Density-functional theory, with and without a magnetic field

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Quantum chemistry

- 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, N₂, F₂, 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 $X \geq 10$
  - clearly, we must choose our orbitals in the best possible manner
### Coupled-cluster convergence

#### Bond distances (pm)

<table>
<thead>
<tr>
<th></th>
<th>RHF</th>
<th>SD</th>
<th>T</th>
<th>Q</th>
<th>5</th>
<th>rel.</th>
<th>theory</th>
<th>exp.</th>
<th>err.</th>
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<tbody>
<tr>
<td>HF</td>
<td>89.70</td>
<td>1.67</td>
<td>0.29</td>
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<tr>
<td>N₂</td>
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<td>2.40</td>
<td>0.67</td>
<td>0.14</td>
<td>0.03</td>
<td>0.00</td>
<td>109.78</td>
<td>109.77</td>
<td>0.01</td>
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<tr>
<td>F₂</td>
<td>132.64</td>
<td>6.04</td>
<td>2.02</td>
<td>0.44</td>
<td>0.03</td>
<td>0.05</td>
<td>141.22</td>
<td>141.27</td>
<td>−0.05</td>
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<tr>
<td>CO</td>
<td>110.18</td>
<td>1.87</td>
<td>0.75</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>112.84</td>
<td>112.84</td>
<td>0.00</td>
</tr>
</tbody>
</table>

#### Harmonic vibrational constants $\omega_e$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>RHF</th>
<th>SD</th>
<th>T</th>
<th>Q</th>
<th>5</th>
<th>rel.</th>
<th>theory</th>
<th>exp.</th>
<th>err.</th>
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</thead>
<tbody>
<tr>
<td>HF</td>
<td>4473.8</td>
<td>−277.4</td>
<td>−50.2</td>
<td>−4.1</td>
<td>−0.1</td>
<td>−3.5</td>
<td>4138.5</td>
<td>4138.3</td>
<td>0.2</td>
</tr>
<tr>
<td>N₂</td>
<td>2730.3</td>
<td>−275.8</td>
<td>−72.4</td>
<td>−18.8</td>
<td>−3.9</td>
<td>−1.4</td>
<td>2358.0</td>
<td>2358.6</td>
<td>−0.6</td>
</tr>
<tr>
<td>F₂</td>
<td>1266.9</td>
<td>−236.1</td>
<td>−95.3</td>
<td>−15.3</td>
<td>−0.8</td>
<td>−0.5</td>
<td>918.9</td>
<td>916.6</td>
<td>2.3</td>
</tr>
<tr>
<td>CO</td>
<td>2426.7</td>
<td>−177.4</td>
<td>−71.7</td>
<td>−7.2</td>
<td>0.0</td>
<td>−1.3</td>
<td>2169.1</td>
<td>2169.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Convergence to $\omega_e$ in $\text{N}_2$
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
The ground-state electronic energy $E[v]$ is a functional of the external potential:

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

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

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

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

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

$$E[v] = \inf_{\rho \to N} \inf_{\Psi \to \rho} \langle \Psi | T + W + \sum_i v(r_i) | \Psi \rangle$$

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

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

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

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

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 calculated the ground-state energy
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:

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

\[E\] 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
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:

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

- \(\rho\) 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:

\[
\partial F[\rho] = \{-v_\rho - c\}, \quad \rho \text{ is a ground-state density of some potential } v_\rho
\]

\[
\partial F[\rho] = \emptyset, \quad \rho \text{ is not a ground-state density of any potential}
\]

- 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:

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

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

- 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

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

- \( \partial E[v] \) 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 $\lambda$:

$$E_{\lambda}[\nu] = \inf_{\rho \to N} (F_{\lambda}[\rho] + (\nu|\rho))$$

Hohenberg–Kohn variation principle

$$F_{\lambda}[\rho] = \inf_{\psi \to \rho} \langle \psi | T + \lambda W | \psi \rangle$$

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

$$T_{s}[\rho] = F_{0}[\rho] = \inf_{\psi \to \rho} \langle \psi | T | \psi \rangle$$

noninteracting kinetic energy

$$J[\rho] = \int \int \rho(r_{1})\rho(r_{2})r_{12}^{-1}dr_{1}dr_{2}$$

Coulomb energy

$$E_{xc}[\rho] = F[\rho] - F_{0}[\rho] - J[\rho]$$

exchange–correlation energy

The noninteracting kinetic energy $T_{s}[\rho]$ can be calculated exactly by introducing orbitals

$$\rho(r) = \sum_{i} \phi_{i}(r)^{*} \phi_{i}(r)$$

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

$$[-\frac{1}{2} \nabla^{2} + v_{\text{eff}}(r)] \phi_{i}(r) = \epsilon_{i} \phi_{i}(r), \quad v_{\text{eff}}(r) = v(r) + v_{J}(r) + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$
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)
    \[ E_{xc}^{\text{LDA}}[\rho] = \int f(\rho(r)) \, dr \]  
    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
    \[ E_{xc}^{\text{GGA}}[\rho] = \int f(\rho(r, \nabla \rho(r))) \, dr \]  
    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
### Table 1. MADs (all energies in eV) for various level of theory for the extended G2 set

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta H_i$</th>
<th>IP</th>
<th>EA</th>
<th>PA</th>
<th>H-Ne, $E_{tot}$</th>
<th>TM $\Delta E$</th>
<th>He$_2$, $\Delta E(R_e)$</th>
<th>Ne$_2$, $\Delta E(R_e)$</th>
<th>(H$_2$O)$_2$, $D_4(R_o \ldots o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>6.47</td>
<td>1.036</td>
<td>1.158</td>
<td>0.15</td>
<td>4.49</td>
<td>1.09</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.161 (3.048)</td>
</tr>
<tr>
<td>G2 or best ab initio</td>
<td>0.07</td>
<td>0.053</td>
<td>0.057</td>
<td>0.05</td>
<td>1.59</td>
<td>0.19</td>
<td><strong>0.0011 (2.993)</strong></td>
<td>0.0043 (3.125)</td>
<td><strong>0.218 (2.912)</strong></td>
</tr>
<tr>
<td>LDA (SVWN)</td>
<td>3.94</td>
<td>0.665</td>
<td>0.749</td>
<td>0.27</td>
<td>6.67</td>
<td>0.54</td>
<td>0.0109 (2.377)</td>
<td>0.0231 (2.595)</td>
<td>0.391 (2.710)</td>
</tr>
<tr>
<td>GGA</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>BP86</td>
<td>0.88</td>
<td>0.175</td>
<td>0.212</td>
<td>0.05</td>
<td>0.19</td>
<td>0.46</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.194 (2.889)</td>
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<td>BLYP</td>
<td>0.31</td>
<td>0.187</td>
<td>0.106</td>
<td>0.08</td>
<td>0.19</td>
<td>0.37</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.181 (2.952)</td>
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<td>BPW91</td>
<td>0.34</td>
<td>0.163</td>
<td>0.094</td>
<td>0.05</td>
<td>0.16</td>
<td>0.60</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.156 (2.946)</td>
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<td>PW91PW91</td>
<td>0.77</td>
<td>0.164</td>
<td>0.141</td>
<td>0.06</td>
<td>0.35</td>
<td>0.52</td>
<td>0.0100 (2.645)</td>
<td>0.0137 (3.016)</td>
<td>0.235 (2.886)</td>
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<td>mPW91PW91</td>
<td>0.65</td>
<td>0.161</td>
<td>0.122</td>
<td>0.05</td>
<td>0.16</td>
<td>0.38</td>
<td>0.0052 (2.823)</td>
<td>0.0076 (3.178)</td>
<td>0.194 (2.911)</td>
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<tr>
<td>mPW1PW1</td>
<td>0.74</td>
<td>0.156</td>
<td>0.101</td>
<td>0.06</td>
<td>1.25</td>
<td>0.34</td>
<td>0.0032 (2.752)</td>
<td>0.0048 (3.097)</td>
<td>0.222 (2.899)</td>
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<tr>
<td>XLYP</td>
<td>0.33</td>
<td>0.186</td>
<td>0.117</td>
<td>0.09</td>
<td>0.95</td>
<td>0.24</td>
<td><strong>0.0010 (2.805)</strong></td>
<td><strong>0.0030 (3.126)</strong></td>
<td>0.192 (2.953)</td>
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<tr>
<td>Hybrid methods</td>
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<tr>
<td>BH &amp; HLYP</td>
<td>0.94</td>
<td>0.207</td>
<td>0.247</td>
<td>0.07</td>
<td>0.08</td>
<td>0.72</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.214 (2.905)</td>
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<tr>
<td>B3P86</td>
<td>0.78</td>
<td>0.636</td>
<td>0.593</td>
<td>0.03</td>
<td>2.80</td>
<td>0.34</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.206 (2.878)</td>
</tr>
<tr>
<td>B3LYPm</td>
<td>0.13</td>
<td>0.168</td>
<td>0.103</td>
<td>0.06</td>
<td>0.38</td>
<td>0.25</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.198 (2.926)</td>
</tr>
<tr>
<td>B3PW91n</td>
<td>0.15</td>
<td>0.161</td>
<td>0.100</td>
<td>0.03</td>
<td>0.24</td>
<td>0.38</td>
<td>Unbound</td>
<td>Unbound</td>
<td>0.175 (2.923)</td>
</tr>
<tr>
<td>PW1PWo</td>
<td>0.23</td>
<td>0.160</td>
<td>0.114</td>
<td>0.04</td>
<td>0.30</td>
<td>0.30</td>
<td>0.0066 (2.660)</td>
<td>0.0095 (3.003)</td>
<td>0.227 (2.884)</td>
</tr>
<tr>
<td>mPW1PW1p</td>
<td>0.17</td>
<td>0.160</td>
<td>0.118</td>
<td>0.04</td>
<td>0.16</td>
<td>0.31</td>
<td>0.0020 (3.052)</td>
<td>0.0023 (3.254)</td>
<td>0.199 (2.898)</td>
</tr>
<tr>
<td>PBE1PBEq</td>
<td>0.21</td>
<td>0.162</td>
<td>0.126</td>
<td>0.04</td>
<td>1.09</td>
<td>0.30</td>
<td>0.0018 (2.818)</td>
<td>0.0026 (3.118)</td>
<td>0.216 (2.896)</td>
</tr>
<tr>
<td>O3LYPr</td>
<td>0.18</td>
<td>0.139</td>
<td>0.107</td>
<td>0.05</td>
<td><strong>0.06</strong></td>
<td>0.49</td>
<td>0.0031 (2.860)</td>
<td>0.0047 (3.225)</td>
<td>0.139 (3.095)</td>
</tr>
<tr>
<td>X3LYPp</td>
<td><strong>0.12</strong></td>
<td>0.154</td>
<td><strong>0.087</strong></td>
<td>0.07</td>
<td>0.11</td>
<td><strong>0.22</strong></td>
<td><strong>0.0010 (2.726)</strong></td>
<td><strong>0.0028 (2.904)</strong></td>
<td><strong>0.216 (2.908)</strong></td>
</tr>
<tr>
<td>Experimental</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$\Delta H_i$, heat of formation at 298 K; PA, proton affinity; $E_{tot}$, 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$_2$, Ne$_2$, and (H$_2$O)$_2$. The best DFT results are in boldface, as are the most accurate answers [experiment except for (H$_2$O)$_2$].

*Ref. 5.*

*Ref. 37.*

*Ref. 7.*

*Ref. 10.*

*Ref. 32.*

*Ref. 12*
**Reaction Enthalpies (kJ/mol)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>B3LYP</th>
<th>CCSD(T)</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$</td>
<td>$-543$</td>
<td>$-543$</td>
<td>$-544(2)$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$</td>
<td>$-208$</td>
<td>$-206$</td>
<td>$-203(2)$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2 + 3\text{H}_2 \rightarrow 2\text{CH}_4$</td>
<td>$-450$</td>
<td>$-447$</td>
<td>$-446(2)$</td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2 \rightarrow \text{CH}_2\text{O}$</td>
<td>$-34$</td>
<td>$-23$</td>
<td>$-21(1)$</td>
</tr>
<tr>
<td>$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_2$</td>
<td>$-166$</td>
<td>$-165$</td>
<td>$-164(1)$</td>
</tr>
<tr>
<td>$\text{F}_2 + \text{H}_2 \rightarrow 2\text{HF}$</td>
<td>$-540$</td>
<td>$-564$</td>
<td>$-563(1)$</td>
</tr>
<tr>
<td>$\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$</td>
<td>$-909$</td>
<td>$-946$</td>
<td>$-933(2)$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$</td>
<td>$-234$</td>
<td>$-250$</td>
<td>$-251(1)$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$</td>
<td>$-346$</td>
<td>$-362$</td>
<td>$-365(2)$</td>
</tr>
<tr>
<td>$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$</td>
<td>$-268$</td>
<td>$-273$</td>
<td>$-272(1)$</td>
</tr>
<tr>
<td>$\text{HCN} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_2$</td>
<td>$-320$</td>
<td>$-321$</td>
<td>$-320(3)$</td>
</tr>
<tr>
<td>$\text{HNO} + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{NH}_2$</td>
<td>$-429$</td>
<td>$-446$</td>
<td>$-444(1)$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$</td>
<td>$-211$</td>
<td>$-244$</td>
<td>$-244(1)$</td>
</tr>
<tr>
<td>$2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$</td>
<td>$-845$</td>
<td>$-845$</td>
<td>$-844(3)$</td>
</tr>
</tbody>
</table>
The Kohn–Sham adiabatic connection

Consider again the Levy constrained-search formula

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

- \( \lambda \) 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 \( F'_0[\rho] \):

\[
F_0[\rho] = \langle \Psi_\rho^0 | T | \Psi_\rho^0 \rangle = T_s[\rho] \leftarrow \text{noninteracting kinetic energy} \\
F'_0[\rho] = \langle \Psi_\rho^0 | W | \Psi_\rho^0 \rangle = J[\rho] + E_x[\rho] \leftarrow \text{Coulomb and exchange energies} \\
F_\lambda[\rho] = T_s[\rho] + \lambda J[\rho] + \lambda E_x[\rho] + E_{c,\lambda}[\rho] \leftarrow \text{correlation energy} 
\]

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

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

- 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
H$_2$ dissociation: from dynamical to static correlation

- Near equilibrium, correlation is predominantly **dynamic**
  - nearly linear curve since correlation is dominated by doubles ($\lambda^2$ in PT)
- Towards dissociation, static correlation becomes important
  - increased curvature form 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$_2$

R = 1.4 bohr

R = 3.0 bohr

R = 5.0 bohr

R = 10.0 bohr
Molecular magnetism

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

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

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

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

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

![Graph showing energy vs. distance for H2 molecule in magnetic fields](image)
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)
The Hamiltonian in a magnetic field (without the Zeeman term):

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

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

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

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

\[ E[\nu, \mathbf{A}] = \inf_{\psi} \langle \psi | H[\nu, \mathbf{A}] | \psi \rangle \]

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:

\[
\begin{array}{cccc}
-0.04 & -0.02 & 0.02 & 0.04 \\
\end{array}
\]

- 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 depend on the scalar and vector potentials:

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

- how can DFT be adapted to magnetic fields?

**CDFT: current-density-functional theory**

- We perform convex conjugation with respect to both \( v \) and \( A \):

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

- \( F_{CDFT} \) depends on \( \rho \) and the (nonobservable) paramagnetic current density \( \kappa \)

- note: only the total current \( j = \kappa + \rho A \) 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

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

- \( F_{BDFT} \) depends on \( \rho \) and the vector potential (magnetic field) \( A \)

- Grayce and Harris (1994)
CDFT: the basic variables

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

  ![Graph of concave function]

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

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

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

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

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

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

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

- Tellgren et al. PRA 86, 062506 (2012)

- The variables conjugate to \((u, \mathbf{A})\) are the density and paramagnetic current density \((\rho, \kappa)\):

  \[
  \rho(r) = \psi^*(r) \psi(r)
  \]

  \[
  \kappa(r) = \text{Re} \psi^*(r) \mathbf{p} \psi(r) \neq \text{Re} \psi^*(r) (\mathbf{p} + \mathbf{A}) \psi(r) = \mathbf{j}(r)
  \]

- unlike the physical current, the paramagnetic current is uniquely determined by the wave function
Consider the field-free system with Hamiltonian $\tilde{H}[u, 0]$

Adding a uniform magnetic field along the z axis with vector potential

$$A = \frac{1}{2} Be_z \times r$$

we obtain the new Hamiltonian

$$\tilde{H}[u, A] = \tilde{H}[u, 0] + \frac{1}{2} BL_z + BS_z$$

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

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

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

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

- there can be no Hohenberg–Kohn theorem for the paramagnetic current density
- observe also:

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

On the other hand, the physical current densities $j = \kappa + \rho A$ of the two systems differ:

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

- a Hohenberg–Kohn theorem for $j$ is not excluded but the purported proofs are wrong
A Kohn–Sham decomposition of the CDFT functional yields (Vignale and Rasolt):

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

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

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

\[ E_{VRG}[\nu] = \int \frac{k_F(r_s)}{24 \pi^2} \left[ g(r_s) - 1 \right] |\nu(r)|^2 \, dr, \]

- 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 $\text{H}_2$ molecule in a strong magnetic field (normal to image plane)
  - density $\rho$ (top), physical current $j^2$ (middle), and vorticity $\nu$ (bottom) of $\text{H}_2$

Hartree–Fock       Full CI

![Hartree–Fock and Full CI images for $\text{H}_2$ molecule]
BDFT: the adiabatic connection

- We may describe magnetic phenomena by setting up a separate DFT for each $B$:
  \[ E_0[v, B] = \inf_\rho (F[\rho, B] + (v|\rho)) \]

- The density functional now depends on the density and on the field strength
  \[ F[\rho, B] = \min_{\psi \to \rho} \langle \psi | T_\pi(B) + W | \psi \rangle = T_s[\rho, B] + J[\rho] + E_{xc}[\rho, B] \]

  - the noninteracting magnetic response is exactly taken care of by $T_s[\rho, B]$

- AC correlation curves of $H_2$ in a perpendicular magnetic field
  - $E_{xc}[\rho, B]$ differs 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