Current-Density-Functional Theory of Molecules in Weak and Strong Magnetic Fields

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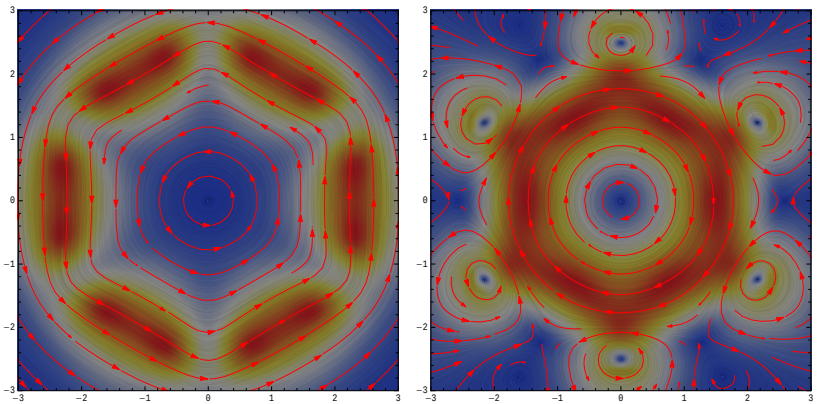
Current-Density-Functional Theory (CDFT)

- In standard DFT, everything depends on the density ρ and universal density functional F:

$$E(v) = \inf_\rho \left(F(\rho) + (v|\rho) \right)$$

  - the density ρ interacts with the external potential v as $(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}$

- In an external magnetic field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, currents $\boldsymbol{\kappa}$ are induced in the electronic system
  - density and current density in benzene above (left) and in (right) the plane in a perpendicular field



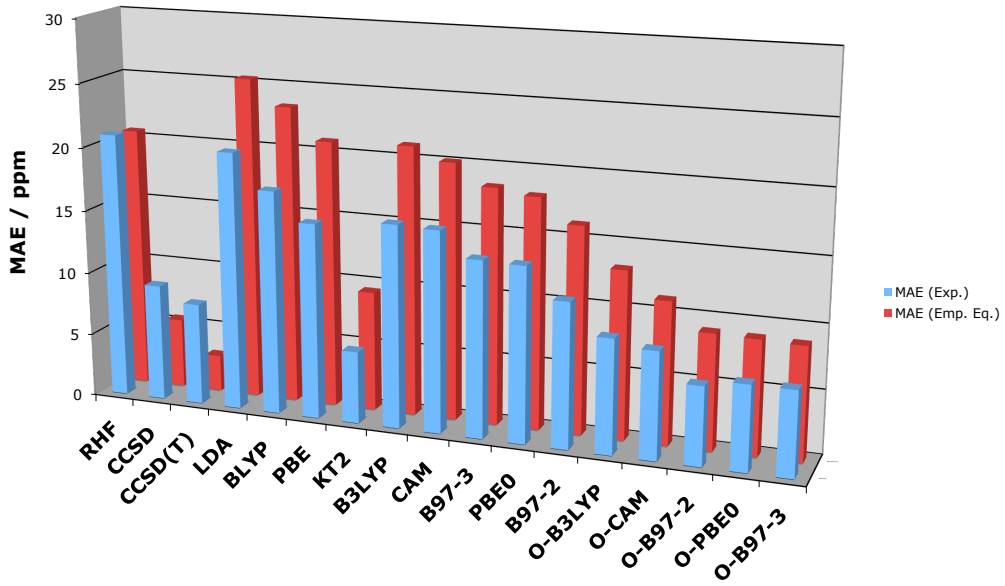
- These induced currents interact with the vector potential $\mathbf{A}$ representing the field
  - it is tempting to set up a DFT-like theory that incorporates the current

$$E(v, \mathbf{A}) = \inf_{\rho,\boldsymbol{\kappa}} \left(F(\rho, \boldsymbol{\kappa}) + (v + \tfrac{1}{2}A^2|\rho) + (\mathbf{A}|\boldsymbol{\kappa}) \right)$$

  - but first: is there a need for such a current-density-functional theory (CDFT)?

DFT in weak magnetic fields

- Errors in shielding constants relative to experimental (blue) and equilibrium (red) values



- Standard Kohn–Sham DFT calculations give shielding constants of uneven quality
  - Teale *et al.* JCP **138**, 024111 (2013)
- Errors arising from a poor density response and from neglected currents are similar

$$\sigma_{\text{tot}} = \sigma_{\text{dia}}(\text{density}) + \sigma_{\text{para}}(\text{density response}) + \sigma_{\text{para}}(\text{current response})$$
$$-10\,\text{ppm} = 0\,\text{ppm} \qquad -6\,\text{ppm} \qquad -4\,\text{ppm}$$

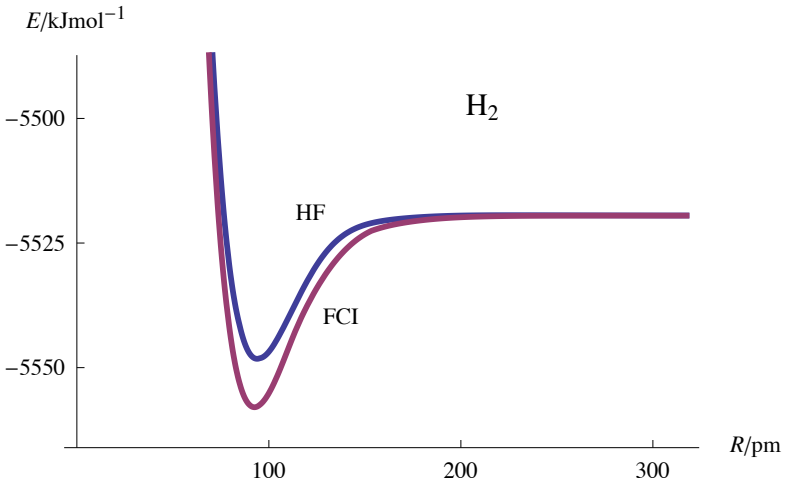
  - Reimann *et al.*, PCCP **17**, 18834 (2015)

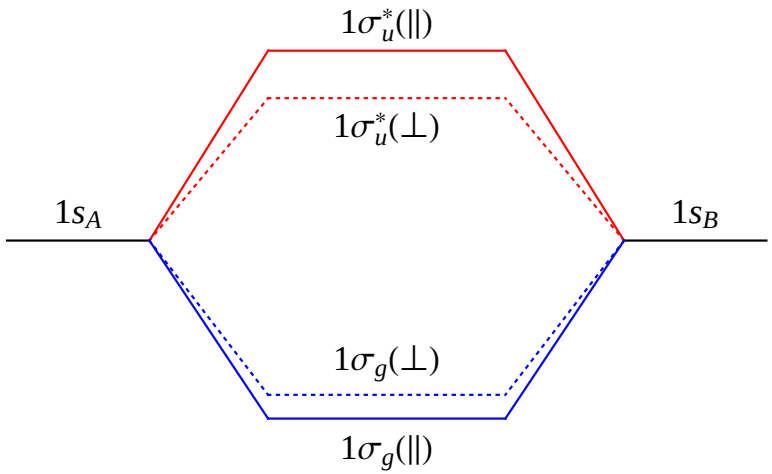
Molecules in strong magnetic fields

- Fascinating chemistry occurs in magnetic fields of strength one atomic unit $B_0 \approx 235\,\mathrm{kT}$
  - Coulomb and magnetic interactions are equally important in such fields
  - the motion of the electrons relative to the field affects chemistry
- Antibonding orbitals are stabilised in a perpendicular field orientation
  - can be understood from the behaviour of $1\sigma_u^*$ in the united-atom limit

$$\lim_{R\to 0} 1\sigma_u^* = \begin{cases} 2p_0, & \text{parallel orientation (no stabilisation)} \\ 2p_{-1}, & \text{perpendicular orientation (stabilised)} \end{cases}$$

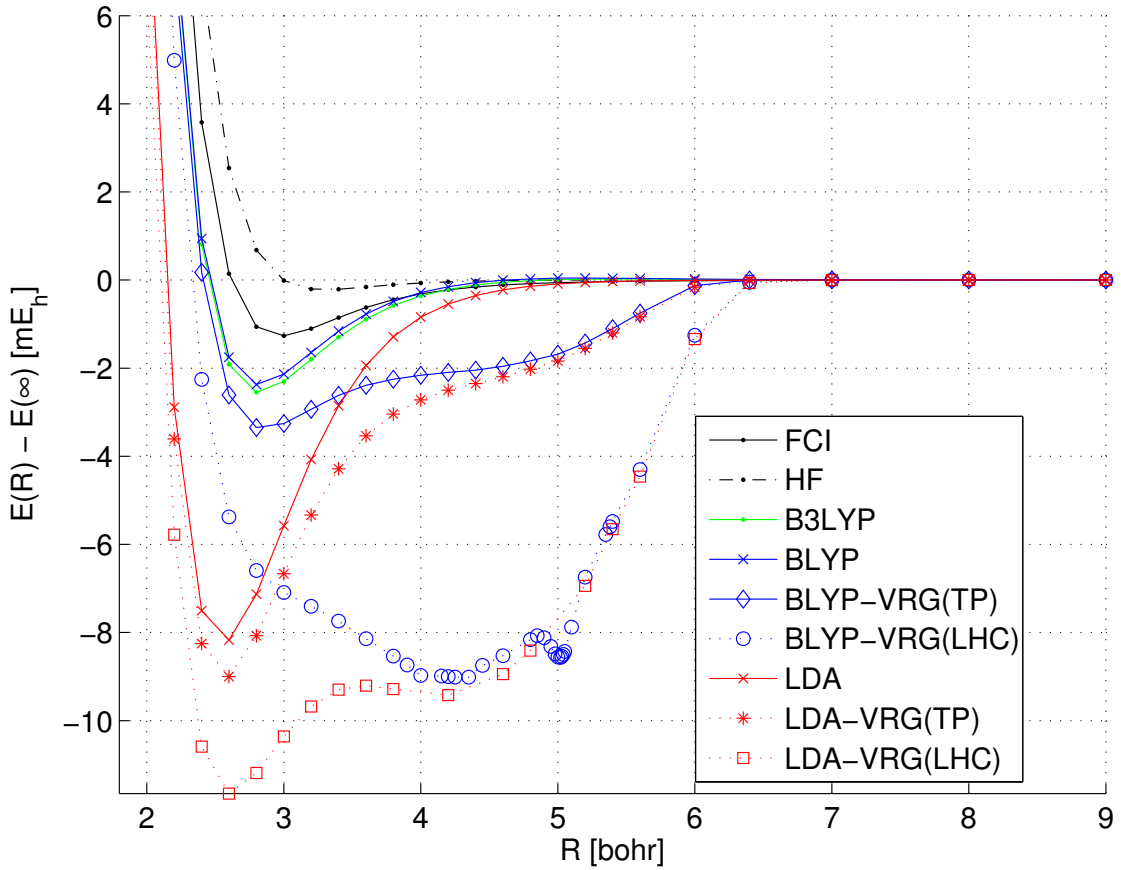
  - H_2 in the $|1\sigma_g 1\sigma_u^*|$ triplet state becomes bound in the magnetic field: zero-bond-order bond





DFT in strong magnetic fields

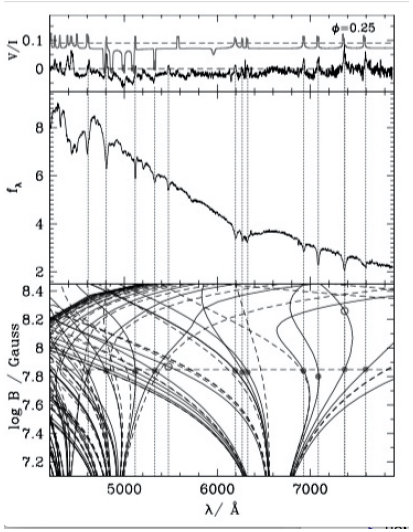
- By stabilisation of antibonding orbitals, rare-gas atoms bind in ultrastrong fields
  - dissociation curve of He_2 in a field of strength B_0
  - u-aug-cc-pVTZ basis with curves aligned at $R = 9a_0$



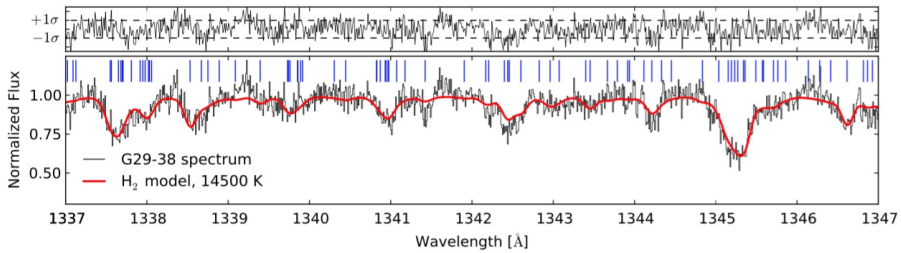
- DFT is now DeFiniTely out of its comfort zone . . .
  - Tellgren *et al.*, JCP **140**, 034101 (2014)

Atoms and molecules in white dwarf atmospheres

- Spectra of the hydrogen atom from a magnetised white dwarf PG 1015+014
  - comparison of observed and predicted visible spectra determines field strength



- In 2013, H_2 molecules were detected in nonmagnetised white dwarfs
  - $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transitions in the UV spectrum of white dwarf G29–38



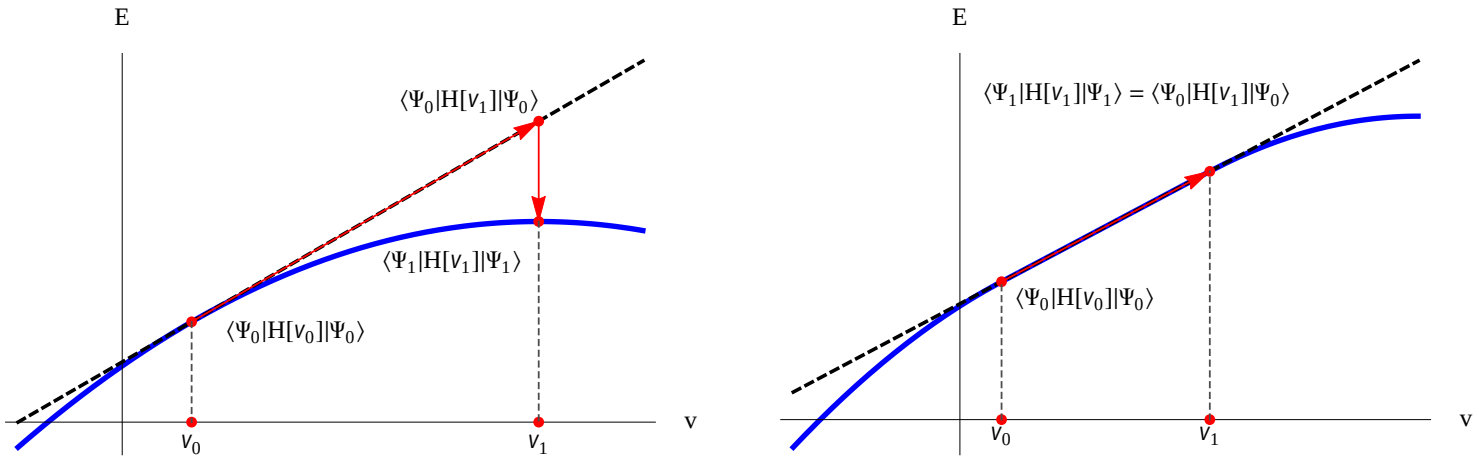
  - calculated spectra are needed to detect in H_2 in magnetised white dwarfs

Overview

- Overview
  - some DFT background
    - Hohenberg–Kohn theorem and energy concavity
  - from DFT to CDFT
    - what are the natural variables?
    - what is the role of the Hohenberg–Kohn theorem?
    - can noninteracting systems be represented by a Slater determinant?
  - exchange–correlation functionals in magnetic fields
    - Vignale–Rasolt–Geldart functional
    - meta-GGA functionals
- London code for molecules in magnetic fields
  - complex wave functions and London atomic orbitals for gauge-origin invariance
  - HF, CASSCF, MP2, CCSD, CCSD(T), FCI, DFT, BDFT and CDFT
  - first Kohn–Sham CDFT code for molecules in magnetic fields
  - http://londonprogram.org (E. Tellgren, K. Lange, S. Stopkowicz)

Hohenberg–Kohn theorem and energy concavity

- The ground-state energy $E(v)$ is concave in the potential for the following reasons:
  - the linearity of the Hamiltonian $H(v) = H_0 + v$ in the external potential v
  - the Rayleigh–Ritz variation principle for the electronic ground state Ψ



  - we have strict concavity of $E(v)$ (left) except when $v_1 - v_0 = c$ is scalar (right)
- The derivative of $E(v)$ is the electronic density ρ (in absence of degeneracies):

$$\frac{\delta E(v)}{\delta v(\mathbf{r})} = \rho(\mathbf{r}) \quad \leftarrow \text{a map from potentials to densities}$$

  - derivative is monotonically decreasing and can therefore be inverted
- This inverse map is also monotonic and is hence the derivative of another concave function: $-F$

$$-\frac{\delta F(\rho)}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) \quad \leftarrow \text{a map from densities to potentials}$$

  - Hohenberg–Kohn theorem: the density determines the potential up to a constant

Hohenberg–Kohn and Lieb variation principles

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

$$\underbrace{E(v) = \inf_\rho \big(F(\rho) + (v|\rho)\big)}_{\text{Hohenberg–Kohn minimisation}} \Leftrightarrow E(v) \leq F(\rho) + (v|\rho)$$

$$\Leftrightarrow F(\rho) \geq E(v) - (v|\rho) \Leftrightarrow \overbrace{F(\rho) = \sup_v \big(E(v) - (v|\rho)\big)}^{\text{Lieb maximisation}}$$

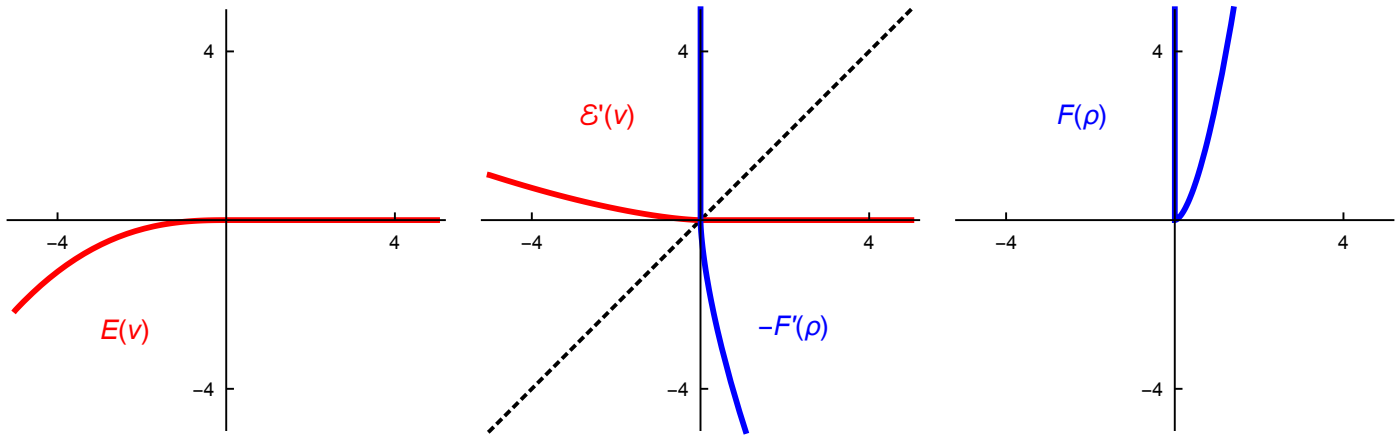
  - concavity of $E(v)$ is the key — it then has a unique conjugate convex partner: $F(\rho)$

- Assuming differentiability, we have the stationary conditions:

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

  - in reality the derivatives do not exist — only subgradients (slopes of supporting lines)

- Graphical illustration of conjugation: differentiate → invert → integrate



Hohenberg–Kohn and Lieb variation principles

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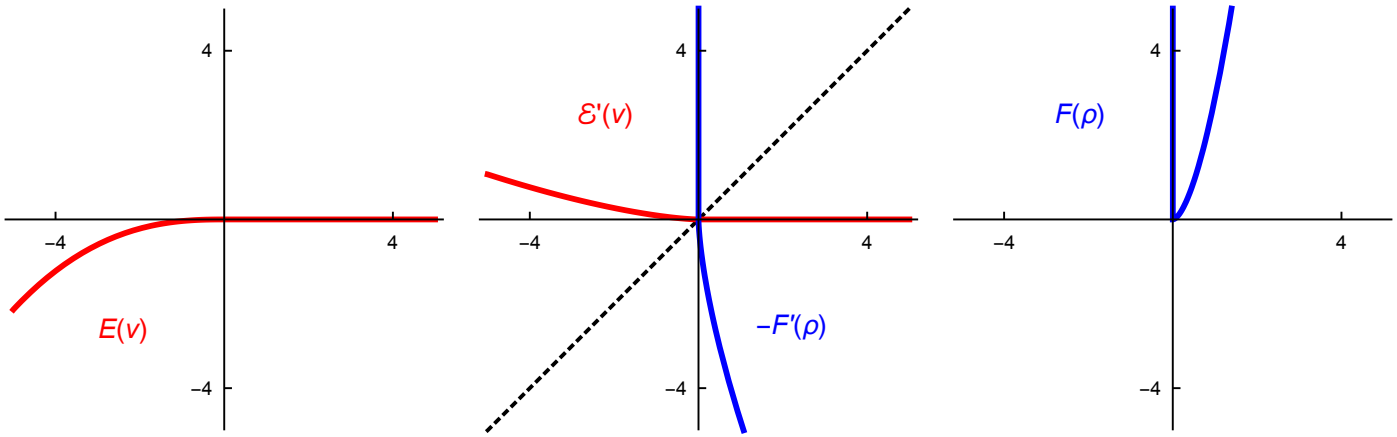
  - concavity of $E(v)$ is the key — it then has a unique conjugate convex partner: $F(\rho)$

- The exact relation between densities and potentials may be expressed in terms of subgradients:

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

  - does not assume differentiability or even continuity – but (non-strict) concavity is essential

- Graphical illustration of conjugation: differentiate → invert → integrate

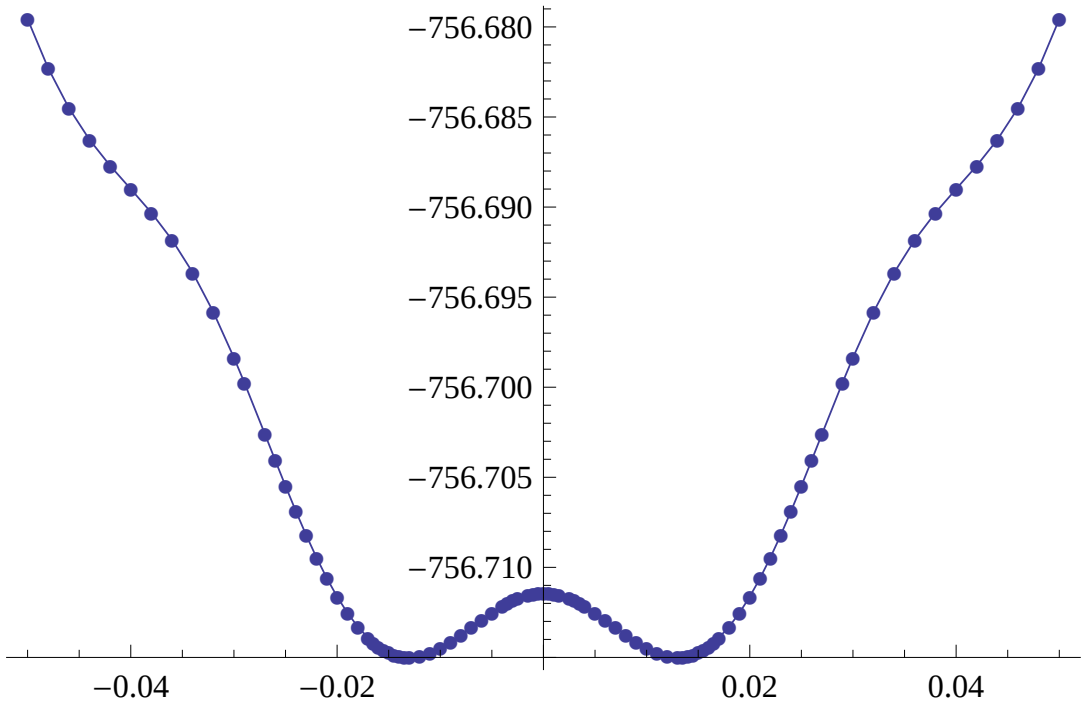


Nonconcavity of energy in a magnetic field

- A magnetic field $\mathbf{B}$ is represented by a vector potential $\mathbf{A}$ such that $\mathbf{B} = \nabla \times \mathbf{A}$
- However, the resulting Hamiltonian $H(v, \mathbf{A})$ is nonlinear in $\mathbf{A}$:

$$H(v, \mathbf{A}) = H_0 + v + \tfrac{1}{2}A^2 + \mathbf{A} \cdot \mathbf{p}$$

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



- the ground-state is paramagnetic for small fields and then becomes diamagnetic
- Tellgren, Helgaker and Soncini, PCCP **11**, 5489 (2009)

Basic variables of CDFT

- A simple reparameterisation of the potentials restores linearity of H and concavity of E:

$$H(u,\mathbf{A}) = H_0 + u + \mathbf{A}\cdot\mathbf{p}, \quad u = v + \tfrac{1}{2}A^2, \quad \mathbf{p} = -\mathrm{i}\boldsymbol{\nabla}$$

  - the basic potentials of CDFT are u and $\mathbf{A}$ (Tellgren *et al.* PRA **86**, 062506 (2012))
- Proceeding as for DFT, we arrive at the Hohenberg–Kohn and Lieb variation principles:

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

$$F(\rho,\boldsymbol{\kappa}) = \sup_{u,\mathbf{A}} \big(E(u,\mathbf{A}) - (u|\rho) - (\mathbf{A}|\boldsymbol{\kappa})\big)$$

  - the universal functional depends on the density and paramagnetic current density

$$\rho(\mathbf{r}) = \Psi^*(\mathbf{r})\Psi(\mathbf{r}) \quad \leftarrow \text{density}$$

$$\boldsymbol{\kappa}(\mathbf{r}) = \mathrm{Re}\Psi^*(\mathbf{r})\mathbf{p}\Psi(\mathbf{r}) \quad \leftarrow \text{paramagnetic current density}$$

  - these quantities are uniquely determined by the electronic structure
  - F was obtained by Hohenberg–Kohn-type arguments by Vignale and Rasolt (1987)
- Why is the physical current density not the basic current variable in CDFT?

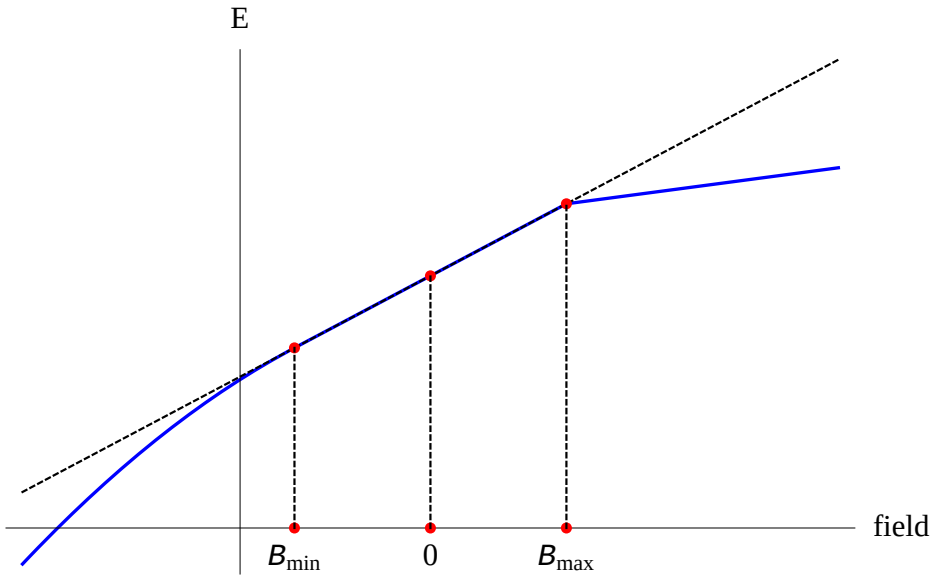
$$\mathbf{j} = \boldsymbol{\kappa} + \rho\,\mathbf{A}$$

  - $\mathbf{j}$ is observable but not uniquely determined by the electronic structure, depending also on $\mathbf{A}$
  - CDFT variables should be the distillation of Ψ information needed for evaluation of interactions

No Hohenberg–Kohn theorem in CDFT

- HK theorem in DFT: the ρ determines the potential v up to a constant
- Adding a uniform magnetic field to a spherical system, we obtain

$$H_B = H_0 + \tfrac{1}{2}BL_z + BS_z \;\Rightarrow\; [H_0, H_B] = 0 \;\Rightarrow\; \text{same ground state } \Psi \text{ in } B_{\min} \leq B \leq B_{\max}$$



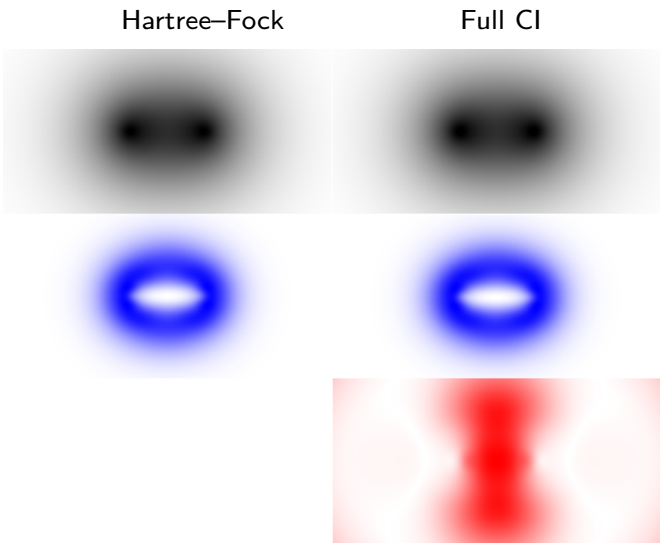
  - the variables $\rho = \Psi^*\Psi$ and $\boldsymbol{\kappa} = \mathrm{Re}\Psi^*\mathbf{p}\Psi$ are constant in the interval since Ψ is constant
  - but the potentials $u = v + \frac{1}{2}A^2$ and $\mathbf{A}$ change in the interval since $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ changes
- No HK theorem: densities $(\rho, \boldsymbol{\kappa})$ do not determine $(u, \mathbf{A})$, even up to a constant
  - von Barth and Hedin (1972), Eschrig and Pickett (2001), Capelle and Vignale (2001,2002)
- But the physical current density $\mathbf{j} = \boldsymbol{\kappa} + \rho\mathbf{A}$ does change in the interval since $\mathbf{A}$ changes
  - HK theorem for $\mathbf{j}$ is not ruled out but purported proofs are flawed (Tellgren *et al.* (2012))

Kohn–Sham CDFT and representability

- A Kohn–Sham decomposition of the CDFT functional yields:

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

  - the exchange–correlation functional depends on the density and the gauge-invariant vorticity
  - Vignale and Rasolt, PRL **59**, 2360 (1987)
- Warning: closed-shell two-electron systems are not representable by a single determinant
  - density ρ (top), physical current j^2 (middle), and vorticity ν (bottom) of H_2



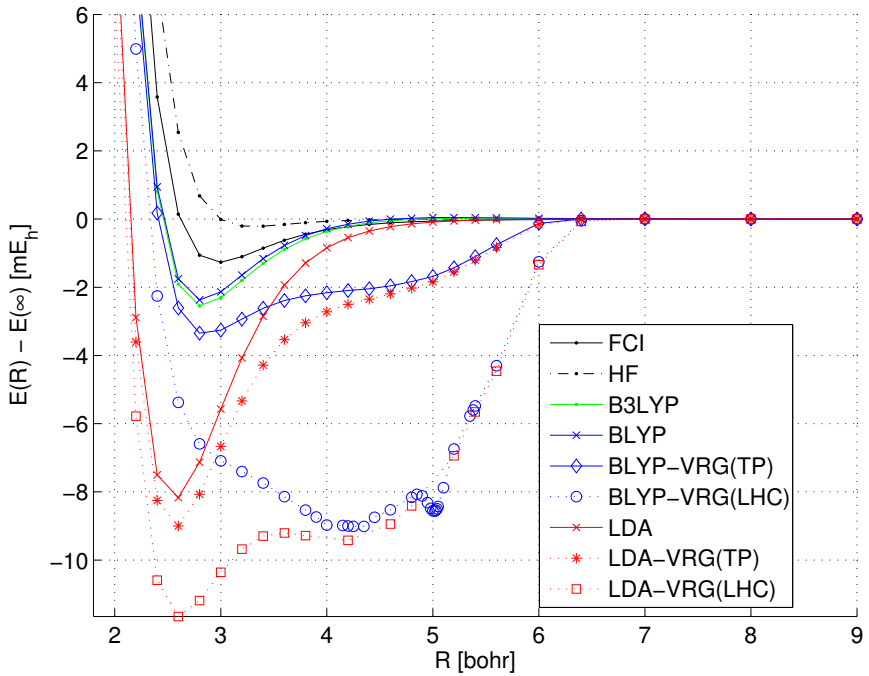
- When are $(\rho, \boldsymbol{\kappa})$ representable by a Slater determinant?
  - Lieb and Schrader (2013): by a single Slater determinant for $N \geq 4$ particles
  - Tellgren, Kvaal and Helgaker (2014): by an ensemble of Slater determinants for $N \geq 1$ particles

VRG functional

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

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

  - based on the response of a uniform electron gas to a uniform magnetic field
  - the function $g(\rho(\mathbf{r}))$ fitted to RPA reference values but no data for $\rho \lesssim 10^{-4}$
  - Lee–Handy–Colwell (LHC) and Tao–Perdew (TP) parameterisations decay slowly as $-\rho^{1/3}$
  - evaluation of vorticity problematic for small densities (regularisation necessary)
- Dissociation of He dimer 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))



  - something else is needed...

Current meta-GGA functionals

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

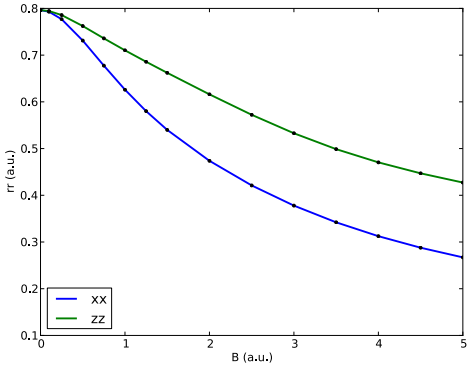
$$\tau_\sigma(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} |\boldsymbol{\nabla}\varphi_{i\sigma}(\mathbf{r})|^2 \text{ (fermionic)} \;\geq\; \tau_\sigma^{\text{W}}(\mathbf{r}) = \frac{1}{4}\frac{|\nabla\rho_\sigma(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} \text{ (bosonic)}$$

  - bosonic/fermionic ratio is a useful iso-orbital indicator to avoid self interaction

$$z_\sigma(\mathbf{r}) = \frac{\tau_\sigma^{\text{W}}(\mathbf{r})}{\tau_\sigma(\mathbf{r})}, \quad 0 \leq z_\sigma(\mathbf{r}) \leq 1$$

  - $z_\sigma(\mathbf{r}) \approx 1$ in iso-orbital regions with one-electron character (tail, single bonds, lone pairs)
  - Becke (1998), Tao–Perdew–Staroverov–Scuseria (2003)

- Self-interaction problems exacerbated in a magnetic field by confinement of A^2 (here He):

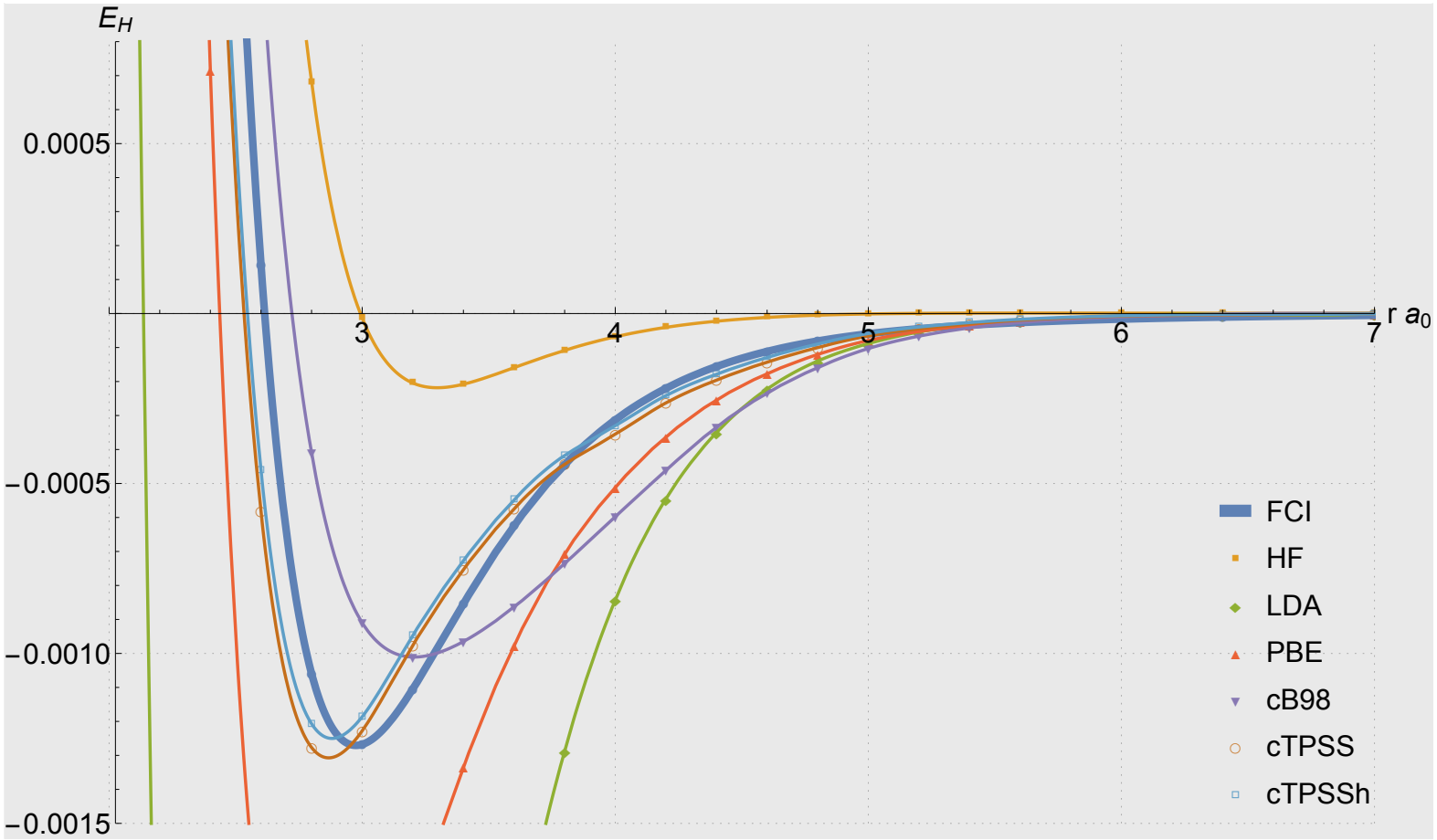


- Gauge invariance requires a modification of τ_σ (not unique) in meta-GGA functionals

$$\tau_\sigma(\mathbf{r}) \to \tilde{\tau}_\sigma(\mathbf{r}) = \tau_\sigma(\mathbf{r}) - \frac{|\boldsymbol{\kappa}_\sigma(\mathbf{r})|^2}{2\rho_\sigma(\mathbf{r})}, \quad \text{(paramagnetic current density } \boldsymbol{\kappa}_\sigma\text{)}$$

  - Dobson (1993), Becke (2002), Tao (2005)
  - Maximoff and Scuseria (2006): NMR shieldings with $-\mathrm{i}\boldsymbol{\nabla} \to -\mathrm{i}\boldsymbol{\nabla} + \mathbf{A}$ in $\tau_\sigma(\mathbf{r})$

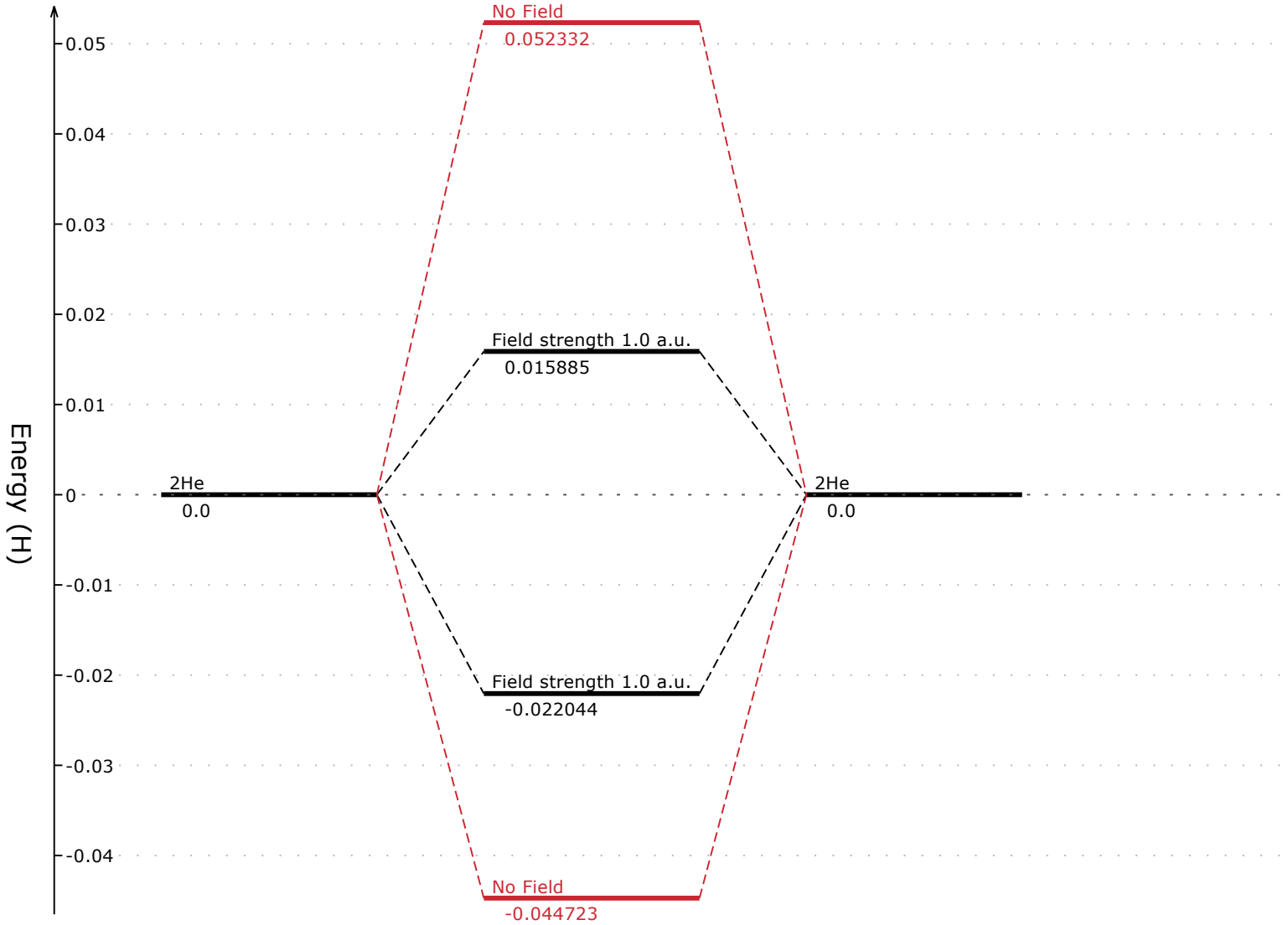
CDFT-mGGA for He_2 in a perpendicular field



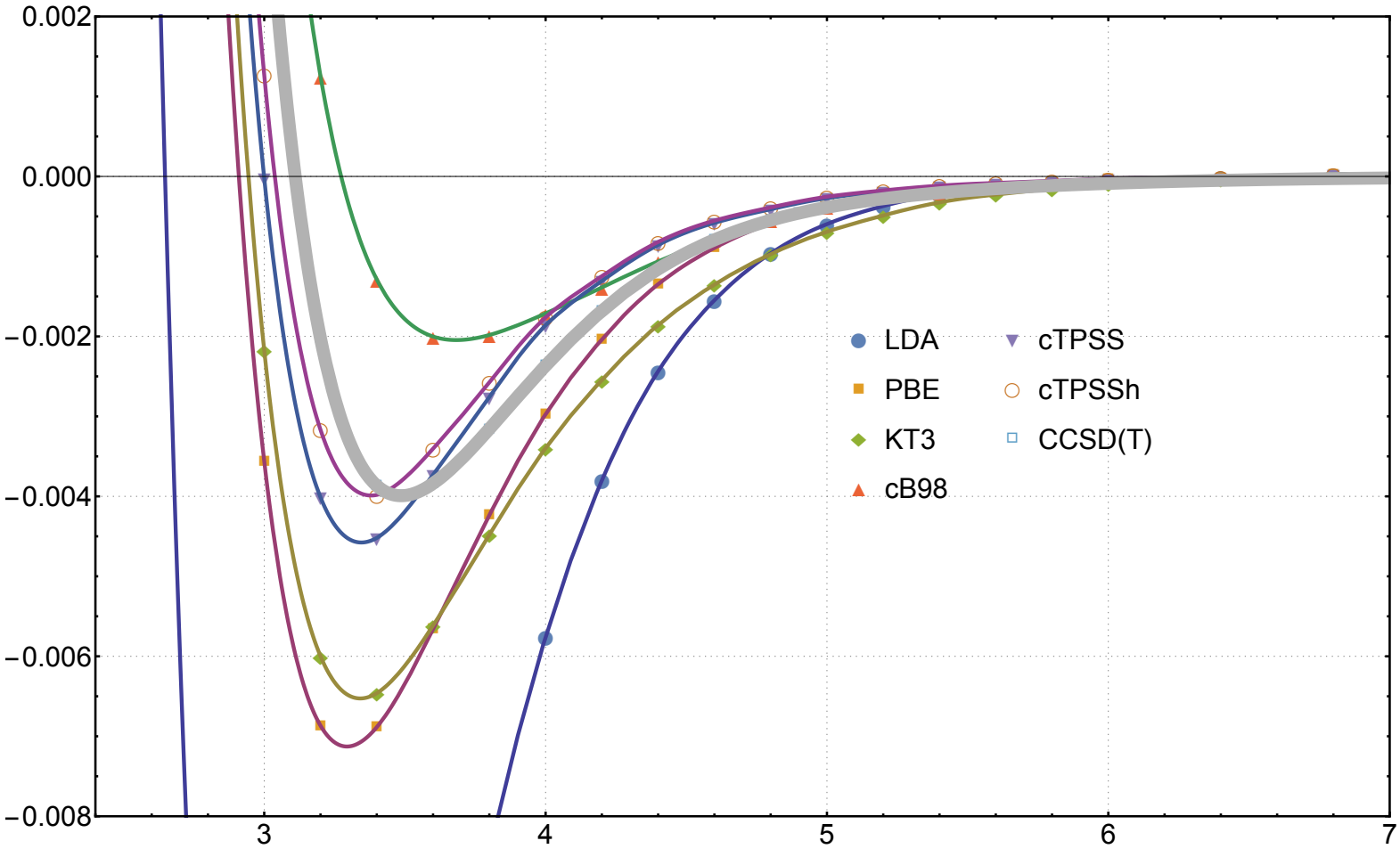
- Three meta-GGA functionals: cB98, cTPSS, and cTPSSh functionals
  - cTPSS for excitation energies in response theory: Bates and Furche JCP **137** 164105 (2012)
  - TPSS for atoms in magnetic fields: Zhu, Zhang and Trickey, PRA **90** 022504 (2014)
  - cTPSS for molecules in magnetic fields: Furness *et al.*, JCTC **11**, 4169 (2015)

cTPSS orbital energy level diagram of He_2

- Stabilisation of antibonding orbitals dominate destabilisation of bonding orbitals

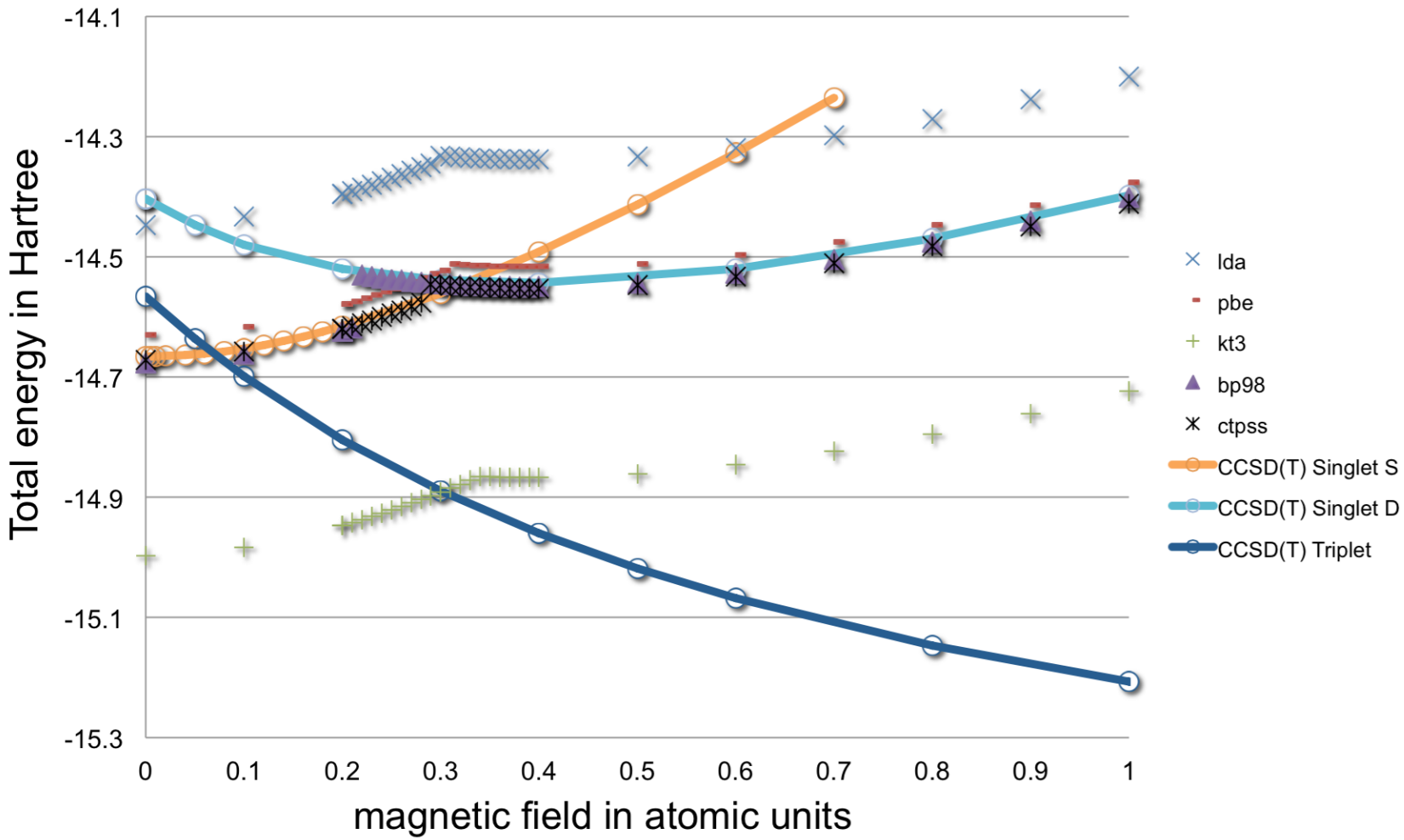


CDFT-mGGA for Ne_2 in a perpendicular field



- TPSS-based forms give a remarkable accuracy
  - mGGAs seem to deliver a reliable description of strong-field effects
  - in strong fields, systems are contracted and self interaction becomes more problematic
  - Zhu, Zhang and Trickey, PRA **90** 022504 (2014)

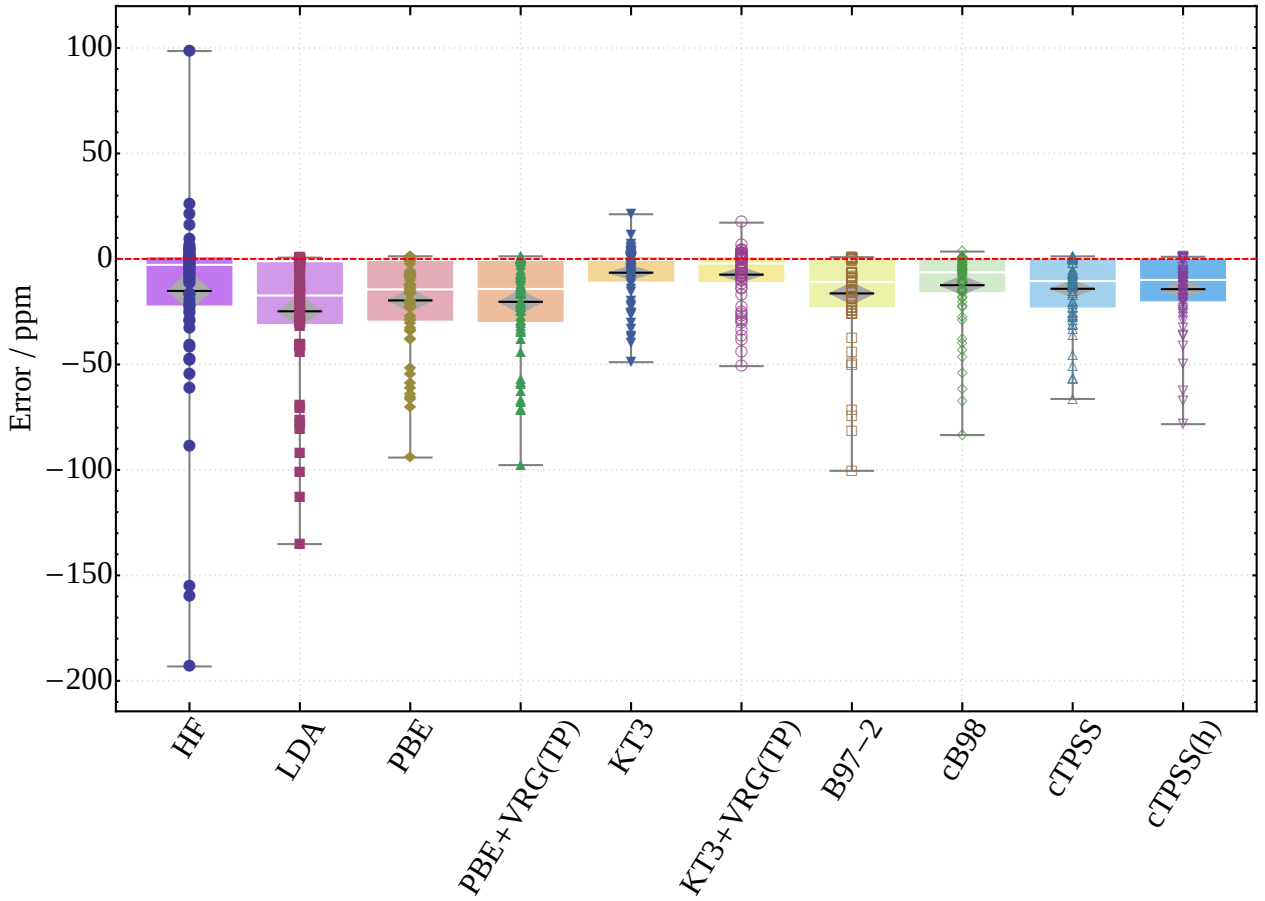
Be atom in lowest singlet S, singlet D, and triplet states



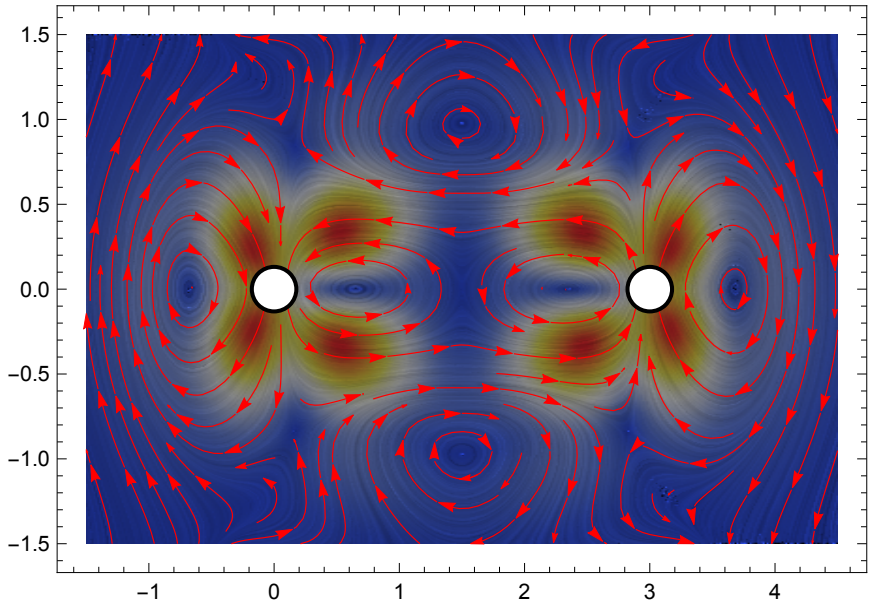
- Stella Stopkowicz *et al.* JCP **143**, 074110 (2015)

CDFT-mGGA shielding constants

- Box-whisker plot of errors in (C)DFT NMR shielding constants relative to extrapolated CCSD(T) values
- All calculations use the aug-cc-pCVTZ basis set.



- Observations
  - functionals are numerically stable to evaluate and physically motivated
  - only modest improvements—underlying flaws of functionals may dominate

Conclusions

- We have considered DFT with and without magnetic fields
  - Hohenberg–Kohn and Lieb variation principles
  - Hohenberg–Kohn theorem
  - CDFT: current-density-functional theory
  - variables, Hohenberg–Kohn theorem, representability
  - CDFT with VRG and meta-GGA
- Acknowledgements:
  - Research Council of Norway (RCN), European Research Council (ERC)