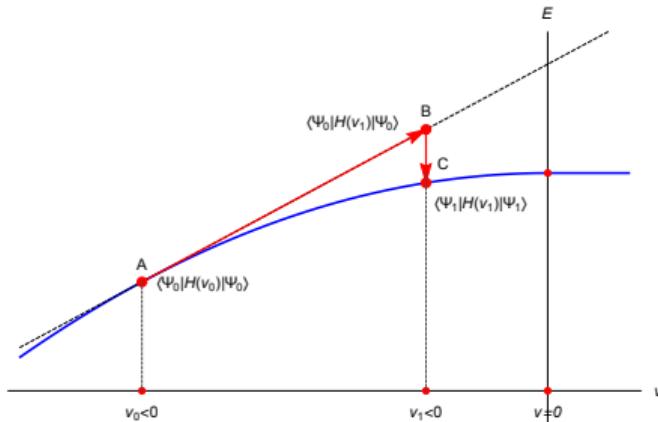
*With very best regards Elliott*



# Concavity of the ground-state energy

- The ground-state energy is continuous and concave in the external potential

$$E(v) = \inf_{\Psi} \langle \Psi | H(v) | \Psi \rangle = \inf_{\Psi} \langle \Psi | T + W + v(\mathbf{r}) | \Psi \rangle$$



- Concavity of  $E(v)$  may be understood in the following two-step manner:
  - from A to B, energy increases linearly since  $H(v)$  is linear in  $v$  and  $\Psi_0$  is fixed
  - from B to C, energy decreases as wave function relaxes to the ground state  $\Psi_1$
- Concavity arises from the Rayleigh–Ritz variation principle and the linearity of  $v \mapsto H(v)$

# DFT by convex analysis

- ▶ DFT now follows from a fundamental result of convex analysis: **biconjugation theorem** (Lieb 1983)
  - ▶ since  $E(v)$  is **concave and continuous** in  $v$ , there exists a convex lower-semi continuous function  $F(\rho)$  such that

$$F(\rho) = \sup_{v \in X^*} (E(v) - (v|\rho)) \quad \text{Lieb variation principle}$$

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

- ▶ vector spaces of densities and potentials are given by the Lebesgue spaces

$$\rho \in X = L^3 \cap L^1, \quad v \in X^* = L^{3/2} + L^\infty$$

- ▶  $E$  and  $F$  are **conjugate functions** – generalization of Legendre transforms
  - ▶ they contain the same information, only encoded in different ways
- ▶ DFT is thus a direct consequence of **the concavity and continuity of the ground-state energy**
  - ▶ DFT was not so much invented as it was discovered
  - ▶ there is no need for the Hohenberg–Kohn theorem – but where is the Hohenberg–Kohn mapping?
- ▶ Lieb's '**amusing fact**':

$$F(\rho) = \min_{\gamma \mapsto \rho} \text{tr}(\gamma H(0))$$

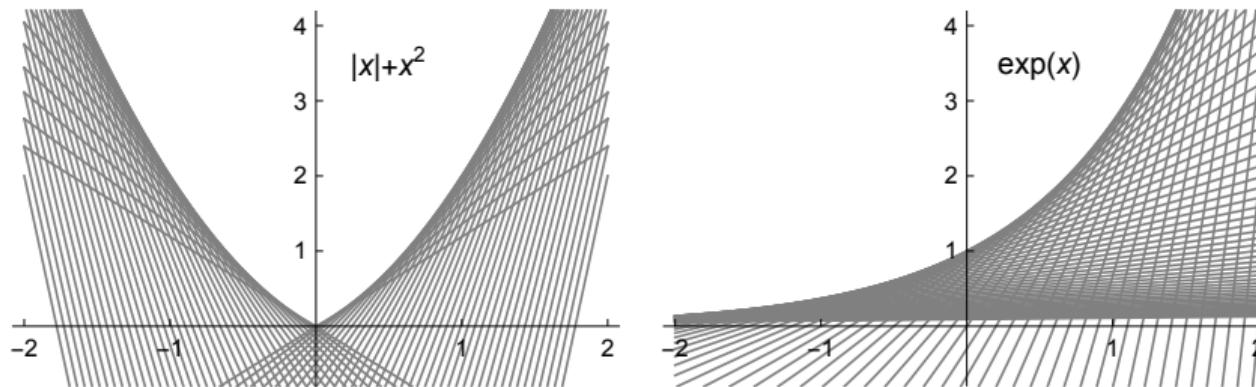
## Convexity of $F$ from the Lieb variation principle

- In the same manner the **Lieb variation principle** constructs, for each  $\rho$ , the universal density functional

$$F(\rho) = \sup_{v \in X^*} (E(v) - (v|\rho))$$

by a **maximization over a set of linear functions**, as illustrated below:

$$\{\rho \mapsto -(v|\rho) + E(v) \mid v \in X^*\}$$



# Convex conjugation: one-dimensional differentiable model

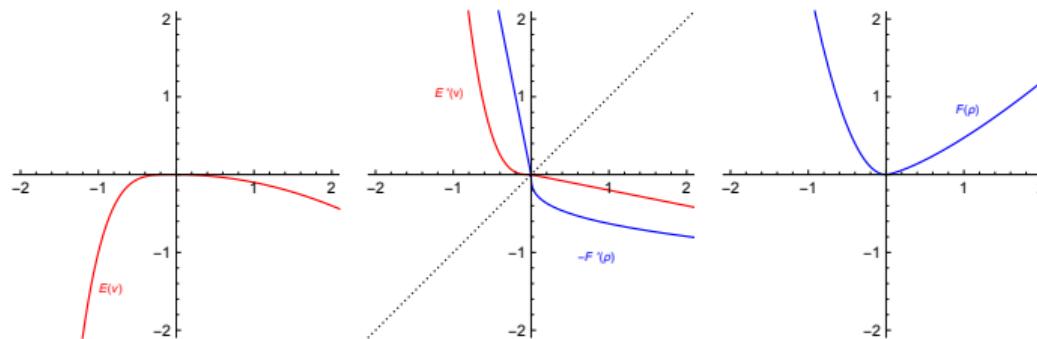
- The  $E(v)$  and  $F(\rho)$  are related in a symmetric manner:

$$E(v) = \inf_{\rho} (F(\rho) + (v|\rho)) \leftrightarrow F(\rho) = \sup_v (E(v) - (v|\rho))$$

- Assuming (for the time being) differentiability, we have the stationary conditions:

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

- $E$  and  $F$  are functions whose derivatives are each other's inverse functions (up to a sign)

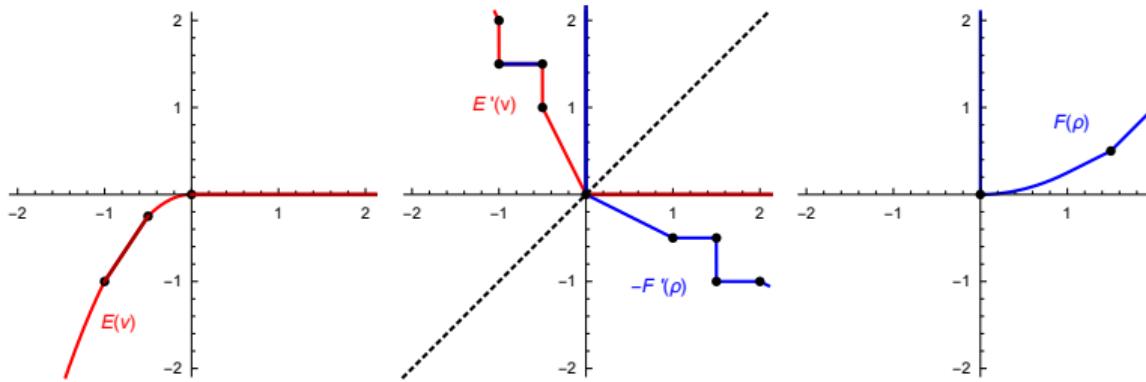


- graphical illustration: differentiate  $\leftrightarrow$  invert  $\leftrightarrow$  integrate

# Convex conjugation: one-dimensional nondifferentiable model

- Hohenberg–Kohn and Lieb variation principles with **nondifferentiable** and **not strictly concave**  $E$

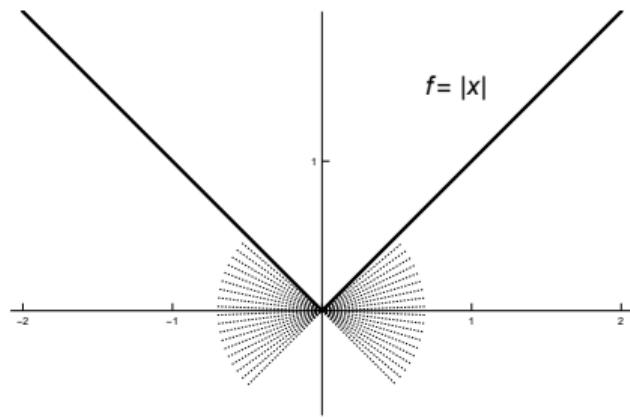
$$E(v) = \inf_{\rho} (F(\rho) + (v|\rho)) \leftrightarrow F(\rho) = \sup_v (E(v) - (v|\rho))$$



- nondifferentiable points** are transformed into **linear line segments** and vice versa
- $F$  is therefore **convex** but **not differentiable** nor **strictly convex**
- $F$  is **lower semi-continuous** but not continuous
- Mappings between potentials and densities cannot be expressed in terms of derivatives:

$$-v(\mathbf{r}) = \frac{\delta F(\rho)}{\delta \rho(\mathbf{r})} \leftrightarrow \rho(\mathbf{r}) = \frac{\delta E(v)}{\delta v(\mathbf{r})}$$

# Subgradients and subdifferentials



- ▶ The subgradients of  $f$  at  $x$  are the slopes of the supporting lines to  $f$  at  $x$
- ▶ The subdifferential  $\partial f(x)$  is the set of all subgradients of  $f$  at  $x$ :

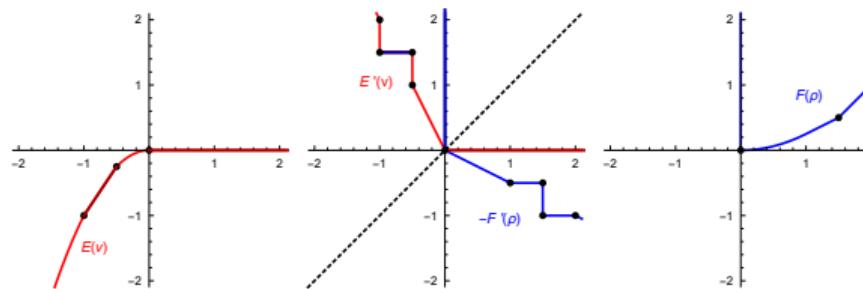
$$\partial f(x) = \begin{cases} \{-1\}, & x < 0, \\ [-1, 1], & x = 0, \\ \{1\}, & x > 0. \end{cases}$$

- ▶ Subgradients generalize derivatives to convex functions that are not differentiable

# Optimality conditions and $v$ -representability

- Hohenberg–Kohn and Lieb variation principles:

$$E(v) = \inf_{\rho} (F(\rho) + (v|\rho)) \iff F(\rho) = \sup_v (E(v) - (v|\rho))$$



- Optimality conditions in terms of subdifferentials:

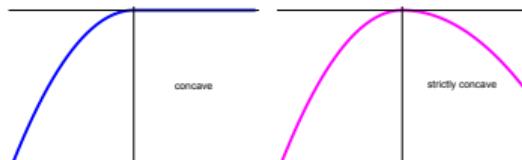
$$-v \in \partial F(\rho) \iff \rho \in \partial E(v) \quad \leftarrow \text{inverse multifunctions}$$

- The subdifferentials are nonempty on dense subsets of their domains and are given by

$$\begin{aligned} \partial F(\rho) &= \{-v_\rho + c \mid \rho \text{ is a ground-state density of } v_\rho, c \in \mathbb{R}\} && \leftarrow \text{Hohenberg–Kohn mapping} \\ \partial E(v) &= \{\rho \mid \rho \text{ is an ensemble ground-state density of } v\} && \leftarrow \text{ground-state densities of } v \end{aligned}$$

# Moreau–Yosida regularization of DFT

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



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

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

- caveat:  $\gamma$  can be as small as we like but  $v$  must be square integrable (Coulomb potential in a box)
- We now introduce the **density functional**  $F_\gamma$  in the usual manner:

$$F_\gamma(\rho) = \max_v (E_\gamma(v) - (v|\rho)), \quad E_\gamma(v) = \min_\rho (F_\gamma(\rho) + (v|\rho))$$

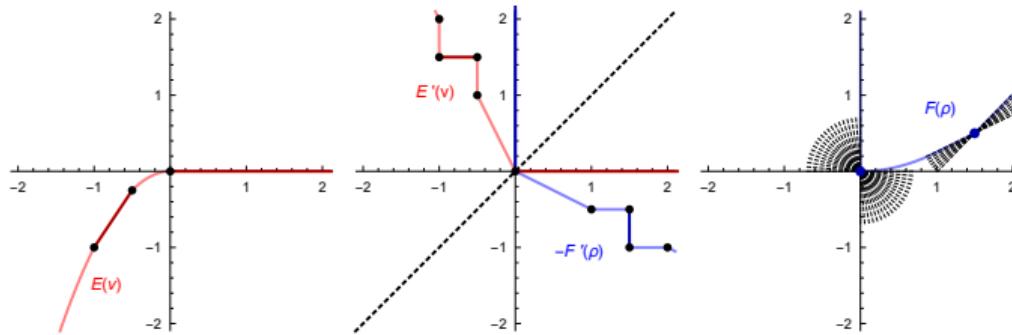
- Unlike  $F$ , the regularized density functional  $F_\gamma$  is **continuous and differentiable**

$$\frac{\delta F_\gamma(\rho)}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) - \mu \quad \text{Euler equation well defined}$$

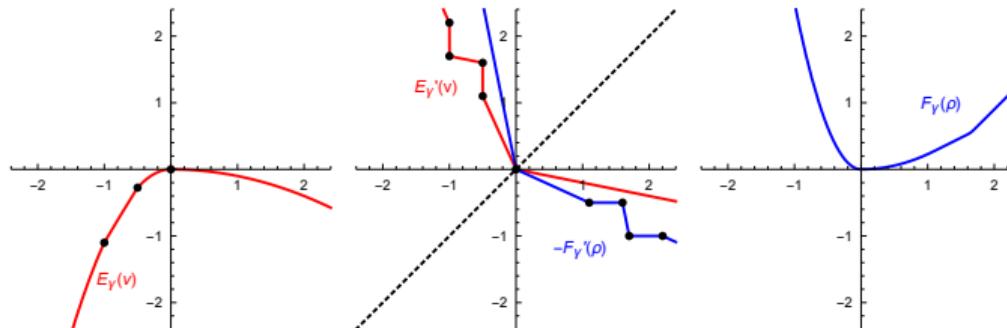
- This procedure is known as **Moreau–Yosida regularization**
  - Kvaal, Ekström, Teale, and Helgaker, *J. Chem. Phys.* **140**, 18A518 (2014)

# Illustration of Moreau–Yosida regularization

- Standard DFT with concave but not strictly concave energy  $E(v)$



- Regularized DFT with strictly concave energy  $E_\gamma(v)$

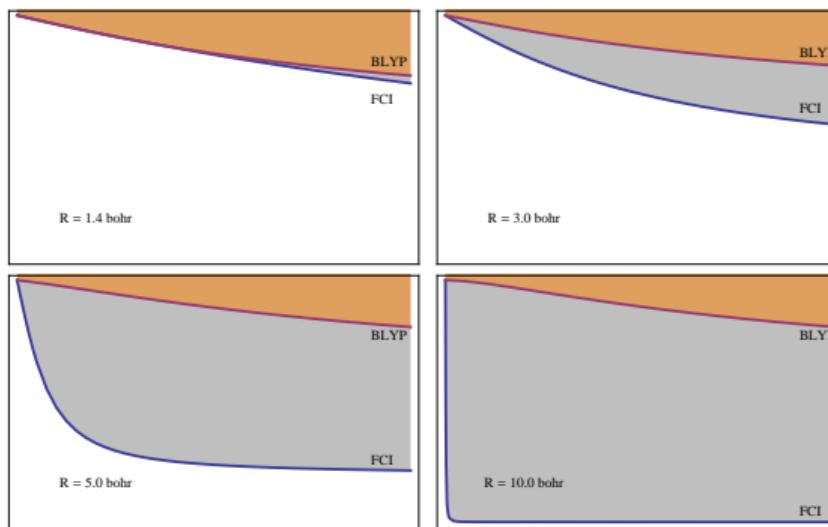


# Ab initio calculation of the universal-density functional

- ▶ Lieb variation principle can be used for ab initio calculation of  $F(\rho)$  to high accuracy

$$F(\rho) = \sup_v (E(v) - (v|\rho)) \leftarrow \text{practical tool for calculating universal density functional}$$

- ▶ first performed by Colonna and Savin on atoms (1999) and later by Yang and Wu for noninteracting systems (2002)
  - ▶ Teale, Coriani, and Helgaker (2010) for molecules at all interaction strengths
- ▶ Illustration: FCI and BLYP adiabatic-connection correlation curves for the dissociation of H<sub>2</sub>



# Summary DFT

- The functions  $E$  and  $F$  are conjugate functions, while the variables  $v$  and  $\rho$  are conjugate variables:

$$E(v) = \inf_{\rho} (F(\rho) + (v|\rho)) \iff F(\rho) = \sup_v (E(v) - (v|\rho))$$

- Optimality conditions are expressed in terms of inverse subdifferentials:

$$E(v) = F(\rho) + (v|\rho) \iff -v \in \partial F(\rho) \iff \rho \in \partial E(v)$$

- Hohenberg–Kohn variation principle is faithful to the Rayleigh–Ritz variation principle (Kvaal & Helgaker, 2015)

$E(v) = \inf_{\rho} (F(\rho) + (v|\rho)) \leftarrow$  convex minimization problem – at most one (degenerate) minimum

- minimum and minimizers are precisely the Rayleigh–Ritz ground-state energy and densities

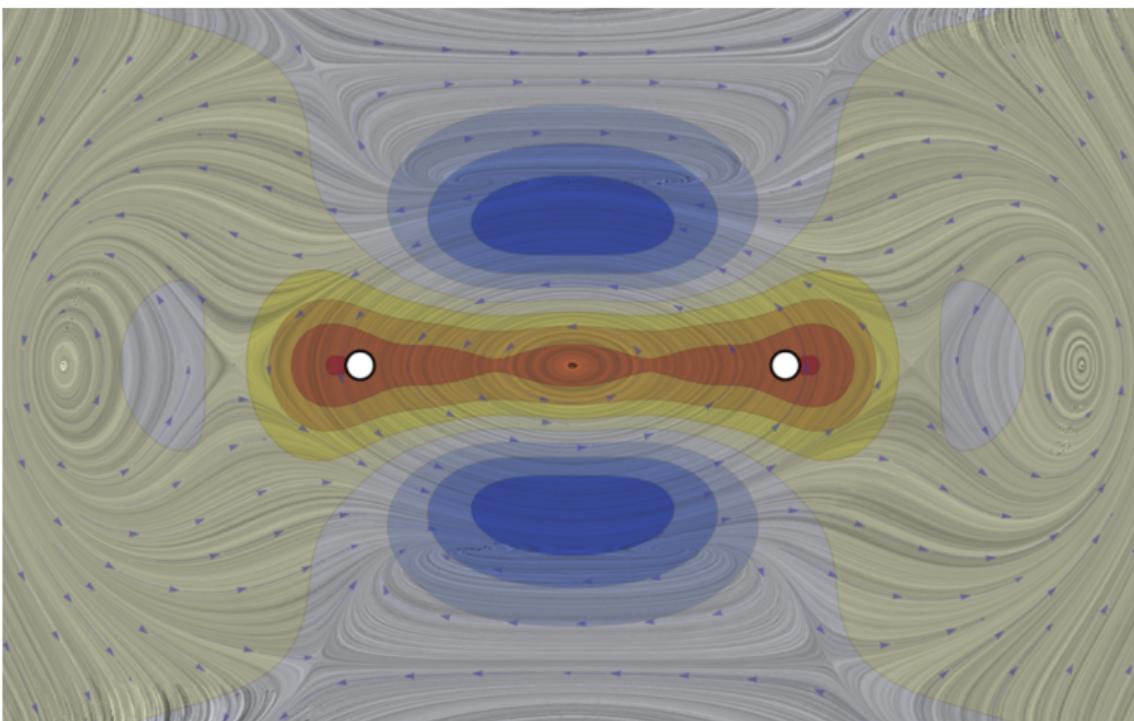
- The universal density functional may be obtained in two equivalent ways

$$F(\rho) = \begin{cases} \min_{\gamma \mapsto \rho} \text{tr}(\gamma H(0)) & \text{Levy's constrained search (good for understanding)} \\ \sup_v (E(v) - (v|\rho)) & \text{Lieb maximization (useful for calculations)} \end{cases}$$

- Hohenberg–Kohn theorem may be expressed as follows:

$$\partial F(\rho) = - \begin{cases} v_{\rho} + \mathbb{R}, & \rho \text{ ensemble } v\text{-representable} \\ \emptyset & \text{otherwise} \end{cases}$$

# DFT in a magnetic field



# Nonconcavity of energy in a magnetic field

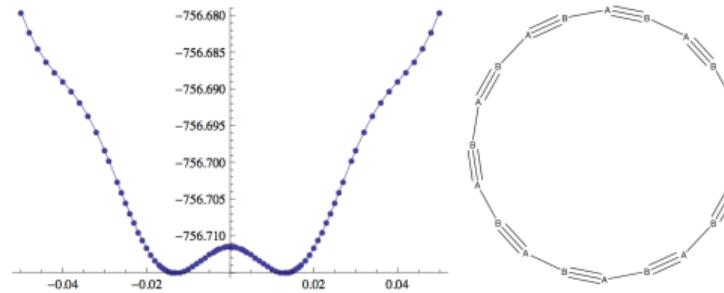
- ▶ A magnetic field  $\mathbf{B}$  modifies the kinetic-energy operator:

$$T(\mathbf{A}) = \frac{1}{2}(\mathbf{p} + \mathbf{A}) \cdot (\mathbf{p} + \mathbf{A}), \quad \mathbf{p} = -i\nabla, \quad \mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$$

- ▶ note: one atomic unit field strength is  $B_0 = 2.35 \times 10^5$  T
- ▶ The Hamiltonian in a magnetic field is therefore quadratic in the vector potential  $\mathbf{A}$ :

$$H(v, \mathbf{A}) = H(0, \mathbf{0}) + v + \frac{1}{2}A^2 + \mathbf{A} \cdot \mathbf{p}$$

- ▶ Consequently,  $E(v, \mathbf{A})$  is not concave in  $\mathbf{A}$  as illustrated for  $C_{20}$  in a perpendicular field



- ▶ Tellgren, Helgaker and Soncini, PCCP **11**, 5489 (2009)

# Concavification of ground-state energy

- The ground-state energy is **quadratic** in the vector potential:

$$E(v, \mathbf{A}) = \inf_{\Psi} \langle \Psi | T(\mathbf{0}) + W + v + \frac{1}{2} A^2 + \mathbf{A} \cdot \mathbf{p} | \Psi \rangle,$$

- To set up DFT, we therefore work with a **reparameterized, concave energy function**:

$$\bar{E}(u, \mathbf{A}) = \inf_{\Psi} \langle \Psi | T(\mathbf{0}) + W + u + \mathbf{A} \cdot \mathbf{p} | \Psi \rangle$$

- reparameterized energy is not bounded below but **upper semi-continuous concave**

$$E(v, \mathbf{A}) = \bar{E}(v + \frac{1}{2} A^2, \mathbf{A})$$

- Tellgren, Kvaal, Sagvolden, Ekström, Teale and Helgaker, *Phys. Rev. A* **86**, 062506 (2012)

- The **paramagnetic current density**  $\kappa$  and the **physical current density**  $\mathbf{j}$  are given by

$$\kappa = N \operatorname{Re} \int \Psi^* \mathbf{p} \Psi d\tau_{-1}, \quad \mathbf{j} = N \operatorname{Re} \int \Psi^* (\mathbf{p} + \mathbf{A}) \Psi d\tau_{-1}, \quad \mathbf{j} = \kappa + \rho \mathbf{A},$$

- Potentials  $(u, \mathbf{A})$  interact with **charge density** and **paramagnetic current density**  $(\rho, \kappa) \leftarrow \Psi$  in the manner

$$\langle \Psi | u | \Psi \rangle = (u | \rho), \quad \langle \Psi | \mathbf{A} \cdot \mathbf{p} | \Psi \rangle = (\mathbf{A} | \kappa)$$

# DFT in a magnetic field: BDFT and CDFT

- ▶  $\bar{E}(u, \mathbf{A})$  is concave in  $u$  and  $\mathbf{A}$ , separately and jointly – we can then do partial or full transformations
- ▶ Magnetic-field DFT (BDFT) (Grayce & Harrison 1994)
  - ▶ partial transformation with respect to first coordinate gives a semi-universal convex-concave density functional

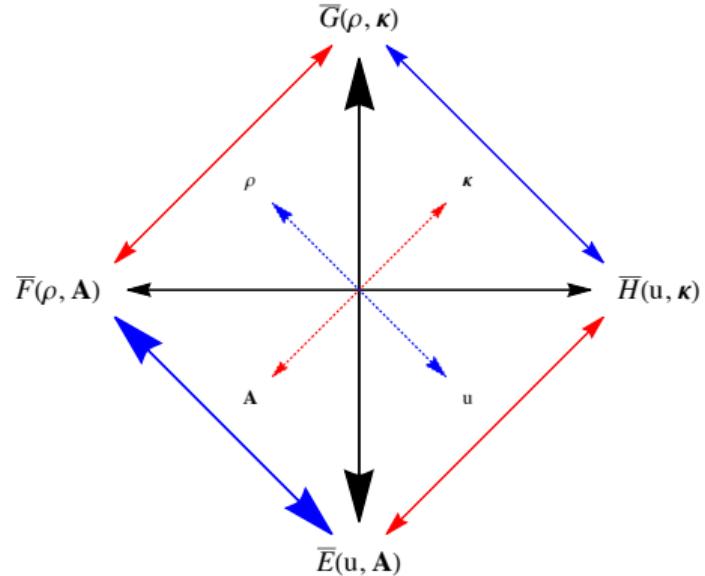
$$\bar{F}(\rho, \mathbf{A}) = \sup_u (\bar{E}(u, \mathbf{A}) - (u|\rho))$$

$$\bar{E}(u, \mathbf{A}) = \inf_{\rho} (\bar{F}(\rho, \mathbf{A}) + (u|\rho))$$

- ▶ Current DFT (CDFT) (Vignale & Rasolt 1987)
  - ▶ full transformation with respect to both coordinates gives a universal convex-convex density functional

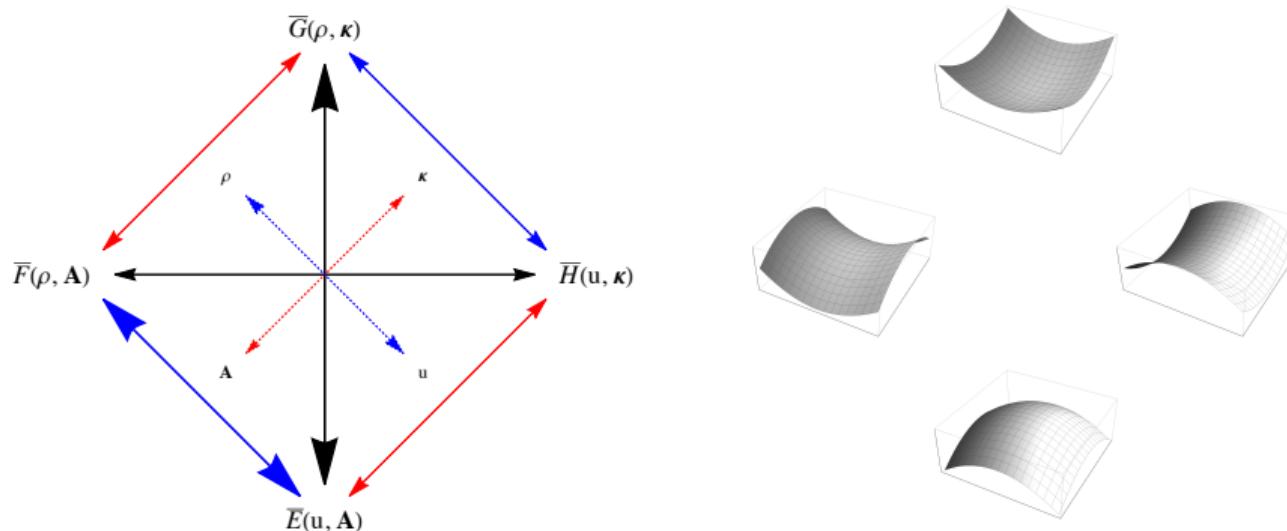
$$\bar{G}(\rho, \kappa) = \sup_{u, \mathbf{A}} (\bar{E}(u, \mathbf{A}) - (u|\rho) - (\mathbf{A}|\kappa))$$

$$\bar{E}(u, \mathbf{A}) = \inf_{\rho, \kappa} (\bar{G}(\rho, \kappa) + (u|\rho) + (\mathbf{A}|\kappa))$$



# Four-way correspondence of convex conjugation

- ▶ Four-way correspondence generated by convex–convex and concave–concave parents
  - ▶ partial transformations generate concave–convex and convex–concave saddle functions



- ▶ Magnetic-Field Density-Functional Theory (BDFT): Lessons from the Adiabatic Connection,  
Reimann, Borgoo, Tellgren, Teale, and Helgaker, *J. Chem. Theory Comput.* **13**, 4089–4100 (2017)

# Constrained-search functionals in a magnetic field

- ▶ In Levy's constrained-search approach, we may treat the kinetic-energy terms in two different ways

$$T(\mathbf{A}) = T(\mathbf{0}) + \frac{1}{2} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{1}{2} A^2, \quad T(\mathbf{0}) = \frac{1}{2} p^2$$

- ▶ in BDFT, we retain all  $T(\mathbf{A})$  in the constrained search:

$$E(v, \mathbf{A}) = \inf_{\rho} (F(\rho, \mathbf{A}) + (v|\rho))$$

$$F(\rho, \mathbf{A}) = \min_{\gamma \mapsto \rho} \text{tr}(\gamma(T(\mathbf{A}) + W)) = \bar{F}(\rho, \mathbf{A}) + \frac{1}{2}(A^2|\rho)$$

- ▶ in CDFT, we retain only  $T(\mathbf{0})$  in the constrained search:

$$E(v, \mathbf{A}) = \inf_{\rho, \kappa} (G(\rho, \kappa) + (\mathbf{A}|\kappa) + (v + \frac{1}{2} A^2|\rho))$$

$$G(\rho, \kappa) = \min_{\gamma \mapsto \rho, \kappa} \text{tr}(\gamma(T(\mathbf{0}) + W)) = \bar{G}(\rho, \kappa)$$

- ▶ The constrained-search functionals are equivalent to the corresponding Legendre–Fenchel functions (in green)
- ▶ convexity and lower semi-continuity have been shown, as well as existence of constrained-search minimizers
- ▶ Kvaal, Laestadius, Tellgren, and Helgaker, *J. Phys. Chem. Lett.* **12**, 1421–1425 (2021)
- ▶ BDFT and CDFT are both faithful to the Rayleigh–Ritz variation principle:
  - ▶ they give exact ground-state energies and densities by a convex minimization problem

# No Hohenberg–Kohn theorem in CDFT

- ▶ Let  $H_0$  be the field-free Hamiltonian and apply  $\mathbf{B} = \nabla \times \mathbf{A}$  in the  $z$  direction
- ▶ After adjusting the scalar potential to remove the diamagnetic term  $A^2/2$ , the new Hamiltonian takes the form

$$H_B = H_0 + \frac{1}{2}BL_z$$

- ▶ If the system is spherically symmetric, then  $H_0$  commutes with  $L_z$  and hence also with  $H_B$ :

$$[H_0, H_B] = 0$$

- ▶ There then exists an interval  $[B_{\min}, B_{\max}]$  where  $H_0$  and  $H_B$  share the ground-state wave function  $\Psi$
- ▶ On this interval,  $\mathbf{A}$  changes while  $\rho$  and  $\kappa$  are constant since they are determined by  $\Psi$ :

$$\rho = N \int \Psi^* \Psi d\tau_{-1}, \quad \kappa = N \operatorname{Re} \int \Psi^* \mathbf{p} \Psi d\tau_{-1}$$

- ▶ There is no Hohenberg–Kohn theorem:  $(\rho, \kappa)$  may be associated with many  $(u, \mathbf{A})$ 
  - ▶ von Barth and Hedin (1972), Eschrig and Pickett (2001), Capelle and Vignale (2001,2002)
- ▶ But physical current density  $\mathbf{j} = \kappa + \rho \mathbf{A}$  does change in the interval
  - ▶ HK theorem for  $\mathbf{j}$  is not ruled out but all purported proofs are flawed (Tellgren et al. (2012))

# CDFT: physical or paramagnetic current density

- The **physical current density** consists of gauge-dependent paramagnetic and diamagnetic parts:

$$\mathbf{j} = \boldsymbol{\kappa} + \rho \mathbf{A}$$

- Vignale and Rasolt (1987,1988) proposed CDFT based on the **paramagnetic current**  $\boldsymbol{\kappa}$ :

$$E(v, \mathbf{A}) = \inf_{\rho, \boldsymbol{\kappa}} (G_{\text{VR}}(\rho, \boldsymbol{\kappa}) + (v + \frac{1}{2} A^2 |\rho|) + (\mathbf{A} | \boldsymbol{\kappa}))$$

$$G_{\text{VR}}(\rho, \boldsymbol{\kappa}) = \inf_{\Psi \mapsto (\rho, \boldsymbol{\kappa})} \langle \Psi | T(\mathbf{0}) + W | \Psi \rangle$$

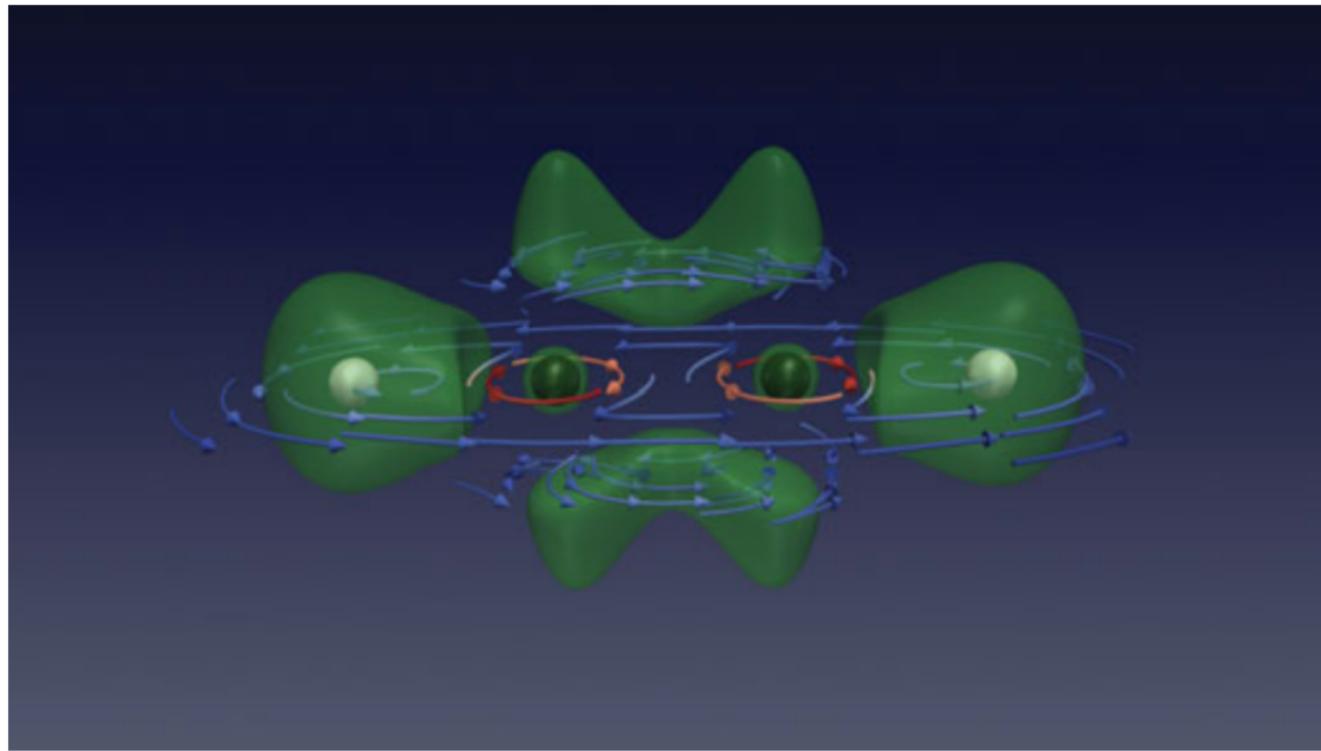
- $\boldsymbol{\kappa}$  is **not observable** and there is no Hohenberg–Kohn theorem
- Pan and Sahni (2010) proposed CDFT based on the **physical current**  $\mathbf{j}$ :

$$E(v, \mathbf{A}) = \inf_{\rho, \mathbf{j}} (G_{\text{PS}}(\rho, \mathbf{j}) + (v - \frac{1}{2} A^2 |\rho|) + (\mathbf{A} | \mathbf{j}))$$

$$G_{\text{PS}}(\rho, \mathbf{j}) = \inf_{\Psi \mapsto (\rho, \mathbf{j})} \langle \Psi | T(\mathbf{0}) + W | \Psi \rangle$$

- $\mathbf{j}$  is **observable**, unlike the paramagnetic current
- unproven HK-like theorem needed to obtain  $\mathbf{A}$  and reconstruct  $(\rho, \boldsymbol{\kappa})$  from  $(\rho, \mathbf{j})$

# Kohn-Sham theory in a magnetic field



# Kohn–Sham decomposition in a magnetic field

- ▶ The Kohn–Sham decomposition of the constrained-search functionals follow in the usual manner:

$$F(\rho, \mathbf{A}) = \mathcal{T}_s(\rho, \mathbf{A}) + J(\rho) + F_{xc}(\rho, \mathbf{A}) \quad \leftarrow \text{Kohn–Sham BDFT}$$

$$G(\rho, \kappa) = K_s(\rho, \kappa) + J(\rho) + G_{xc}(\rho, \kappa) \quad \leftarrow \text{Kohn–Sham CDFT}$$

- ▶ The noninteracting kinetic energy functionals are given by:

$$\mathcal{T}_s(\rho, \mathbf{A}) = \min_{\gamma \mapsto \rho} \text{tr} (\gamma T(\mathbf{A})) \leftarrow \text{noninteracting physical kinetic energy}$$

$$K_s(\rho, \kappa) = \min_{\gamma \mapsto (\rho, \kappa)} \text{tr} (\gamma T(\mathbf{0})) \leftarrow \text{noninteracting canonical kinetic energy}$$

- ▶ The exchange and correlation energies are separately gauge invariant

- ▶ BDFT and CDFT ground-state exchange–correlation energies are related as

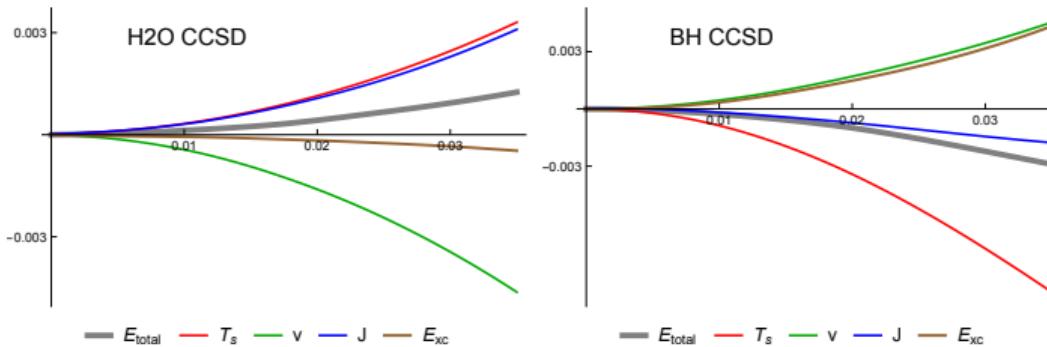
$$F_{xc}(\rho, \mathbf{A}) \geq G_{xc}(\rho, \kappa)$$

- ▶ they give the same ground-state energy in the density-only approximation:

$$F_{xc}(\rho, \mathbf{A}) = G_{xc}(\rho, \kappa) = E_{xc}(\rho)$$

# Kohn–Sham decomposition in a magnetic field

- ▶ Dependence of BDFT energy components on perpendicular  $B$  of diamagnetic H<sub>2</sub>O and paramagnetic BH:
  - ▶ Kohn–Sham components calculated by CCSD Lieb maximization
  - ▶ changes driven by the kinetic energy, which depends explicitly on the field



- ▶ Density of H<sub>2</sub>O is compressed in the field, while that of BH is decompressed
  - ▶  $T_s(\rho) + J(\rho)$  change in the opposite direction of  $(v|\rho) + E_{\text{xc}}(\rho)$
- ▶ The density must be accurately described to give good magnetizabilities
- ▶ Reimann, Borgoo, Austad, Tellgren, Teale, Helgaker, and Stopkowicz, *Mol. Phys.* **117**, 97–109 (2019)

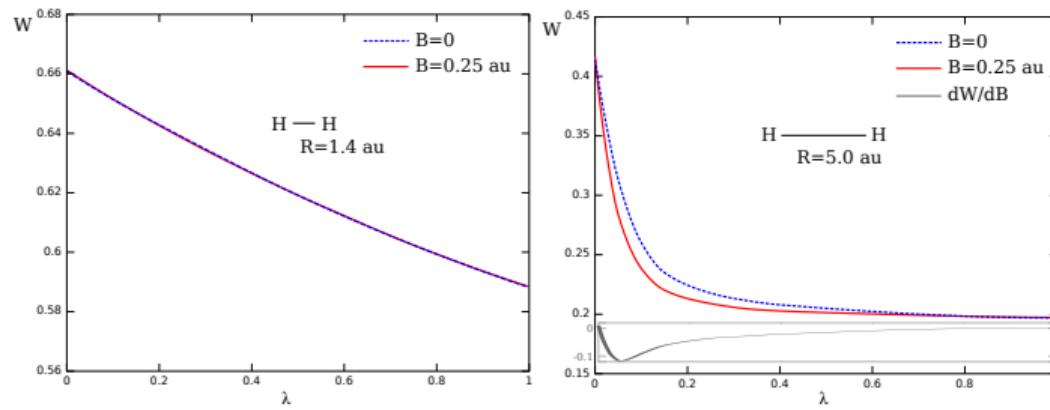
# BDFT adiabatic–connection curves in a magnetic field

- The adiabatic connection (AC) in a magnetic field can be studied using Lieb maximization

$$F_{xc}(\rho, \mathbf{A}) = \int_0^1 \mathcal{W}_\lambda(\rho, \mathbf{A}) d\lambda - J(\rho), \quad \mathcal{W}_\lambda(\rho, \mathbf{A}) \leftarrow \text{AC integrand at interaction strength } \lambda$$

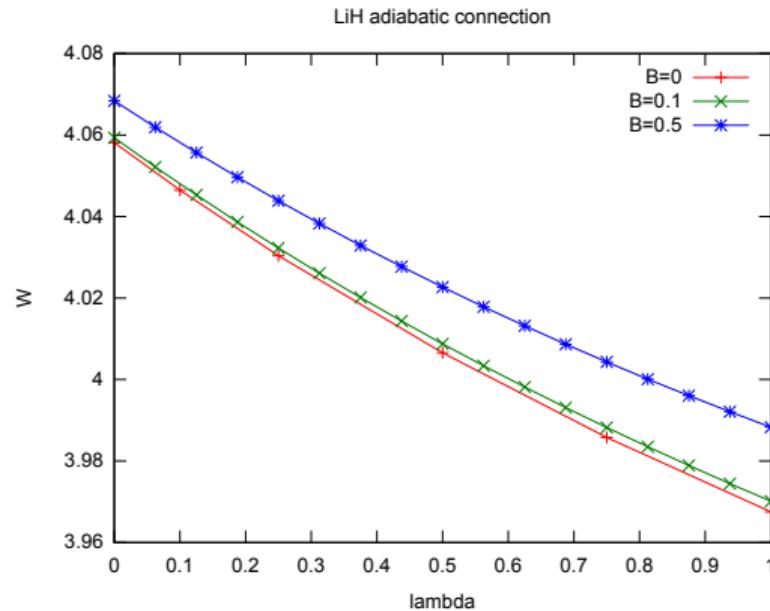
- Exchange–correlation integrand of H<sub>2</sub> in a perpendicular magnetic field

- curves change appreciably only at stretched geometries
- earlier onset of static correlation in a strong magnetic field



# BDFT adiabatic-connection curve for LiH in a magnetic field

- ▶ AC curves of LiH in a perpendicular magnetic field at a fixed bond length
  - ▶ compressed atomic densities gives less dynamical and more static correlation



# Kohn–Sham equations in a magnetic field

- The Kohn–Sham equations in an external potential  $(v_{\text{ext}}, \mathbf{A}_{\text{ext}})$  are given by

$$\left[ \frac{1}{2} p^2 + \frac{1}{2} (\mathbf{p} \cdot \mathbf{A}_s + \mathbf{A}_s \cdot \mathbf{p}) + \mathbf{s} \cdot (\nabla \times \mathbf{A}_s) + v_s \right] \varphi_p = \varepsilon_p \varphi_p$$

- the Kohn–Sham potentials contain contributions from external and exchange–correlation potentials

$$v_s = v_{\text{ext}} + \frac{1}{2} A_{\text{ext}}^2 + v_J + v_{\text{xc}},$$

$$\mathbf{A}_s = \mathbf{A}_{\text{ext}} + \mathbf{A}_{\text{xc}},$$

- the exchange–correlation potentials differ in BDFT and CDFT:

$$v_{\text{xc}} = \frac{\delta F_{\text{xc}}(\rho, \mathbf{A})}{\delta \rho(\mathbf{r})}, \quad \mathbf{A}_{\text{xc}} = \mathbf{0} \qquad \longleftarrow \quad \text{BDFT exchange–correlation potentials}$$

$$v_{\text{xc}} = \frac{\delta G_{\text{xc}}(\rho, \kappa)}{\delta \rho(\mathbf{r})}, \quad \mathbf{A}_{\text{xc}} = \frac{\delta G_{\text{xc}}(\rho, \kappa)}{\delta \kappa(\mathbf{r})} \quad \longleftarrow \quad \text{CDFT exchange–correlation potentials}$$

- BDFT and CDFT equations are identical in the density-only approximation, when  $F_{\text{xc}}(\rho, \mathbf{A}) = G_{\text{xc}}(\rho, \kappa) = E_{\text{xc}}(\rho)$
- Molecular orbitals expanded in London atomic orbitals for gauge invariance
- Furness, Verbeke, Tellgren, Stopkowicz, Ekström, Helgaker, and Teale, JCTC 11, 4169–4181 (2015)  
Reimann, Borgoo, Tellgren, Teale, and Helgaker, JCTC 13, 4089–4100 (2017)

# $N$ -representability in Kohn–Sham CDFT

- ▶ Given  $\rho$  and  $\kappa$ , does there exist an ensemble  $\gamma$  such that  $\gamma \mapsto (\rho, \kappa)$ ?
  - ▶ Lieb and Schrader (2013): by a single Slater determinant for  $N \geq 4$  particles
  - ▶ Tellgren, Kvaal and Helgaker (2014): by an ensemble of Slater determinants for  $N \geq 1$  particles
- ▶ Closed-shell two-electron systems are **not representable by a single determinant**
- ▶ Consider the gauge-invariant vorticity:

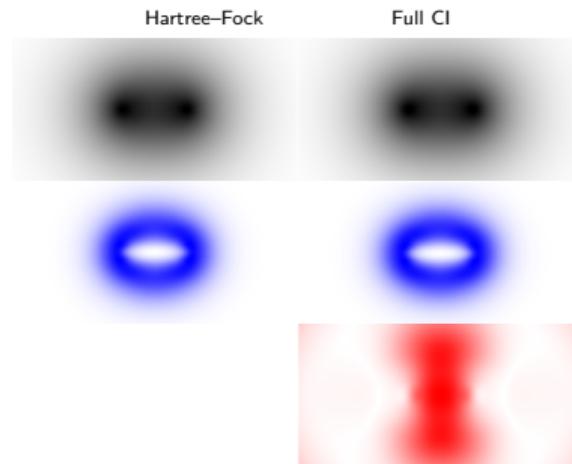
$$\nu(\mathbf{r}) = \nabla \times \frac{\kappa(\mathbf{r})}{\rho(\mathbf{r})}$$

- ▶  $\rho$  and  $\nu$  determine the xc energy:

$$G_{xc}(\rho, \kappa) \rightarrow G_{xc}(\rho, \nu)$$

- ▶ Vignale and Rasolt, PRL 59, 2360 (1987)
- ▶ Plots for H<sub>2</sub> in Hartree–Fock and FCI theories:

density  $\rho$  (top)  
 physical current  $j^2$  (middle)  
 vorticity  $\nu$  (bottom)



# VRG functional

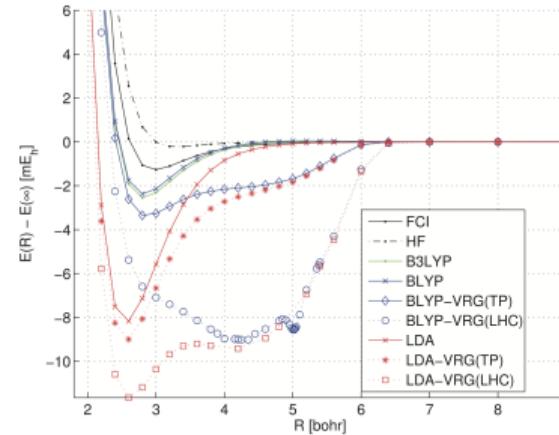
- Vignale–Rasolt–Geldart (VRG) local vorticity functional

$$E_{\text{VRG}}(\boldsymbol{\nu}) = \int g(\rho(\mathbf{r})) |\boldsymbol{\nu}(\mathbf{r})|^2 d\mathbf{r}, \quad \boldsymbol{\nu}(\mathbf{r}) = \nabla \times \frac{\boldsymbol{\kappa}(\mathbf{r})}{\rho(\mathbf{r})}$$

- uniform electron gas in a uniform magnetic field (RPA); several parameterizations exist
- regularization necessary for small values
- He<sub>2</sub> in a perpendicular field of strength  $B_0$ 
  - u-aug-cc-pVTZ curves aligned at  $R = 9a_0$
  - Tellgren *et al.*, JCP **140**, 034101 (2014)

*“numerical problems arise from the vorticity variable ... the vorticity variable is rather difficult computationally ... the difficulty may be deep enough that it could be profitable to seek an alternative gauge-invariant formulation of the current dependence in DFT”*

Zhu and Trickey, JCP **125**, 094317 (2006)



# meta-GGA functionals in a magnetic field

- ▶ The meta-GGA functionals depend on the kinetic-energy density:

$$\tau_\sigma(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \quad \leftarrow \quad \text{from expansion of spherically averaged exchange hole}$$

- ▶ Gauge invariant modification by Dobson (1993) by inclusion of paramagnetic current

$$\tau_\sigma^c(\mathbf{r}) = \tau_\sigma(\mathbf{r}) - \frac{|\kappa_\sigma(\mathbf{r})|^2}{2\rho_\sigma(\mathbf{r})}$$

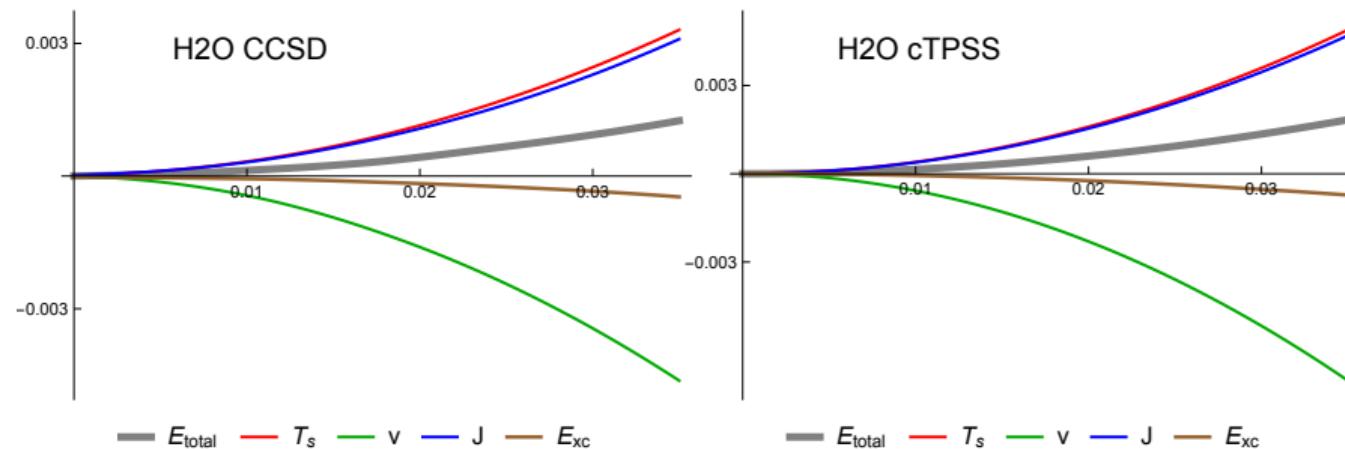
- ▶ Maximoff and Scuseria (2006) constructed kinetic-energy density from the canonical momentum

$$\tau_\sigma^a(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} | -i\nabla \varphi_{i\sigma}(\mathbf{r}) + \mathbf{A}(\mathbf{r}) |^2,$$

- ▶ We here consider three meta-GGA functionals: B98, TPSS, TPSSh
- ▶ The gauge-invariant (current-dependent) forms are denoted cB98, cTPSS and cTPSSh
  - ▶ cTPSS has been used for excitation energies in response theory
  - ▶ Bates and Furche JCP **137** 164105 (2012)

# BDFT/cTPSS for diamagnetic H<sub>2</sub>O

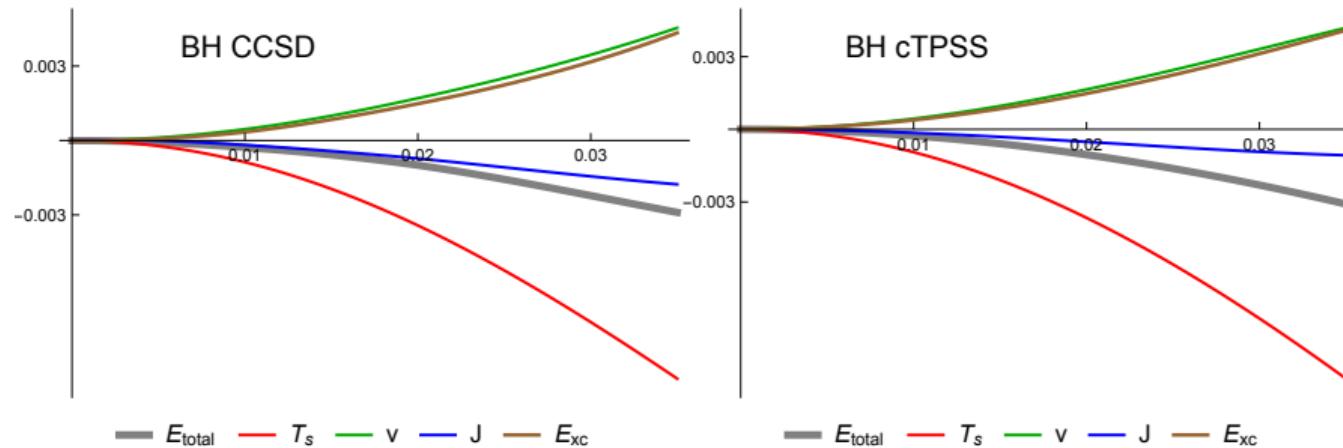
- Dependence of the CCSD and cTPSS Kohn–Sham BDFT energy components on field strength



- cTPSS performs well but overestimates the overall energy variation
  - good-quality density is important for a correct diamagnetic behaviour
- Reimann, Borgoo, Austad, Tellgren, Teale, Helgaker, and Stopkowicz, *Mol. Phys.* **117**, 97–109 (2019)

# BDFT/cTPSS for paramagnetic BH

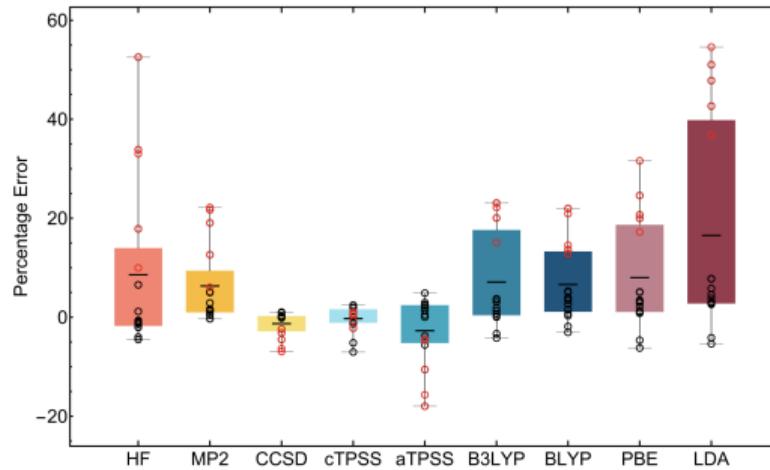
- Dependence of the CCSD and cTPSS Kohn–Sham BDFT energy components on field strength



- Large contribution from exchange–correlation functional
  - cTPSS performs well but error cancellation between exchange and correlation
- Reimann, Borgoo, Austad, Tellgren, Teale, Helgaker, and Stopkowicz, *Mol. Phys.* **117**, 97–109 (2019)

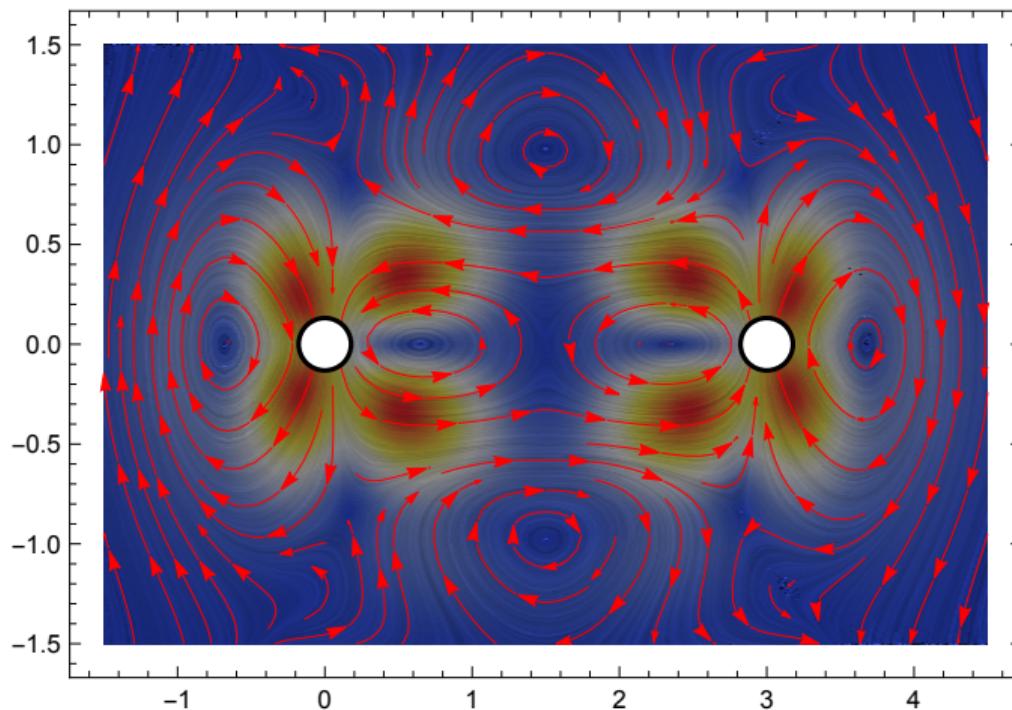
# BDFT magnetizabilities

- ▶ Errors in perpendicular component of the magnetizability  $d^2E/dB^2$  at  $B = 0$ 
  - ▶ uncontracted aug-cc-pVTZ basis relative to CCSD(T)/aug-cc-pCV5Z
  - ▶ diamagnetic He, Be, Ne, H<sub>2</sub>, He<sub>2</sub>, N<sub>2</sub>, CO, HF, H<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub> (black circles)
  - ▶ paramagnetic BH, CH<sup>+</sup>, AIH, SiH<sup>+</sup>, BeH<sup>-</sup> (red circles)



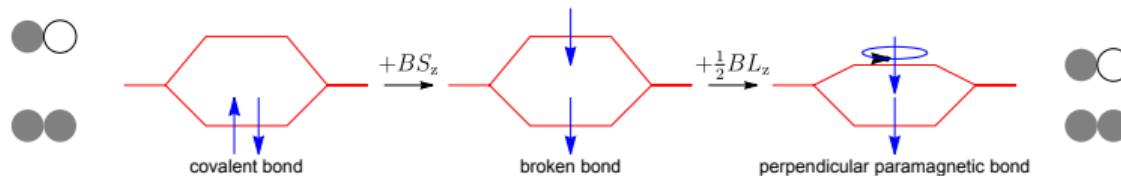
- ▶ Reimann, Borgoo, Austad, Tellgren, Teale, Helgaker, and Stopkowicz, *Mol. Phys.* **117**, 97–109 (2019)

# Quantum chemistry in a strong magnetic field



# Perpendicular magnetic bonding

- Let us consider the ground-state  $\text{H}_2$  molecule in an increasing magnetic field

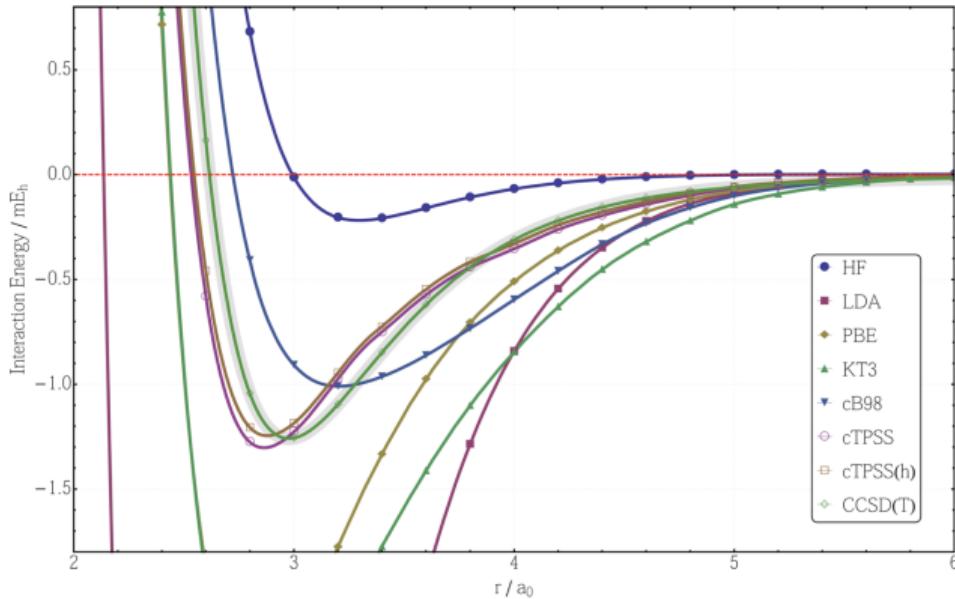


- Spin Zeeman interaction  $Bs_z$  breaks the covalent bond
  - the magnetic field favours beta spin over alpha spin
  - eventually, the alpha electron undergoes a spin flip, forcing it into the antibonding orbital
- Orbital Zeeman interaction  $\frac{1}{2}BL_z$  makes a paramagnetic bond
  - $1\sigma_u^*$  has the shape of a  $2p_{-1}$  orbital, if properly oriented
  - $1\sigma_u^*$  is increasingly lowered as the atoms come together
  - eventually, the triplet  $1\sigma_g 1\sigma_u^*$  configuration becomes bonding
- Perpendicular paramagnetic bonding
  - Lange, Tellgren, Hoffmann and Helgaker, *Science* **337** 327 (2012)



# He<sub>2</sub> in a perpendicular field: paramagnetic bonding

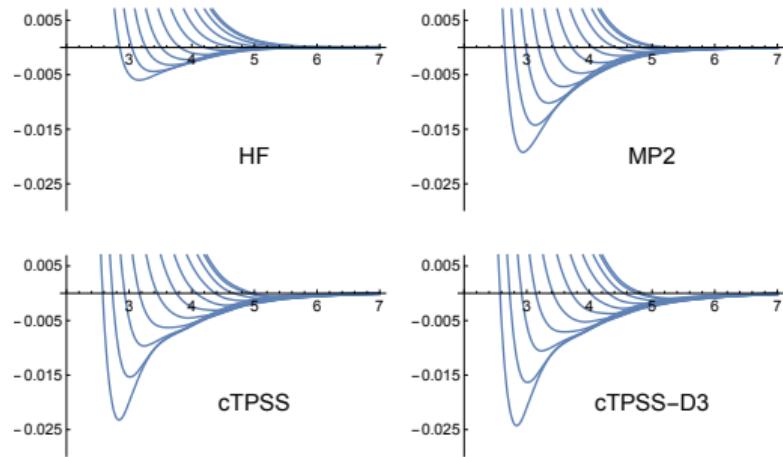
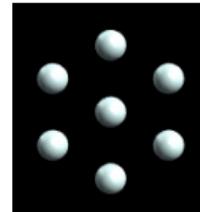
- ▶ Singlet He<sub>2</sub> in a perpendicular magnetic field of strength  $B_0 = 2.35 \times 10^5$  T
  - ▶ calculations in uncontracted aug-cc-pCVTZ basis with curves aligned at dissociation



- ▶ Furness, Verbeke, Tellgren, Stopkowicz, Ekström, Helgaker, and Teale, *JCTC* **11**, 4169–4181 (2015)

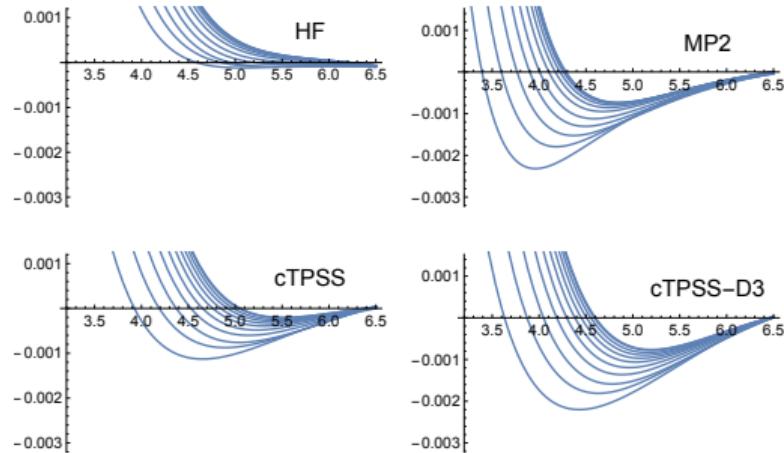
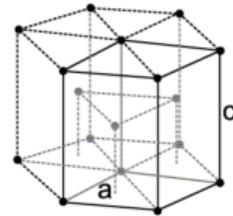
# Symmetric in-plane dissociation of He<sub>7</sub> flake

- ▶ Planar He<sub>7</sub> flake in perpendicular fields from 0 to  $B_0$ 
  - ▶ calculations with QUEST in u-aug-cc-pVTZ basis
- ▶ Paramagnetic bonding – dispersion unimportant
  - ▶ good agreement between MP2 and DFT/cTPSS



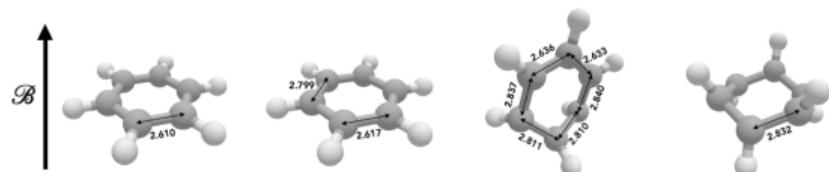
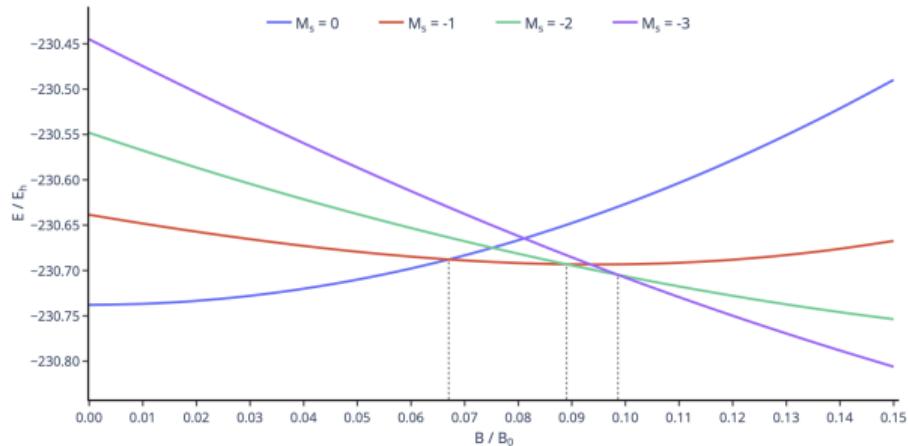
# Interlayer dissociation of $\text{He}_{17}$ cluster

- ▶ hcp-like  $\text{He}_{17}$  cluster in a perpendicular field from 0 to  $1B_0$ 
  - ▶ energy against interlayer distance
- ▶ Weak dispersion only – no paramagnetic bonding
  - ▶ good agreement between MP2 and DFT/cTPSS-D3



# Benzene in a strong magnetic field

- CDFT calculations with Quest on benzene with 0, 2, 4, and 6 unpaired beta electrons



- Tom Irons, David Gregoire, and Andy Teale, JCTC 17, 2166-2185 (2021). (CDFT gradients)

# Conclusions and acknowledgements

## ► Concluding remarks

- ▶ DFT in a magnetic field can be set up by analogy with standard DFT
- ▶ magnetic-field DFT (BDFT) and current-DFT (CDFT)
- ▶ Legendre–Fenchel and constrained-search functionals are equivalent
- ▶ vorticity functionals are unstable – meta-GGA works well, in particular cTPSS
- ▶ better densities needed to improve properties (magnetizabilities, shieldings)
- ▶ CDFT/cTPSS works well in a strong magnetic field

## ► Co-workers

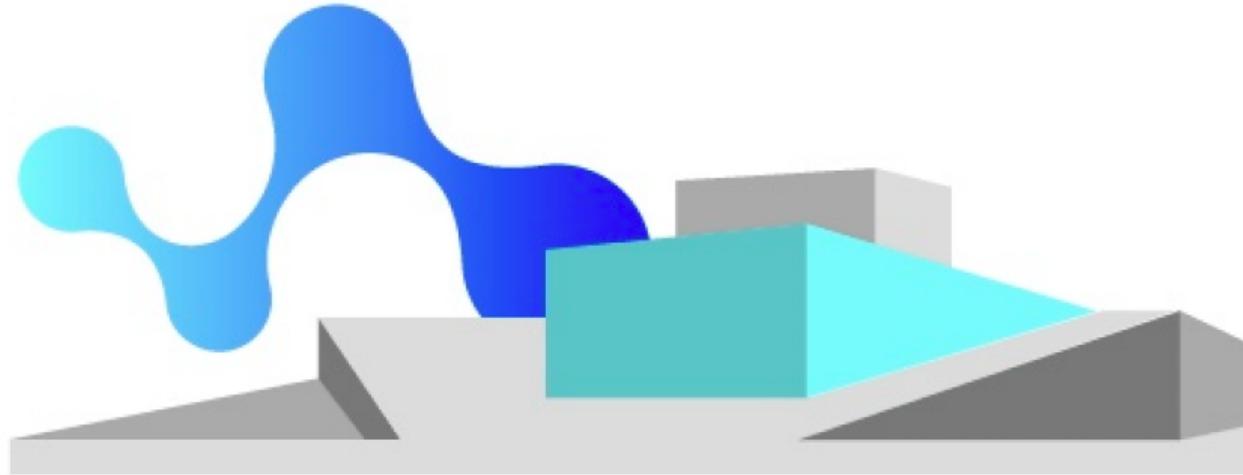
- ▶ Erik Tellgren, Simen Kvaal, André Laestadius (University of Oslo)
- ▶ Andy Teale, Tom Irons, Miles Pemberton (University of Nottingham)

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