

## Density-functional theory, with and without a magnetic field

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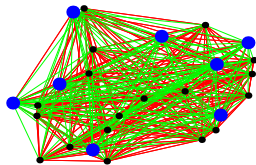
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Advances in Many-Body Theory: from Nuclei to Molecules  
Institute for Nuclear Theory (INT),  
University of Washington, Seattle, Washington  
April 3–5, 2013

- ▶ Molecules are difficult but well understood **many-body systems**:

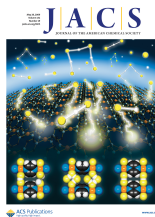
“The underlying physical laws necessary for the mathematical theory of a large part of physics and **the whole of chemistry** are thus **completely known**, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” **P. A. M. Dirac**



- ▶ Today, **quantum-chemical calculations** are routinely carried out by **nonspecialists**:

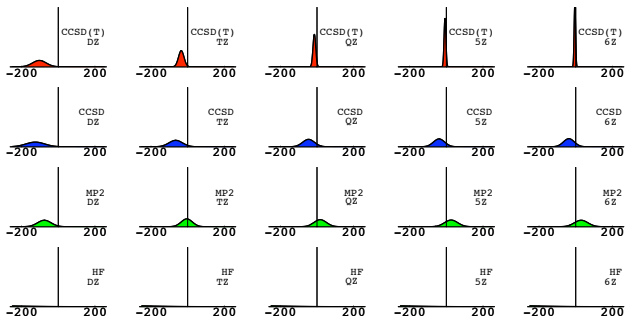
About 40% of all articles in the Journal of American Chemical Society are supported by computation, many of electronic structure:

- ▶ molecular structure
- ▶ spectroscopic constants
- ▶ interaction with electromagnetic fields
- ▶ reactivity, reaction rates, and dynamics



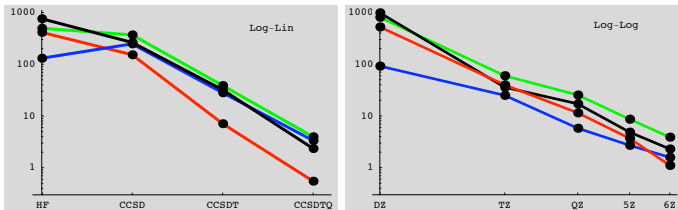
# History of quantum chemistry

- ▶ **Ab initio molecular electronic-structure theory** has developed since the 1960s:
  - ▶ Hartree–Fock (HF) self-consistent field (SCF) theory (1960s)
  - ▶ configuration-interaction (CI) theory (1970s)
  - ▶ multiconfigurational SCF (MCSCF) theory (early 1980s)
  - ▶ many-body perturbation theory (1980s)
  - ▶ coupled-cluster theory (late 1980s)
  - ▶ density-functional theory (1990s)
- ▶ **Coupled-cluster theory** is the most successful wave-function theory
  - ▶ introduced from nuclear physics (Bartlett)
  - ▶ size extensive treatment of dynamical correlation, unlike truncated CI theory
  - ▶ high cost, near-degeneracy (strong correlation) problems
  - ▶ the exact solution can be approached in systematic manner (AE errors, kJ/mol)



# Energy contributions to atomization energies (kJ/mol)

- ▶ Contributions of each CC excitation level (left) and AO basis-set shell (right)



- ▶ color code: HF, N<sub>2</sub>, F<sub>2</sub>, and CO

- ▶ The excitation-level convergence is approximately linear (log-linear plot)
  - ▶ each new excitation level reduces the error by about an order of magnitude
  - ▶ the contributions from quintuples are negligible (about 0.1 kJ/mol)
- ▶ The basis-set convergence is much slower (log-log plot)
  - ▶ each shell contributes an energy proportional to  $X^{-4}$  where  $X$  is the cardinal number
  - ▶ a similarly small error (0.1 kJ/mol) requires  $X > 10$
  - ▶ clearly, we must choose our orbitals in the best possible manner

# Coupled-cluster convergence

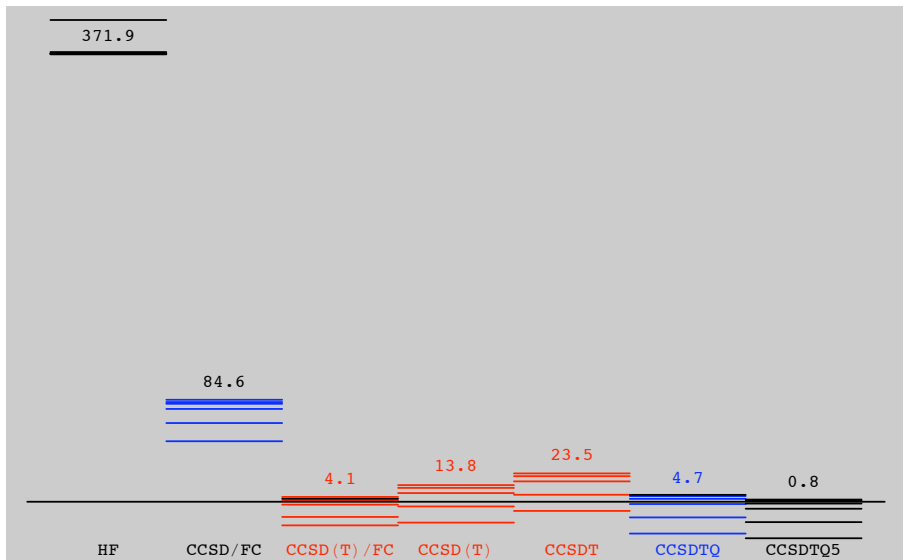
## Bond distances (pm)

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	89.70	1.67	0.29	0.02	0.00	0.01	91.69	91.69	0.00
N <sub>2</sub>	106.54	2.40	0.67	0.14	0.03	0.00	109.78	109.77	0.01
F <sub>2</sub>	132.64	6.04	2.02	0.44	0.03	0.05	141.22	141.27	-0.05
CO	110.18	1.87	0.75	0.04	0.00	0.00	112.84	112.84	0.00

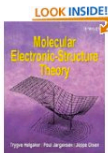
## Harmonic vibrational constants $\omega_e$ (cm<sup>-1</sup>)

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	4473.8	-277.4	-50.2	-4.1	-0.1	-3.5	4138.5	4138.3	0.2
N <sub>2</sub>	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	2358.0	2358.6	-0.6
F <sub>2</sub>	1266.9	-236.1	-95.3	-15.3	-0.8	-0.5	918.9	916.6	2.3
CO	2426.7	-177.4	-71.7	-7.2	0.0	-1.3	2169.1	2169.8	0.7

# Convergence to $\omega_e$ in $N_2$



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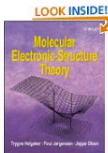
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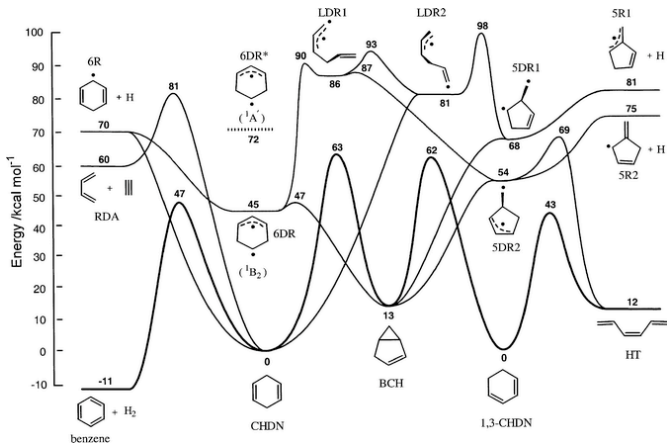
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# The emergence of density-functional theory (DFT)

- ▶ The traditional methods of quantum chemistry are capable of high accuracy
  - ▶ nevertheless, most calculations are performed using **density-functional theory (DFT)**
- ▶ What is the reason for the popularity of DFT?
  - ▶ the standard methods are (at least for high accuracy) very expensive





# Density-functional theory (DFT)

- ▶ The ground-state electronic energy  $E[v]$  is a functional of the **external potential**:

$$v(\mathbf{r}) = - \sum_K \frac{Z_K}{r_K} \quad \text{Coulomb potential}$$

- ▶ The **ground-state energy** with **external potential**  $v$ :

$$E[v] = \inf_{\Psi \rightarrow N} \langle \Psi | H[v] | \Psi \rangle$$

$$H[v] = T + W + \sum_i v(\mathbf{r}_i), \quad W = \sum_{i>j} r_{ij}^{-1}$$

- ▶ It is possible to perform the Rayleigh–Ritz minimization in **two nested steps**:

$$E[v] = \inf_{\rho \rightarrow N} \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W + \sum_i v(\mathbf{r}_i) | \Psi \rangle$$

$$= \inf_{\rho \rightarrow N} \left[ \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle + (\rho|v) \right]$$

- ▶ In the **Hohenberg–Kohn variation principle**, we minimize over all densities  $\rho$ :

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

$$F[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T + W | \Psi \rangle \quad \text{Levy constrained-search functional}$$

- ▶ The **universal density functional**  $F[\rho]$  depends only on the density

- ▶ the density depends only on three spatial coordinates
- ▶ it contains all information needed to calculate the ground-state energy

# The Hohenberg–Kohn and Lieb variation principles

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

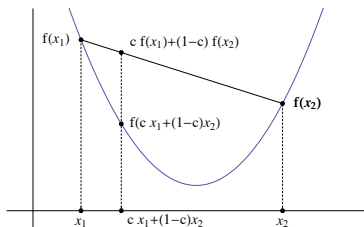
$$E[v] = \inf_{\rho} (F[\rho] + (v|\rho)) \quad \text{the Hohenberg–Kohn variation principle (1964)}$$

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

- ▶ 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  $\rho$ , respectively
  - ▶ the extrinsic and intrinsic energies, respectively
- ▶ The possibility of expressing  $E$  in terms of  $F$  follows from the convexity of  $-E[v]$  in  $v$ :

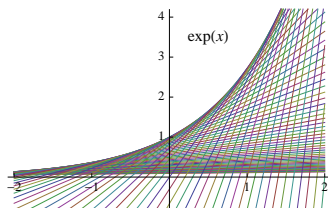
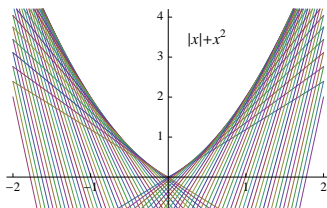
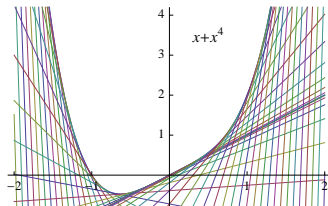
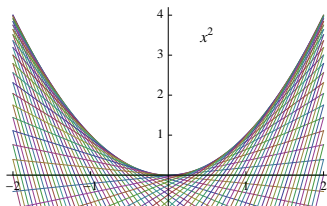


# What characterizes a convex function?

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

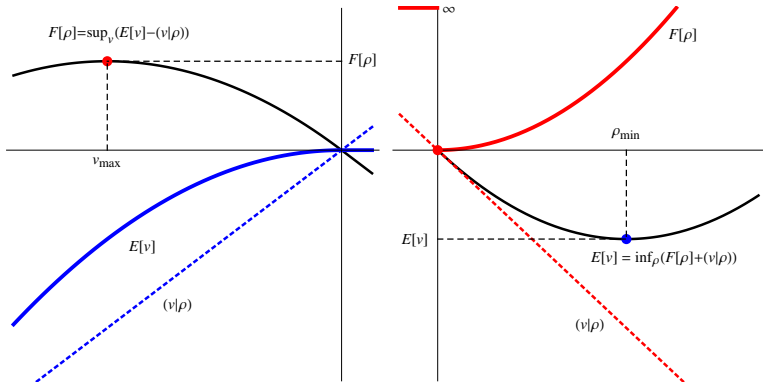
$$f(x) = \sup_y [xy - g(y)] \leftarrow \text{pointwise supremum of all supporting lines}$$

- ▶ 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**  $F[\rho]$ :  $E[v] \leftrightarrow F[\rho]$



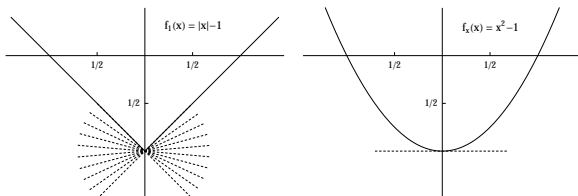
- ▶ **Mathematical characterization** of  $E$  and  $F$ :

- ▶  $E$  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  $L^3 \cap L^1$

# Stationary conditions and subgradients

- ▶ Concavity of  $E$  and convexity of  $F$  imply **great simplicity**
  - ▶ all minima and maxima in the Hohenberg–Kohn and Lieb variation principles are **global**
  - ▶ methods of **convex optimization** theory can be used
- ▶ However, convex functions are **not necessarily differentiable**
  - ▶ minima are not characterized by derivatives but by 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  $x_0$

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

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

# DFT stationary conditions: the Hohenberg–Kohn theorem

- ▶ The DFT variation principles are **convex optimization problems**:

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

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

- ▶ The condition of zero subgradient gives the following **reciprocal stationary relations**:

$$E[v] = F[\rho] + (v|\rho) \Leftrightarrow -v \in \partial F[\rho] \Leftrightarrow \rho \in \partial E[v]$$

- ▶  $\rho$  and  $v$  are **conjugate variables** and  $\partial F[\rho]$  and  $\partial E[v]$  are **inverse functions**
- ▶ note:  $F$  and  $E$  are not differentiable
- ▶ The subdifferential  $\partial F[\rho]$  contains the associated potentials:
  - $\partial F[\rho] = \{-v_{\rho} - c\}$ ,  $\rho$  is a ground-state density of some potential  $v_{\rho}$
  - $\partial F[\rho] = \emptyset$ ,  $\rho$  is not a ground-state density of any potential
- ▶ **Hohenberg–Kohn theorem**: the ground-state density determines the potential to within a constant
- ▶ not all densities are ground-state densities of any potential
- ▶ the set of ground-state densities is dense in the set of all  $N$ -electron densities
- ▶ The subdifferential  $\partial E[v]$  contains the associated (degenerate) ground-state densities:

$$\partial E[v] = \text{co}\{\rho_1, \rho_2, \dots, \rho_n\}, \quad v \text{ supports a ground state}$$

$$\partial E[v] = \emptyset, \quad v \text{ does not support a ground state}$$

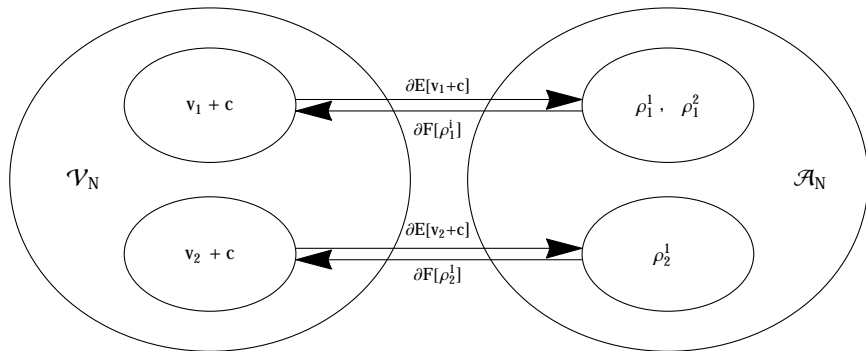
- ▶ not all potentials support a ground state
- ▶ the set of potentials with a ground state is dense in the set of all potentials

# $v$ -representability densities and $\rho$ -representable potentials

- ▶  $E[v]$  and  $F[\rho]$  are functions whose **subdifferentials are inverse functions**

$$E[v] = F[\rho] + (v|\rho) \Leftrightarrow -v \in \partial F[\rho] \Leftrightarrow \rho \in \partial E[v]$$

- ▶  $\partial E[v]$  gives the ground-state densities (if any) associated with  $v$
- ▶  $\partial F[\rho]$  gives the ground-state potential (if any) associated with  $\rho$  (uniquely)



# Kohn–Sham theory

- ▶ We may set up DFT at **arbitrary interaction strengths**  $\lambda$ :

$$E_\lambda[v] = \inf_{\rho \rightarrow N} (F_\lambda[\rho] + (v|\rho)) \quad \text{Hohenberg–Kohn variation principle}$$

$$F_\lambda[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T + \lambda W | \Psi \rangle \quad \text{universal density functional}$$

- ▶ In **Kohn–Sham theory**, we relate the complicated  $F_1[\rho]$  to the much simpler  $F_0[\rho]$ :

$$F_1[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

where

$$T_s[\rho] = F_0[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | T | \Psi \rangle \quad \text{noninteracting kinetic energy}$$

$$J[\rho] = \iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_1d\mathbf{r}_2 \quad \text{Coulomb energy}$$

$$E_{xc}[\rho] = F[\rho] - F_0[\rho] - J[\rho] \quad \text{exchange–correlation energy}$$

- ▶ The **noninteracting kinetic energy**  $T_s[\rho]$  can be calculated exactly by introducing orbitals

$$\rho(\mathbf{r}) = \sum_i \phi_i(\mathbf{r})^* \phi_i(\mathbf{r})$$

- ▶ the **Kohn–Sham orbitals** are eigenfunctions of an effective **Kohn–Sham potential**:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$



# The exchange–correlation functional

- ▶ The exact exchange–correlation functional is unknown
  - ▶ we must rely on approximations

- ▶ **Local-density approximation (LDA)**

- ▶ XC functional modeled after the uniform electron gas (which is known exactly)

$$E_{xc}^{\text{LDA}}[\rho] = \int f(\rho(\mathbf{r})) \, d\mathbf{r} \quad \text{local dependence on density}$$

- ▶ widely applied in condensed-matter physics
  - ▶ not sufficiently accurate to compete with traditional methods of quantum chemistry

- ▶ **Generalized-gradient approximation (GGA)**

- ▶ introduce a dependence also on the density gradient

$$E_{xc}^{\text{GGA}}[\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \, d\mathbf{r} \quad \text{local dependence on density and its gradient}$$

- ▶ **Becke's gradient correction to exchange** (1988) changed the situation
  - ▶ the accuracy became sufficient to compete in chemistry
  - ▶ indeed, surprisingly high accuracy for energetics

- ▶ A bewildering variety of functionals has been developed

- ▶ sometimes chosen to satisfy **exact conditions**, other times **fitted to data**

# A plethora of exchange–correlation functionals

Table 1. MADs (all energies in eV) for various level of theory for the extended G2 set

Method	G2(MAD)				H-Ne, $E_{\text{tot}}$	TM $\Delta E$	He <sub>2</sub> , $\Delta E(R_e)$	Ne <sub>2</sub> , $\Delta E(R_e)$	(H <sub>2</sub> O) <sub>2</sub> , $D_e(R_{\text{O} \dots \text{O}})$
	$\Delta H_f$	IP	EA	PA					
HF	6.47	1.036	1.158	0.15	4.49	1.09	Unbound	Unbound	0.161 (3.048)
G2 or best <i>ab initio</i>	0.07 <sup>a</sup>	0.053 <sup>b</sup>	0.057 <sup>b</sup>	0.05 <sup>b</sup>	1.59 <sup>c</sup>	0.19 <sup>d</sup>	<b>0.0011 (2.993)<sup>e</sup></b>	0.0043 <b>(3.125)<sup>e</sup></b>	<b>0.218 (2.912)<sup>f</sup></b>
LDA (SVWN)	3.94 <sup>a</sup>	0.665	0.749	0.27	6.67	0.54 <sup>g</sup>	0.0109 (2.377)	0.0231 (2.595)	0.391 (2.710)
GGA									
BP86	0.88 <sup>a</sup>	0.175	0.212	0.05	0.19	0.46	Unbound	Unbound	0.194 (2.889)
BLYP	0.31 <sup>a</sup>	0.187	0.106	0.08	0.19	0.37 <sup>g</sup>	Unbound	Unbound	0.181 (2.952)
BPW91	0.34 <sup>a</sup>	0.163	0.094	0.05	0.16	0.60	Unbound	Unbound	0.156 (2.946)
PW91PW91	0.77	0.164	0.141	0.06	0.35	0.52	0.0100 (2.645)	0.0137 <b>(3.016)</b>	0.235 (2.886)
mPWPW <sup>h</sup>	0.65	0.161	0.122	0.05	0.16	0.38	0.0052 (2.823)	0.0076 <b>(3.178)</b>	0.194 <b>(2.911)</b>
PBEPBE <sup>i</sup>	0.74 <sup>i</sup>	0.156	0.101	0.06	1.25	0.34	0.0032 (2.752)	0.0048 <b>(3.097)</b>	0.222 (2.899)
XLYP <sup>j</sup>	0.33	0.186	0.117	0.09	0.95	0.24	<b>0.0010 (2.805)</b>	<b>0.0030 (3.126)</b>	0.192 (2.953)
Hybrid methods									
BH & HLYP <sup>k</sup>	0.94	0.207	0.247	0.07	0.08	0.72	Unbound	Unbound	0.214 <b>(2.905)</b>
B3P86 <sup>l</sup>	0.78 <sup>a</sup>	0.636	0.593	<b>0.03</b>	2.80	0.34	Unbound	Unbound	0.206 (2.878)
B3LYP <sup>m</sup>	0.13 <sup>a</sup>	0.168	0.103	0.06	0.38	0.25 <sup>g</sup>	Unbound	Unbound	0.198 (2.926)
B3PW91 <sup>n</sup>	0.15 <sup>a</sup>	0.161	0.100	<b>0.03</b>	0.24	0.38	Unbound	Unbound	0.175 (2.923)
PW1PW <sup>o</sup>	0.23	0.160	0.114	0.04	0.30	0.30	0.0066 (2.660)	0.0095 <b>(3.003)</b>	0.227 (2.884)
mPW1PW <sup>p</sup>	0.17	0.160	0.118	0.04	0.16	0.31	0.0020 <b>(3.052)</b>	0.0023 (3.254)	0.199 (2.898)
PBE1PBE <sup>q</sup>	0.21 <sup>i</sup>	0.162	0.126	0.04	1.09	0.30	0.0018 (2.818)	0.0026 <b>(3.118)</b>	<b>0.216 (2.896)</b>
O3LYP <sup>r</sup>	0.18	<b>0.139</b>	0.107	0.05	<b>0.06</b>	0.49	0.0031 (2.860)	0.0047 (3.225)	0.139 (3.095)
X3LYP <sup>s</sup>	<b>0.12</b>	0.154	<b>0.087</b>	0.07	0.11	<b>0.22</b>	<b>0.0010 (2.726)</b>	<b>0.0028 (2.904)</b>	<b>0.216 (2.908)</b>
Experimental	—	—	—	—	—	—	<b>0.0010 (2.970)<sup>t</sup></b>	<b>0.0036 (3.091)<sup>t</sup></b>	0.236 <sup>u</sup> (2.948) <sup>v</sup>

$\Delta H_f$ , heat of formation at 298 K; PA, proton affinity;  $E_{\text{tot}}$ , total energies (H-Ne); TM  $\Delta E$ , s to d excitation energy of nine first-row transition metal atoms and nine positive ions. Bonding properties ( $\Delta E$  or  $D_e$  in eV and  $(R_e)$  in Å) are given for He<sub>2</sub>, Ne<sub>2</sub>, and (H<sub>2</sub>O)<sub>2</sub>. The best DFT results are in boldface, as are the most accurate answers [experiment except for (H<sub>2</sub>O)<sub>2</sub>].

# Reaction Enthalpies (kJ/mol)

	B3LYP		CCSD(T)		exp.
$\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	-543	1	-543	1	-544(2)
$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	-208	-5	-206	-3	-203(2)
$\text{C}_2\text{H}_2 + 3\text{H}_2 \rightarrow 2\text{CH}_4$	-450	-4	-447	-1	-446(2)
$\text{CO} + \text{H}_2 \rightarrow \text{CH}_2\text{O}$	-34	-13	-23	-2	-21(1)
$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_2$	-166	-2	-165	-1	-164(1)
$\text{F}_2 + \text{H}_2 \rightarrow 2\text{HF}$	-540	23	-564	-1	-563(1)
$\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$	-909	24	-946	-13	-933(2)
$\text{CH}_2\text{O} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-234	17	-250	1	-251(1)
$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$	-346	19	-362	3	-365(2)
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-268	4	-273	-1	-272(1)
$\text{HCN} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_2$	-320	0	-321	-1	-320(3)
$\text{HNO} + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{NH}_2$	-429	15	-446	-2	-444(1)
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-211	33	-244	0	-244(1)
$2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$	-845	-1	-845	-1	-844(3)

# The Kohn–Sham adiabatic connection

- ▶ Consider again the **Levy constrained-search formula**

$$F_\lambda[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + \lambda W | \Psi \rangle = \langle \Psi_\rho^\lambda | T + \lambda W | \Psi_\rho^\lambda \rangle$$

- ▶  $\lambda$  is the **coupling-strength parameter**
- ▶ We may now connect the interacting and noninteracting systems

$$F_\lambda[\rho] = F_0[\rho] + \int_0^\lambda F'_\mu[\rho] d\mu, \quad F'_\lambda[\rho] = \langle \Psi_\rho^\lambda | W | \Psi_\rho^\lambda \rangle \leftarrow \text{Hellmann–Feynman theorem}$$

- ▶ at  $\lambda = 0$ , we have the noninteracting system
  - ▶ at  $\lambda = 1$ , we have the fully interacting system
- ▶ We next perform the **Kohn–Sham decomposition** by introducing  $F_0[\rho]$  and  $F'_0[\rho]$ :

$$F_0[\rho] = \langle \Psi_\rho^0 | T | \Psi_\rho^0 \rangle = T_s[\rho] \quad \leftarrow \text{noninteracting kinetic energy}$$

$$F'_0[\rho] = \langle \Psi_\rho^0 | W | \Psi_\rho^0 \rangle = J[\rho] + E_x[\rho] \quad \leftarrow \text{Coulomb and exchange energies}$$

$$F_\lambda[\rho] = T_s[\rho] + \lambda J[\rho] + \lambda E_x[\rho] + E_{c,\lambda}[\rho] \quad \leftarrow \text{correlation energy}$$

- ▶ We can thus extract the correlation energy by **coupling-strength integration**

$$E_{c,\lambda}[\rho] = \int_0^\lambda \langle \Psi_\rho^\mu | W | \Psi_\rho^\mu \rangle d\mu - \lambda J[\rho] - \lambda E_x[\rho]$$

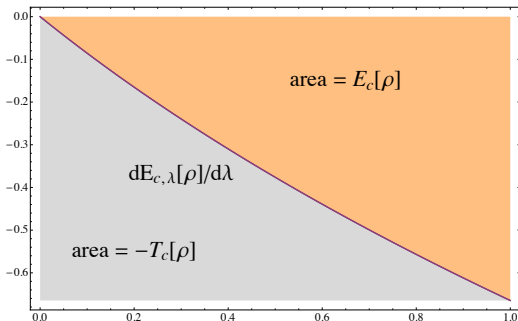
- ▶ in the **adiabatic approximation**, the integrand is assumed to change smoothly with  $\lambda$

# The adiabatic connection: the correlation energy

- ▶ In KS theory, the **correlation energy** is the only term that depends nontrivially on  $\lambda$ :

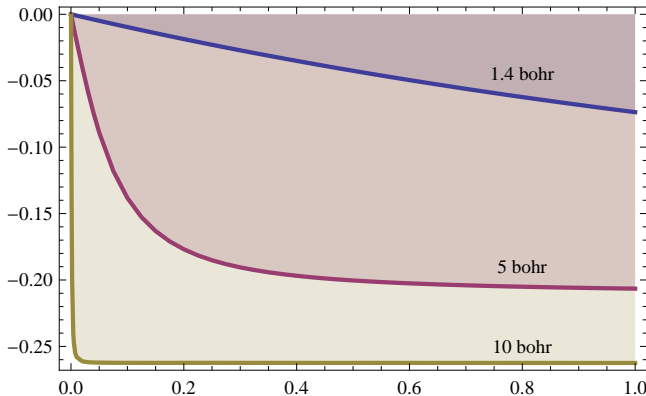
$$E_{c,\lambda}[\rho] = \int_0^\lambda (\langle \Psi_\rho^\mu | W | \Psi_\rho^\mu \rangle - \langle \Psi_\rho^0 | W | \Psi_\rho^0 \rangle) d\mu$$

- ▶ as  $\lambda$  increases, the wave function relaxes under the constraint of a fixed density
- ▶ Adiabatic-connection curve for the CCSD(T) correlation energy of the neon atom
  - ▶ calculated by the Lieb variation principle
  - ▶ Teale *et al.* JCP **130**, 104111 (2009); *ibid* **132**, 164115 (2010)



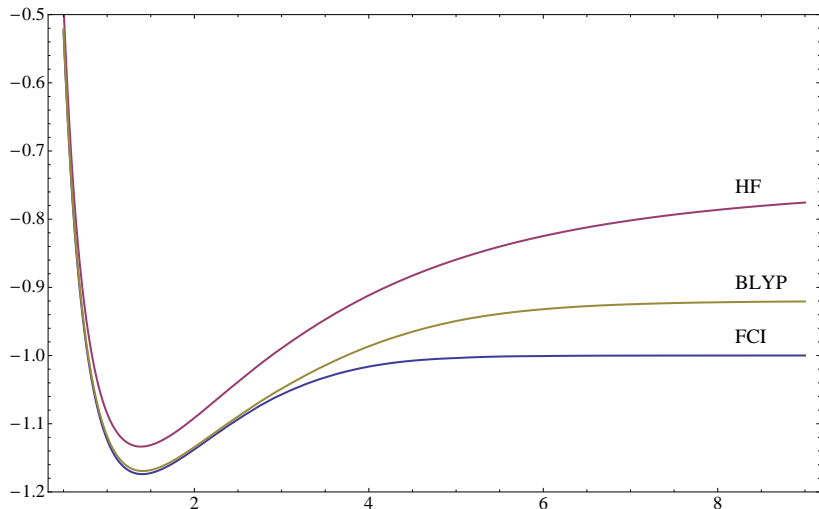
# H<sub>2</sub> dissociation: from dynamical to static correlation

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

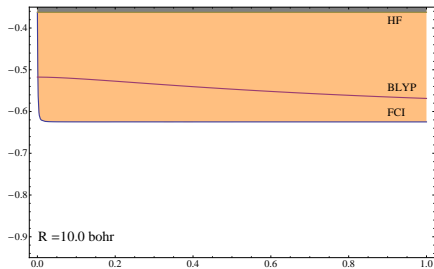
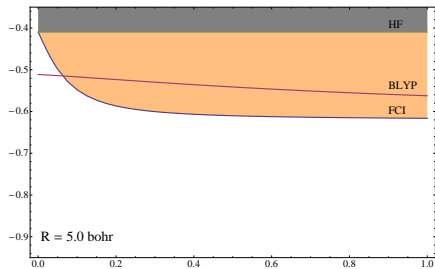
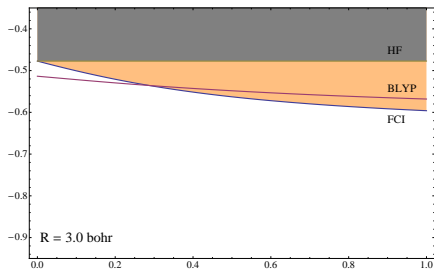
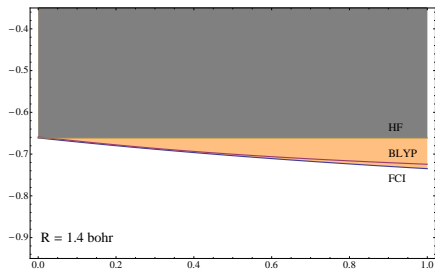


# The adiabatic connection: the dissociation of $H_2$

- ▶ To study static and dynamic correlation, we consider  $H_2$  dissociation
  - ▶ RHF, BLYP, and FCI levels of theory in the aug-cc-pVQZ basis



# Adiabatic connection: XC curves for $H_2$





# Molecular magnetism

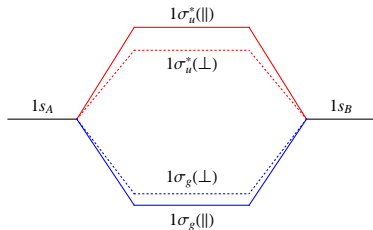
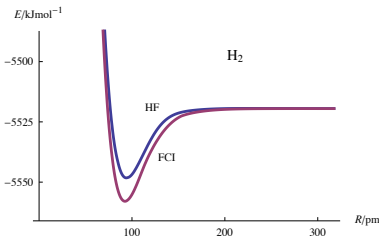
- ▶ A magnetic field  $\mathbf{B}$  modifies the **kinetic-energy operator**:

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

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

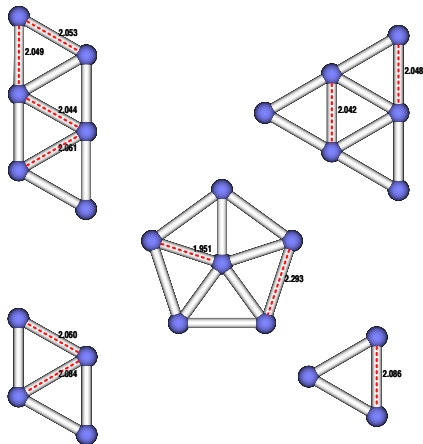
$$\boldsymbol{\pi}_i = -i\nabla_i + \mathbf{A}(\mathbf{r}_i), \quad \mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$$

- ▶ 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  $\text{H}_2$  and singlet  $\text{He}_2$  in strong fields
  - ▶ Lange *et al.* Science **337**, 327 (2012)



# 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



- ▶ Tellgren *et al.* PCCP 14, 9492 (2012)

# 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:

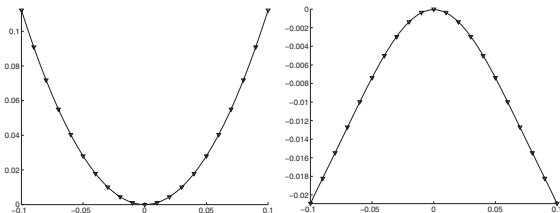
$$H[v, \mathbf{A}] = \frac{1}{2} \sum_i p_i^2 + \sum_i \mathbf{A}(r_i) \cdot \mathbf{p}_i + \frac{1}{2} \sum_i A(r_i)^2 + \sum_i v(r_i) + W$$

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

$$E[v, \mathbf{A}] = \inf_{\Psi} \langle \Psi | H[v, \mathbf{A}] | \Psi \rangle$$

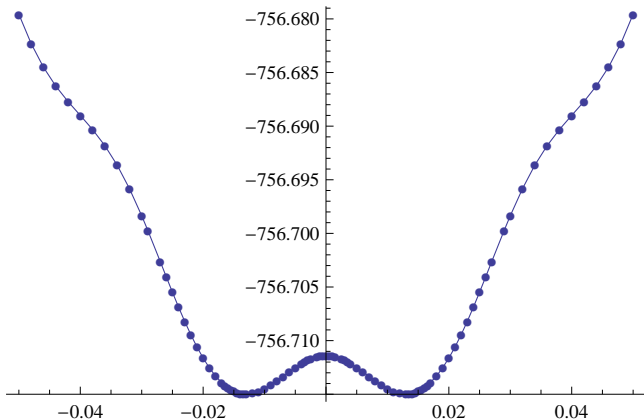
- ▶ The energy is **not necessarily concave** in the vector potential:

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



# Diamagnetism and paramagnetism

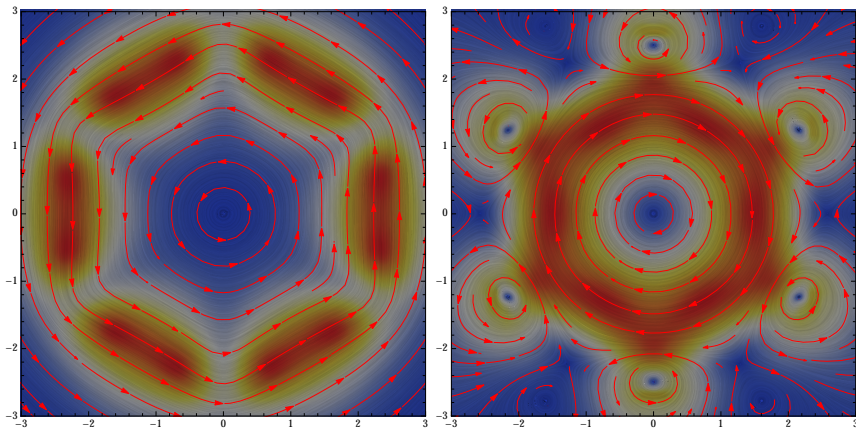
- ▶ The complicated field dependence results from an **interplay of linear and quadratic terms**
- ▶  $C_{20}$  in a perpendicular magnetic field:



- ▶ All molecules become diamagnetic at a **critical field strength**  $B_c$
- ▶ Tellgren *et al.* PCCP **11**, 5489 (2009)

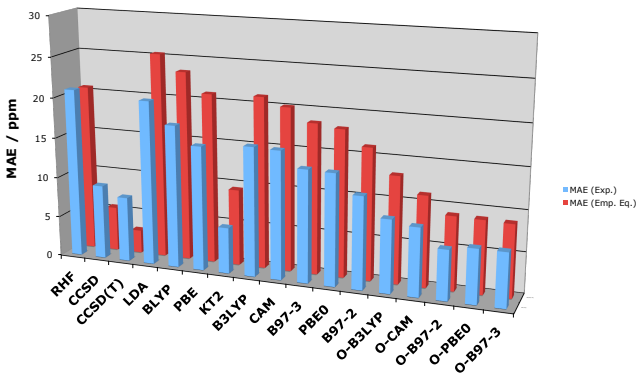
# Current densities in magnetic fields

- ▶ In an external magnetic field, **currents** are induced in the electronic system
- ▶ Below, we have plotted induced currents in **benzene** in a perpendicular field
  - ▶ current density in the  $\pi$  system (above the molecular plane) to the left
  - ▶ current density in the  $\sigma$  system (in the molecular plane) to the right



# Nuclear magnetic shielding constants

- ▶ The most important use of magnetism in chemistry is NMR spectroscopy
  - ▶ nuclear spin transitions in an externally applied field shielded by the electrons
  - ▶ the shielding is determined by the response of the electronic system to the external field
  - ▶ shielding constants give important information about molecular structure
- ▶ Kohn–Sham calculations of shielding constants are of uneven quality
  - ▶ these calculations neglect the field/current dependence of the exchange–correlation functional



- ▶ Mean absolute errors (in ppm) for NMR shielding constants relative to experimental (blue) and empirical equilibrium values (red). Teale *et al.* JCP **138**, 024111 (2013)

# DFT in magnetic fields

- ▶ The electronic energy and Hamiltonian now depends on the **scalar and vector potentials**:

$$E[v, \mathbf{A}] = \inf_{\Psi} \langle \Psi | H[v, \mathbf{A}] | \Psi \rangle$$

- ▶ how can DFT be adapted to magnetic fields?

## CDFT: current-density-functional theory

- ▶ We perform convex conjugation with respect to both  $v$  and  $\mathbf{A}$ :

$$E[v, \mathbf{A}] \leftrightarrow F_{\text{CDFT}}[\rho, \kappa]$$

- ▶  $F_{\text{CDFT}}$  depends on  $\rho$  and the (nonobservable) **paramagnetic current density**  $\kappa$
- ▶ note: only the total current  $\mathbf{j} = \kappa + \rho\mathbf{A}$  is gauge invariant and observable
- ▶ Vignale and Rasolt (1987,1988)

## BDFT: magnetic-field density-functional theory

- ▶ We perform convex conjugation with respect to  $v$  only

$$E[v, \mathbf{A}] \leftrightarrow F_{\text{BDFT}}[\rho, \mathbf{A}]$$

- ▶  $F_{\text{BDFT}}$  depends on  $\rho$  and the vector potential (magnetic field)  $\mathbf{A}$
- ▶ Grayce and Harris (1994)

# CDFT: the basic variables

- ▶ The ground-state energy  $E[v, \mathbf{A}]$  is not concave in  $(v, \mathbf{A})$ :



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

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

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

$$\bar{E}[u, \mathbf{A}] = \inf_{\Psi} \langle \Psi | \bar{H}[u, \mathbf{A}] | \Psi \rangle = E[u - \frac{1}{2}A^2, A]$$

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

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

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

- ▶ Tellgren *et al.* PRA **86**, 062506 (2012)
- ▶ The variables conjugate to  $(u, \mathbf{A})$  are the **density and paramagnetic current density**  $(\rho, \kappa)$ :

$$\rho(\mathbf{r}) = \Psi^*(\mathbf{r})\Psi(\mathbf{r})$$

$$\kappa(\mathbf{r}) = \text{Re}\Psi^*(\mathbf{r})\mathbf{p}\Psi(\mathbf{r}) \neq \text{Re}\Psi^*(\mathbf{r})(\mathbf{p} + \mathbf{A})\Psi(\mathbf{r}) = \mathbf{j}(\mathbf{r})$$

- ▶ unlike the physical current, the paramagnetic current is uniquely determined by the wave function



# CDFT: the Hohenberg–Kohn theorem

- ▶ Consider the field-free system with Hamiltonian  $\bar{H}[u, \mathbf{0}]$
- ▶ Adding a **uniform magnetic field** along the z axis with vector potential

$$\mathbf{A} = \frac{1}{2} B \mathbf{e}_z \times \mathbf{r}$$

we obtain the new Hamiltonian

$$\bar{H}[u, \mathbf{A}] = \bar{H}[u, \mathbf{0}] + \frac{1}{2} B L_z + B S_z$$

- ▶ If  $u$  is spherical, then the two Hamiltonians **commute** and have the **same eigenstates**:

$$[\bar{H}[u, \mathbf{0}], \bar{H}[u, \mathbf{A}]] = 0$$

- ▶ Since  $(\rho, \kappa)$  are determined by the eigenstates, **they are the same in the two cases**:

$$(u, \mathbf{0}) \rightarrow (\rho, \kappa) \leftarrow (u, \mathbf{A})$$

- ▶ there can be **no Hohenberg–Kohn theorem for the paramagnetic current density**
- ▶ Eschrig (2001), Capelle and Vignale (2001,2002)
- ▶ observe also:

$$u = v + c \Leftrightarrow [H[u], H[v]] = 0$$

- ▶ On the other hand, the **physical current densities**  $\mathbf{j} = \kappa + \rho \mathbf{A}$  of the two systems differ:

$$(u, \mathbf{0}) \rightarrow (\rho, \kappa + \mathbf{0}) \neq (\rho, \kappa + \rho \mathbf{A}) \leftarrow (u, \mathbf{A})$$

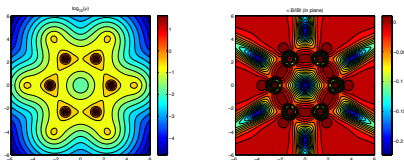
- ▶ a Hohenberg–Kohn theorem for  $\mathbf{j}$  is not excluded but the purported proofs are wrong

# CDFT: Kohn–Sham theory

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

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

- ▶ the exchange–correlation functional depends on the **density** and **vorticity**



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

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

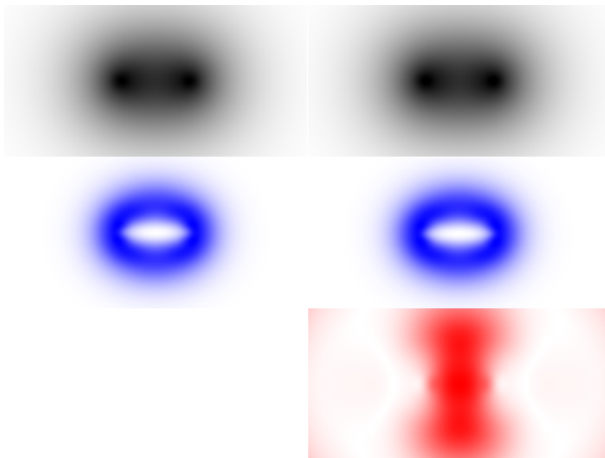
- ▶ local approximation expressed in terms of the gauge-invariant vorticity
- ▶ based on the response of a uniform electron gas to a uniform magnetic field
- ▶ the parametrization is numerically difficult, with arbitrary cutoffs
- ▶ it gives too negative contributions to the molecular electronic energy
- ▶ shielding errors typically increase by 20%–30% ...
- ▶ CDFT Kohn–Sham **representability problem**
  - ▶ a noninteracting Slater determinant may not be able to represent simultaneously  $\rho$  and  $\nu$

# CDFT: noninteracting representability

- ▶ 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  $\rho$  (top), physical current  $j^2$  (middle), and vorticity  $\nu$  (bottom) of  $H_2$

Hartree-Fock

Full CI



# BDFT: the adiabatic connection

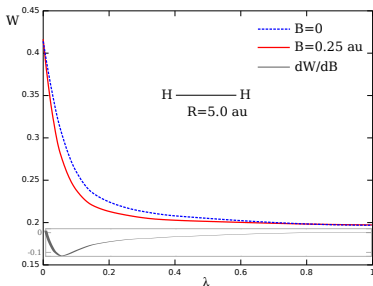
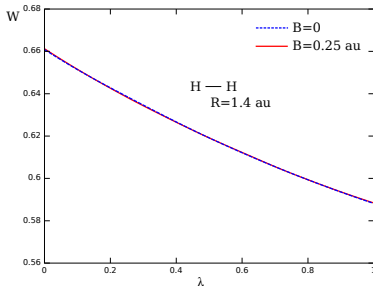
- ▶ We may describe magnetic phenomena by setting up a separate DFT for each  $\mathbf{B}$ :

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

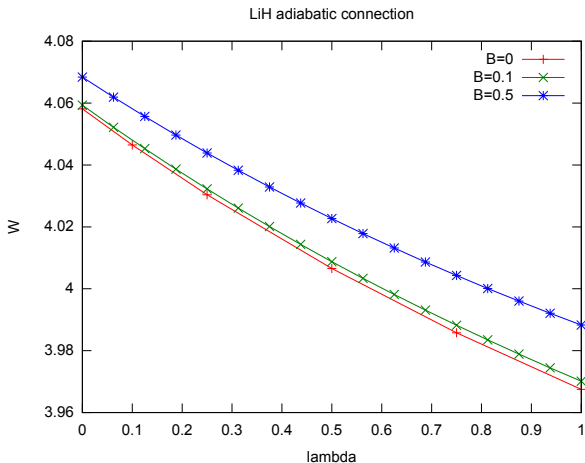
- ▶ The density functional now depends on the **density** and on the **field strength**

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

- ▶ the **noninteracting magnetic response** is exactly taken care of by  $T_s[\rho, \mathbf{B}]$
- ▶ AC correlation curves of  $\text{H}_2$  in a perpendicular magnetic field
  - ▶  $E_{xc}[\rho, \mathbf{B}]$  differs strongly 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

