Calculation and modeling of adiabatic-connection curves

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The universal density functional and Lieb’s theory

Evaluation of density functionals by Lieb maximization

The adiabatic connection

Dynamical correlation in the adiabatic connection

Static correlation in the adiabatic connection

Range-separated methods and the generalized adiabatic connection

Conclusions
The Levy constrained-search functional

- The ground-state energy with external potential $v$ and coupling strength $\lambda$:
  \[
  E_\lambda[v] = \inf_{\psi \to N} \langle \psi | H_\lambda[v] | \psi \rangle
  \]
  \[
  H_\lambda[v] = T + \lambda W + \sum_i v(r_i), \quad W = \sum_{i>j} r_{ij}^{-1}, \quad 0 \leq \lambda \leq 1
  \]

- It is possible to perform this minimization in two steps
  \[
  E_\lambda[v] = \inf_{\rho \to N} \left( F_\lambda[\rho] + \int v(r) \rho(r) \, dr \right)
  \]
  Hohenberg–Kohn variation principle
  \[
  F_\lambda[\rho] = \inf_{\psi \to \rho} \langle \psi | H_\lambda[0] | \psi \rangle
  \]
  Levy constrained-search functional

- In applications of DFT, approximations to $F_\lambda[\rho]$ are made
  - typically assessed by comparison with experiment

- We are going to present rigorous evaluations of $F_\lambda[\rho]$
  - provide insight into $F_\lambda[\rho]$ and its dependence on static and dynamical correlation
  - test approximate $F_\lambda[\rho]$ and suggest new ones

- Our tool will be the adiabatic connection
  - the dependence of $F_\lambda[\rho]$ on $\lambda$ for fixed $\rho$: $F_0[\rho] \to F_1[\rho]$

- For such studies, a slightly different formulation of DFT is useful
The Lieb convex-conjugate functional

- In Lieb’s theory (1983), \( F_\lambda [\rho] \) is defined as the convex conjugate to \( E_\lambda [v] \):

\[
F_\lambda [\rho] = \sup_v (E_\lambda [v] - \int \nu(r) \rho(r) \, dr)
\]

the Lieb variation principle

\[
E_\lambda [v] = \inf_\rho (F_\lambda [\rho] + \int \nu(r) \rho(r) \, dr)
\]

the Hohenberg–Kohn variation principle

- The two variation principles are Legendre–Fenchel (LF) transforms

- The possibility of the LF formulation follows from the convexity of \(-E_\lambda [v]\) in \(v\):

\[
\int f(x_1) - f(x_2) \geq \int f(c x_1 + (1-c) x_2) - f(c x_1 + (1-c) x_2)
\]

- it then has a convex conjugate partner: the Lieb functional \( F_\lambda [\rho] \)

- Conjugate functions have inverse first derivatives

- A convex functional and its conjugate partner satisfy Fenchel’s inequality:

\[
F_\lambda [\rho] \geq E_\lambda [v] - \int \nu(r) \rho(r) \, dr \quad \Leftrightarrow \quad E_\lambda [v] \leq F_\lambda [\rho] + \int \nu(r) \rho(r) \, dr
\]

- Either variation principle sharpens Fenchel’s inequality into an equality

- We shall use Lieb’s variation principle to calculate \( F_\lambda [\rho] \) at different levels of theory
Lieb’s theory for approximate energies

- Lieb’s theory may be applied to any exact or approximate energy that is concave:

\[
F_{\lambda}^{\text{mod}}[\rho] \quad \overset{\text{LF}}{\leftrightarrow} \quad E_{\lambda}^{\text{mod}}[\nu]
\]

- examples: the lowest state of any spin symmetry
- examples: all variationally determined energies such as \( E_{\lambda}^{\text{HF}}[\nu] \) and \( E_{\lambda}^{\text{FCI}}[\nu] \)

- For nonconcave energies, \( F_{\lambda}^{\text{mod}}[\rho] \) is well-defined but not strictly conjugate to \( E_{\lambda}^{\text{mod}}[\nu] \)
- instead, \( F_{\lambda}^{\text{mod}}[\rho] \) is conjugate to the least concave upper bound to the energy

\[
E_{\lambda}^{\text{mod}}[\nu] \overset{\text{LF}}{\rightarrow} F_{\lambda}^{\text{mod}}[\rho] \overset{\text{LF}}{\leftarrow} \tilde{E}_{\lambda}^{\text{mod}}[\nu] \geq E_{\lambda}^{\text{mod}}[\nu]
\]

- examples: \( E_{\lambda}^{\text{MP2}}[\nu] \) and \( E_{\lambda}^{\text{CCSD}}[\nu] \)
For a given density $\rho(r)$ and chosen level of theory $E_\lambda[v]$, we wish to calculate

$$F_\lambda[\rho] = \max_v \left( E_\lambda[v] - \int v(r) \rho(r) \, dr \right)$$

by maximizing the right-hand side with respect to variations in the potential $v(r)$.

The potential is parameterized as

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

where the three terms are

- the physical, external potential $v_{\text{ext}}(r)$
- the Fermi–Amaldi reference potential to ensure correct asymptotic behaviour

$$v_{\text{ref}}(r) = \left( 1 - \frac{1}{N} \right) \int \frac{\rho(r')}{|r - r'|} \, dr'$$

- an expansion in Gaussians $g_t(r)$ with coefficients $c_t$
- we use large orbital basis sets, typically augmented with diffuse functions

Implemented levels of theory of $E_\lambda[v]$ are: HF, MP2, CCD, CCSD, CCSD(T), FCI.

Wu and Yang (2003), Teale, Coriani and Helgaker (2009)
We determine $v_c(r)$ and hence $F_{\lambda}[\rho]$ by maximizing with respect to $c_t$ the quantity

$$G_{\lambda,\rho}(c) = E_{\lambda}[v_c] - \int v_c(r) \rho(r) \, dr$$

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

Our convergence target is a gradient norm smaller than $10^{-6}$.

The quasi-Newton method requires only the gradient

$$\frac{\partial G_{\lambda,\rho}(c)}{\partial c_t} = \int [\rho_{\lambda,c}(r) - \rho(r)] g_t(r) \, dr$$

implemented with BFGS update

converges in 100–200 iterations

The Newton method requires also the Hessian

$$\frac{\partial^2 G_{\lambda,\rho}(c)}{\partial c_t \partial c_u} = \int \int g_t(r) g_u(r') \frac{\delta \rho(r)}{\delta v(r')} \, dr \, dr'$$

calculated (exactly or approximately) from (CCSD) linear response theory

expensive but robust convergence in 5–10 iterations

All code is implemented in DALTON
The adiabatic connection

- HF, MP2, CCSD and CCSD(T) plots of $F_\lambda[\rho]$ for the neon atom in the cc-pVQZ basis

These are very boring curves: almost indistinguishable and nearly linear

$$F_\lambda[\rho] = \min_{\psi \to \rho} \langle \psi | T + \lambda W | \psi \rangle \quad \text{slight concavity from variation principle}$$

- Note the noninteracting limit:

$$F_0[\rho] = \min_{\psi \to \rho} \langle \psi | T | \psi \rangle = T_s[\rho] \quad \text{noninteracting kinetic energy}$$
The exchange–correlation functional

- We now subtract off the boring parts: the noninteracting limit and the Coulomb energy:

\[ E_{xc,\lambda}[\rho] = F_{\lambda}[\rho] - T_s[\rho] - \lambda J[\rho] \]

exchange–correlation energy

\[ J[\rho] = \iint \rho(r_1)\rho(r_2) r_{12}^{-1} \, dr_1 dr_2 \]

Coulomb energy

- The resulting curves are negative but still concave since a linear term has been subtracted:

- The exchange energy dominates these curves (this is not always true)
- we can now distinguish the HF curve (top) from the remaining ones
The exchange and correlation functionals

- The exchange–correlation functional is typically dominated by the exchange functional:

\[ E_{x,\lambda}[\rho] = \lambda \left( \langle \psi_0 | W | \psi_0 \rangle - J[\rho] \right) < 0 \quad \text{exchange functional} \]

- the exchange energy depends linearly on \( \lambda \)

- Subtracting the exchange functional, we obtain the correlation functional:

\[ E_{c,\lambda}[\rho] = E_{xc,\lambda}[\rho] - E_{x,\lambda}[\rho] < 0 \quad \text{correlation functional} \]

- The resulting AC correlation curve is negative and concave

- The HF curve is (nearly) horizontal and (nearly) zero
- the MP2, CCSD and CCSD(T) curves are (nearly) quadratic
The AC integrand

- Being concave, \( E_{xc, \lambda}[\rho] \) may be represented in terms of a decreasing AC integrand:

\[
E_{xc, \lambda}[\rho] = \int_0^\lambda E'_{xc, \lambda}[\rho] \, d\lambda = \int_0^\lambda W_{xc, \lambda}[\rho] \, d\lambda \quad (W_{xc, \lambda}[\rho] \text{ monotonically decreasing})
\]

- note: the AC integrand has a large constant exchange contribution (above the horizontal line)

- The Hellmann–Feynman theorem provides an explicit expression for the AC integrand:

\[
W_{xc, \lambda}[\rho] = \langle \psi_\lambda | W | \psi_\lambda \rangle - J[\rho] \quad (\text{AC integrand})
\]

- Langreth and Perdew 1975, Gunnarsson and Lindqvist 1976
A geometrical view of the adiabatic connection

The exchange energy of $\text{H}_2$ at $R = 5a_0$

$$E_X = \langle \psi_0 | W'_{\lambda} | \psi_0 \rangle - J'_{\lambda}[\rho] = E_X$$

$W_0$
A geometrical view of the adiabatic connection

The (total) correlation energy of $\text{H}_2$ at $R = 5a_0$

\[ \langle \psi_0 | W'_\lambda | \psi_0 \rangle - J'_\lambda[\rho] = E_X \]

\[ \langle \psi_1 | W'_\lambda | \psi_1 \rangle - J'_\lambda[\rho] = E_C \]
A geometrical view of the adiabatic connection

The kinetic correlation energy of H$_2$ at $R = 5a_0$

\[ \langle \psi_0 | W'_\lambda | \psi_0 \rangle - J'_\lambda[\rho] = E_X \]

\[ \langle \psi_1 | W'_\lambda | \psi_1 \rangle - J'_\lambda[\rho] = E_C \]
A geometrical view of the adiabatic connection

The exchange–correlation energy of $H_2$ at $R = 5a_0$

\[
\langle \psi_0 | W_\lambda | \psi_0 \rangle - J'_\lambda[\rho] = E_X
\]

\[
\langle \psi_1 | W_\lambda | \psi_1 \rangle - J'_\lambda[\rho]
\]

Helgaker et al. (CTCC, University of Oslo)
Basis-set convergence of the AC integrand
He atom in the aug-cc-pVDZ basis

\[ E_{XC} \text{aug-cc-pVDZ} = -1.04964 \text{ a.u.} \]

\[ E_{XC} \text{aug-cc-pVDZ (FCI)} = -1.04973 \text{ a.u.} \]

\[ 0.00009 \text{ a.u.} \]
Basis-set convergence of the AC integrand
He atom in the aug-cc-pVTZ basis

\[ E_{XC \text{ aug-cc-pVTZ}} = -1.06252 \text{ a.u.} \]

\[ E_{XC \text{ aug-cc-pVTZ (FCI)}} = -1.06253 \text{ a.u.} \]

\[ 0.00001 \text{ a.u.} \]
Basis-set convergence of the AC integrand
He atom in the aug-cc-pVQZ basis

\[ E_{XC \text{ aug-cc-pVQZ}} = -1.06500 \text{ a.u.} \]

\[ E_{XC \text{ aug-cc-pVQZ (FCI)}} = -1.06500 \text{ a.u.} \]
Basis-set convergence of the AC integrand

He atom in the aug-cc-pV5Z basis

\[ E_{XC \text{ aug-cc-pV5Z}} = -1.06597 \text{ a.u.} \]

\[ E_{XC \text{ aug-cc-pV5Z (FCI)}} = -1.06597 \text{ a.u.} \]
Basis-set convergence of the AC integrand

He atom in the aug-cc-pV6Z basis

\[ E_{XC \ fcc-pV6Z} = -1.06631 \text{ a.u.} \]

\[ E_{XC \ fcc-pV6Z \ (FCI)} = -1.06631 \text{ a.u.} \]
Basis-set convergence of the AC integrand

Extrapolated FCI basis-set limit of the He atom

\[ E_{\text{XC Extrap.}} = -1.06677 \text{ a.u.} \]

\[ E_{\text{XC Extrap (FCI)}} = -1.06678 \text{ a.u.} \]
The energy may equivalently be expressed as a functional of density or potential:

\[ E_\lambda[v] = \inf_\rho \left( F_\lambda[\rho] + \int v(r)\rho(r)\,dr \right) \quad \text{the Hohenberg–Kohn variation principle} \]

\[ F_\lambda[\rho] = \sup_v \left( E_\lambda[v] - \int v(r)\rho(r)\,dr \right) \quad \text{the Lieb variation principle} \]

- we normally generate \( E_\lambda[v] \) by minimization with respect to \( \rho(r) \)
- here we consider the opposite, generating \( F_\lambda[\rho] \) by maximization with respect to \( v(r) \)

This conjugate relationship holds at all levels for which \( E_\lambda[v] \) is concave:

\[ E_\lambda[v] \xrightarrow{\text{LF}} F_\lambda[\rho] \xrightarrow{\text{LF}} \con E_\lambda[v] \geq E_\lambda[v] \]

- We have discussed the general shape of AC curves
  - Coulomb, exchange and correlation
- We shall now calculate \( F_\lambda[\rho] \) at different levels of theory
  - different basis sets and basis-set convergence
  - neon and water (dynamic correlation)
  - dissociation of \( \text{H}_2 \) (static correlation)
- We shall finally consider generalized adiabatic connections
  - spatial decomposition of the exchange–correlation energy
The Hartree–Fock universal density functional

- We first consider the universal density functional in Hartree–Fock (HF) theory

\[
E_{\lambda}^{\text{HF}}[\nu] = \inf_{\rho} \left( F_{\lambda}^{\text{HF}}[\rho] + \int \nu(r) \rho(r) \, dr \right) \quad \text{the HF Hohenberg–Kohn variation principle}
\]

\[
F_{\lambda}^{\text{HF}}[\rho] = \sup_{\nu} \left( E_{\lambda}^{\text{HF}}[\nu] - \int \nu(r) \rho(r) \, dr \right) \quad \text{the HF Lieb variation principle}
\]

- In HF theory, the wave function remains one-determinantal at all \( 0 \leq \lambda \leq 1 \)
  - the effective potential changes smoothly so as to reproduce the HF density at all \( \lambda \)
    \[\nu_{s}(r) \quad \text{(local potential at } \lambda = 0) \quad \rightarrow \quad \hat{\nu}_{\text{HF}} \quad \text{(nonlocal potential at } \lambda = 1)\]
  - the orbitals and orbital energies become \( \lambda \)-dependent

- The HOMO–LUMO gap opens up as the KS potential transforms into the Fock potential

![Graph showing eigenvalues and orbitals as a function of \( \lambda \)]
The Hartree–Fock adiabatic-connection curve

- The HF energy has a tiny 'correlation' contribution ($-2.1 \text{ mH for water}$)
  - the orbitals change with increasing $\lambda$ but always provide the same density
  - at $\lambda = 0$, the kinetic energy is minimized; at $\lambda = 1$, the total energy is minimized
  - the associated orbital-relaxation energy is proportional to $\lambda^2$

- The AC correlation curve is therefore very nearly a straight line

- In HF-OEP theory, the energy is slightly higher than the HF energy (by $2.2 \text{ mH}$)
  - in OEP, we insist on a local potential for an explicit exchange functional
  - we likewise have a local potential but have no constraints on the functional
The MP2 and CCSD correlation energies

the neon atom

▶ The MP2 and CCSD curves are not straight but bend slightly upwards
  ▶ the MP2 curve lies below the CCSD curve

▶ A linear curve would reflect a $\lambda^2$ dependence of the correlation energy
  ▶ why does the curve bend?

![Diagram showing the relationship between $W_{XC,\lambda}$ and $-T_{C}[\rho]$]
The MP2 and CCSD correlation energies
the water molecule

- The MP2 and CCSD curves are not straight but bend slightly upwards
  - the MP2 curve lies below the CCSD curve

A linear curve would reflect a $\lambda^2$ dependence of the correlation energy
- why does the curve bend?
Two-parameter CCSD correlation curves

- Second-order perturbation theory suggests the following model:

\[ E^{D}_{c,\lambda}[\rho] = -\frac{\lambda^2 w^2}{h + \lambda g} \Rightarrow W^{D}_{c,\lambda}[\rho] = -\frac{w^2 \lambda (2h + g \lambda)}{(h + g \lambda)^2} = -\frac{2w^2}{h} \lambda + \mathcal{O}(\lambda^2) \]

- We set \( w = g \) and then use \( h \) and \( g \) to reproduce exactly initial slope and end point.

- This two-parameter model agrees perfectly with the calculated AC points:
  - curvature follows from increasing HOMO–LUMO gap.
The adiabatic connection: the triples correction
the neon atom

- The CCSD(T) curve lies slightly below the CCSD curve
  - the difference increases with increasing $\lambda$

- An inspection of the triples correction suggests that it behaves like $\lambda^3$
  - the difference between the CCSD and CCSD(T) integrands should behave like $\lambda^2$
  - an almost perfect fit is possible with a one-parameter quadratic curve

$$E_{c,\lambda}[\rho] = -\frac{\lambda^3 w^3}{(h + \lambda g)^2} \quad \Rightarrow \quad W_{c,\lambda}^{\text{CCSD(T)}}[\rho] - W_{c,\lambda}^{\text{CCSD}}[\rho] = -\frac{w^3 \lambda^2 (3h + g \lambda)}{(h + g \lambda)^3} = -\frac{3w^3}{h^2} \lambda^2 + \mathcal{O}(\lambda^3) \approx -0.0189\lambda^2$$
The adiabatic connection: the triples correction
the water molecule

- The CCSD(T) curve lies slightly below the CCSD curve
  - the difference increases with increasing $\lambda$

An inspection of the triples correction suggests that it behaves like $\lambda^3$
  - the difference between the CCSD and CCSD(T) integrands should behave like $\lambda^2$
  - an almost perfect fit is possible with a one-parameter quadratic curve

$$W_{c,\lambda}^T[\rho] \approx -0.0256\lambda^2$$
Part of the motivation for studying the AC is to develop **new functionals**
- simple forms can be turned directly into functionals by integration
- famous example: the Becke HH functional by linear interpolation

Note: all such AC forms are only as good as their **input data**
- we must also provide a recipe for producing input data

Previous work:
- Ernzerhof (1996)
- Burke *et al.* (1997)
- Seidl *et al.* (2000)
- Mori-Sánchez *et al.* (2007)
- Peach *et al.* (2008)

In the **absence of accurate data**, there was little to differentiate the various AC forms
- none of the suggested forms reproduce our data

We have studied the AC curves for systems dominated by **dynamical correlation**
- we shall now see if they are sufficiently flexible for **static correlation**
To study static 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$_2$

At short distances, exchange ($-0.827E_h$) dominates over correlation ($-0.039E_h$) energy.

- BLYP curve performs well, reproducing HF exchange and FCI correlation.
- The BLYP and CI curves are nearly linear, indicative of dynamical correlation.
The overall picture is similar to that at $R = 0.7$ bohr.

Most notably, the exchange energy decreases in magnitude from $-827$ to $-661$ m$E_h$

The correlation energy increases slightly in magnitude, from $-39$ to $-41$ m$E_h$
The exchange energy decreases further in magnitude from $-661$ to $-477 \, mE_h$

The correlation energy increases in magnitude from $-41$ to $-77 \, mE_h$

The FCI curve now curves more strongly, indicative of static correlation

The BLYP functional overestimates exchange but works well by LYP error cancellation
The overall picture is similar to that at $R = 3.0$ bohr.

However, the static-correlation curvature of the FCI curve is now more pronounced.

The (nonconvex) BLYP curve strongly underestimates the magnitude of the XC energy.

The BLYP curve now benefits less from error cancellation.
At $R = 10$ bohr, the two atoms are separated and correlation is essentially static.

- Dynamical correlation is now less than 1 $E_h$ (dispersion).
- The BLYP functional works mostly by overestimating the exchange energy.
- It still has a nonzero slope, indicative of dynamic correlation!

![Graph showing XC curves for $H_2$](image)
Adiabatic connection: correlation-only curves for H₂

\( R = 0.7 \text{ bohr} \)

- The correlation-only AC curve illustrates the performance of the LYP functional
  - it performs in much the same manner for helium and two separated hydrogen atoms
  - its construction was based on the helium atom
- Below, blue and yellow areas represent kinetic and total correlation FCI energies
The correlation-only AC curve illustrates the performance of the LYP functional:
- it performs in much the same manner for helium and two separated hydrogen atoms;
- its construction was based on the helium atom.

Below, blue and yellow areas represent kinetic and total correlation FCI energies.

$R = 1.4$ bohr

$R = 0.7$ bohr
Adiabatic connection: correlation-only curves for H$_2$

$R = 3.0$ bohr

- The correlation-only AC curve illustrates the performance of the LYP functional
  - it performs in much the same manner for helium and two separated hydrogen atoms
  - its construction was based on the helium atom
- Below, blue and yellow areas represent kinetic and total correlation FCI energies
Adiabatic connection: correlation-only curves for H\textsubscript{2}

\( R = 5.0 \) bohr

- The correlation-only AC curve illustrates the performance of the LYP functional
  - it performs in much the same manner for helium and two separated hydrogen atoms
  - its construction was based on the helium atom
- Below, blue and yellow areas represent kinetic and total correlation FCI energies
Adiabatic connection: correlation-only curves for $H_2$

$R = 7.0$ bohr

- The correlation-only AC curve illustrates the performance of the LYP functional
  - it performs in much the same manner for helium and two separated hydrogen atoms
  - its construction was based on the helium atom
- Below, blue and yellow areas represent kinetic and total correlation FCI energies
Adiabatic connection: XC curves for H$_2$

$R = 10.0$ bohr

- The correlation-only AC curve illustrates the performance of the LYP functional.
  - It performs in much the same manner for helium and two separated hydrogen atoms.
  - Its construction was based on the helium atom.
- Below, blue and yellow areas represent kinetic and total correlation FCI energies.

![Graph showing XC curves for H$_2$ with $R = 10.0$ bohr and LYP, HF, and FCI curves.]
The two-parameter model applied to the $H_2$ molecule

- Application of the two-parameter doubles model to the FCI dissociation of $H_2$:

\[ W^{D}_{c,\lambda}[\rho] = -\frac{w^2\lambda(2h + g\lambda)}{(h + g\lambda)^2} \quad \text{based on perturbation theory} \]

- the dashed lines obtained by using the exact initial gradient and exact end point
- the full lines obtained by a least-squares fit to all points

![Graph showing the dissociation of $H_2$]
A two-parameter CI model applied to the $\text{H}_2$ molecule

- A better two-parameter model is obtained from a two-level CI model

\[
\mathcal{E}_{\lambda,c}[\rho] = \frac{1}{2} \Delta E - \frac{1}{2} \sqrt{\Delta E^2 + 4w^2\lambda^2}, \quad \Delta E = h + g\lambda
\]

\[
\mathcal{W}_{\lambda,c}[\rho] = \frac{1}{2} g - \frac{g(h + g\lambda) + 4w^2\lambda}{2\sqrt{(h + g\lambda)^2 + 4w^2\lambda^2}}
\]

- excellent least-square fits with two adjustable parameters
- good fits to initial gradient and end point
Generalized, range-separated adiabatic connection

- Up to now, we have studied the AC with a uniformly scaled two-electron interaction
- We shall now consider range-separated adiabatic interactions

\[ w^s_\lambda(r_{ij}) = \frac{\lambda}{r_{ij}} \]
\[ w^e_\lambda(r_{ij}) = \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} \]
\[ w^g_\lambda(r_{ij}) = \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right) \]

- As \( \lambda \) increases, we build up the full interaction from outer to inner region
  - this provides an alternative view of correlation
  - such ACs are of particular relevance for range-separated methods
Damping with error function

\[ \lambda = 0.0 \]

- Comparison of the full Coulomb potential with the **err** and **err–gau** potentials

\[
\begin{align*}
    w^e_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} \\
    w^g_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right)
\end{align*}
\]

**err potential**

**err–gau potential**
Damping with error function

\( \lambda = 0.1 \)

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
\text{err potential} & \quad w^e_\lambda(r_{ij}) = \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} \\
\text{err–gau potential} & \quad w^g_\lambda(r_{ij}) = \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right)
\end{align*}
\]
Damping with error function

\( \lambda = 0.2 \)

Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
  w_\lambda^e(r_{ij}) &= \text{erf} \left( \frac{\lambda}{1-\lambda} \frac{r_{ij}}{r_{ij}} \right) \\
  w_\lambda^g(r_{ij}) &= \text{erf} \left( \frac{\lambda}{1-\lambda} \frac{r_{ij}}{r_{ij}} \right) - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right)
\end{align*}
\]

\( w_\lambda^e(r_{ij}) \) \textit{err potential}

\( w_\lambda^g(r_{ij}) \) \textit{err–gau potential}
Damping with error function
\( \lambda = 0.3 \)

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
w^e_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} \quad \text{err potential} \\
\lambda^g_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left(\frac{\lambda}{1-\lambda}\right) \exp\left(-\frac{1}{3} \left(\frac{\lambda}{1-\lambda}\right)^2 r_{ij}^2\right) \quad \text{err–gau potential}
\end{align*}
\]
Damping with error function

\[ \lambda = 0.4 \]

- Comparison of the full Coulomb potential with the **err** and **err–gau** potentials

\[
\begin{align*}
    w^e_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} \quad &\text{err potential} \\
    w^g_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right) \quad &\text{err–gau potential}
\end{align*}
\]
Damping with error function

$\lambda = 0.5$

Comparison of the full Coulomb potential with the err and err–gau potentials

\[
\begin{align*}
  w^e_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} \\
  w^g_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left(\frac{\lambda}{1-\lambda}\right) \exp\left(-\frac{1}{3} \left(\frac{\lambda}{1-\lambda}\right)^2 r_{ij}^2\right)
\end{align*}
\]

**err potential**

**err–gau potential**
Damping with error function

\( \lambda = 0.6 \)

- Comparison of the full Coulomb potential with the \text{err} and \text{err–gau} potentials

\[
\begin{align*}
w^e_\lambda(r_{ij}) &= \text{erf}\left( \frac{\lambda}{1-\lambda} r_{ij} \right) \\
w^g_\lambda(r_{ij}) &= \frac{\text{erf}\left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right)
\end{align*}
\]

\text{err potential} \hspace{1em} \text{err–gau potential}
Damping with error function

$\lambda = 0.7$

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
w^e_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} & \text{err potential} \\
w^g_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right) & \text{err–gau potential}
\end{align*}
\]
Damping with error function

\( \lambda = 0.8 \)

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
    w^e_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1 - \lambda} r_{ij}\right)}{r_{ij}} \\
    w^g_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1 - \lambda} r_{ij}\right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left(\frac{\lambda}{1 - \lambda}\right) \exp \left(-\frac{1}{3} \left(\frac{\lambda}{1 - \lambda}\right)^2 r_{ij}^2\right)
\end{align*}
\]

\( w^e_\lambda(r_{ij}) \) - \textit{err potential}

\( w^g_\lambda(r_{ij}) \) - \textit{err–gau potential}
Damping with error function

\( \lambda = 0.9 \)

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
    w^e_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} \quad \text{err potential} \\
    w^g_\lambda(r_{ij}) &= \frac{\text{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left(\frac{\lambda}{1-\lambda}\right) \exp\left(-\frac{1}{3} \left(\frac{\lambda}{1-\lambda}\right)^2 r_{ij}^2\right) \quad \text{err–gau potential}
\end{align*}
\]
Damping with error function
\( \lambda = 1.0 \)

- Comparison of the full Coulomb potential with the \textit{err} and \textit{err–gau} potentials

\[
\begin{align*}
w^e_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} \\
\text{err potential} \\

w^g_\lambda(r_{ij}) &= \frac{\text{erf} \left( \frac{\lambda}{1-\lambda} r_{ij} \right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left( \frac{\lambda}{1-\lambda} \right) \exp \left( -\frac{1}{3} \left( \frac{\lambda}{1-\lambda} \right)^2 r_{ij}^2 \right) \\
\text{err–gau potential}
\end{align*}
\]
AC correlation curves for the He isoelectronic series

$Z = 1$

- **Standard AC curve** on the left
  - linearity increases with increasing $Z$
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

$Z = 2$

- Standard AC curve on the left
  - linearity increases with increasing $Z$
- Range-separated (erf–gau) AC curve on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

$Z = 3$

- **Standard AC curve** on the left
  - linearity increases with increasing $Z$
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

$Z = 4$

- **Standard AC curve** on the left
  - linearity increases with increasing $Z$
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

\( Z = 5 \)

- **Standard AC curve** on the left
  - linearity increases with increasing \( Z \)
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing \( Z \)
AC correlation curves for the He isoelectronic series

$Z = 6$

- **Standard AC curve** on the left
  - linearity increases with increasing $Z$
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

\( Z = 7 \)

- **Standard AC curve** on the left
  - linearity increases with increasing \( Z \)
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing \( Z \)
AC correlation curves for the He isoelectronic series

\( Z = 8 \)

- Standard AC curve on the left
  - linearity increases with increasing \( Z \)
- Range-separated (erf–gau) AC curve on the right
  - curves reveal increasing compactness with increasing \( Z \)
AC correlation curves for the He isoelectronic series

$Z = 9$

- **Standard AC curve** on the left
  - linearity increases with increasing $Z$
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing $Z$
AC correlation curves for the He isoelectronic series

Z = 10

- **Standard AC curve** on the left
  - linearity increases with increasing Z
- **Range-separated (erf–gau) AC curve** on the right
  - curves reveal increasing compactness with increasing Z
Range separation: dissociation of $\text{H}_2$
the total AC curve at internuclear separation 0.7 bohr

- We consider the **total AC curve** first
  - includes Coulomb, exchange and correlation contributions
- **Standard AC curve** on the left
  - it undergoes the usual transition from a sloped to horizontal curve at full separation
  - this reflects the transition from dynamical to static correlation
- **Range-separated erf–gau AC curve** on the right
  - it moves towards small $\lambda$ values with increasing separation
  - at full separation, all total interactions are interatomic

![Graphs showing AC curves](image-url)
Range separation: dissociation of H$_2$
the total AC curve at internuclear separation 1.4 bohr

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Range separation: dissociation of $\text{H}_2$

the total AC curve at internuclear separation 3.0 bohr

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Range separation: dissociation of $H_2$
the total AC curve at internuclear separation 5.0 bohr

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  - at full separation, all total interactions are interatomic
Range separation: dissociation of $H_2$
the total AC curve at internuclear separation 7.0 bohr

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  - includes Coulomb, exchange and correlation contributions

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  - this reflects the transition from dynamical to static correlation

- Range-separated erf–gau AC curve on the right
  - it moves towards small $\lambda$ values with increasing separation
  - at full separation, all total interactions are interatomic
Range separation: dissociation of H\textsubscript{2}
the total AC curve at internuclear separation 10.0 bohr

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  - includes Coulomb, exchange and correlation contributions
- Standard AC curve on the left
  - it undergoes the usual transition from a sloped to horizontal curve at full separation
  - this reflects the transition from dynamical to static correlation
- Range-separated erf–gau AC curve on the right
  - it moves towards small $\lambda$ values with increasing separation
  - at full separation, all total interactions are interatomic
Range separation: dissociation of $\text{H}_2$
the correlation-only AC curve at internuclear separation 0.7 bohr

- We next consider the correlation-only AC curve
- **Standard AC curve** on the left
  - it undergoes the same transition from a sloped to horizontal curve
  - this reflects the transition from dynamical to static correlation
- **Range-separated erf–gau AC curve** on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel

- Static correlation is not easily treated by range separation
Range separation: dissociation of $\text{H}_2$
the correlation-only AC curve at internuclear separation 1.4 bohr

- We next consider the correlation-only AC curve.
- **Standard AC curve** on the left:
  - it undergoes the same transition from a sloped to horizontal curve.
  - this reflects the transition from dynamical to static correlation.
- **Range-separated erf–gau AC curve** on the right:
  - at short bond distance, the interactions are predominantly short-ranged.
  - at long distances, short- and long-ranged interactions partially cancel.

- Static correlation is not easily treated by range separation.
Range separation: dissociation of $H_2$
the correlation-only AC curve at internuclear separation 3.0 bohr

- We next consider the correlation-only AC curve

- Standard AC curve on the left
  - it undergoes the same transition from a sloped to horizontal curve
  - this reflects the transition from dynamical to static correlation

- Range-separated erf–gau AC curve on the right
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- Static correlation is not easily treated by range separation
Range separation: dissociation of $\text{H}_2$

the correlation-only AC curve at internuclear separation 5.0 bohr

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Static correlation is not easily treated by range separation
Range separation: dissociation of $\text{H}_2$
the correlation-only AC curve at internuclear separation 7.0 bohr

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Range separation: dissociation of $\text{H}_2$
the correlation-only AC curve at internuclear separation 10.0 bohr

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  - at long distances, short- and long-ranged interactions partially cancel

Static correlation is not easily treated by range separation
Conclusions

- We have calculated the universal density functional by Lieb maximization
  - Newton and quasi-Newton methods
  - many standard levels of theory: HF, MP2, CCSD, CCSD(T), BLYP
  - many-electron atoms and molecules

- We have presented accurate adiabatic-connection (AC) curves
  - total, exchange–correlation and correlation-only curves

- We have discussed the shape of the AC curves
  - static correlation give horizontal curves
  - dynamical correlation gives slanted curves
  - doubles give approximately linear curves; triples add quadratic correction
  - these curves can be accurately modeled with few parameters

- We have studied the dissociation of H$_2$
  - HF, BLYP and FCI

- We have presented range-separated AC curves
  - short- and long-range correlation
  - static and dynamical correlation