



Current-density-functional theory

basic variables and convex conjugation

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Theory Days on Current-Density-Functional Theory

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- ▶ Density-functional theory (DFT)
 - ▶ ground-state energy in the absence of a field
 - ▶ Levy–Lieb constrained-search theory
 - ▶ DFT by convex conjugation
 - ▶ (sub)differentiability and stationary conditions
- ▶ Current-density-functional theory (CDFT)
 - ▶ ground-state energy in the presence of a magnetic field
 - ▶ CDFT by convex conjugation and the Vignale–Rasolt functional
 - ▶ stationary conditions and the Hohenberg–Kohn theorem
 - ▶ the choice of variables
 - ▶ the rigorous formulation of CDFT (N -representability)
- ▶ Kohn–Sham CDFT
 - ▶ Kohn–Sham theory and the vorticity
 - ▶ the VRG functional and its parametrization
 - ▶ CDFT NMR shieldings
- ▶ Lieb maximizations
 - ▶ optimization techniques: the bundle method
 - ▶ applications to magnetic-field DFT (BDFT)

Density matrix constrained-search theory

- ▶ The **Hamiltonian** of an N -electron system without of a magnetic field:

$$H[v] = T + W + \sum_k v(\mathbf{r}_k)$$

- ▶ The molecular electronic system is described by an **ensemble** of density matrices:

$$\gamma = \sum_i \lambda_i |\Psi_i\rangle \langle \Psi_i|, \quad \lambda_i \geq 0, \quad \sum_i \lambda_i = 1$$

with associated **electron density**:

$$\rho(\mathbf{r}) = \sum_i \lambda_i \rho_i(\mathbf{r}), \quad \rho_i(\mathbf{r}_1) = N \int \Psi_i^* \Psi_i d\tau_{-1}$$

- ▶ The ground-state energy from the **Rayleigh–Ritz variation principle**:

$$E[v] = \inf_{\gamma} \text{tr} \gamma H[v]$$

- ▶ The ground-state energy from the **Hohenberg–Kohn variation principle**:

$$E[v] = \inf_{\rho \in \mathcal{I}_N} (F[\rho] + (\rho|v))$$

in terms of the **Levy–Lieb constrained-search functional**:

$$F[\rho] = \inf_{\gamma \mapsto \rho} \text{tr} \gamma H[0]$$

- ▶ The **vector spaces** of densities and potentials (Lieb 1983):

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

The Hohenberg–Kohn and Lieb variation principles

- ▶ Lieb showed that the energy and density functional are symmetrically related:

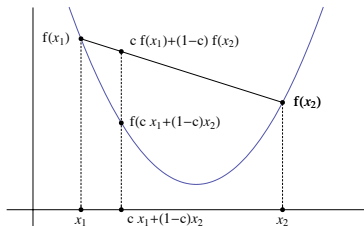
$$E[v] = \inf_{\rho} (F[\rho] + (v|\rho)) \quad \text{the Hohenberg–Kohn variation principle (1964)}$$

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

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

$$F[\rho] \geq E[v] - (v|\rho) \Leftrightarrow E[v] \leq F[\rho] + (v|\rho) \quad \text{Fenchel's inequality}$$

- ▶ E and F are **conjugate functions**: $E(\text{concave}) \leftrightarrow F(\text{convex})$
 - ▶ convex/concave conjugates, Fenchel conjugates, Legendre–Fenchel transforms. . .
 - ▶ they contain same information, expressed as functions of v and ρ , respectively
 - ▶ the extrinsic and intrinsic energies, respectively
- ▶ The possibility of expressing E in terms of F follows from the convexity of $-E[v]$ in v :

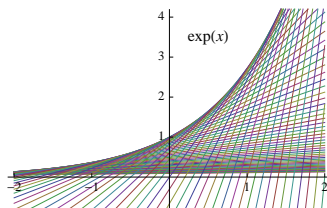
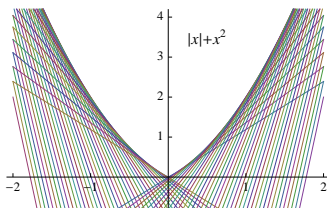
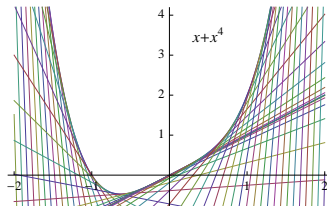
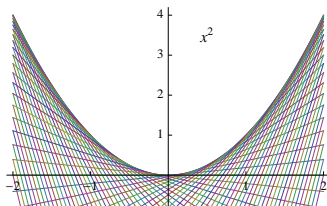


What characterizes convex functions?

- ▶ A function $f : \mathbb{R} \mapsto \mathbb{R}$ is convex if and only if it can be written in the form

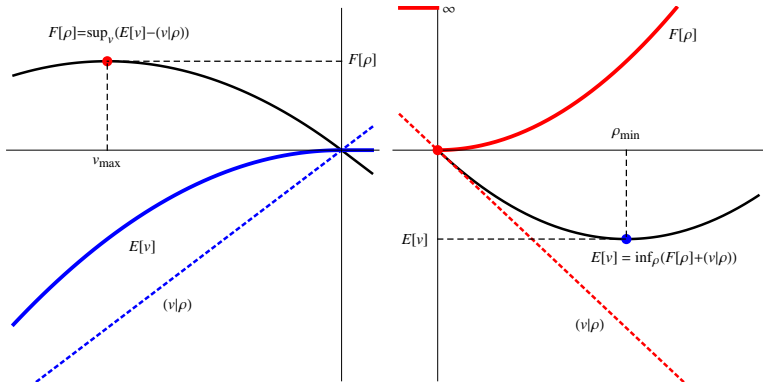
$$f(x) = \sup_y [xy - g(y)] \leftarrow \text{pointwise supremum of all supporting lines}$$

- ▶ The plots below illustrate this construction for x^2 , $x + x^4$, $|x| + x^2$ and $\exp(x)$



Conjugate functions $E \leftrightarrow F$

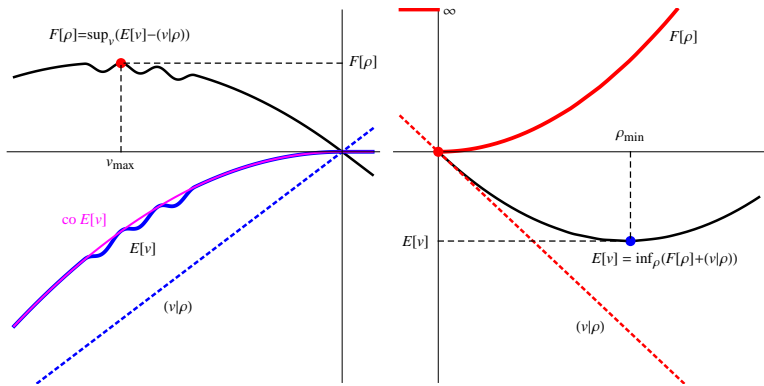
- ▶ The ground-state energy $E[v]$ is **concave** in v by the Rayleigh–Ritz variation principle
 - ▶ it can therefore be exactly represented by its **convex conjugate** $F[\rho]$: $E[v] \leftrightarrow F[\rho]$



- ▶ **Mathematical characterization** of E and F :
 - ▶ E is continuous and concave (not everywhere differentiable) on $L^{3/2} + L^{\infty}$
 - ▶ F is lower semicontinuous and convex (nowhere continuous and nowhere differentiable) on $L^3 \cap L^1$

The concave envelope $E[v] \rightarrow F[\rho] \leftrightarrow \text{co } E[v] \geq E[v]$

- ▶ However, approximate $E[v]$ may **not be concave** (not variationally minimized)
 - ▶ it still generates a **convex** $F[\rho]$, conjugate to the **concave envelope** $\text{co } E[v] \geq E[v]$

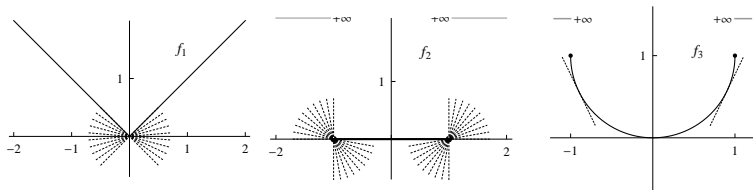


- ▶ The concave envelope $\text{co } E[v]$ is the **least concave upper bound** to $E[v]$
 - ▶ with this caveat, we may introduce **all ab-initio levels of theory** for $E[v]$ into DFT
 - ▶ as $E[v]$ converges to the exact ground-state energy, so does $\text{co } E[v]$

Differentiability and subdifferentiability

- ▶ Concavity of E and convexity of F imply **great simplicity**
 - ▶ all minima and maxima in the Hohenberg–Kohn and Lieb variation principles are **global**
 - ▶ advanced methods of **convex optimization** theory can be used
- ▶ However, convex functions are **not necessarily differentiable**
 - ▶ minima are not characterized by derivatives but subgradients
- ▶ The **subgradients** y_0 of f at x_0 are the **slopes of the supporting lines** to f at x_0 :

$$f(x) \geq f(x_0) + y_0(x - x_0), \quad \forall x$$



- ▶ The set of all subgradients of f at x_0 is the **subdifferential** $\partial f(x_0)$ of f at x_0

$$\partial f_1(0) = -[1, 1], \quad \partial f_2(0) = \{0\}, \quad \partial f_3(0) = \{0\}$$

- ▶ a minimum occurs if and only if the subdifferential contains zero (horizontal supporting line)
- ▶ differentiability follows when ∂f is a singleton and f is continuous

DFT stationary conditions

- ▶ The **Hohenberg–Kohn variation principle** is a convex minimization problem:

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

- ▶ the (global) minimum is attained when the subdifferential of right-hand side contains zero:

$$\begin{aligned} E[v] = F[\rho] + (v|\rho) &\Leftrightarrow \\ 0 \in \partial_{\rho}(F[\rho] + (v|\rho)) &\Leftrightarrow -v \in \partial F[\rho] = \{-v[\rho] - c | c \in \mathbb{R}\} \end{aligned}$$

- ▶ conditions for **v-representability**: $\partial F[\rho] \neq \emptyset$ (this occurs on a dense subset of X)
 - ▶ the **Hohenberg–Kohn theorem**: $\partial F[\rho] = \{-v[\rho] - c\}$
- ▶ The **Lieb variation principle** is a concave maximization problem:

$$F[\rho] = \sup_v (E[v] - (v|\rho))$$

- ▶ the (global) maximum is attained when the subdifferential of right-hand side contains zero:

$$\begin{aligned} F[\rho] = E[v] - (v|\rho) &\Leftrightarrow \\ 0 \in \partial_v(E[v] - (v|\rho)) &\Leftrightarrow \rho \in \partial E[v] = \text{co}\{\rho_1, \rho_2, \dots, \rho_n\} \end{aligned}$$

- ▶ $\partial E[v]$ contains all **ensemble ground-state densities** associated with v
 - ▶ these densities may belong to X (ground state) or $X^{**} \setminus X$ (distribution ground state)
- ▶ The **reciprocal relations**: the subdifferentials are inverse multifunctions:

$$-v \in \partial F[\rho] \Leftrightarrow \rho \in \partial E[v]$$

Molecular magnetism

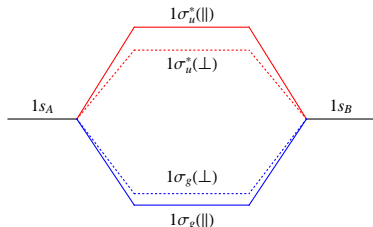
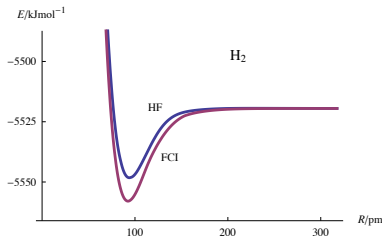
- ▶ A magnetic field \mathbf{B} modifies the **kinetic-energy operator**:

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

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

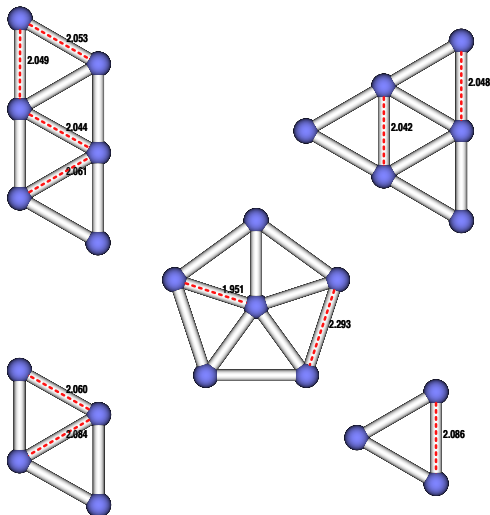
$$\boldsymbol{\pi}_i = -i\nabla_i + \mathbf{A}(\mathbf{r}_i), \quad \mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$$

- ▶ We have recently developed the **LONDON code** for molecular calculations in strong fields
 - ▶ complex wave functions and London atomic orbitals
 - ▶ Hartree–Fock, CASSCF, CCSD, FCI and Kohn–Sham models
- ▶ Molecules in magnetic fields exhibit **many interesting features**:
 - ▶ molecular bonding of triplet H_2 and singlet He_2 in strong fields



Helium clusters in strong magnetic fields

- ▶ RHF/u-aug-cc-pVTZ level of theory
 - ▶ all structures are planar and consist of equilateral triangles
 - ▶ suggestive of hexagonal 2D crystal lattice



Ground-state energy in a magnetic field

- ▶ The **Hamiltonian** in a magnetic field (without the Zeeman term):

$$H[v, \mathbf{A}] = \frac{1}{2} \sum_i \pi_i^2 + \sum_i v(r_i) + W, \quad \pi_i = -i\nabla_i + \mathbf{A}(r_i), \quad \mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$$

- ▶ The Hamiltonian has a **linear and quadratic dependence** on the vector potential:

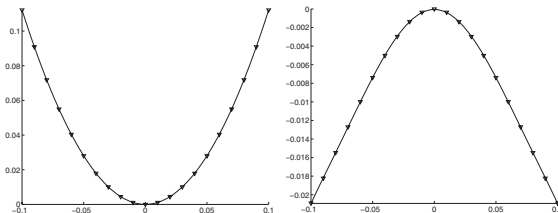
$$H[v, \mathbf{A}] = \frac{1}{2} \sum_i p_i^2 + \sum_i \mathbf{A}(r_i) \cdot \mathbf{p}_i + \frac{1}{2} \sum_i A(r_i)^2 + \sum_i v(r_i) + W$$

- ▶ The **ground-state energy** in a magnetic field from Rayleigh–Ritz variation principle:

$$E[v, \mathbf{A}] = \inf_{\gamma} \text{tr } \gamma H[v, \mathbf{A}]$$

- ▶ The energy is **not necessarily concave** in the vector potential:

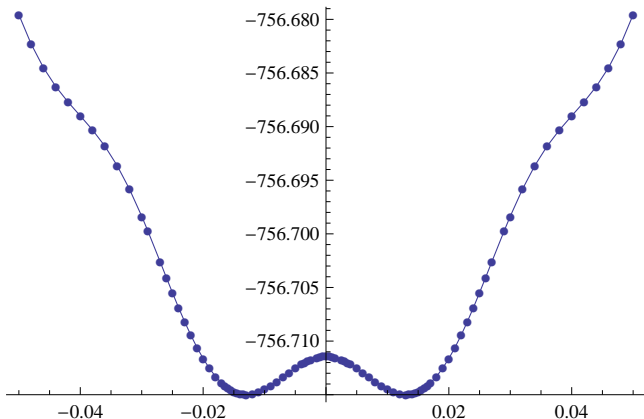
- ▶ **diamagnetic benzene** (convex) to the left and **paramagnetic BH** (concave) to the right



- ▶ It therefore cannot be represented by a conjugate function: $E \nleftrightarrow F$

Diamagnetism and paramagnetism

- ▶ The complicated field dependence results from an **interplay of linear and quadratic terms**
- ▶ C_{20} in a perpendicular magnetic field:



- ▶ All molecules become diamagnetic at a **critical field strength** B_c

CDFT by convex conjugation

- ▶ A simple **reparametrization** yields a Hamiltonian that is linear in the potentials:

$$\bar{H}[u, \mathbf{A}] = \frac{1}{2} \sum_i p_i^2 + W + \sum_i u(r_i) + \sum_i \mathbf{A}(r_i) \cdot \mathbf{p}_i, \quad u = v + \frac{1}{2} A^2$$

- ▶ From the variation principle and this linearity, **concavity of the ground-state energy** follows:

$$\bar{E}[u, \mathbf{A}] = \inf_{\gamma} \text{tr} \gamma \bar{H}[u, \mathbf{A}] = E[v - \frac{1}{2} A^2, A]$$

- ▶ Convex conjugation gives the associated convex **CDFT universal density functional**:

$$F[\rho, \kappa] = \sup_{\mathbf{v}} (\bar{E}[u, \mathbf{A}] - (u|\rho) - (\mathbf{A}|\kappa))$$

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

- ▶ The variables conjugate to (u, \mathbf{A}) are the **paramagnetic ensemble densities** (ρ, κ) :

$$\rho(\mathbf{r}) = \sum_i \lambda_i \rho_i(\mathbf{r}), \quad \rho_i(\mathbf{r}_1) = N \int \Psi_i^* \Psi_i d\tau_{-1}$$

$$\kappa(\mathbf{r}) = \sum_i \lambda_i \kappa_i(\mathbf{r}), \quad \kappa_i(\mathbf{r}_1) = N \text{Re} \int \Psi_i^* \mathbf{p}_1 \Psi_i d\tau_{-1}$$

- ▶ $F[\rho, \kappa]$ is the **Vignale–Rasolt constrained-search functional** in density-matrix form:

$$F_{\text{VR}}[\rho, \kappa] = \inf_{\gamma \mapsto \rho, \kappa} \text{tr} \gamma \bar{H}[0, \mathbf{0}]$$

CDFT and the Hohenberg–Kohn theorem I

- ▶ The conditions for a **minimum in the Hohenberg–Kohn variation principle**:

$$\bar{E}[u, \mathbf{a}] = F[\rho, \kappa] + (u|\rho) + (\mathbf{A}|\kappa) \Leftrightarrow (\rho, \kappa) \in \partial \bar{E}[u, \mathbf{A}] \Leftrightarrow -(u, \mathbf{A}) \in \partial F[\rho, \kappa]$$

- ▶ Consider now the following set of **external potentials**:

$$(u_c, \mathbf{A}_c) = (u_0, \mathbf{A}_0) + c(\Delta u, \Delta \mathbf{A}), \quad (\rho_0, \kappa_0) \in \partial E[u_0, \mathbf{A}_0]$$

- ▶ The **Hamiltonian** in this potential may be written in the form:

$$\bar{H}_c = \bar{H}_0 + cK, \quad K = \sum_i \Delta u(r_i) + \sum_i \Delta A(r_i) \cdot \mathbf{p}_i$$

- ▶ If \bar{H}_0 and K commute, then \bar{H}_c have **the same eigenstates** for all c

- ▶ the ground-state of \bar{H}_c may therefore remain the same in some interval of c :

$$[\bar{H}_0, K] = 0 \Leftrightarrow (\rho_0, \kappa_0) \in \partial E[u_c, \mathbf{A}_c], \quad c_{\min} \leq c \leq c_{\max}$$

- ▶ The **paramagnetic density** (ρ, κ) **does not determine** (u, \mathbf{A}) **uniquely**

- ▶ note: the order of the eigenstates of $H[v, \mathbf{A}]$ and $\bar{H}[u, \mathbf{A}]$ may differ since

$$E_n[v, \mathbf{A}] = \bar{E}_n[v, \mathbf{A}] + \frac{1}{2}(\rho_n|A^2)$$

- ▶ Eschrig (2001), Capelle & Vignale (2001,2002)

- ▶ In DFT, $\mathbf{A} \equiv 0$ and the only commuting K is $K = I \Rightarrow \bar{H}_c = \bar{H}_0 + c$

CDFT and the Hohenberg–Kohn theorem II

- ▶ Consider the following **external scalar and vector potentials** v_B and \mathbf{A}_B :

$$v_B = v_0 - \frac{1}{8}B^2(x^2 + y^2), \quad \mathbf{A}_B = \frac{1}{2}B\mathbf{e}_z \times \mathbf{r}$$

for which

$$\mathbf{A} \cdot \mathbf{p} = \frac{1}{2}BL_z, \quad \frac{1}{2}A^2 = \frac{1}{8}B^2(x^2 + y^2)$$

- ▶ The scalar potential v_B has been **adjusted to cancel the diamagnetic operator** $\frac{1}{2}A^2$:

$$u_B = v_B + \frac{1}{2}A^2 = v_0 \quad \leftarrow \text{spherically symmetric}$$

- ▶ The **electronic Hamiltonian** is therefore given by

$$H[v_B, \mathbf{A}_B] = H_0 + \frac{1}{2}BL_z, \quad [H_0, L_z] = 0$$

- ▶ The system has the **same ground-state wave function** in $B_{\min} \leq B \leq B_{\max}$ with energy

$$E_B = E_0 + \frac{1}{2}BL_z$$

- ▶ It follows that (v_B, \mathbf{A}_B) have the **same ground-state density** (ρ_0, κ_0) in this interval:

$$(\rho_0, \kappa_0) \in \partial E[v_B, \mathbf{A}_B], \quad B_{\min} \leq B \leq B_{\max}$$

- ▶ the density (ρ_0, κ_0) does not determine the potential (v_B, \mathbf{A}_B) uniquely
- ▶ Capelle and Vignale (2001,2002)

CDFT: choice of variables

- ▶ The **physical current** consists of paramagnetic and diamagnetic parts:

$$\mathbf{j} = \boldsymbol{\kappa} + \boldsymbol{\tau} = \boldsymbol{\kappa} + \rho \mathbf{A}, \quad \mathbf{j} = N \operatorname{Re} \int \Psi_i^* \boldsymbol{\pi}_1 \Psi_i d\boldsymbol{\tau}_{-1}$$

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

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

$$F_{\text{VR}}[\rho, \boldsymbol{\kappa}] = \min_{\Psi \mapsto \rho, \boldsymbol{\kappa}} \langle \Psi | T + W | \Psi \rangle$$

- ▶ the paramagnetic current is **not observable** (and gauge dependent)
- ▶ there is no Hohenberg–Kohn theorem
- ▶ **Pan and Sahni** (2010) proposed CDFT based on the **physical current** (ρ, \mathbf{j}) :

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

$$F_{\text{PS}}[\rho, \mathbf{j}] = \min_{\Psi \mapsto \rho, \mathbf{j}} \langle \Psi | T + W | \Psi \rangle$$

- ▶ the total current is **observable** (and gauge independent)
- ▶ unsuccessful attempts at proving a Hohenberg–Kohn theorem

$$E[v, \mathbf{A}] + E[v', \mathbf{A}'] < E[v, \mathbf{A}] + E[v', \mathbf{A}'] + (\rho|(\mathbf{A} - \mathbf{A}')^2)$$

- ▶ the Pan–Sahni functional is problematic
- ▶ We believe the correct formulation is that based on the paramagnetic current

Rigorous formulation of CDFT

- ▶ The formulation of CDFT so far **has not been rigorous**
 - ▶ what is the domain of F_{VR} ?
 - ▶ what are the conditions for N -representability?
- ▶ Lieb laid a **rigorous foundation** for DFT (1983)
 - ▶ what is its generalization to CDFT?
- ▶ In the following, we shall consider a few points regarding the rigorous CDFT:
 - ▶ the set of admissible wave functions Ψ in the constrained search
 - ▶ the conditions for N -representable (ρ, κ)
 - ▶ the vector spaces of densities and potentials
 - ▶ the mathematical characterization of F_{VR}

Well-defined expansion of the kinetic energy

- ▶ A **normalized wave function** of **finite kinetic energy** without field:

$$\left. \begin{aligned} \langle \Psi | \Psi \rangle &= 1 \\ \langle \Psi | p^2 | \Psi \rangle &= \langle \mathbf{p} \Psi | \mathbf{p} \Psi \rangle < +\infty \end{aligned} \right\} \Leftrightarrow \left. \begin{aligned} \Psi &\in L^2 \\ \nabla \Psi &\in L^2 \end{aligned} \right\} \Leftrightarrow \Psi \in H^1 \quad (\text{Sobolev space})$$

- ▶ Sobolev inner product $\langle \Psi_1 | \Psi_2 \rangle_{H^1} = \langle \Psi_1 | \Psi_2 \rangle + \sum_i \langle \nabla_i \Psi_1 | \nabla_i \Psi_2 \rangle$
- ▶ this requirement also ensures a **finite Coulomb energy**
- ▶ A **normalized wave function** of **finite kinetic energy** with field:

$$\left. \begin{aligned} \langle \Psi | \Psi \rangle &= 1 \\ \langle \Psi | \pi_{\mathbf{A}}^2 | \Psi \rangle &= \langle \pi_{\mathbf{A}} \Psi | \pi_{\mathbf{A}} \Psi \rangle < +\infty \end{aligned} \right\} \Leftrightarrow \left. \begin{aligned} \Psi &\in L^2 \\ (\nabla + i\mathbf{A})\Psi &\in L^2 \end{aligned} \right\} \Leftrightarrow \Psi \in H_{\mathbf{A}}^1$$

- ▶ the **magnetic Sobolev** space depends on the field \mathbf{A}
- ▶ The Sobolev spaces H^1 and $H_{\mathbf{A}}^1$ are different—neither set is included in the other
 - ▶ the **expanded kinetic energy** may be **ill defined** due to singularities, “ $+\infty - \infty$ ”

$$\langle \Psi | \pi_{\mathbf{A}}^2 | \Psi \rangle \neq \langle \Psi | p^2 | \Psi \rangle + \langle \rho_{\Psi} | A^2 \rangle + 2\langle \kappa_{\Psi} | \mathbf{A} \rangle$$

- ▶ However, H^1 and $H_{\mathbf{A}}^1$ have a common subset of **smooth functions with compact support**:

$$C_0^\infty \subset H^1 \cap H_{\mathbf{A}}^1$$

- ▶ for $\Psi \in C_0^\infty$ (which is dense in H^1 and $H_{\mathbf{A}}^1$), the expanded kinetic energy is well defined

Well-defined CDFT constrained search

- ▶ The **Vignale–Rasolt constrained-search functional** is well defined:

$$\begin{aligned} E[v, \mathbf{A}] &= \inf_{\Psi \in L^2} \langle \Psi | H[v, \mathbf{A}] | \Psi \rangle \quad \leftarrow \text{normalized wave functions} \\ &= \inf_{\Psi \in H_{\mathbf{A}}^1} \langle \Psi | \frac{1}{2} \pi_{\mathbf{A}}^2 + W | \Psi \rangle + (\rho_{\Psi} | v) \quad \leftarrow \text{normalized wave functions of finite energy} \\ &= \inf_{\Psi \in C_0^\infty \subset H^1} \langle \Psi | \frac{1}{2} \pi_{\mathbf{A}}^2 + W | \Psi \rangle + (\rho_{\Psi} | v) \quad \leftarrow \text{search domain independent of } \mathbf{A} \\ &= \inf_{(\rho, \kappa) \in \mathcal{J}_N} \inf_{\substack{\Psi \in H^1 \\ \Psi \mapsto (\rho, \kappa)}} \langle \Psi | \frac{1}{2} \rho^2 + W | \Psi \rangle + (\rho | v + \frac{1}{2} A^2) + (\kappa | \mathbf{A}) \quad \leftarrow N\text{-rep. densities} \\ &= \inf_{(\rho, \kappa) \in \mathcal{J}_N} F_{\text{VR}}[\rho, \kappa] + (v + \frac{1}{2} A^2 | \rho) + (\kappa | \mathbf{A}) \quad \leftarrow \text{universal density functional} \end{aligned}$$

- ▶ Its **domain** the set of N -representable paramagnetic densities:

$$\mathcal{J}_N = \{(\rho, \kappa) \mid (\rho, \kappa) \text{ can be obtained from some } \Psi \in H^1\}$$

- ▶ Furthermore, it may be shown that the corresponding **density-matrix functional**

$$F_{\text{VR}}[\rho, \kappa] = \inf_{\gamma \mapsto \rho, \kappa} \text{tr } \gamma \bar{H}[0, \mathbf{0}]$$

is **lower semi-continuous convex** and that the infimum is a minimum

N -representability in CDFT

- ▶ We have identified the **domain** of the universal density functional

$$\mathcal{J}_N = \{(\rho, \kappa) \mid (\rho, \kappa) \text{ can be obtained from some } \Psi \in H^1\}$$

- ▶ This is simple generalization of the set of N -representable densities:

$$\mathcal{I}_N = \{\rho \mid \rho \text{ can be obtained from some } \Psi \in H\}$$

- ▶ An explicit characterization of N -representable densities in DFT:

$$\mathcal{I}_N = \{\rho \mid \rho \geq 0, \int \rho(\mathbf{r}) \, d\mathbf{r} = N, T_W[\rho] < \infty\}$$

in terms of the **von Weizsäcker kinetic energy**:

$$T_W[\rho] = \frac{1}{8} \int |\nabla \rho(\mathbf{r})|^2 \rho^{-1}(\mathbf{r}) \, d\mathbf{r}.$$

- ▶ In CDFT, N -representable densities have a finite **generalized von Weizsäcker kinetic energy**

$$(\rho, \kappa) \in \mathcal{J}_N \Rightarrow T_W[\rho, \kappa] < \infty$$

where

$$T_W[\rho, \kappa] = \int (\rho^{-1} |\nabla \rho|^2 + \rho^{-1} |\kappa|^2) \, d\mathbf{r}$$

- ▶ However, it has not been shown that $T_W[\rho, \kappa] < \infty$ is sufficient for N -representability

Summary CDFT

- ▶ CDFT may be established by **convex conjugation** by introducing $u = v + A^2/2$:

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

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

where the concave energy \bar{E} is related to the **physical ground-state energy** as

$$E[v, A] = \bar{E}[v + \frac{1}{2}A^2, A].$$

- ▶ These may be translated into the following **Vignale–Rasolt and Lieb variation principles**:

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

$$F[\rho, \kappa] = \sup_{v, \mathbf{A}} (E[v, \mathbf{A}] - (v + \frac{1}{2}A^2|\rho) - (\mathbf{A}|\kappa))$$

- ▶ **Ground-state densities and potentials** related by the reciprocal relations (no HK theorem):

$$(\rho, \kappa) \in \partial \bar{E}[u, \mathbf{A}] \Leftrightarrow -(u, \mathbf{A}) \in \partial F[\rho, \kappa]$$

- ▶ Valid **vector spaces of densities and potentials** are given by

$$(\rho, \kappa) \in X \cap L^1[(1+r^{2n})dr] \times \mathbf{L}^1[(1+r^n)dr], \quad X = L^3 \cap L^1$$

$$(u, \mathbf{A}) \in (X^* + L^\infty[(1+r^{2n})^{-1}dr]) \times \mathbf{L}^\infty[(1+r^n)^{-1}dr]$$

Kohn–Sham CDFT with the VRG functional

- ▶ A **Kohn–Sham decomposition** of the CDFT functional yields (Vignale and Rasolt):

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

- ▶ 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
- ▶ We assume the **density–vorticity separation** of the XC functional:

$$E_{xc}[\rho, \boldsymbol{\nu}] = E_{xc}^0[\rho] + E_{VRG}[\boldsymbol{\nu}]$$

- ▶ The **Vignale–Rasolt–Geldart (VRG)** local vorticity exchange–correlation functional

$$E_{VRG}[\boldsymbol{\nu}] = \int \frac{k_F(r_s)}{24\pi^2} [g(r_s) - 1] |\boldsymbol{\nu}(\mathbf{r})|^2 d\mathbf{r},$$

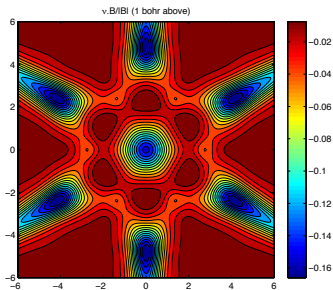
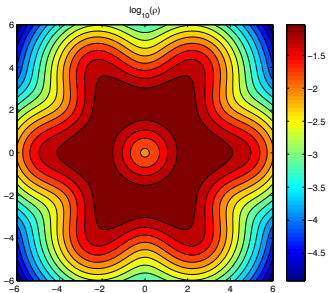
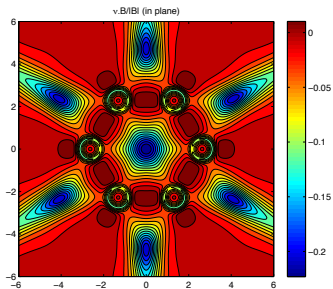
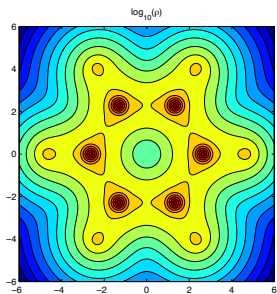
is expressed in terms of the **vorticity** and

$$k_F(r_s) = \left(\frac{9\pi}{4}\right)^{1/3} r_s^{-1} \text{ Fermi wave vector}$$

$$g(r_s) = \frac{\chi_L}{\chi_L^0}(r_s) \quad \text{Landau diamagnetic susceptibilities enhancement factor}$$

where $r_s = \left(\frac{3}{4\pi\rho(\mathbf{r})}\right)^{1/3}$ is the Wigner–Seitz radius

Density and vorticity in benzene

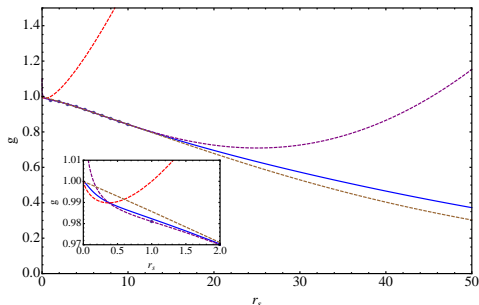


Forms for enhancement factor $g(r_s)$

- ▶ The exact **high-density limit** (small r_s) is known but of limited use

$$g_{\text{hd}}(r_s(r)) = 1 + 0.027643r_s \ln r_s + \dots$$

- ▶ RPA data is available for $r_s < 10$, **several forms** have been proposed to fit this data
 - ▶ **Lee–Colwell–Handy (LCH)**, **Orestes–Maracasso–Capelle (OMC)**, **Tao–Perdew (TP)**



- ▶ **OMC** does not respect the high density limit and **LCH** is a poor fit to the RPA data for smaller r_s
- ▶ **OMC** better fits the available RPA data over the range it is available
- ▶ For $r_s > 10$ **OMC** and **LCH** disagree, the **LCH** curve appears the more sensible low-density limit
- ▶ **TP** “stitches together” the best aspects of each (g_{LCH} is slightly re-parameterized)

G. Vignale, M. Rasolt and D. J. W. Geldart, PRB **37**, 2502 (1988)
E. Orestes, T. Maracasso and K. Capelle, PRA **68**, 022105 (2003)

A. M. Lee, S. M. Colwell and N. C. Handy, CPL **229**, 225 (1994)
J. Tao and J. P. Perdew, PRL **95**, 196403 (2005)

Nonperturbative evaluation of magnetic properties

- ▶ We have performed **CDFT calculations** of shielding constants with London
- ▶ We use the **VRG correction** with the LCH parameterization of the susceptibility ratio
- ▶ Here we consider **LDA** and **KT3** functionals each with and without the VRG correction
 - ▶ LDA is not expected to be accurate for shielding constants
 - ▶ KT3 is an empirical GGA form designed to deliver reasonable shielding constants
- ▶ Properties calculated **nonperturbatively** using the ground-state energies for a given field B
- ▶ The **nuclear shielding tensor** for a nucleus K obtained from finite differences:

$$\sigma_{K;\alpha\beta} = \frac{\partial^2 E(\mathbf{B}, \mathbf{M}_K)}{\partial B_\alpha \partial M_{K\beta}} \Big|_{\mathbf{B}=0, \mathbf{M}=0}, \quad \sigma_K^{\text{iso}} = \frac{1}{3} \text{tr} \sigma_K$$

- ▶ We consider the following set of molecules for preliminary calculations:

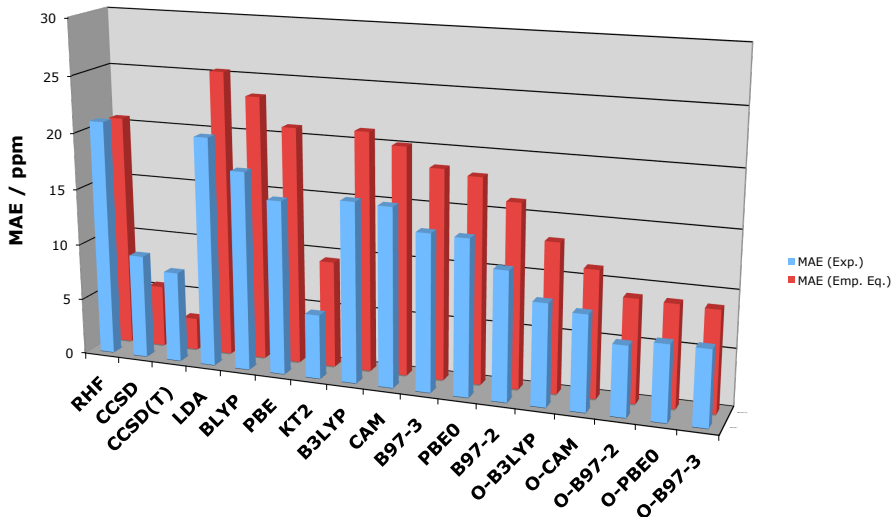
HF, CO, N₂, H₂O, NH₃, CH₄, AlF, FCN, H₂S, HFCO, LiF, LiH

- ▶ Shielding constants compared against a recent benchmark set of CCSD(T) values

T. W. Keal and D. J. Tozer, JCP **121**, 5654 (2004)
A. M. Lee, N. C. Handy and S. M. Colwell, JCP **103**, 10095 (1995)
U. Ekström, L. Visscher, R. Bast, A. J. Thorvaldsen and K. Ruud, JCTC **6**, 1971 (2010)

T. W. Keal and D. J. Tozer, JCP **119**, 3015 (2003)
E. I. Tellgren, A. Soncini and T. Helgaker, JCP **129**, 154114 (2008)
A. M. Teale, O. B. Lutnæs, D. J. Tozer, J. Gauss and T. Helgaker, JCP, (2012)

Shieldings: mean absolute errors relative to experiment



- ▶ Mean absolute errors (in ppm) for NMR shielding constants relative to experimental (blue) and empirical equilibrium values (red). The inclusion of vibrational corrections in the empirical equilibrium values leads to a degradation of the quality of the RHF and DFT results but to a notable improvement for the CCSD and CCSD(T) methods. (Teale *et al.*, JCP)

NMR Isotropic Shielding Constants

Mol	Nuc	LDA	LDA-VRG	KT3	KT3-VRG	CCSD(T)	Exp	Vib	Emp. Eq.
HF	H	29.4	29.5	30.2	30.3	29.2	28.5	-0.3	28.84
	F	416.9	416.6	412.2	411.9	419.8	409.6	-11.8	421.4
CO	C	-20.7	-25.1	5.6	1.8	3.8	0.9	-2.4	3.3
	O	-87.1	-94.0	-54.5	-60.9	-51.0	-62.7	-5.8	-57.0
N ₂	N	-90.1	-95.7	-59.9	-64.9	-59.1	-61.6	-4.3	-57.3
H ₂ O	O	335.1	335.3	327.8	328.0	337.5	323.6	-14.2	337.8
	H	31.0	31.0	31.5	31.7	31.0	30.1	-0.5	30.6
NH ₃	N	267.6	268.4	263.2	264.2	270.6	264.5	-8.7	273.3
	H	31.6	31.6	32.1	32.1	31.7	30.7	-0.6	31.3
CH ₄	C	193.9	194.0	193.5	193.6	200.0	195	-3.7	198.7
	H	31.3	31.3	31.7	31.7	31.5	30.6	-0.6	31.2
AlF	Al	532.1	528.3	566.4	562.8	576.7			
	F	141.3	135.4	174.7	169.2	225.6			
FCN	F	344.7	344.6	337.5	337.2	379.1			
	C	64.9	62.9	83.2	81.3	85.2			
	N	91.9	90.0	122.2	120.6	118.4			
H ₂ S	S	727.1	726.5	724.6	723.9	740.0			
	H	30.4	30.4	31.1	31.1	30.7	30.5	-0.4	30.9
HFCO	O	-138.8	-146.9	-89.3	-96.8	-92.9			
	C	17.4	15.3	37.1	35.2	43.2			
	F	84.5	78.0	116.3	110.0	178.2	147.7	-12.3	160.0
	H	22.9	22.9	23.6	23.5	24.1			
LiF	Li	85.4	82.3	89.9	85.7	90.1	87.5	0.1	87.4
	F	341.8	281.8	359.3	295.9	387.0	374.3	1.1	373.2
LiH	H	25.8	25.4	26.8	26.5	26.5	25.7	-0.1	25.8
	Li	86.4	81.7	92.2	89.6	89.9	90.6	0.1	90.5
ME		-21.2	-25.6	-9.2	-13.5				
MAE		21.2	25.6	10.3	13.9				

- ▶ LDA significantly and systematically underestimates the shieldings
- ▶ KT3 halves the errors but still systematically underestimates
- ▶ The VRG corrections tend to reduce the shieldings on average, worsening the results

NMR Isotropic Shielding Constants

- ▶ Our observations are **consistent with previous perturbative implementations**
 - ▶ A. M. Lee, N. C. Handy and S. M. Colwell, JCP **103**, 10095 (1995)
 - ▶ although the trend is reproduced exact reproduction of the results is problematic
- ▶ The **XC functionals should be adapted** to work with the VRG correction
 - ▶ KT3 was derived empirically for good results with neglect of these corrections
 - ▶ the paramagnetic contribution to shieldings is sensitive to the HOMO–LUMO gap

Mol	LDA	KT3	KS[CCSD(T)]
HF	0.327	0.318	0.375
CO	0.251	0.269	0.264
N ₂	0.300	0.316	0.310
H ₂ O	0.238	0.231	0.271
NH ₃	0.206	0.200	0.231
CH ₄	0.337	0.333	0.380
AlF	0.152	0.153	0.157
FCN	0.268	0.257	0.277
H ₂ S	0.202	0.197	0.219
HFCO	0.201	0.214	0.221
LiF	0.182	0.156	0.263
LiH	0.106	0.094	0.117

- ▶ the ME and MAE are -0.026 and 0.026 for LDA
- ▶ the ME and MAE are -0.029 and 0.031 for KT3
- ▶ both systematically underestimate the gaps... room for further improvement
- ▶ the accurate values provide a guide to avoid error cancellations by overinflating the gaps

- ▶ The VRG functional is **numerically difficult** to deal with: **cutoffs** must be imposed
 - ▶ no obvious convergence with respect to the variation of the cutoff is observed
 - ▶ *“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 & Trickey JCP **125**, 094317 (2006)

Lieb maximization in DFT

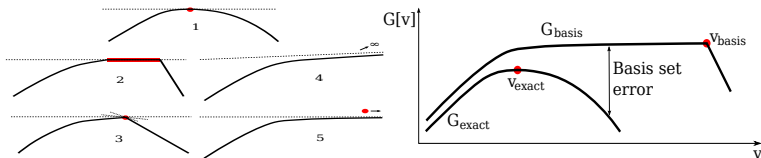
- ▶ For a given **density** $\rho(\mathbf{r})$ and **model** $E_\lambda[v]$ at **interaction strength** λ , we wish to calculate

$$F_\lambda[\rho] = \max_v (E_\lambda[v] - (v|\rho)), \quad E_\lambda = \inf_{\Psi} \langle \Psi | T + \lambda W + \sum_i v(\mathbf{r}_i) | \Psi \rangle$$

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

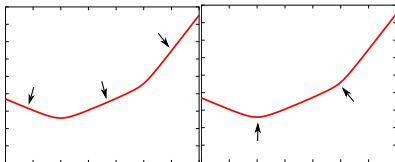
$$v_c(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + (1 - \lambda)v_{\text{ref}}(\mathbf{r}) + \sum_t c_t g_t(\mathbf{r})$$

- ▶ the **physical, external potential** $v_{\text{ext}}(\mathbf{r})$
 - ▶ the **Fermi-Amaldi reference potential** to ensure correct asymptotic behaviour
 - ▶ an **expansion in Gaussians** $g_t(\mathbf{r})$ with coefficients c_t
 - ▶ implemented in DALTON and LONDON for HF, MP2, CCSD, and CCSD(T)
- ▶ The Lieb maximization is carried out by the **bundle method**
 - ▶ because of concavity, **all maxima are global maxima**
 - ▶ v -representability in a given basis is obtained when $(g_t|\rho - \rho_\lambda) = 0$
 - ▶ E_λ is not necessarily differentiable (with ensembles)
 - ▶ difficulties may arise in small basis sets and for small λ

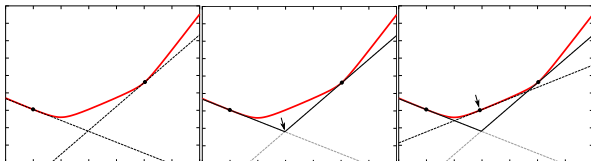


The bundle method for near piecewise linear functions

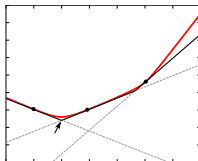
- ▶ The goal function contains alternating regions of **small and large curvature**



- ▶ The **cutting-plane method** minimizes linearized functions (supporting hyperplanes)



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



Kohn–Sham theory and the adiabatic connection

- ▶ We introduce **Kohn–Sham theory** by expanding about $\lambda = 0$:

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

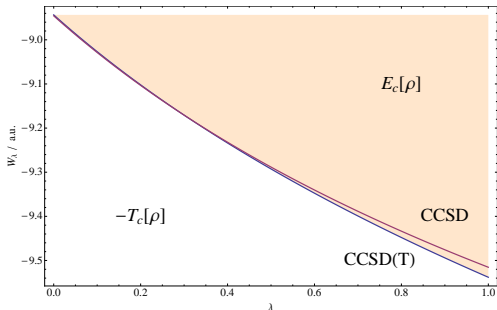
- ▶ The **correlation energy** is the only term that depends on λ in a nontrivial manner:

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

- ▶ The correlation energy obtained by integration over the **AC integrand**:

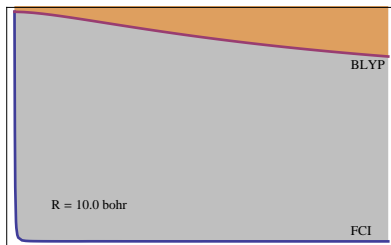
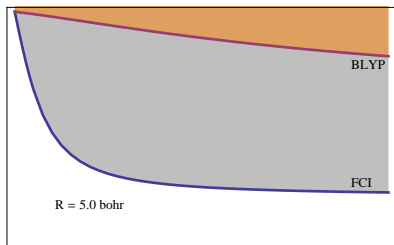
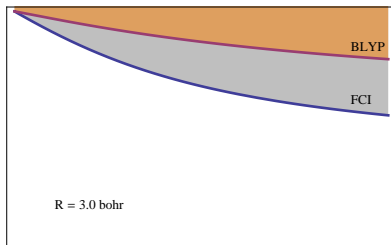
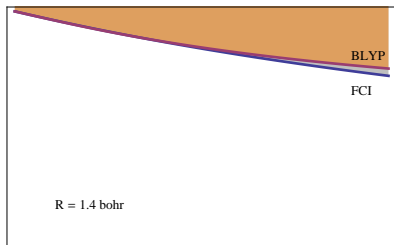
$$E_c[\rho] = \int_0^1 W_\lambda[\rho] d\lambda$$

- ▶ CCSD and CCSD(T) AC curves for the water molecule:



BLYP and FCI correlation AC curves for H_2

- ▶ 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**



Lieb maximization in magnetic-field DFT (BDFT)

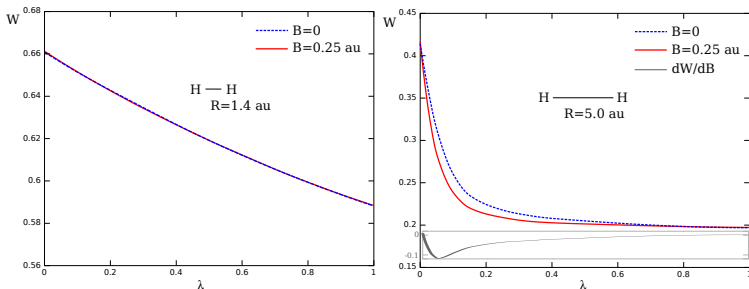
- ▶ We may describe magnetic phenomena by setting up a separate DFT for each \mathbf{B} :

$$E_0[v, \mathbf{B}] = \inf_{\rho} (F[\rho, \mathbf{B}] + (v|\rho))$$

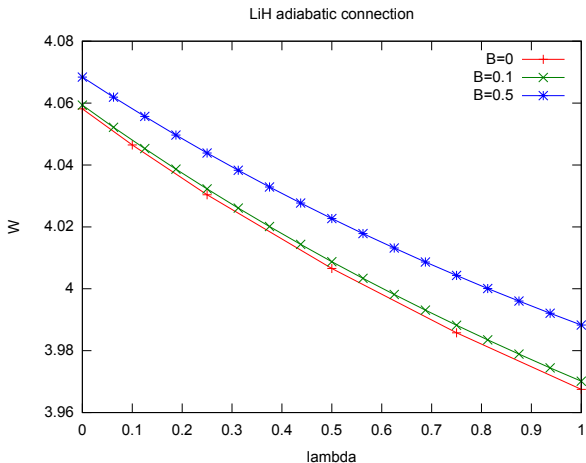
- ▶ **magnetic-field DFT (BDFT)** (Grayce & Harris 1994) as an alternative to CDFT
- ▶ The density functional now depends on the **density** and on the **field strength**

$$F[\rho, \mathbf{B}] = \min_{\Psi \mapsto \rho} \langle \Psi | T_{\pi}(\mathbf{B}) + W | \Psi \rangle = T_s[\rho, \mathbf{B}] + J[\rho] + E_{xc}[\rho, \mathbf{B}]$$

- ▶ the **noninteracting magnetic response** is exactly taken care of by $T_s[\rho, \mathbf{B}]$
- ▶ AC correlation curves of H_2 in a perpendicular magnetic field
 - ▶ $E_{xc}[\rho, \mathbf{B}]$ differs from $E_{xc}[\rho]$ only at stretched geometries
 - ▶ an earlier onset of static correlation in strong magnetic fields



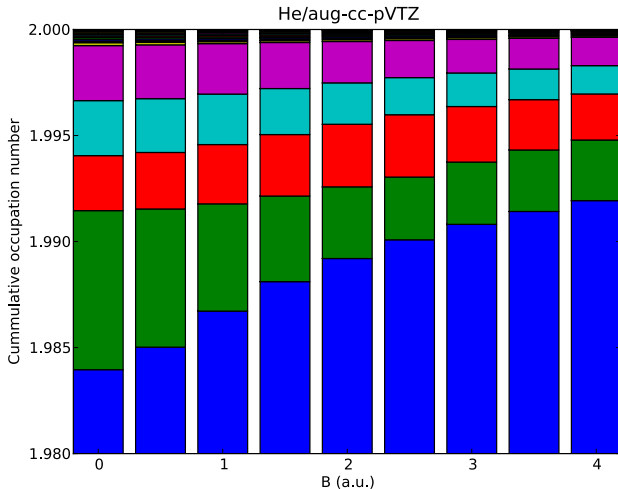
BDFT AC curve for LiH



- ▶ Increased magnetic field has a definite effect on the AC curve.
 - ▶ less dynamical correlation energy, slightly more “static” correlation at fixed bond length
 - ▶ consistent with shortening of bond lengths in the field

Dynamical correlation in magnetic fields

- ▶ The FCI occupation numbers of He approach 2 and 0 strong fields
 - ▶ diminishing importance of dynamical correlation in magnetic fields
 - ▶ the two electrons rotate in the same direction about the field direction



Lieb formulation of CDFT

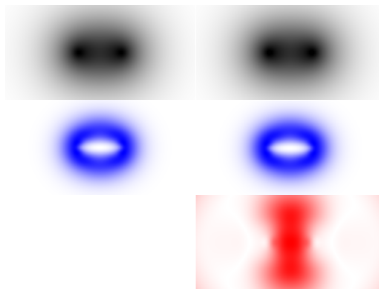
- ▶ We are working towards **Lieb maximizations in CDFT**

$$F_\lambda[\rho, \kappa] = \sup_{u, \mathbf{A}} E_\lambda[u, \mathbf{A}] - (\rho|u) - (\mathbf{A}|\kappa)$$

- ▶ should shed light on the importance of the current contribution and adequacy of VRG
- ▶ We expect Lieb maximizations in CDFT to be **more challenging** than in DFT
 - ▶ in CDFT, the Kohn–Sham system will more often exhibit **small or zero gaps**
- ▶ Closed-shell two-electron systems are not representable by a single determinant in a field
 - ▶ consider the H_2 molecule in a strong magnetic field (normal to image plane)
 - ▶ density ρ (top), physical current j^2 (middle), and vorticity ν (bottom) of H_2

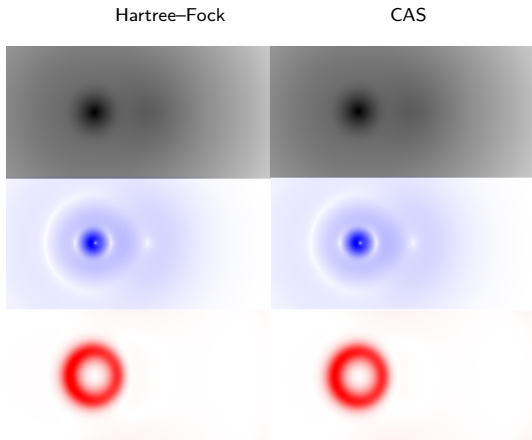
Hartree–Fock

Full CI



Density, current and vorticity in BH

- ▶ Many-electron systems exhibit fewer representability problems related to the vorticity
 - ▶ the BH molecule in a strong magnetic field (normal to image plane)
 - ▶ density ρ (top), physical current j^2 (middle), and vorticity ν (bottom) of H_2
 - ▶ some regions are still single-orbital dominated (not visible in plot)



Summary

- 1 Lieb's theory of DFT (convex conjugation)
- 2 Lieb's theory adapted to CDFT
- 3 The choice of variables: $u \leftrightarrow v$, $\kappa \leftrightarrow j$
- 4 CDFT (KS–VRG) calculations of shieldings
- 5 Lieb maximizations (bundle methods, finite basis sets)
- 6 Applications of Lieb variation principle to BDFT
- 7 Future: Application of Lieb variation principle for CDFT