RPA and the adiabatic connection

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Université Pierre et Marie Curie, Jussieu campus, Paris, France

Outline

- Calculating $F_\lambda[\rho]$
  - The Levy constrained-search and Lieb convex-conjugate functionals
  - Performing the Lieb maximization
- The Adiabatic Connection
  - The Decomposition of $F_\lambda[\rho]$ and coupling-strength dependence of $T_\lambda[\rho]$ and E_{xc}
  - The Adiabatic Connection Integrand
- The Adiabatic Connection and the Random Phase Approximation
  - The RPA correlation energy and the adiabatic connection fluctuation theorem
  - The relationship between RPA and coupled cluster techniques
  - Calculation of RPA and TDHF adiabatic connections
  - Comparison with standard DFT functionals
- Range-Dependent Adiabatic Connections
  - Generalized adiabatic connections (Erf, Erf-Gau)
  - The description of static correlation
- Modelling the Adiabatic Connection
  - A Constructive Route to new exchange–correlation functionals
  - Models based on Perturbation-Theory and Configuration-Interaction

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  - The RPA correlation energy in density-functional theory
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The Levy Constrained Search Functional

- The ground-state energy with external potential v and coupling strength λ:

$$E_\lambda[v] = \inf_{\Psi \to N} \langle \Psi | H_\lambda[v] | \Psi \rangle$$

$$H_\lambda[v] = T + W_\lambda + \sum_i v(\mathbf{r}_i), \quad W_\lambda = \sum_{i>j} \lambda / r_{ij}, \quad 0 \leq \lambda \leq 1$$

- It is possible to perform this minimization in two steps

$$E_\lambda[v] = \inf_{\rho \to N} \left(F_\lambda[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} \right) \quad \text{Hohenberg–Kohn variation principle}$$

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- In applications of DFT, approximations to $F_\lambda[\rho]$ are made
  - typically developed by comparison with experiment
- We are going to present evaluations of $F_\lambda[\rho]$ using wavefunction techniques
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  - test approximate $F_\lambda[\rho]$ and a constructive route to new ones
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The Lieb Convex-Conjugate Functional

- In Lieb's theory, $F_\lambda[\rho]$ is defined as the convex conjugate to $E_\lambda[v]$:

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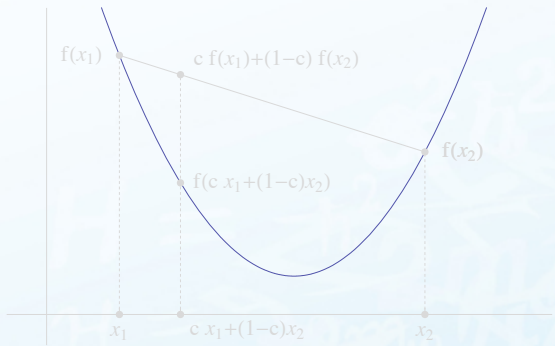
  - the two variation principles are Legendre–Fenchel (LF) transforms
- The possibility of the LF formulation follows from the convexity of $-E_\lambda[v]$ in v:



  - 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:

$$F_\lambda[\rho] \geq E_\lambda[v] - \int v(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \quad \Leftrightarrow \quad E_\lambda[v] \leq F_\lambda[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

  - 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

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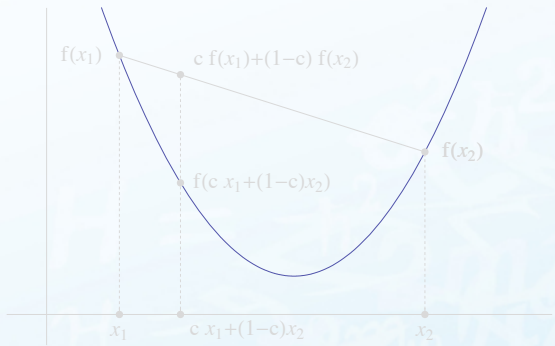

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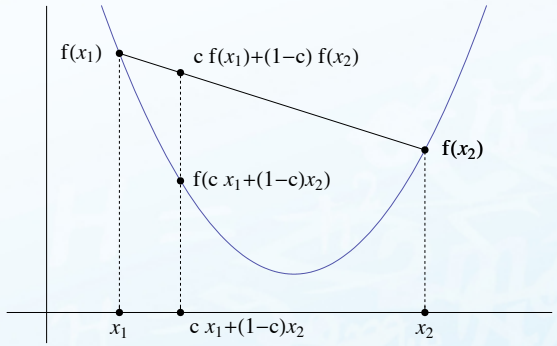

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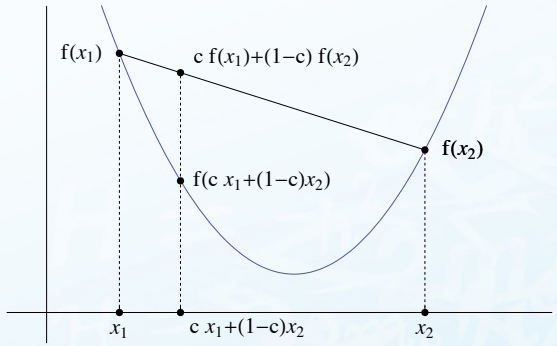

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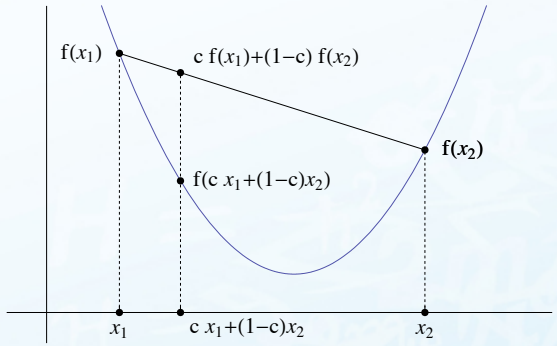

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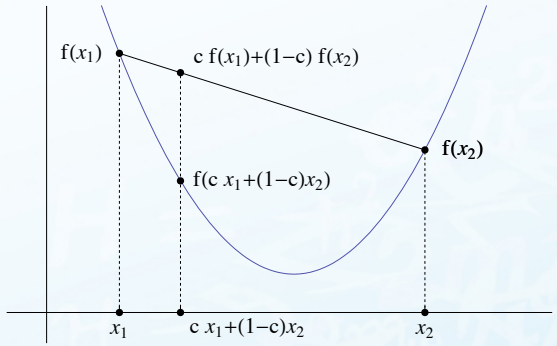

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- We shall use Lieb's variation principle to calculate $F_\lambda[\rho]$ at different levels of theory

The Lieb Convex-Conjugate Functional

- In Lieb's theory, $F_\lambda[\rho]$ is defined as the convex conjugate to $E_\lambda[v]$:

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

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

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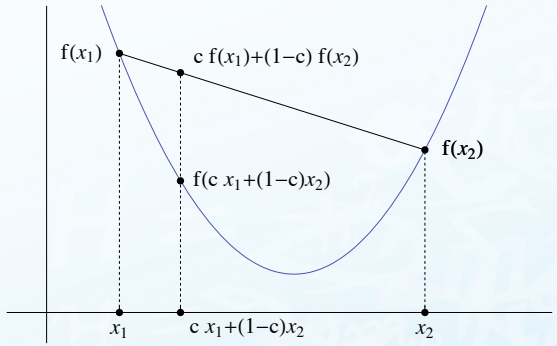

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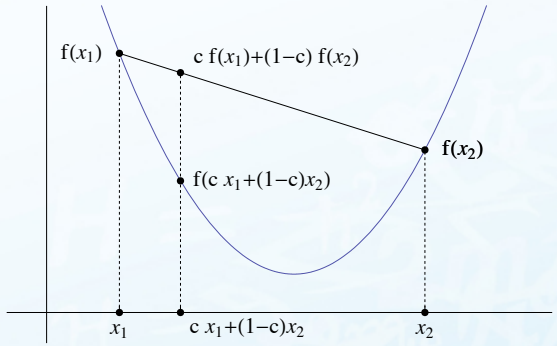

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Performing the Lieb Maximization

- For a given density $\rho(\mathbf{r})$ and chosen level of theory $E_\lambda[v]$, we wish to calculate

$$F_\lambda[\rho] = \max_v \left(E_\lambda[v] - \int v(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \right)$$

  by maximizing the right-hand side with respect to variations in the potential $v(\mathbf{r})$

- Direct-Optimization techniques are used. The potential is parameterized as

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

  where the three terms are
  - the physical, external potential $v_{\mathrm{ext}}(\mathbf{r})$
  - the Fermi–Amaldi reference potential to ensure correct asymptotic behaviour

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

  - an expansion in Gaussians $g_t(\mathbf{r})$ with coefficients c_t
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- Implemented levels of theory of $E_\lambda[v]$ are: HF, RPA, dRPA, MP2, CCD, CCSD, CCSD(T)

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First- and second-order Lieb maximizations

- We determine $v_{\mathbf{c}}(\mathbf{r})$ and hence $F_\lambda[\rho]$ by maximizing with respect to c_t the quantity

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- Our convergence target is a gradient norm smaller than 10^{-6}
- The quasi-Newton method requires only the gradient

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  - Implemented with BFGS update
  - Converges in 100–200 iterations
- The Newton method also requires the Hessian

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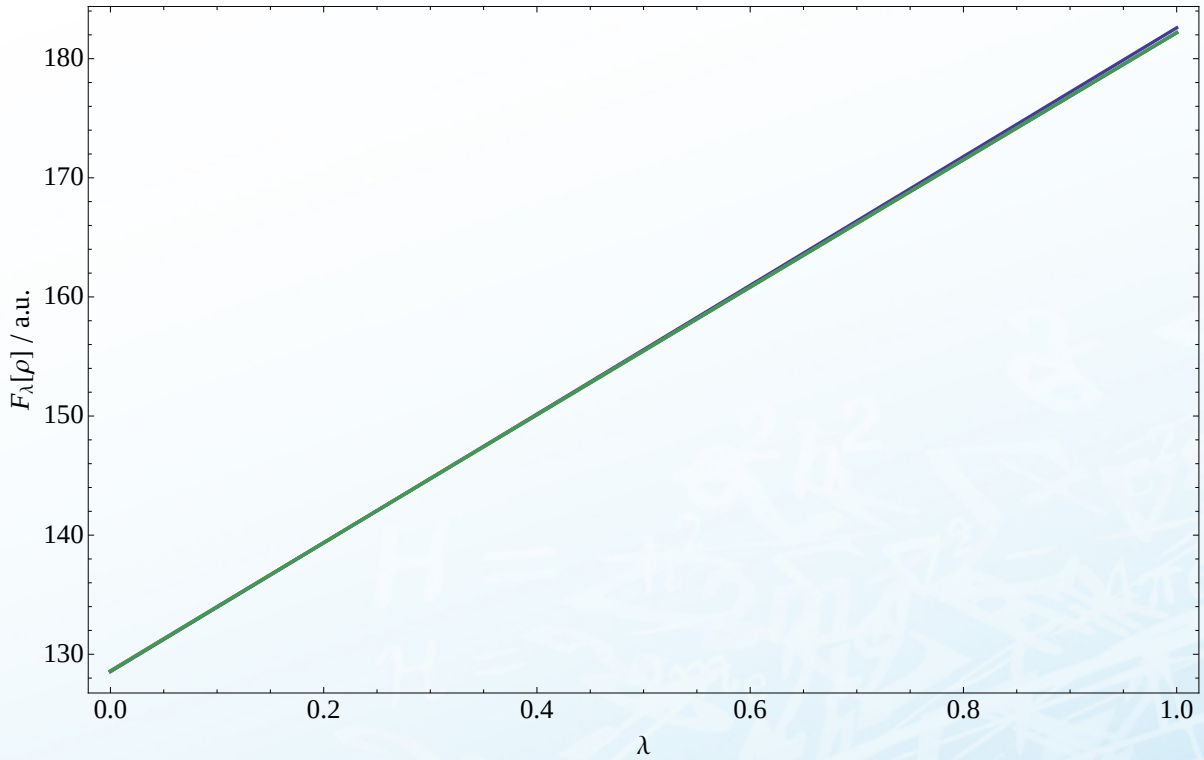
Calculating $F_\lambda[\rho]$

- 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

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

- Note the noninteracting limit:

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

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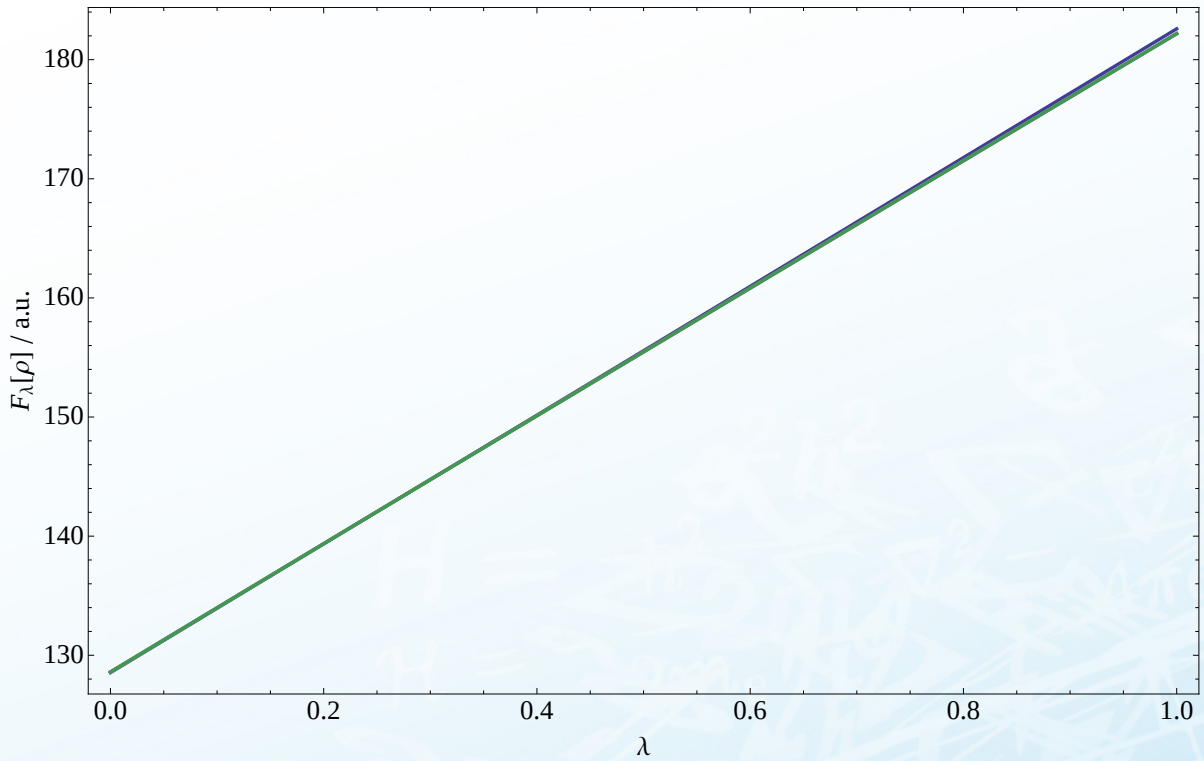

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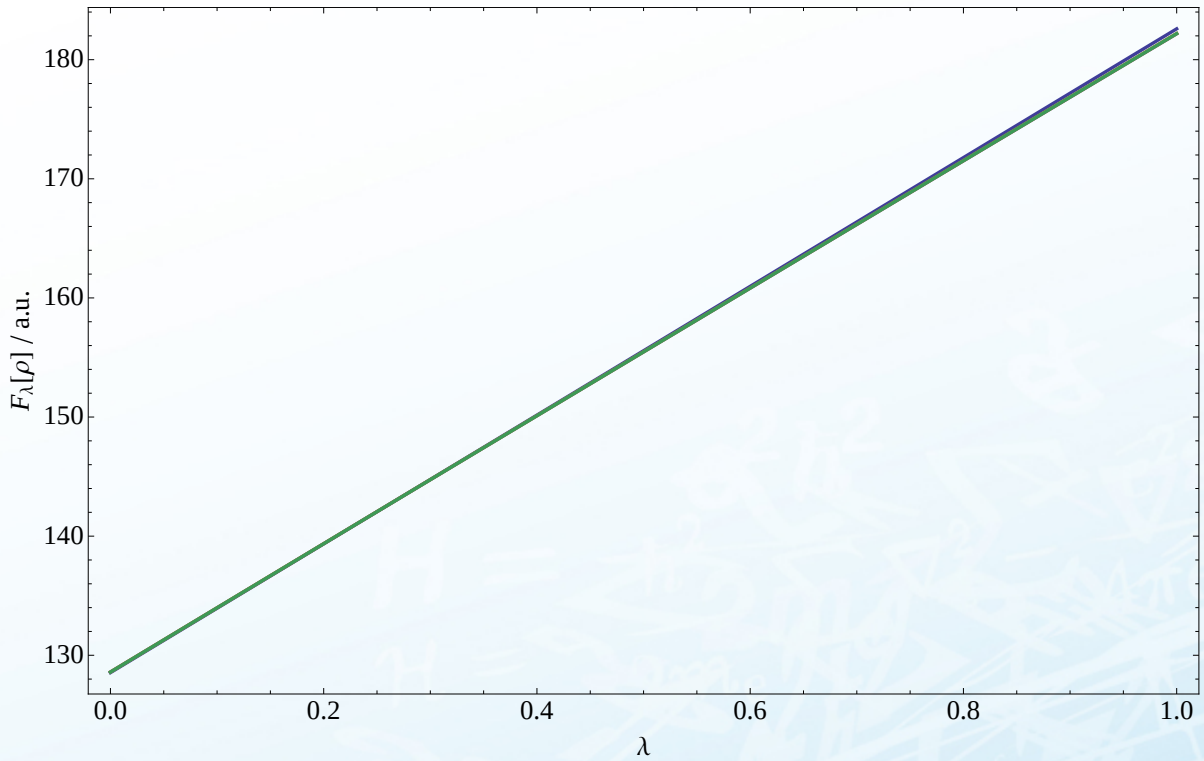

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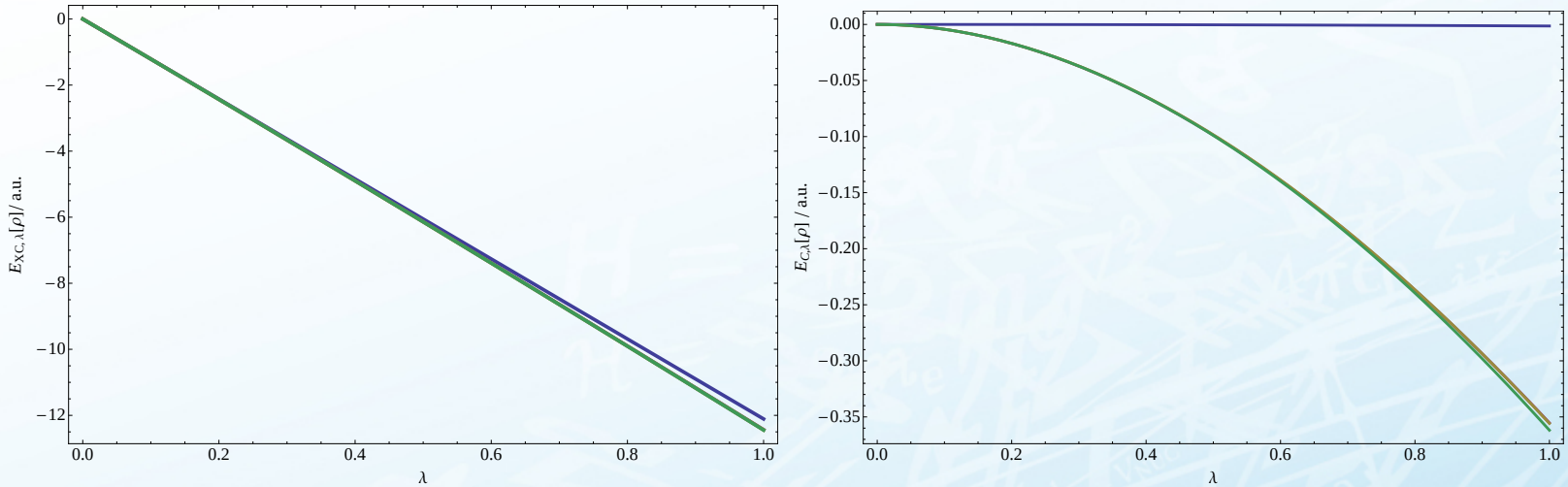
The Decomposition of $F_\lambda[\rho]$

- We usually decompose $F_\lambda[\rho]$ into known and unknown contributions

$$F_\lambda[\rho] = T_\mathrm{s}[\rho] + J_\lambda[\rho] + E_{\mathrm{x},\lambda}[\rho] + E_{\mathrm{c},\lambda}[\rho]$$

- Let's focus on the latter two components of interest ($E_{\mathrm{xc},\lambda}$ on the left, $E_{\mathrm{c},\lambda}$ on the right)



- For $E_{\mathrm{xc},\lambda}$ the exchange energy dominates in this example $\longrightarrow$ almost linear
- Removing the exchange contribution shows the dependence of the correlation energy on $\lambda \longrightarrow$ almost quadratic
- Importantly, both are concave in λ

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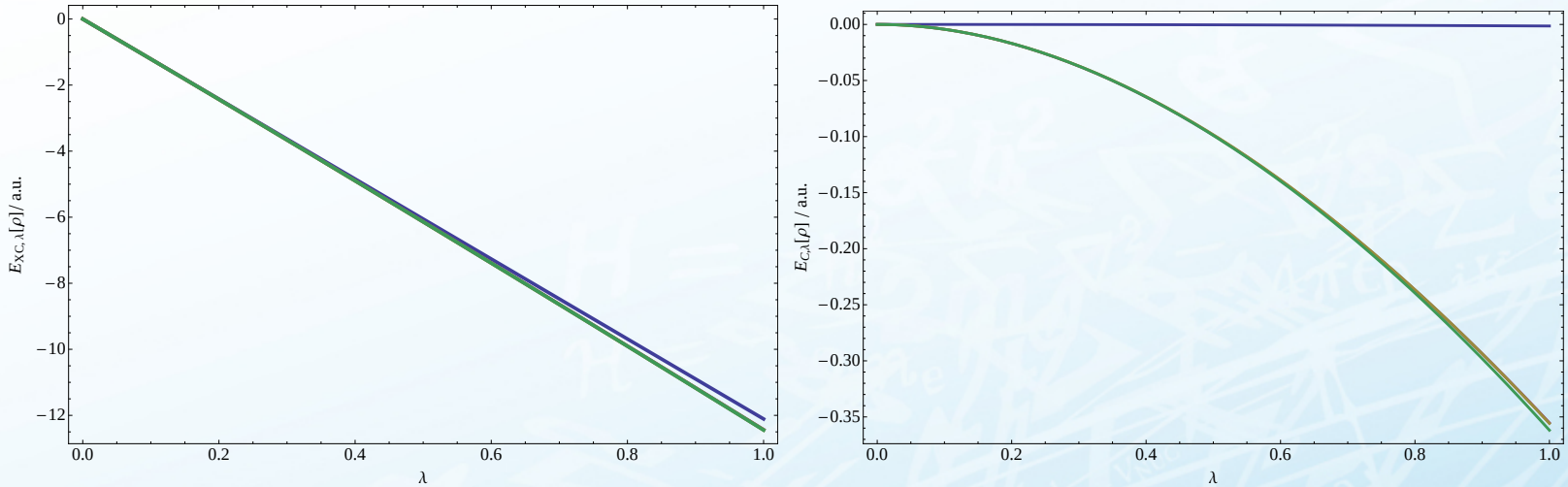

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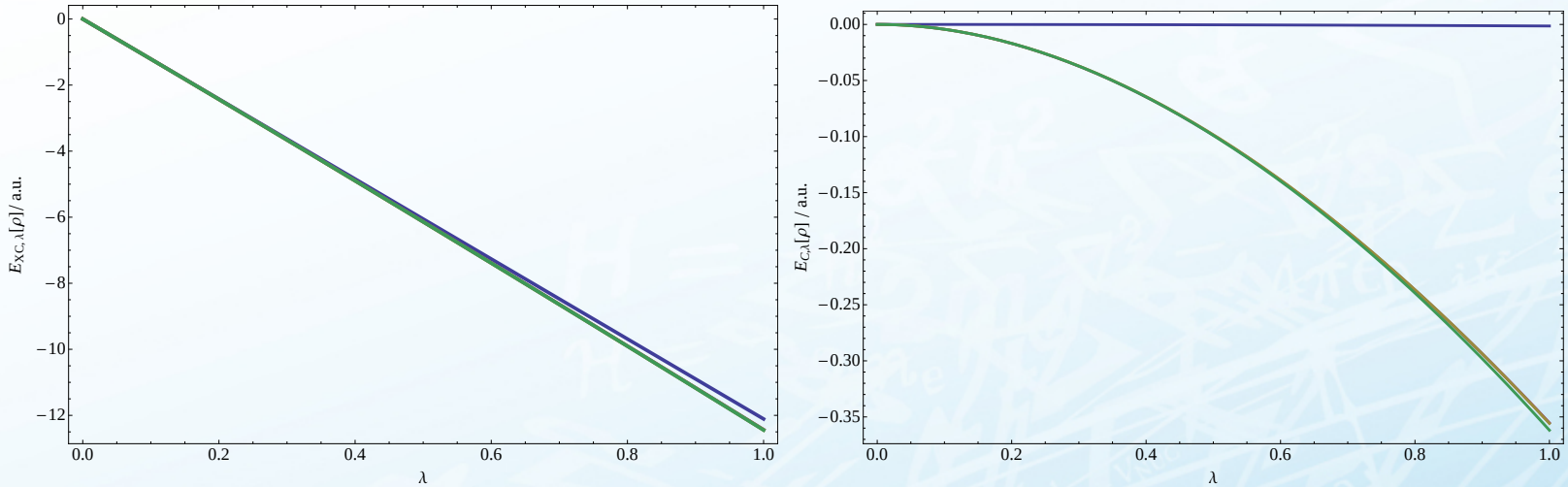

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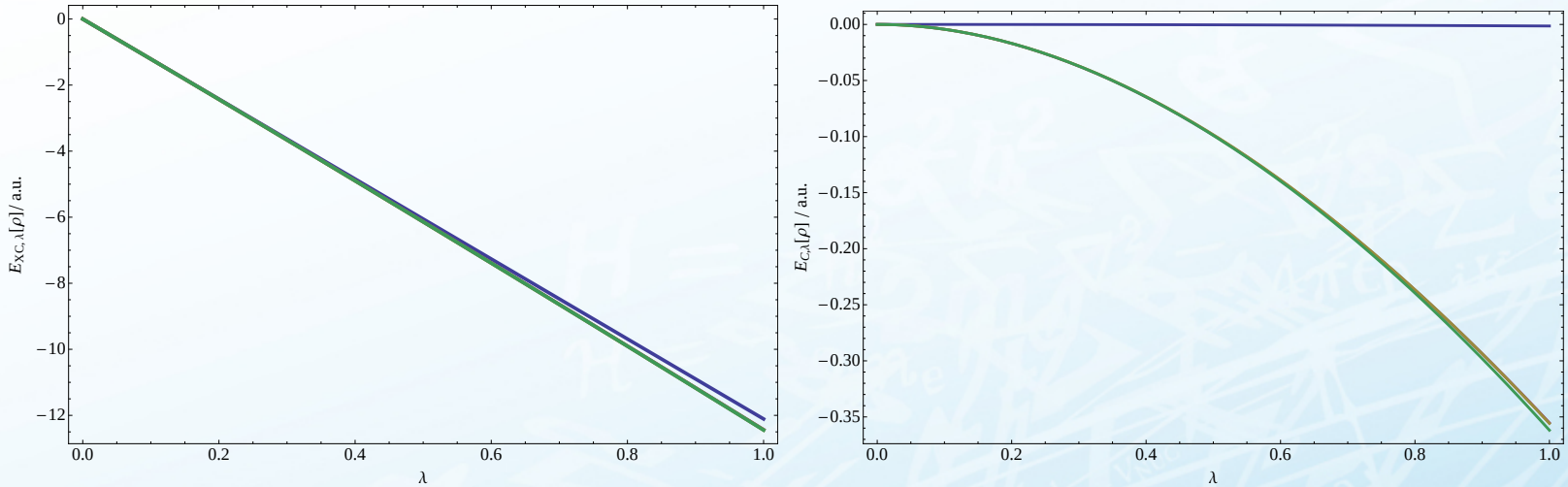

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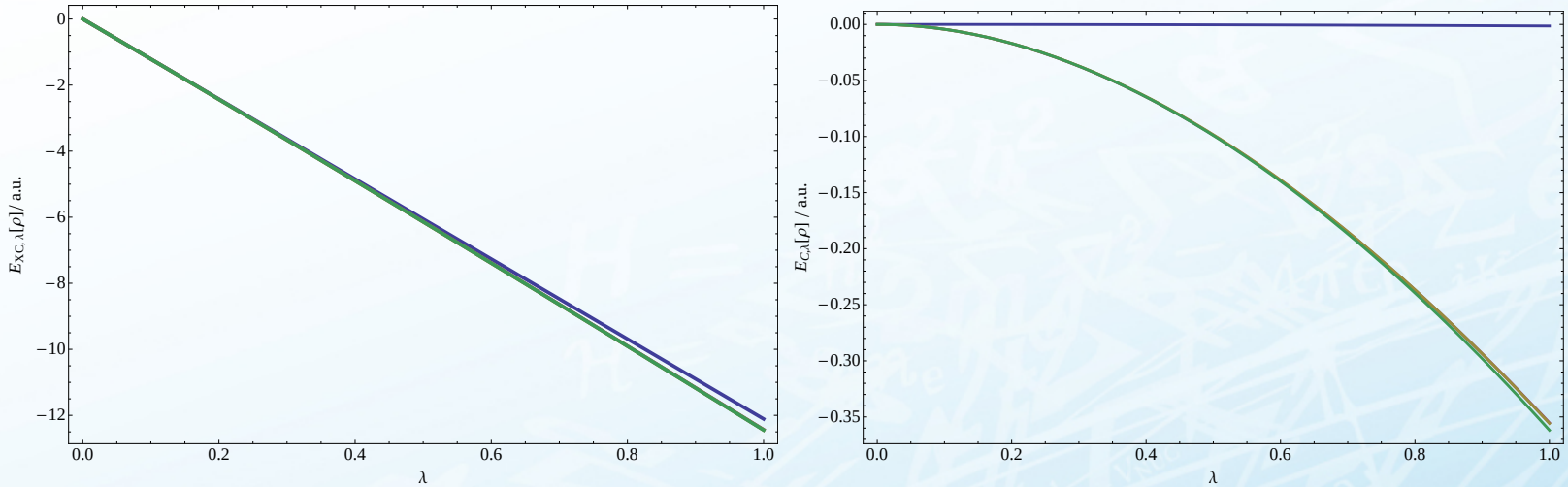

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The Adiabatic Connection

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

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

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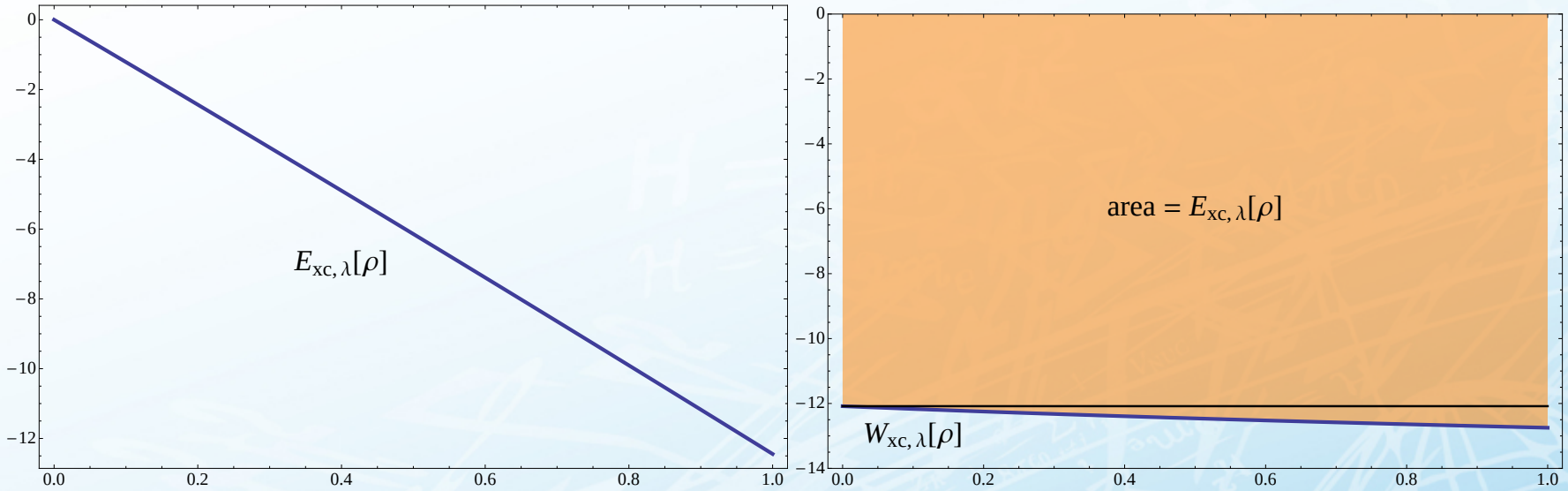

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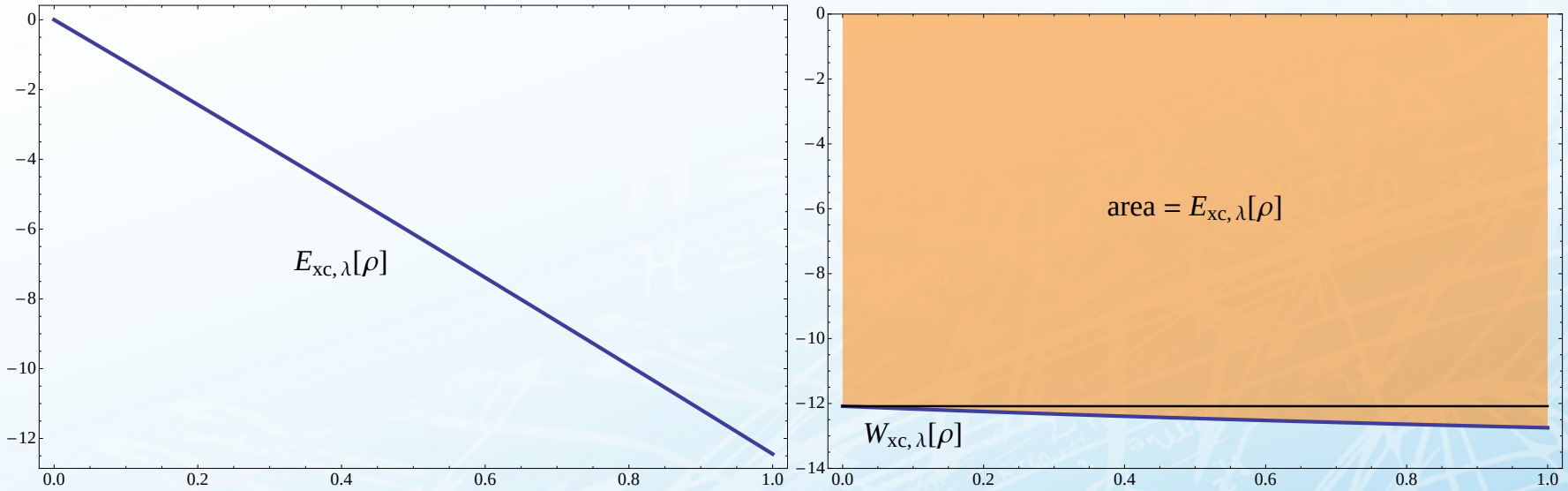

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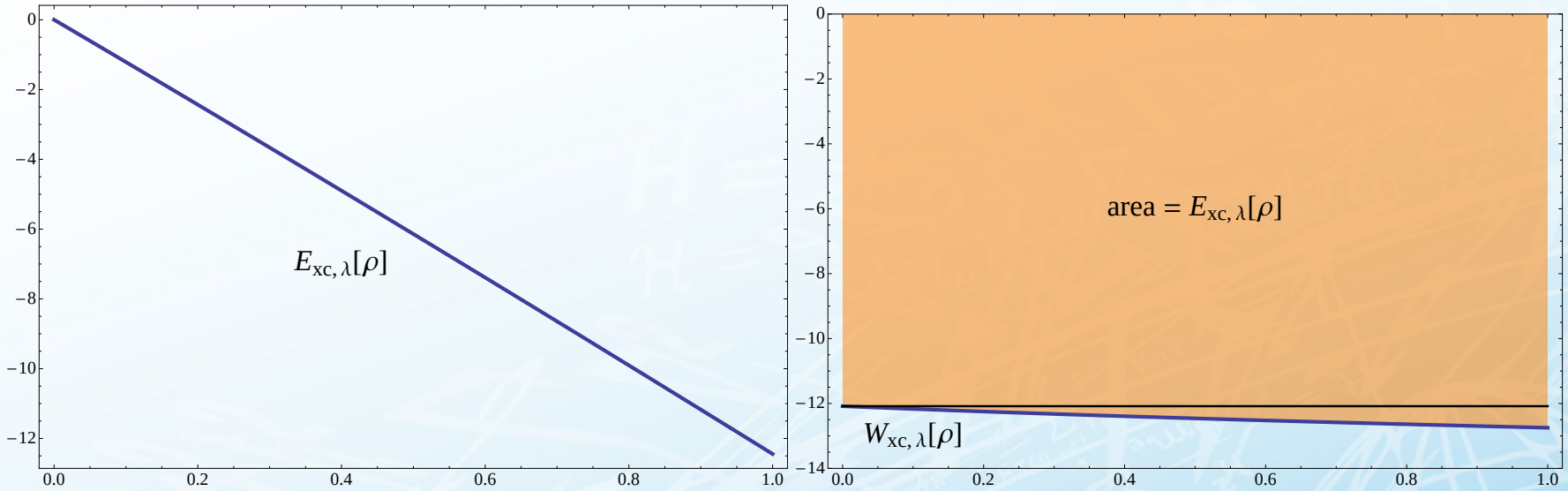

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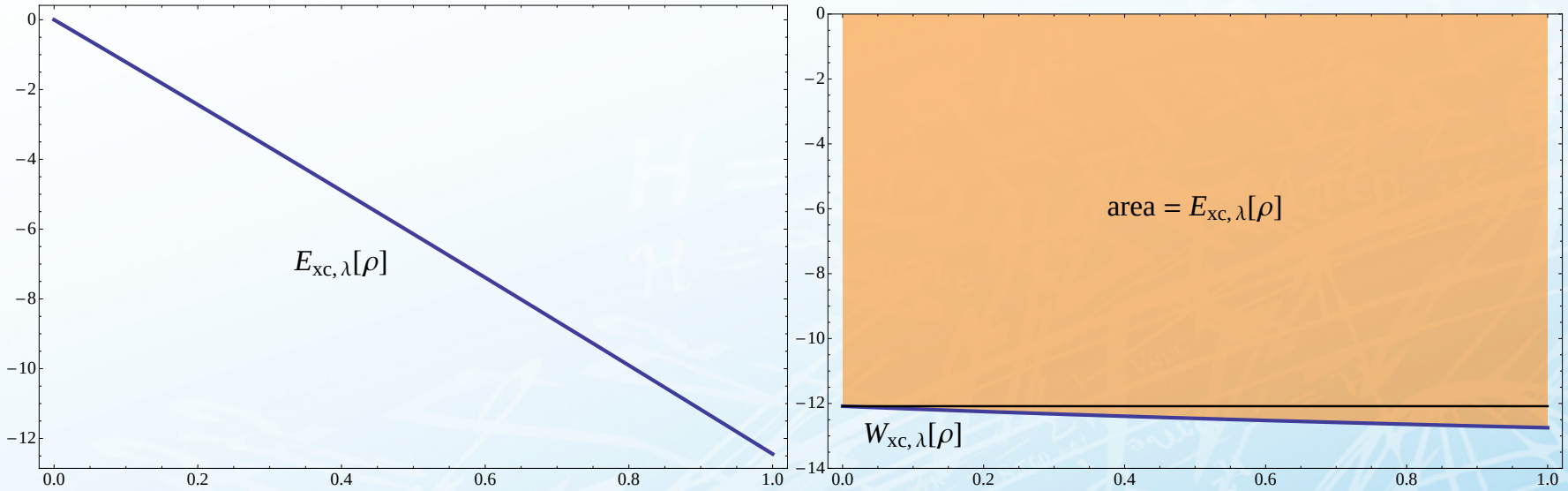

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The Adiabatic Connection Integrand

- Just as for the exchange–correlation integrand which gives E_{xc} on integration
- We may construct integrand for the sum of the Coulomb, exchange and correlation energies:

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- Using our approach we may employ any of the armoury of wavefunction techniques to accurately calculate the AC
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The RPA Correlation Energy in DFT

- The *closed-shell* RPA excitation problem requires the solution of

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \boldsymbol{\omega}$$

$$A_{ai,bj} = (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + L_{aijb} \qquad B_{ai,bj} = -L_{aibj} \qquad L_{pqrs} = 2g_{pqrs} - g_{psrq}$$

- The Tamn-Dancoff approximation (TDA) sets $\mathbf{B} = 0$ and solves $\mathbf{AZ} = \mathbf{Z}v$.
- The RPA contains both excitation and de-excitation operators, the latter of which can be thought of as correlating the ground state, whilst TDA contains only excitation operators.
- The ground state correlation energy in RPA is then given by the plasmonic formula

$$E_c^{\mathrm{RPA}} = \frac{1}{2}\mathrm{Tr}(\boldsymbol{\omega} - \mathbf{A})$$

- The above equations correspond to the 'full' RPA, making the replacement $L_{pqrs} = 2g_{pqrs}$ gives so called 'direct' RPA (dRPA)

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The Relationship of RPA to Coupled-Cluster Techniques

- It has long been known numerically and recently proved analytically that the (d)RPA correlation energy may be obtained by solving a so called (d)ring-CCD problem
- Following Scuseria *et al.* we introduce the quantities $\mathbf{Z} = \mathbf{Y}\mathbf{X}^{-1}$ and $\mathbf{R} = \mathbf{X}\omega\mathbf{X}^{-1}$ (assuming that $\mathbf{X}$ is non-singular) the RPA problem may be re-written as

$$\mathbf{B} + \mathbf{A}\mathbf{Z} + \mathbf{Z}\mathbf{A} + \mathbf{Z}\mathbf{B}\mathbf{Z} = \mathbf{0}$$

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- We begin with the dynamically correlated atomic systems He and Ne, before examining the H_2 molecule (u-aug-cc-pCVTZ basis)
- For comparison we will also present the ACs for HF, MP2, CCD, and CCSD

Calculating RPA and dRPA ACs

- The (d)RPA is an attractive non-local but relatively inexpensive correlation contribution for use in DFT
- The dRPA can be derived directly from a consideration of the adiabatic connection. However the AC can be calculated both for RPA and dRPA
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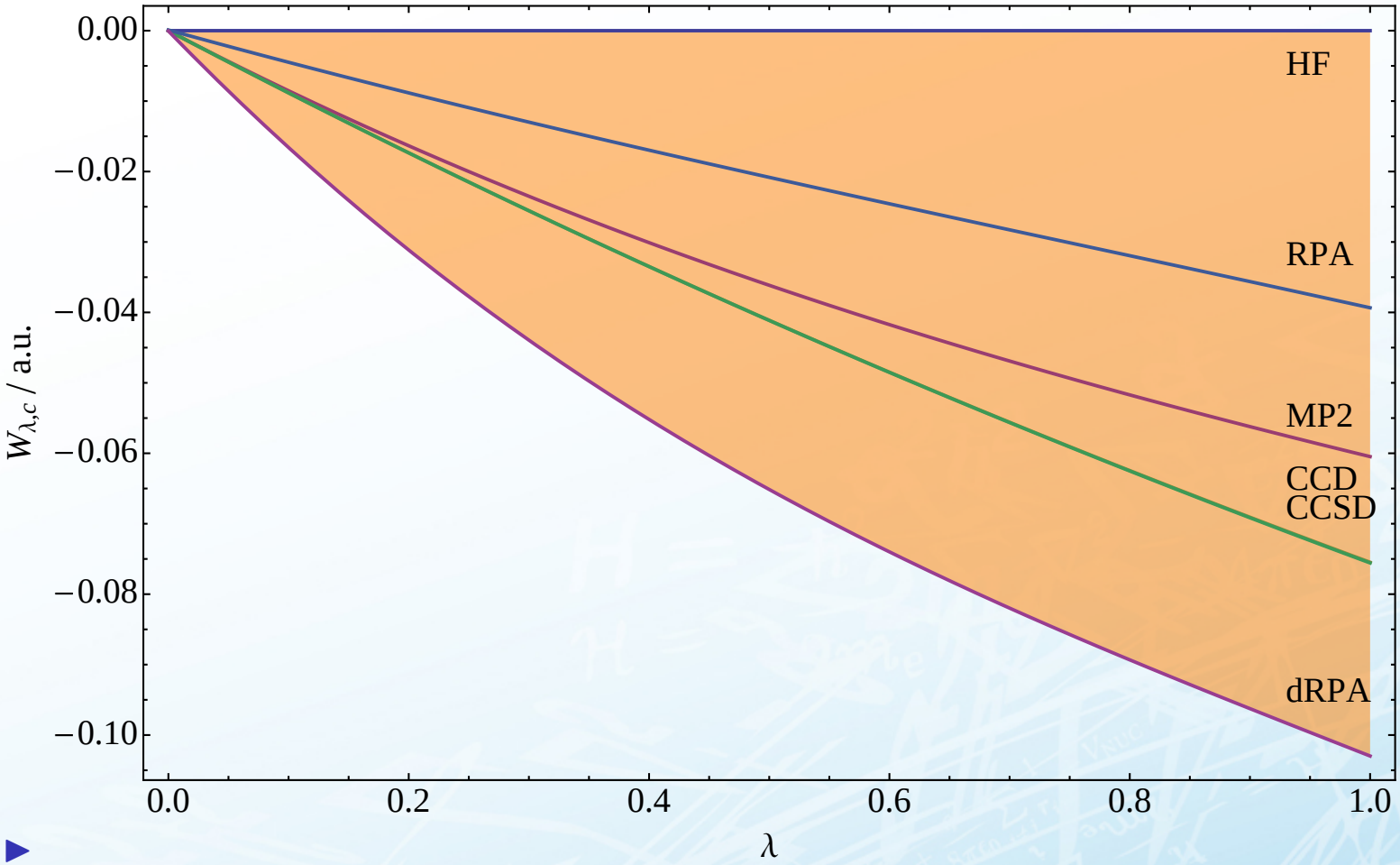
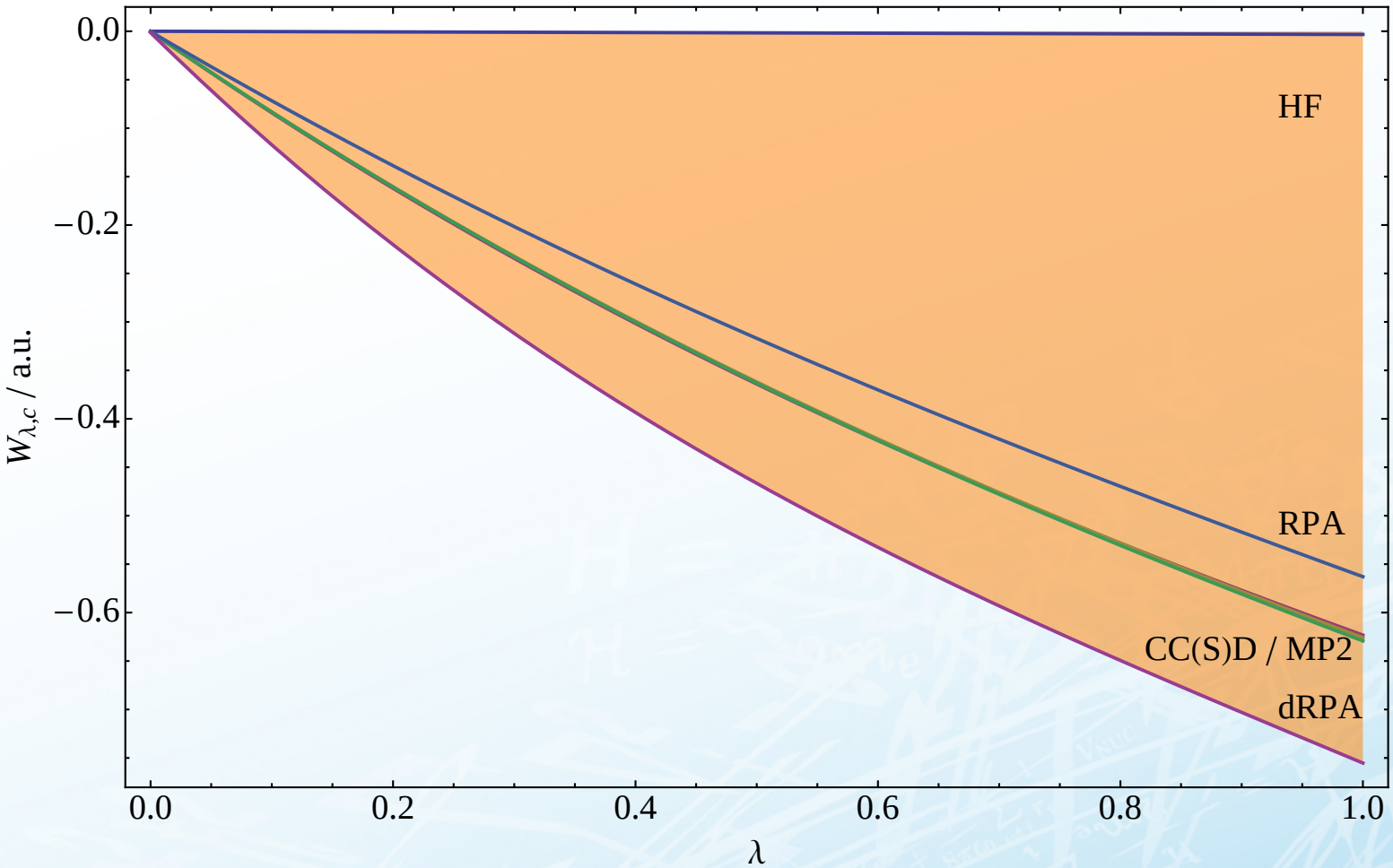
RPA ACs: He



- RPA gives a much too positive correlation energy, whilst dRPA gives a significantly too negative correlation energy for atoms

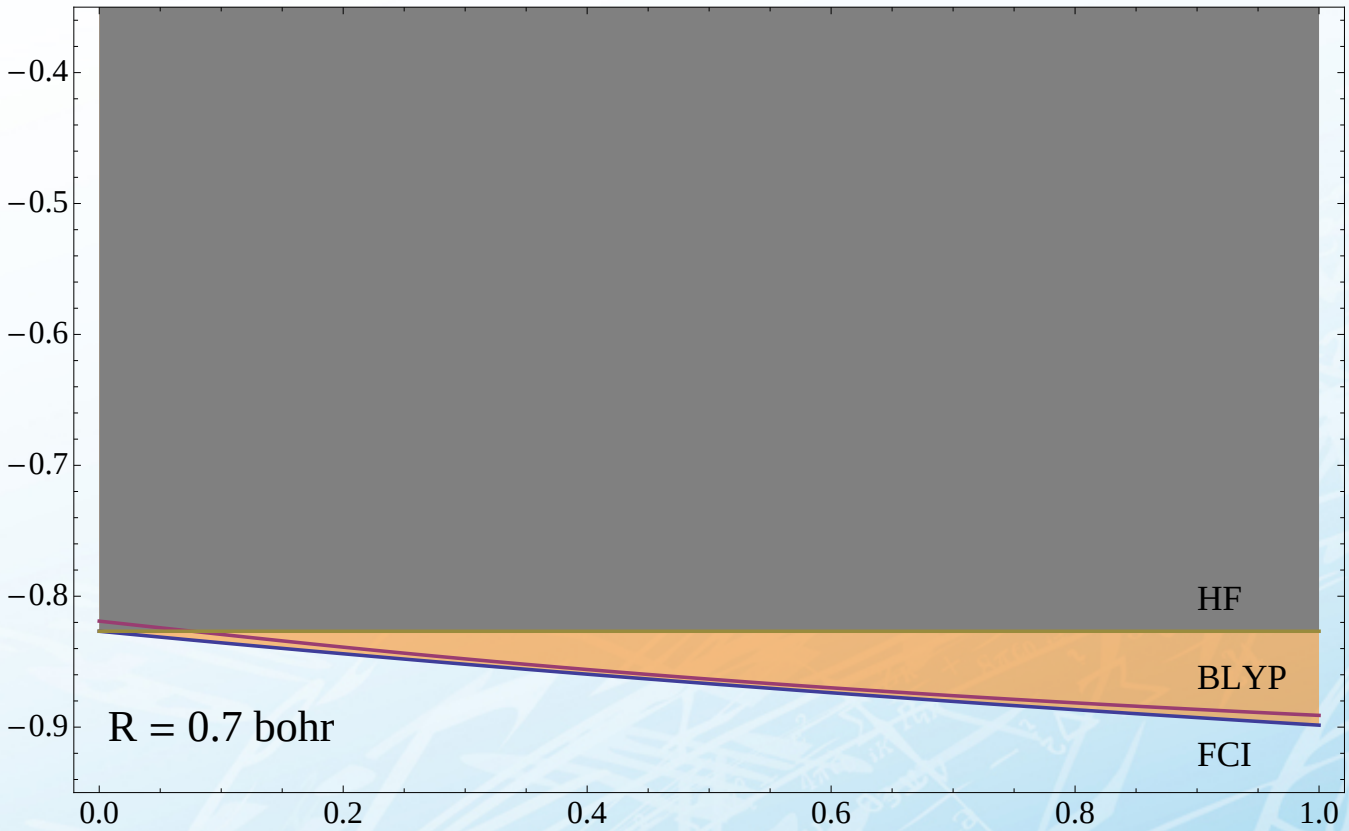
RPA ACs: Ne



- RPA gives a much too positive correlation energy, whilst dRPA gives a significantly too negative correlation energy for atoms

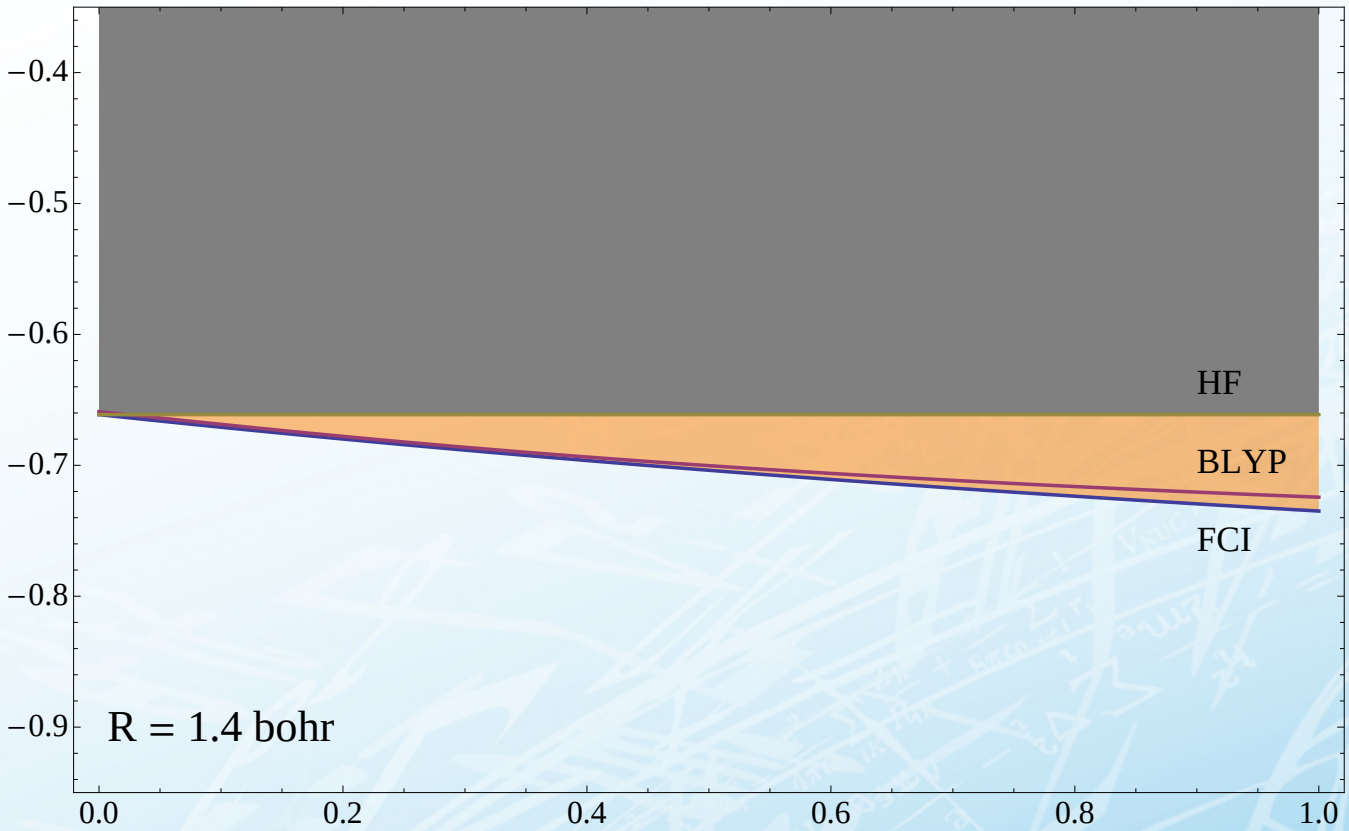
The H_2 Molecule: BLYP

- 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 FCI curves are nearly linear, indicative of dynamical correlation



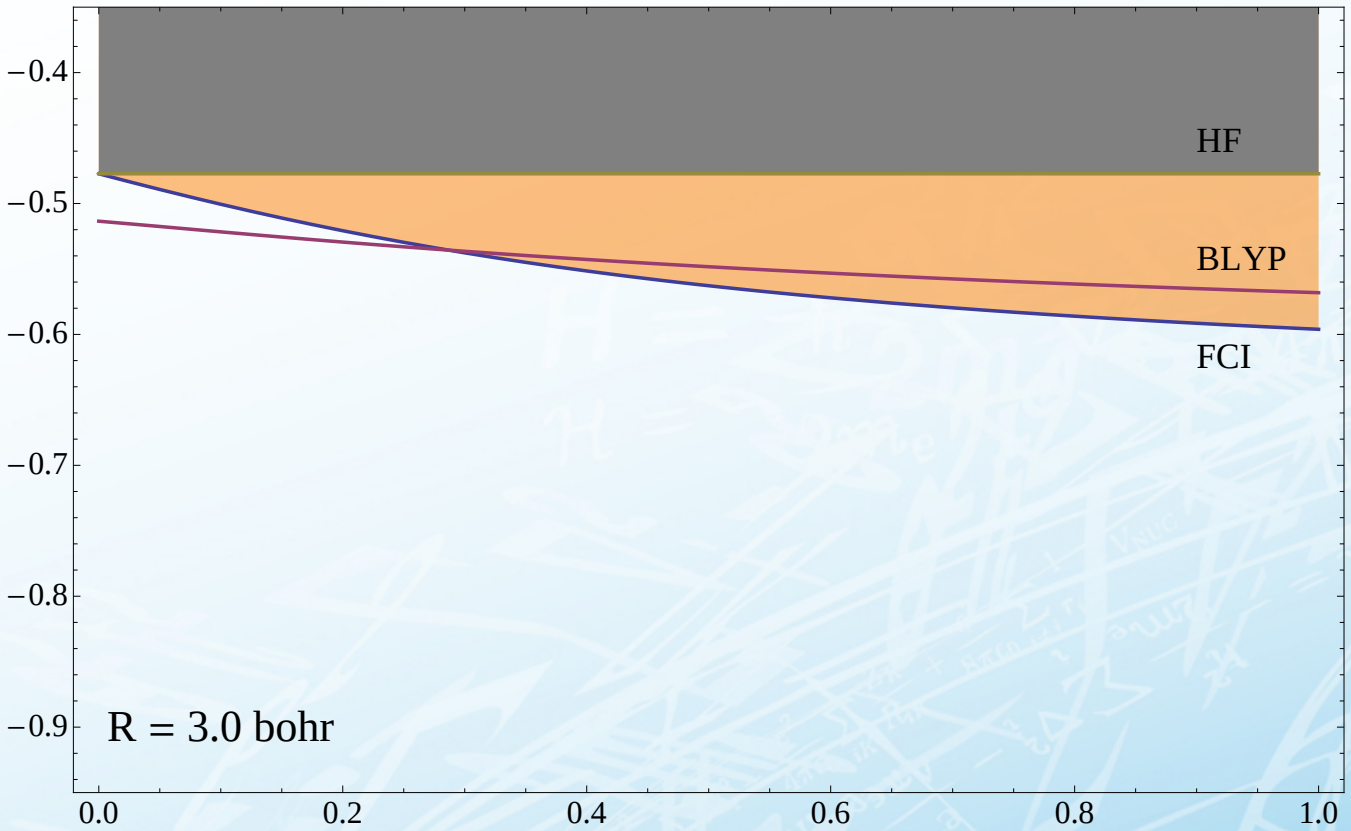
The H_2 Molecule: BLYP

- The overall picture is similar to that at $R = 0.7$ bohr
- Most notably, $E_x \Uparrow$ from -827 to -661 mE_h
- $E_c \Downarrow$, from -39 to -41 mE_h



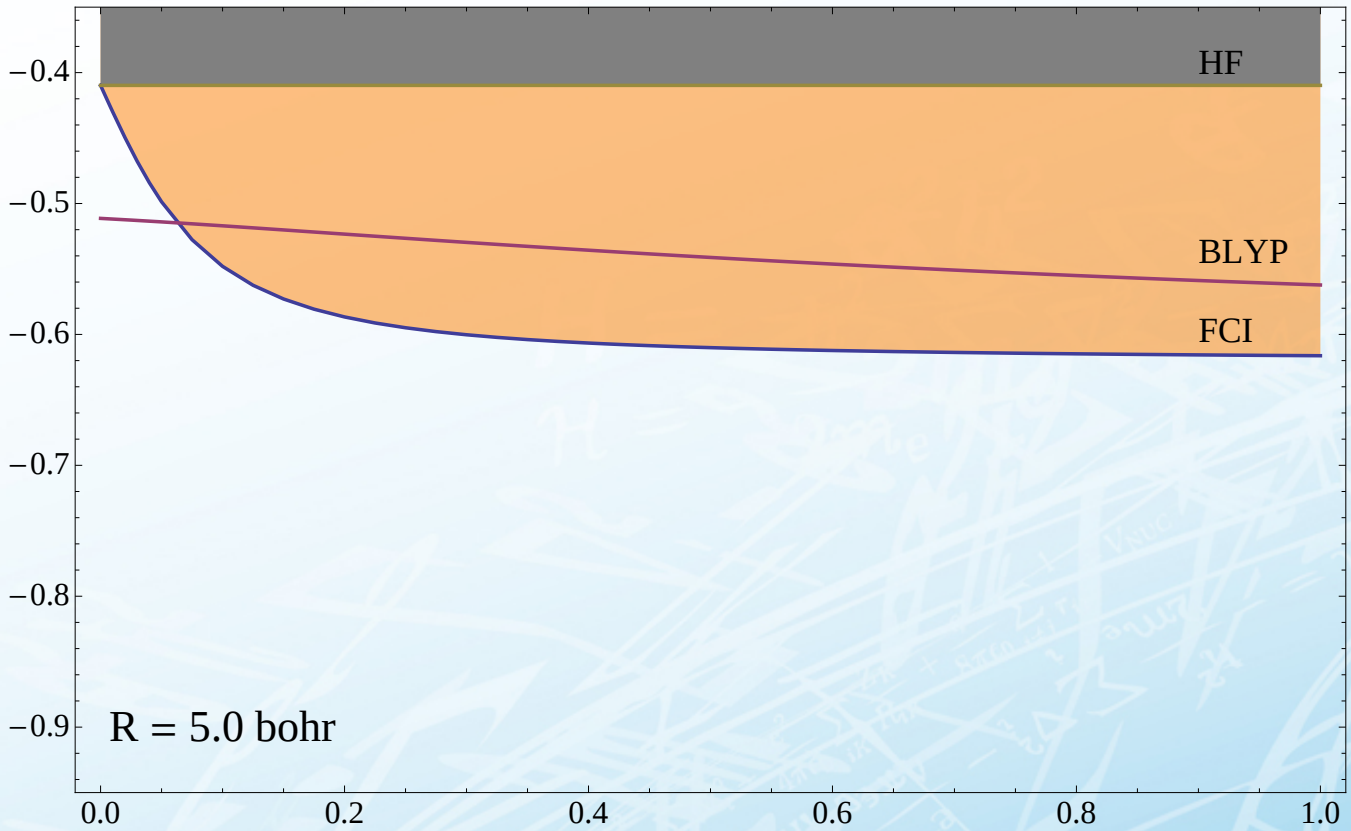
The H_2 Molecule: BLYP

- $E_x \Uparrow$ further from -661 to -477 mE_h and $E_c \Downarrow$, -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 error cancellation



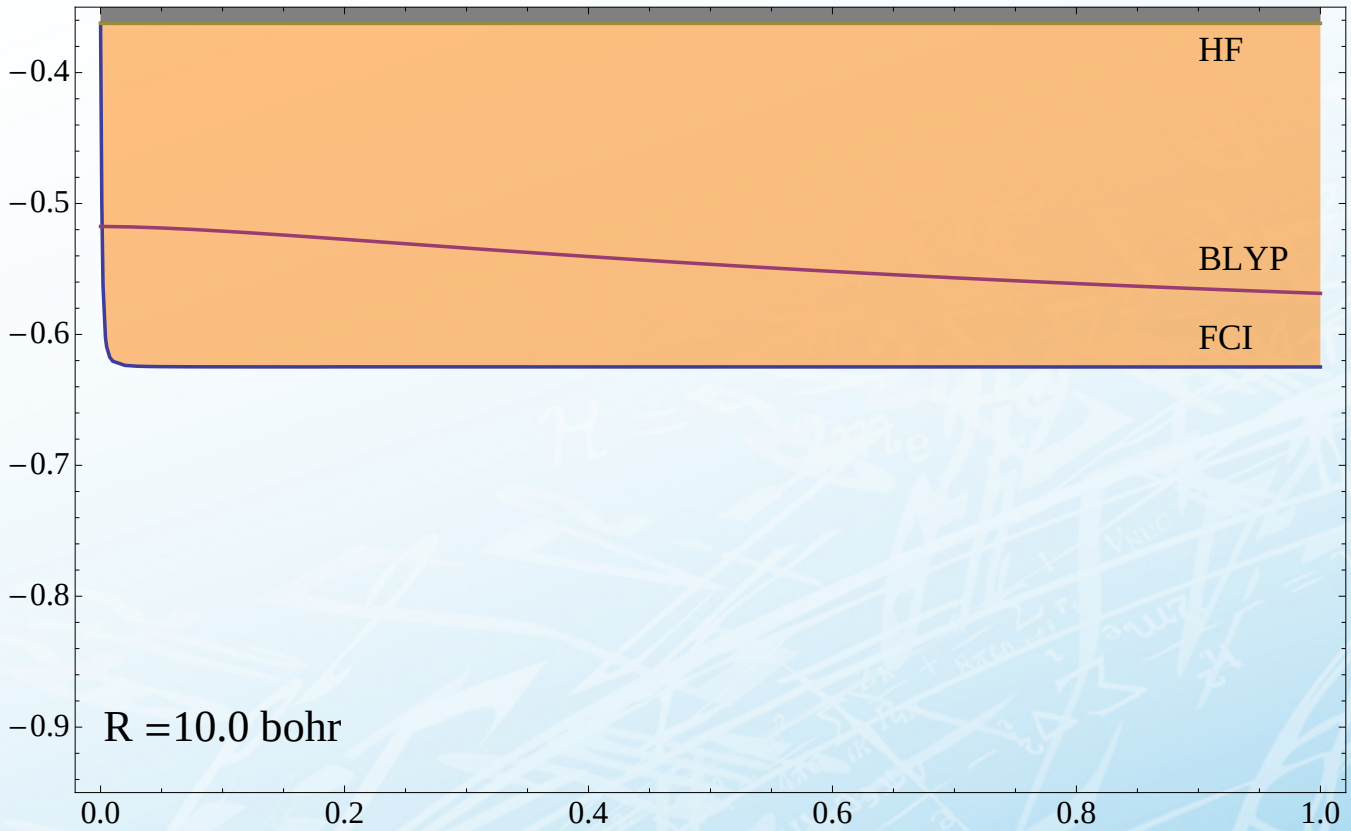
The H_2 Molecule: BLYP

- 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 BLYP curve now benefits less from error cancellation, underestimating the XC energy

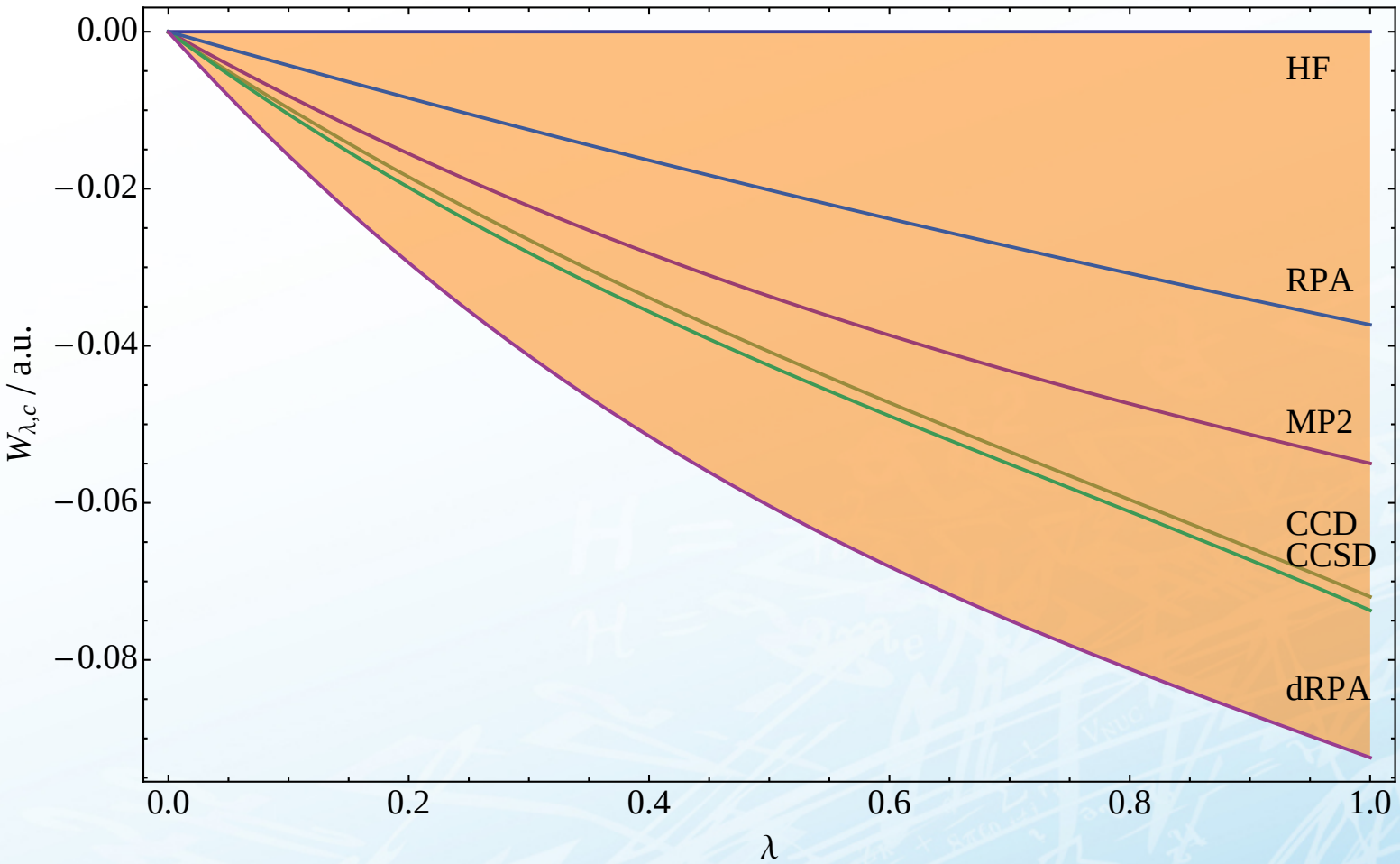


The H_2 Molecule: BLYP

- At $R = 10$ bohr, the two atoms are separated and correlation is essentially static
- Dynamical correlation is now less than 1 mE_h (dispersion)
- The BLYP functional works mostly by overestimating the exchange energy

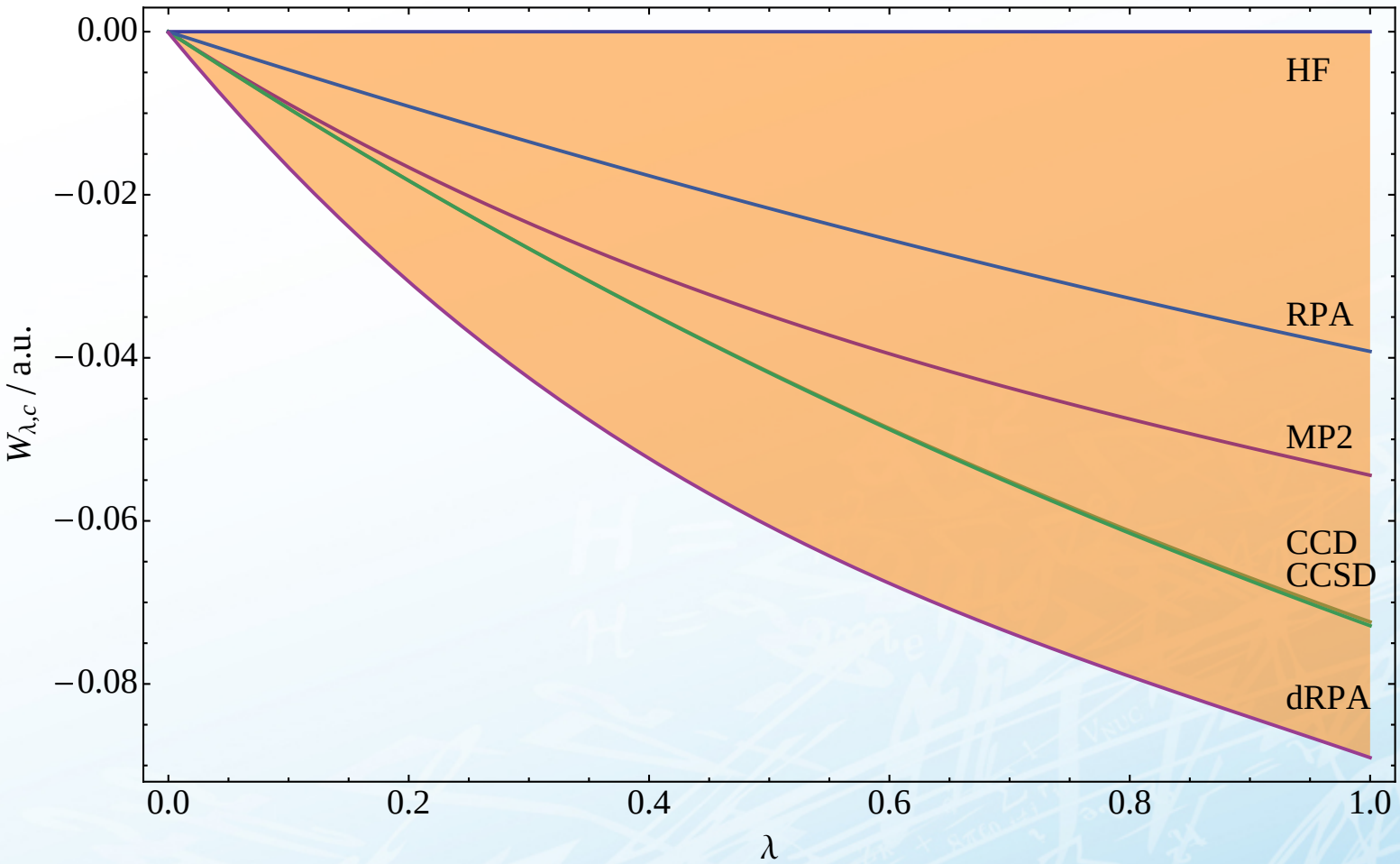


RPA ACs: H_2



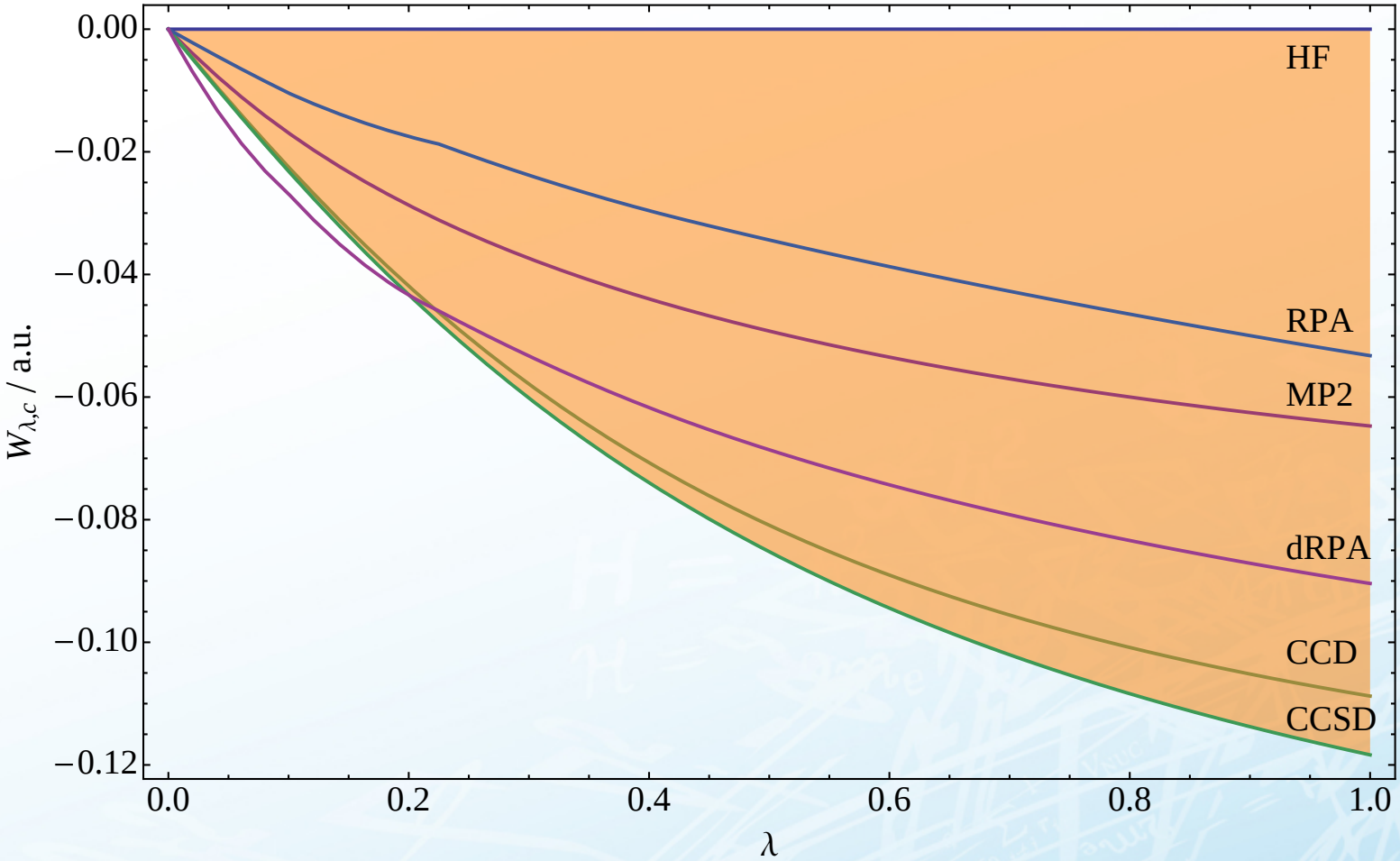
- At $R = 0.7$ bohr, half equilibrium bond length, the picture is similar to He atom

RPA ACs: H_2



- Stretching to $R = 1.4$ bohr, equilibrium bond length, little changes

RPA ACs: H_2



- Stretching to $R = 3.0$ bohr, the correlation energy grows and the AC begins to display more pronounced curvature. Both RPA and dRPA now give a too positive correlation energy. However, both display some curvature.

Generalized, range-dependent adiabatic connection

- Up to now, we have studied the AC with uniformly scaled two-electron interaction

$$W_\lambda = \sum_{i \neq j} w_\lambda(r_{ij}), \qquad w^{\mathrm{s}}_\lambda(r_{ij}) = \frac{\lambda}{r_{ij}}$$

- We shall now consider range-dependent generalized adiabatic interaction

$$w^{\mathrm{e}}_\lambda(r_{ij}) = \frac{\mathrm{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}}$$

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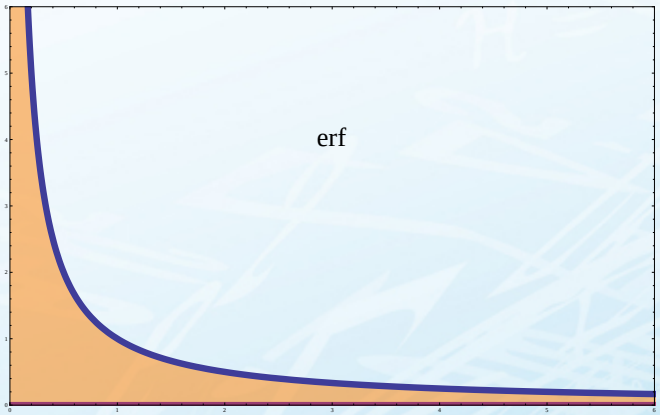
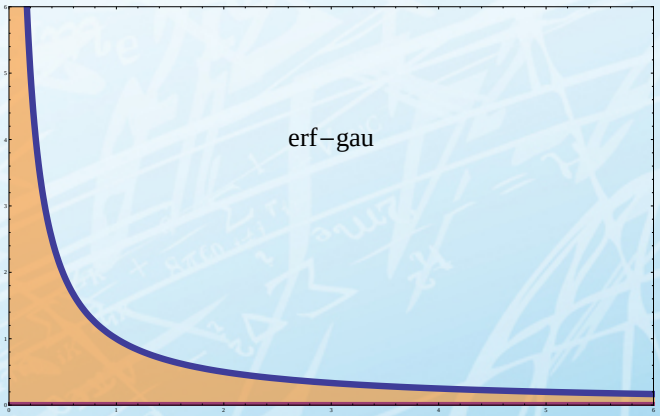
  - $\lambda = 0.0$





- Savin (1996), Yang, JCP **109**, 10107 (1998), Toulouse et al. PRA **70**, 062505 (2004)

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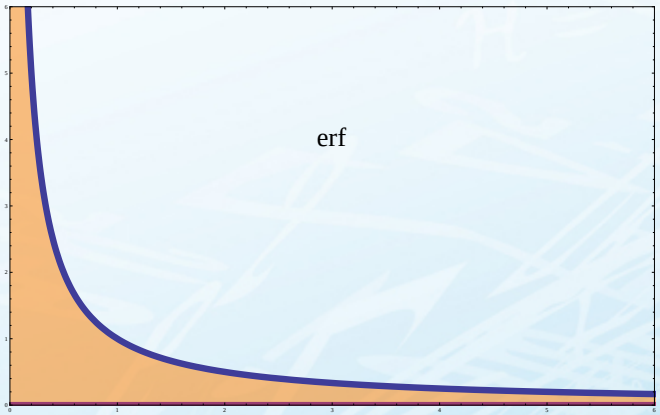

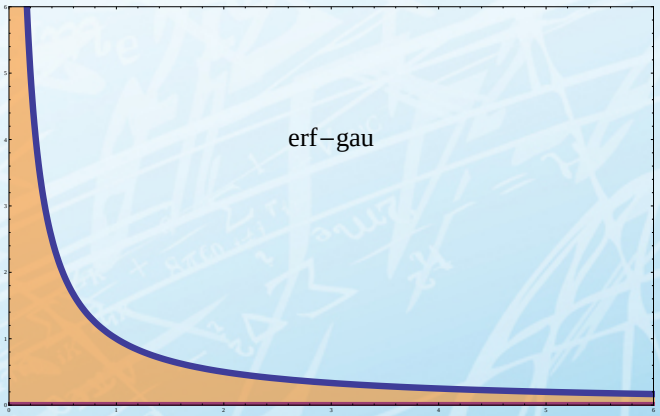

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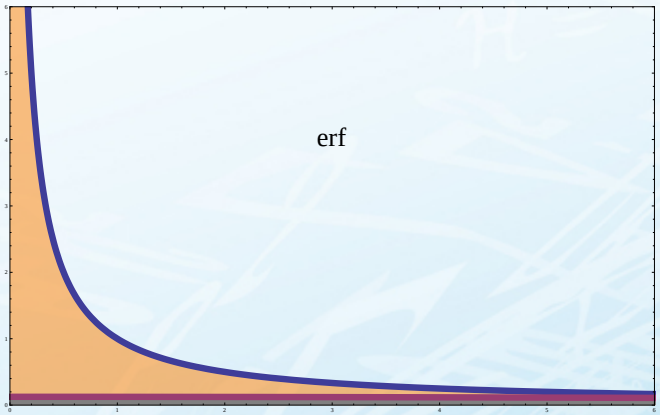

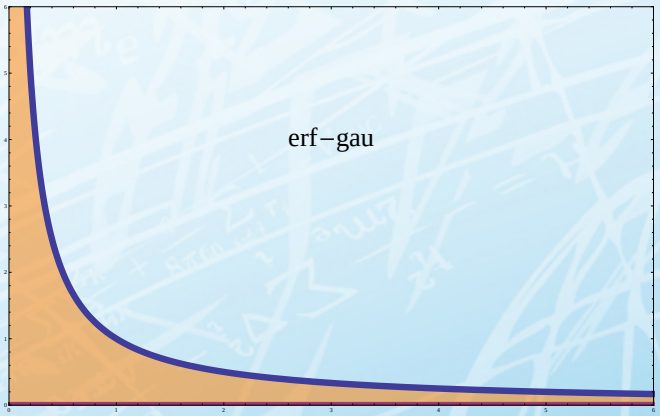

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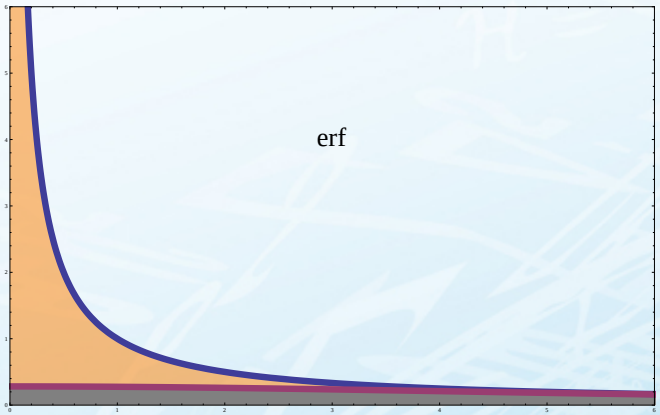
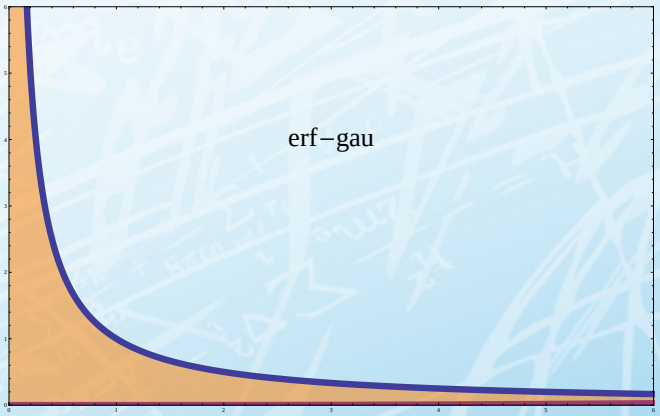
  - $\lambda = 0.2$





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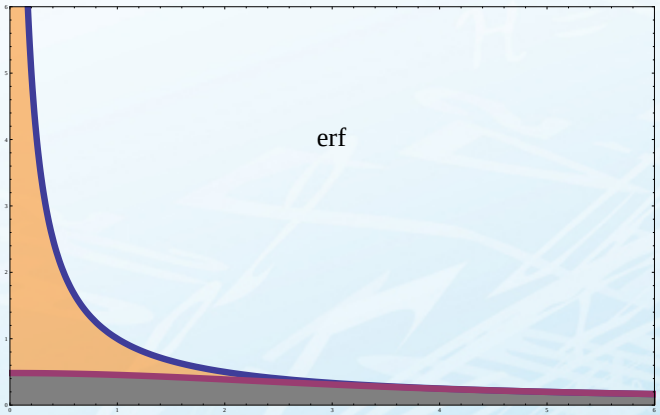
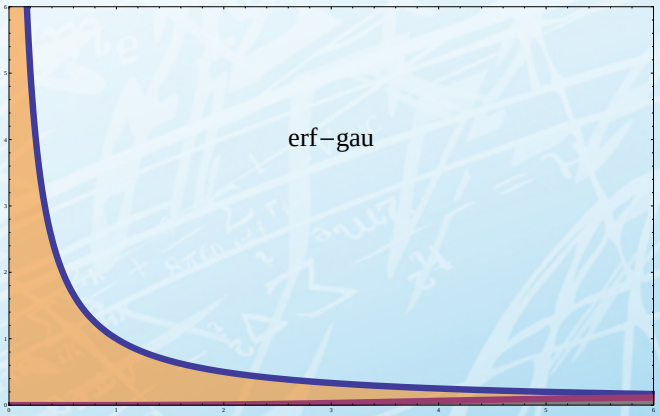
  - $\lambda = 0.3$





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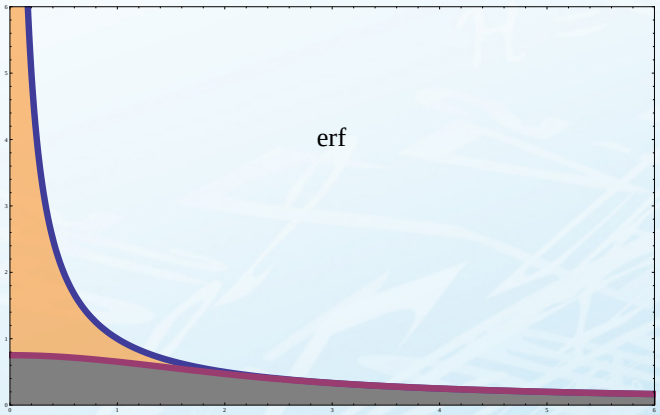
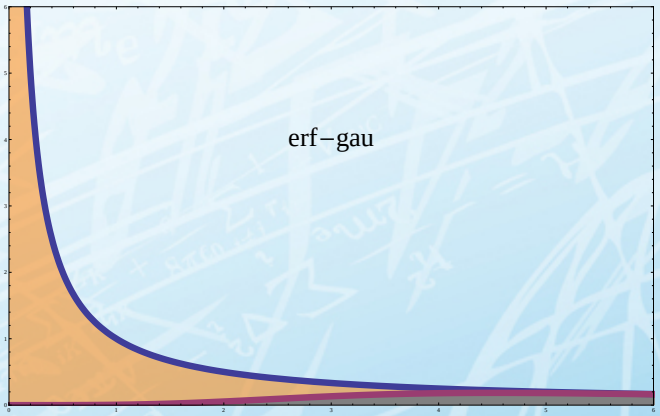
  - $\lambda = 0.4$





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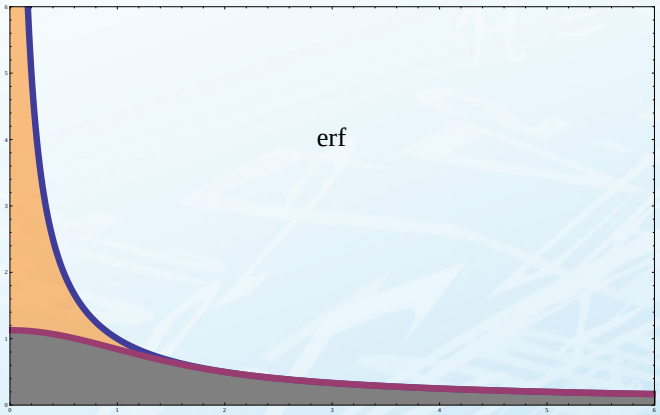
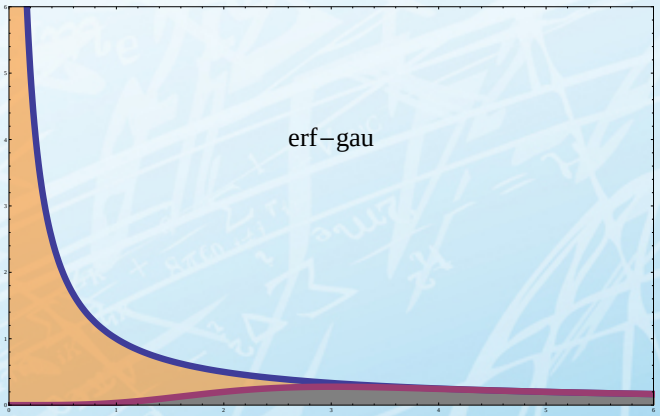
  - $\lambda = 0.5$





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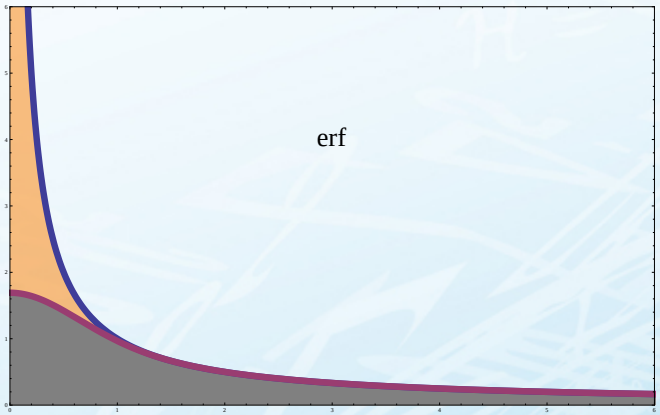
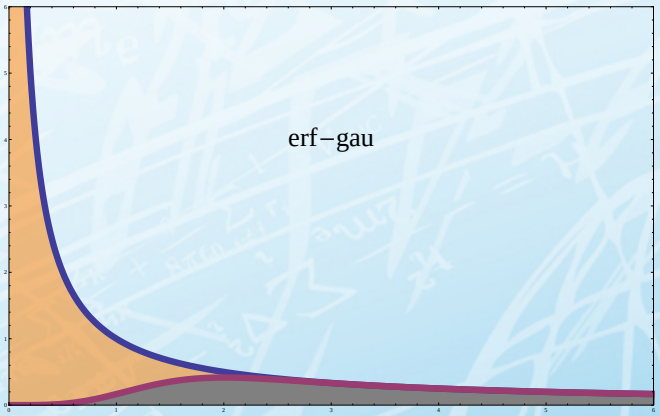
  - $\lambda = 0.6$





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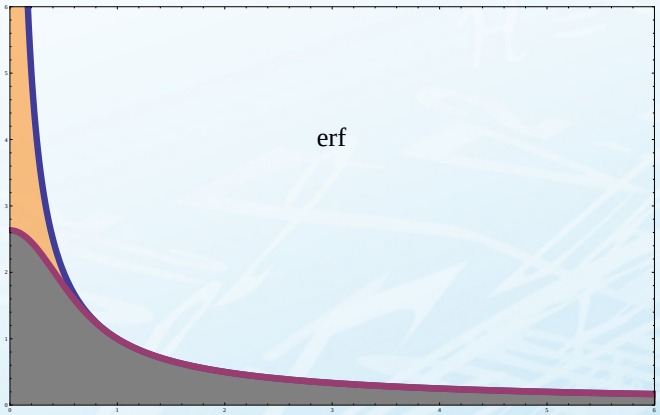
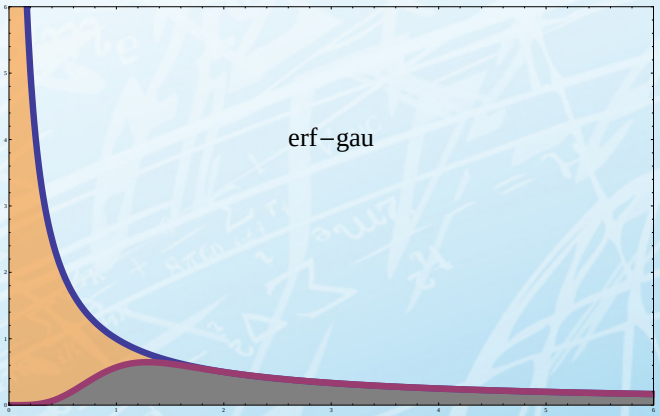
  - $\lambda = 0.7$





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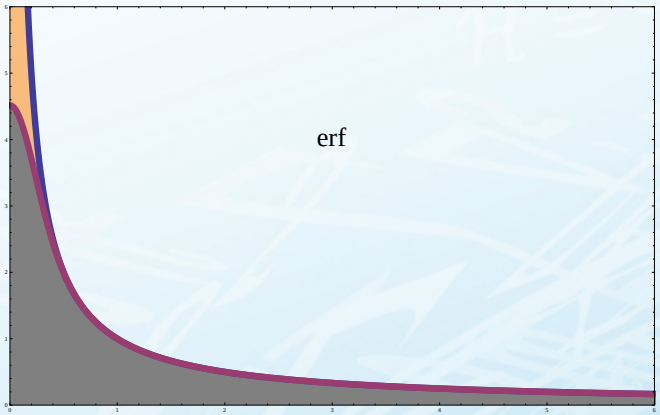
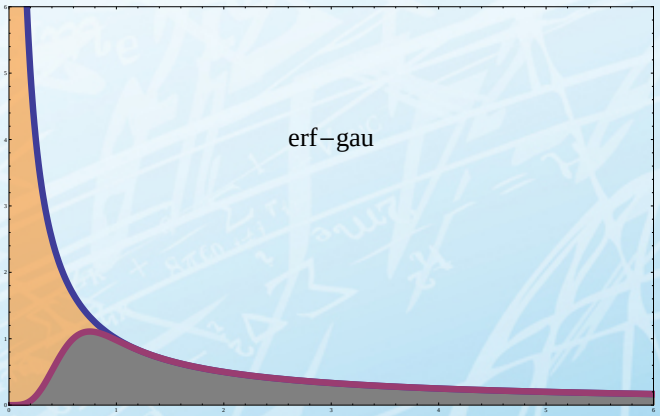
  - $\lambda = 0.8$





- Savin (1996), Yang, JCP **109**, 10107 (1998), Toulouse *et al.* PRA **70**, 062505 (2004)

Generalized, range-dependent adiabatic connection

- Up to now, we have studied the AC with uniformly scaled two-electron interaction

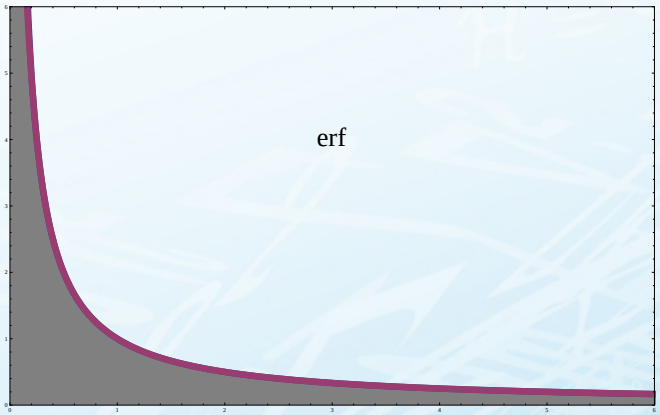
$$W_\lambda = \sum_{i \neq j} w_\lambda(r_{ij}), \qquad w^{\mathrm{s}}_\lambda(r_{ij}) = \frac{\lambda}{r_{ij}}$$

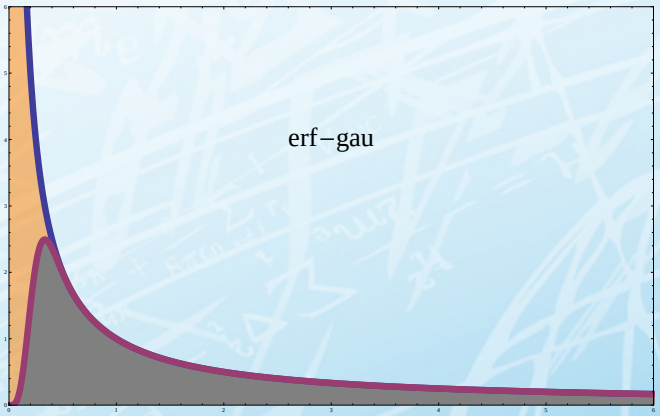
- We shall now consider range-dependent generalized adiabatic interaction

$$w^{\mathrm{e}}_\lambda(r_{ij}) = \frac{\mathrm{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}}$$

$$w^{\mathrm{g}}_\lambda(r_{ij}) = \frac{\mathrm{erf}\left(\frac{\lambda}{1-\lambda} r_{ij}\right)}{r_{ij}} - \frac{2}{\sqrt{\pi}} \left(\frac{\lambda}{1-\lambda}\right) \exp\left(-\frac{1}{3}\left(\frac{\lambda}{1-\lambda}\right)^2 r_{ij}^2\right)$$

  - $\lambda = 0.9$





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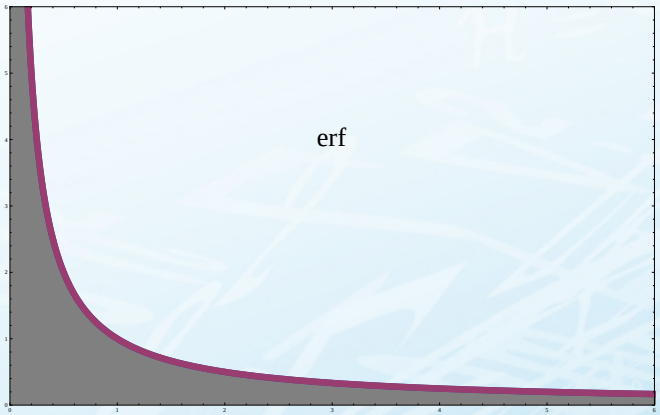
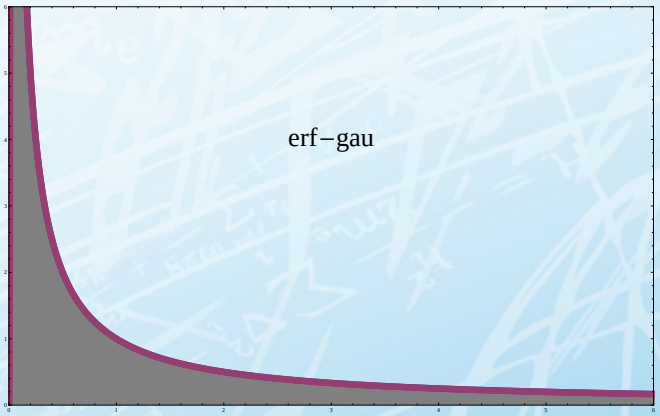
  - $\lambda = 1.0$

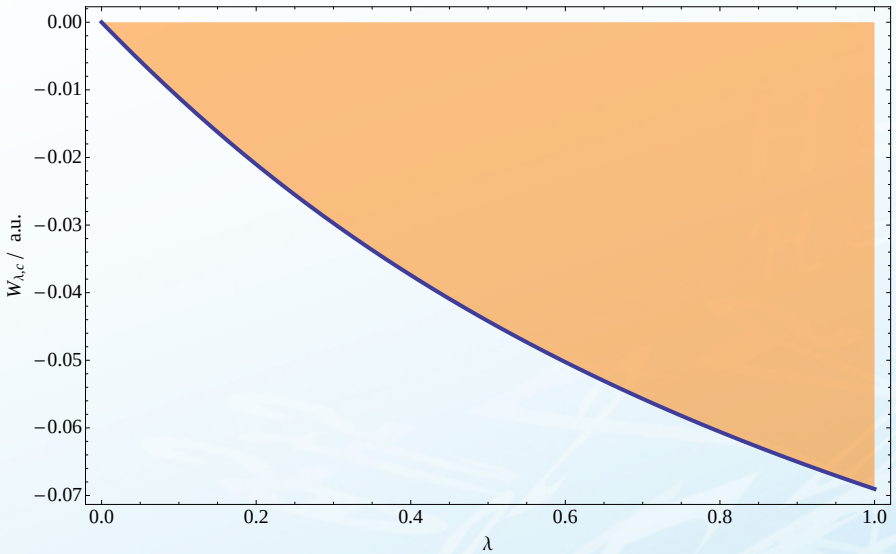


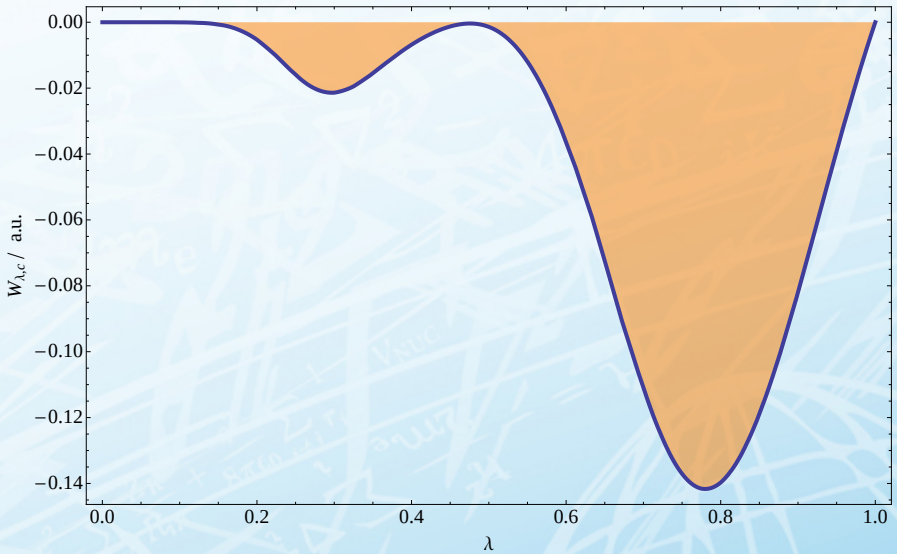


- Savin (1996), Yang, JCP **109**, 10107 (1998), Toulouse *et al.* PRA **70**, 062505 (2004)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 1$

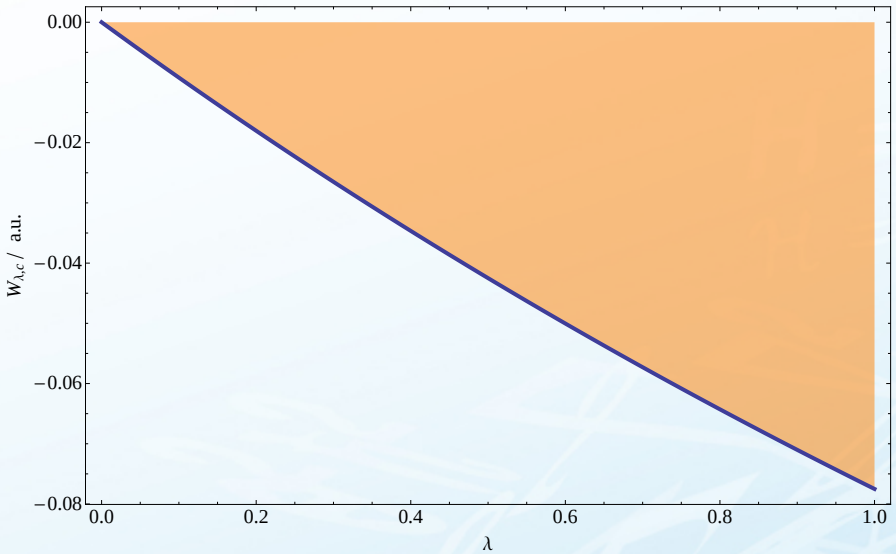


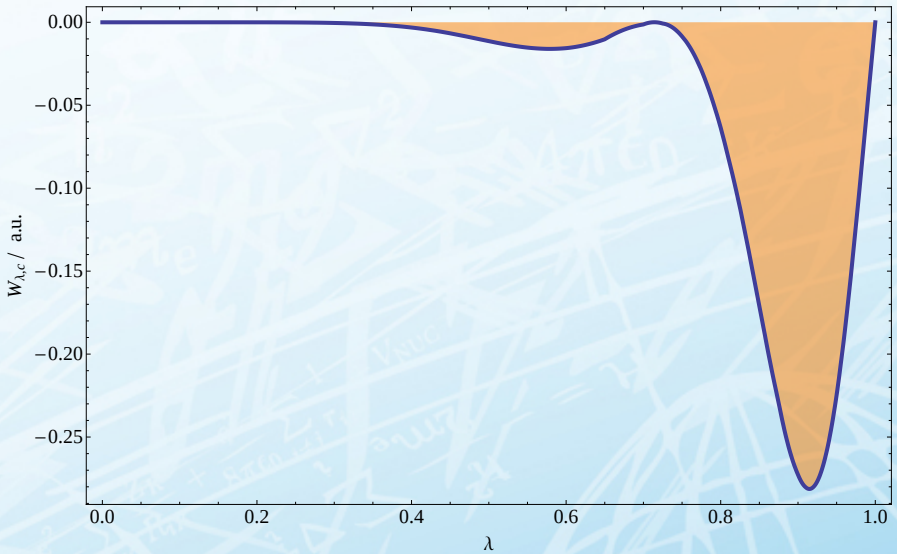


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 2$

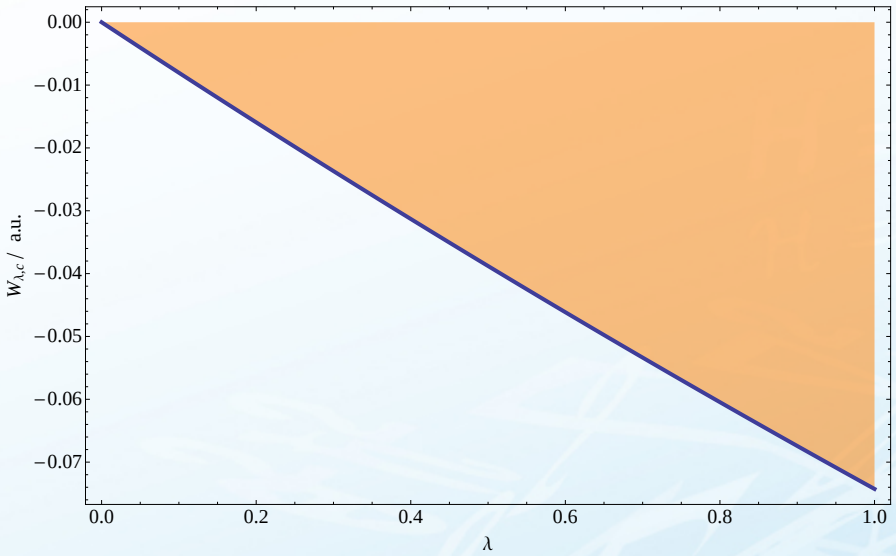


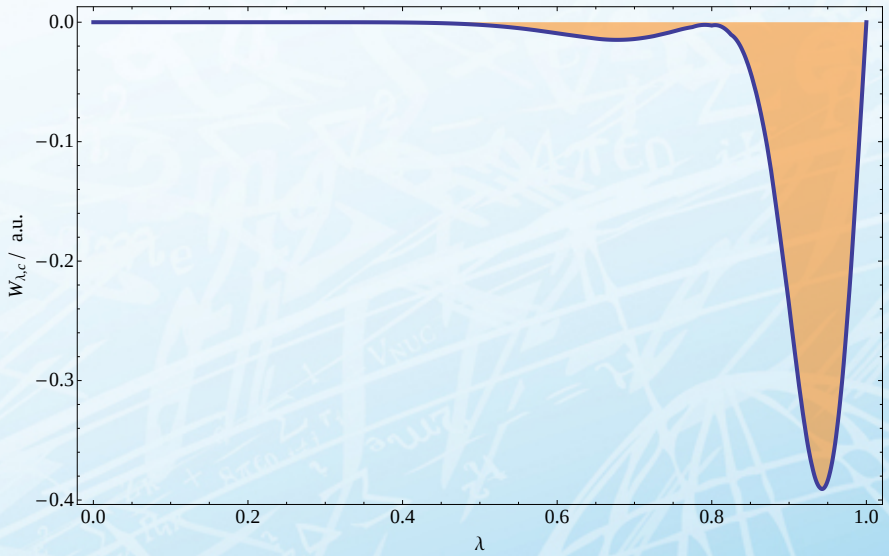


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 3$

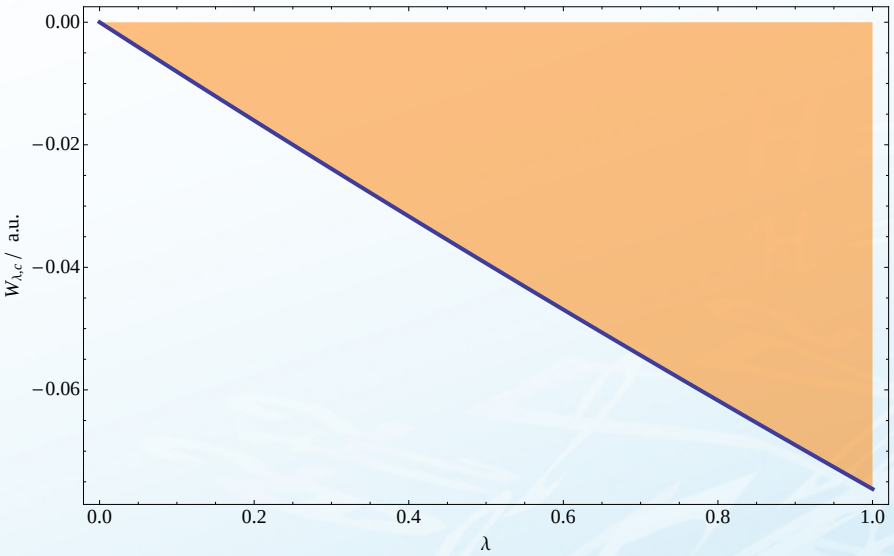


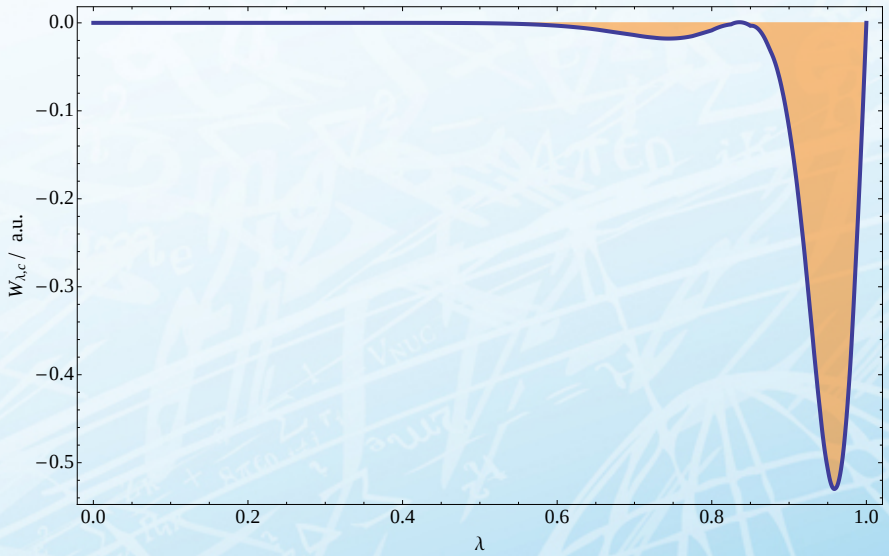


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 4$

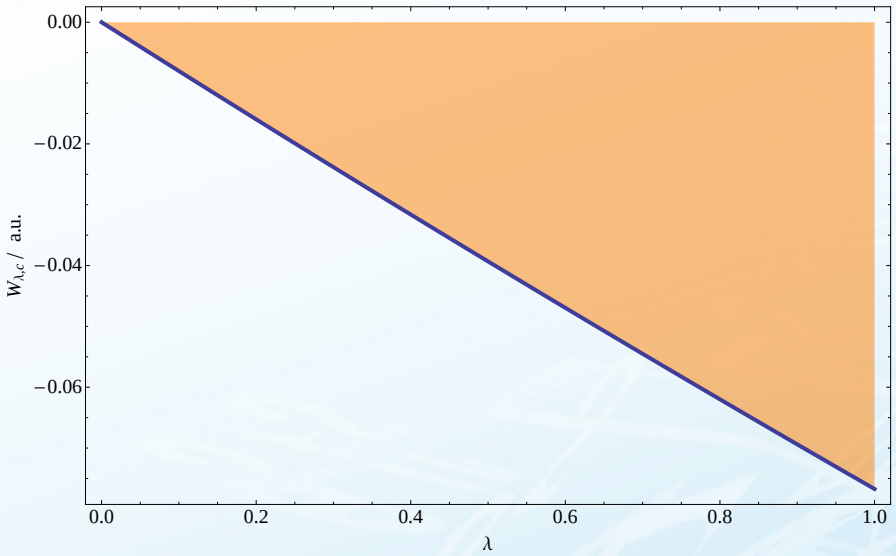


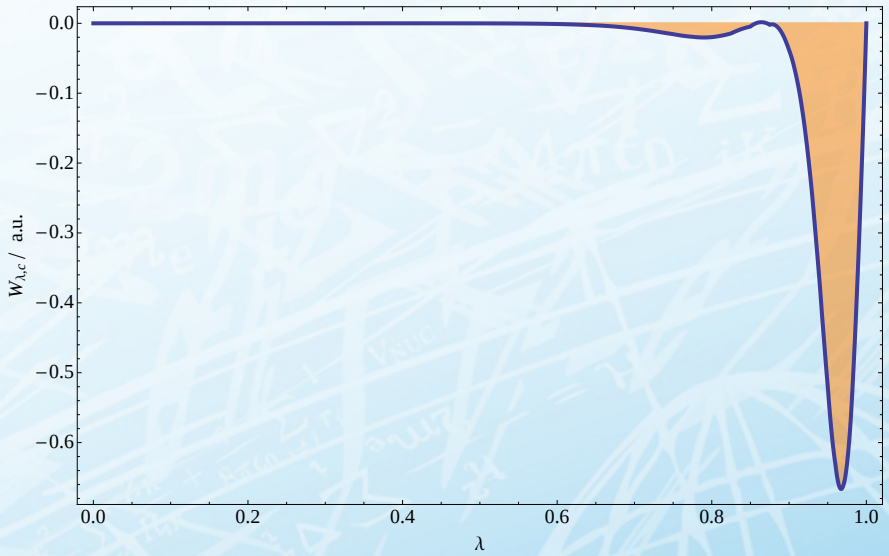


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 5$

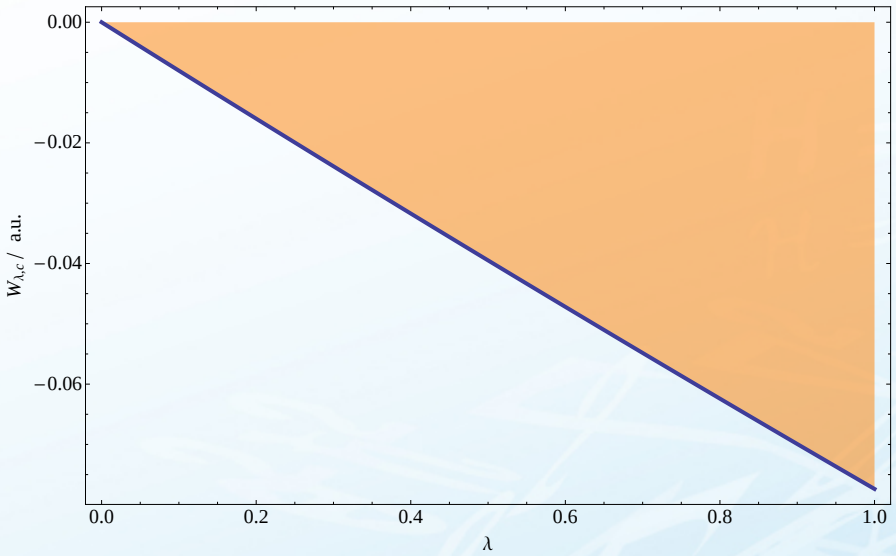


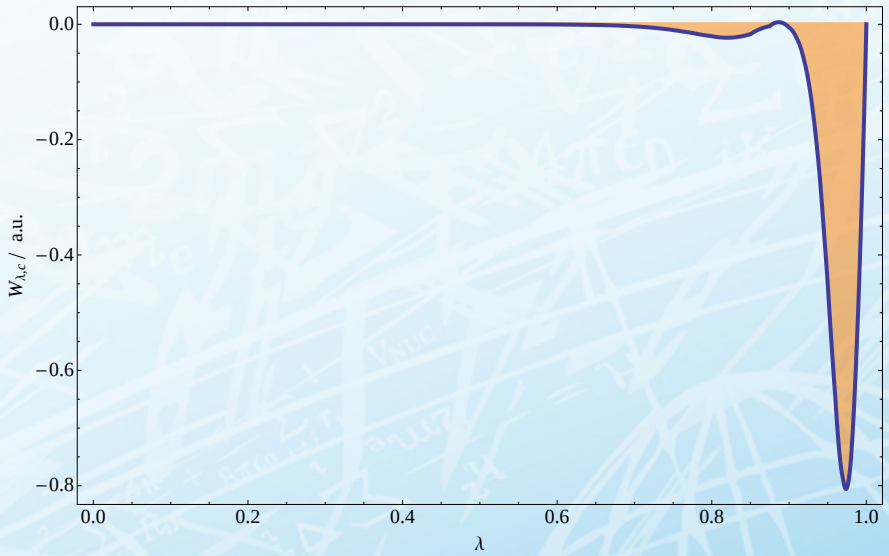


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 6$

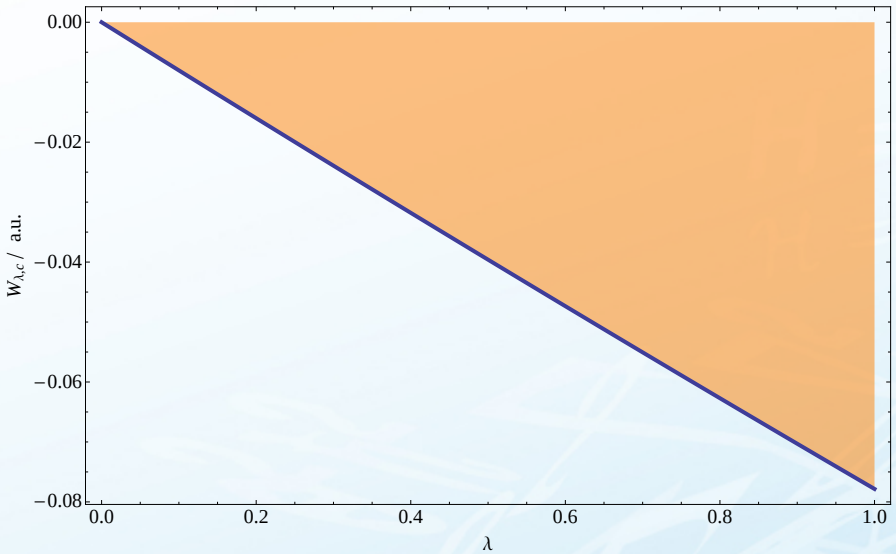


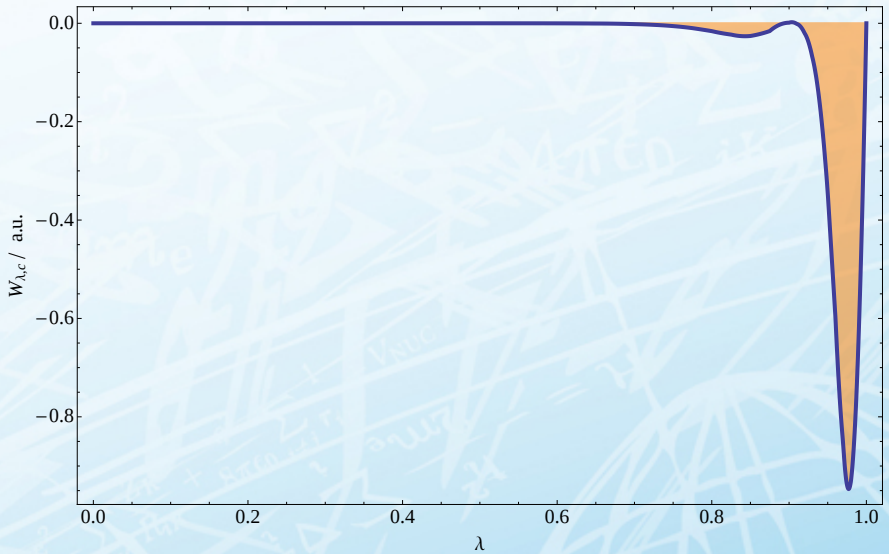


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 7$

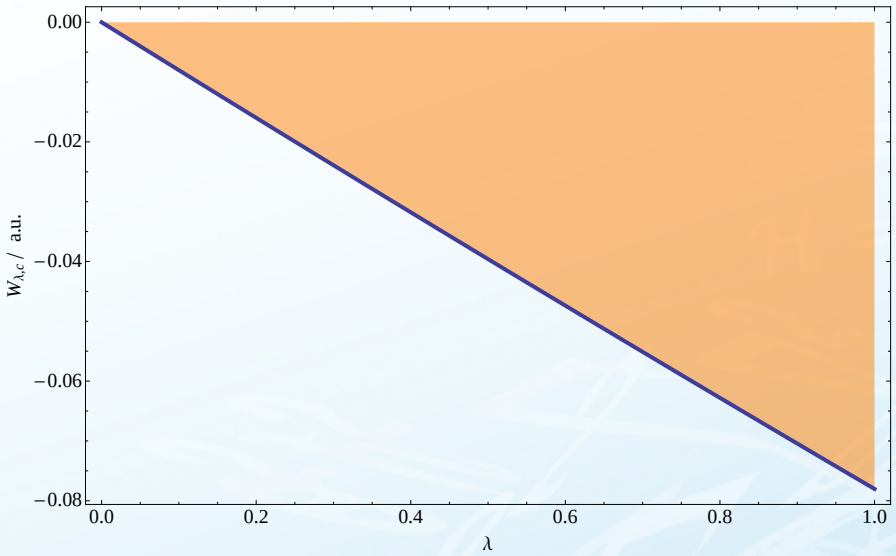


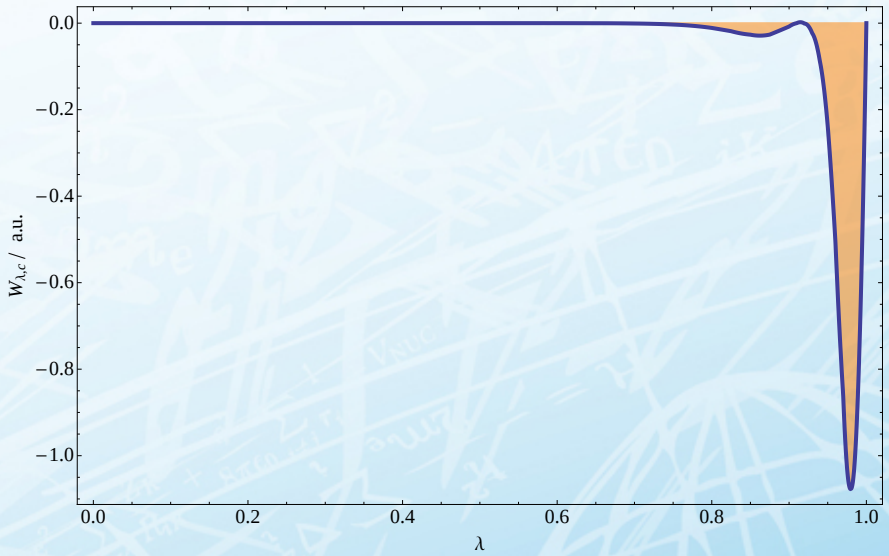


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 8$

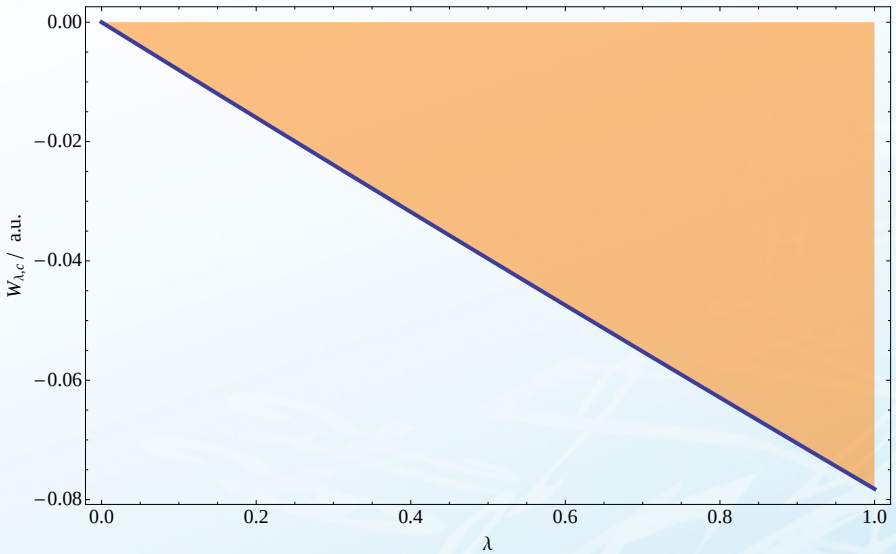


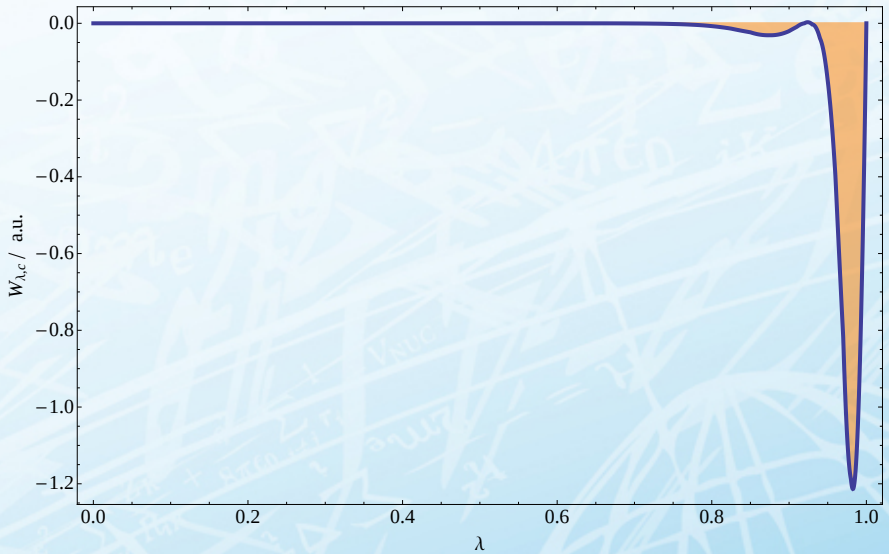


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- 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
- $Z = 9$





- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

AC correlation curves for the He isoelectronic series

- Standard AC curve on the left
  - linearity increases with increasing Z
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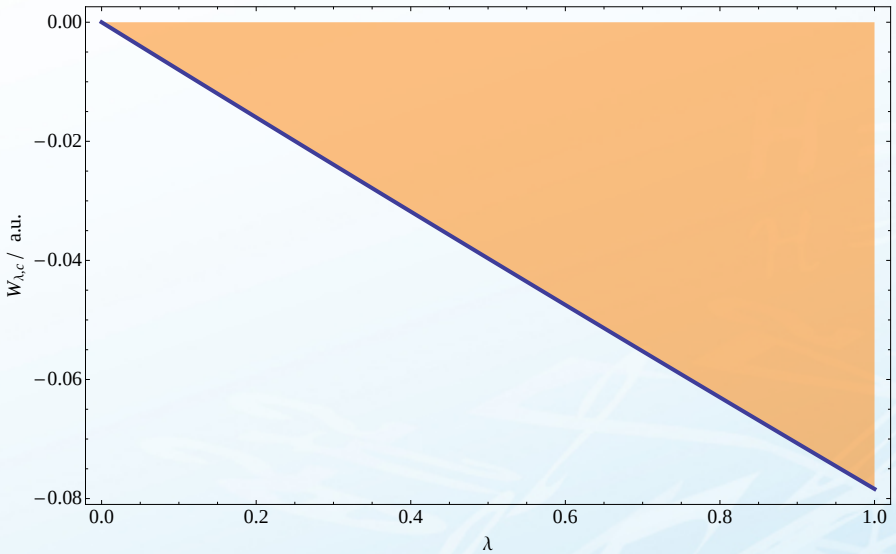
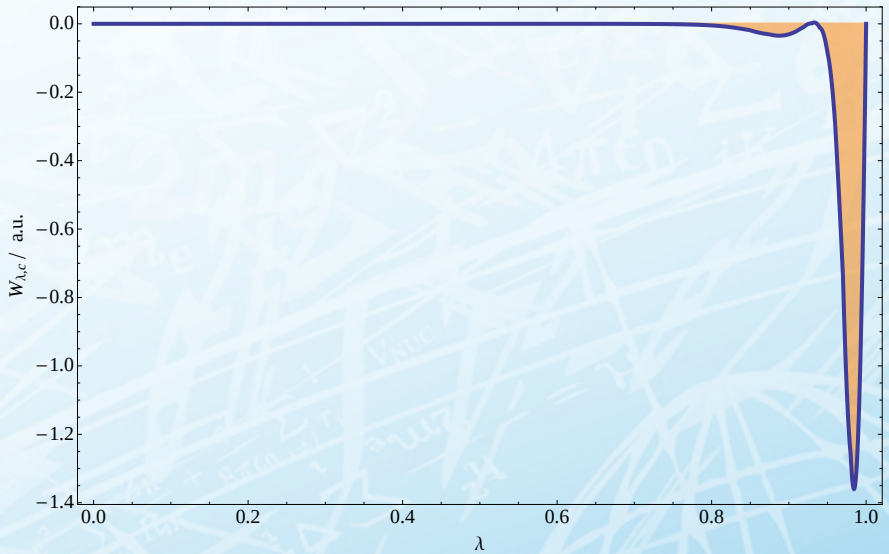
- $Z = 10$

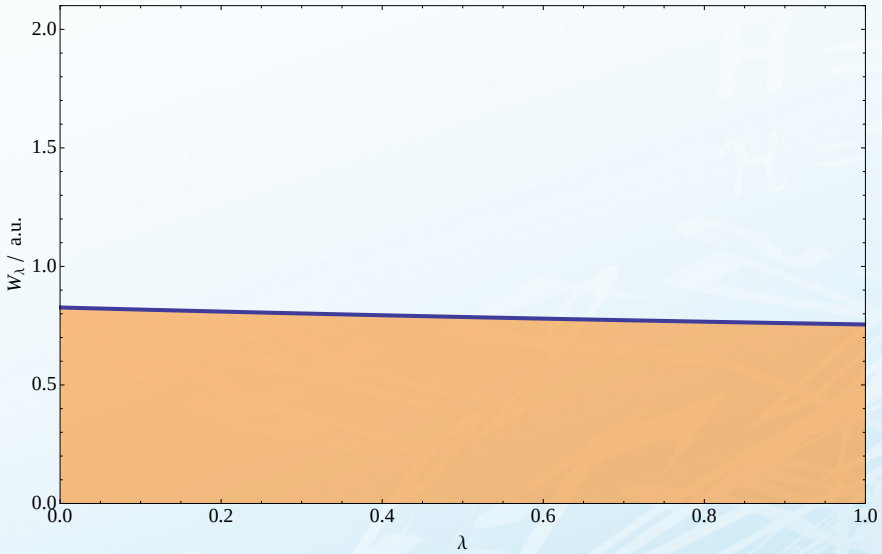


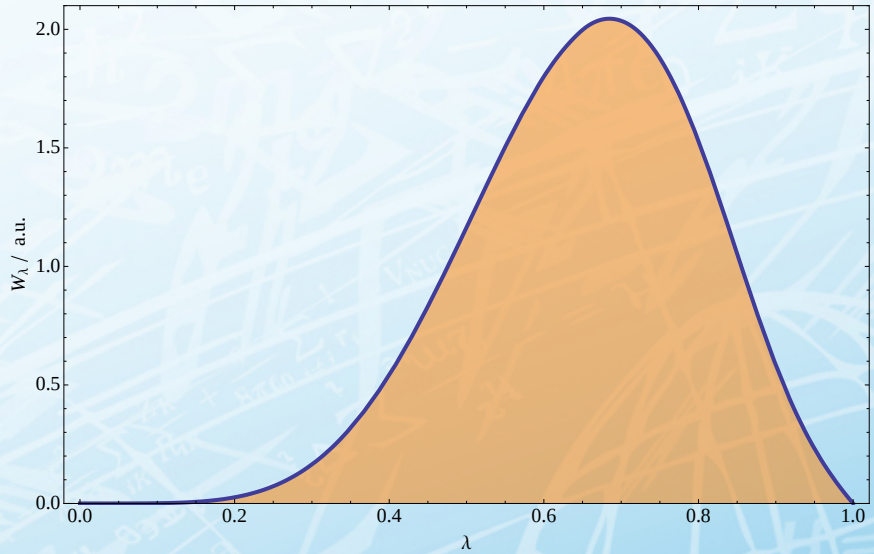


- Teale, Coriani, Helgaker, AIP Conf. Proc. (2009)

Range-dependent AC: Total curve, dissociating H_2

- We consider the total AC curve first
  - includes Coulomb, exchange and correlation
- Standard 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 curve on the right
  - it moves towards small λ values with increasing separation
  - at full separation, all total interactions are interatomic
- $R = 0.7$ bohr





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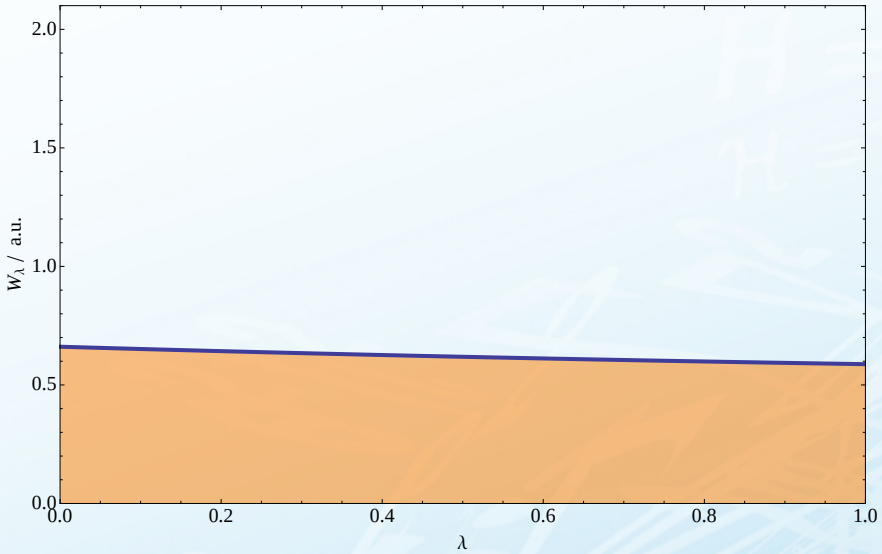
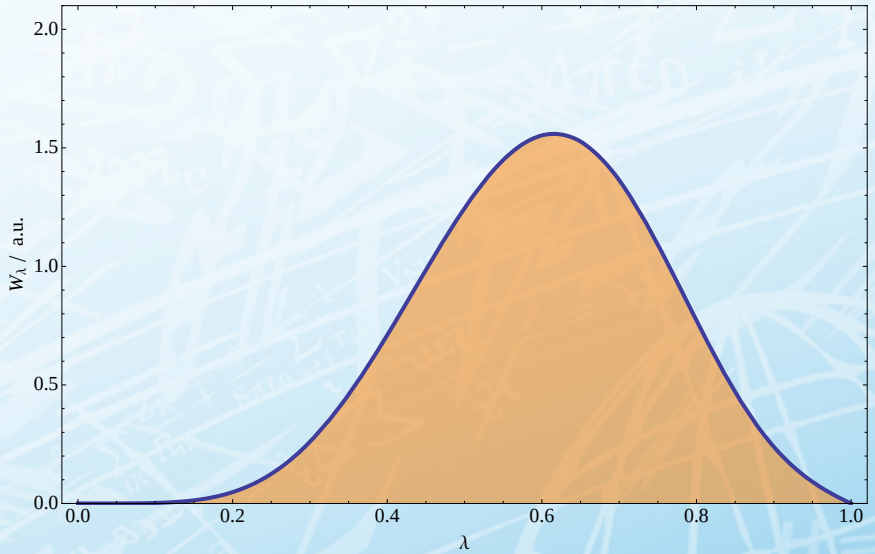
- $R = 1.4$ bohr





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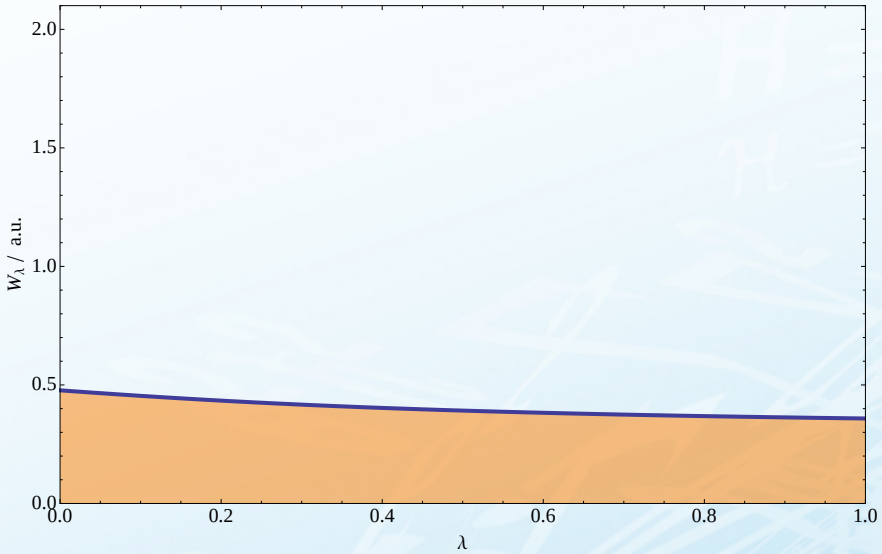
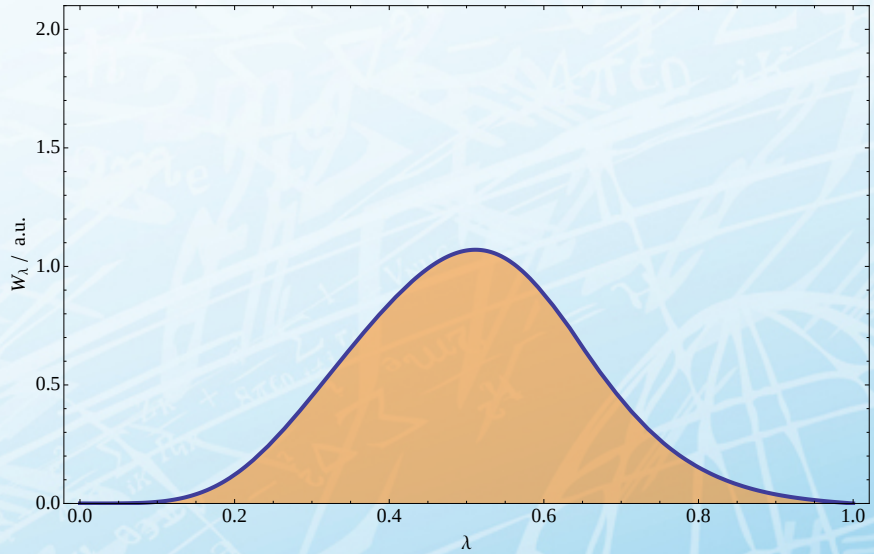
- $R = 3.0$ bohr





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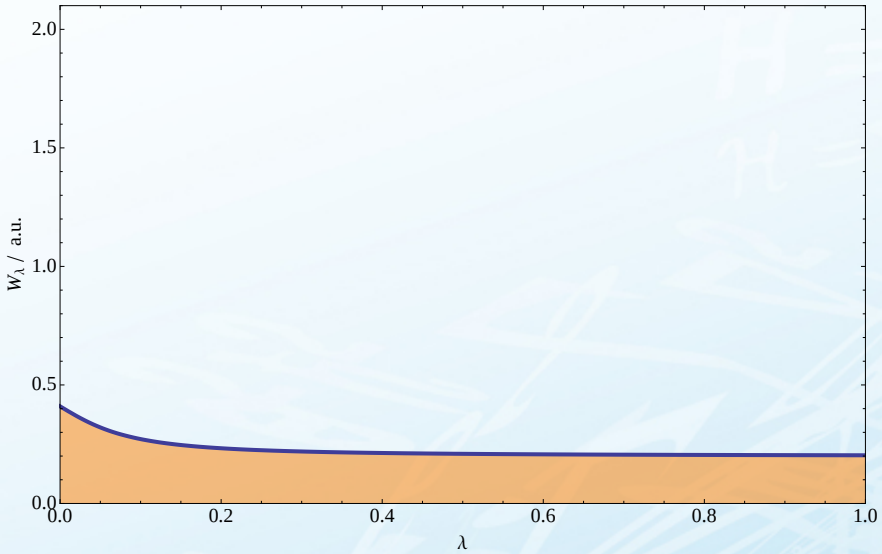

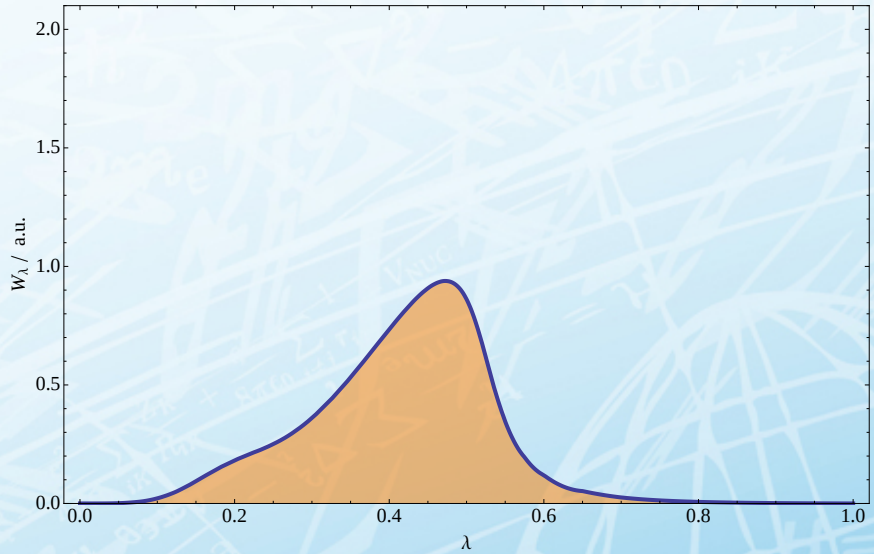

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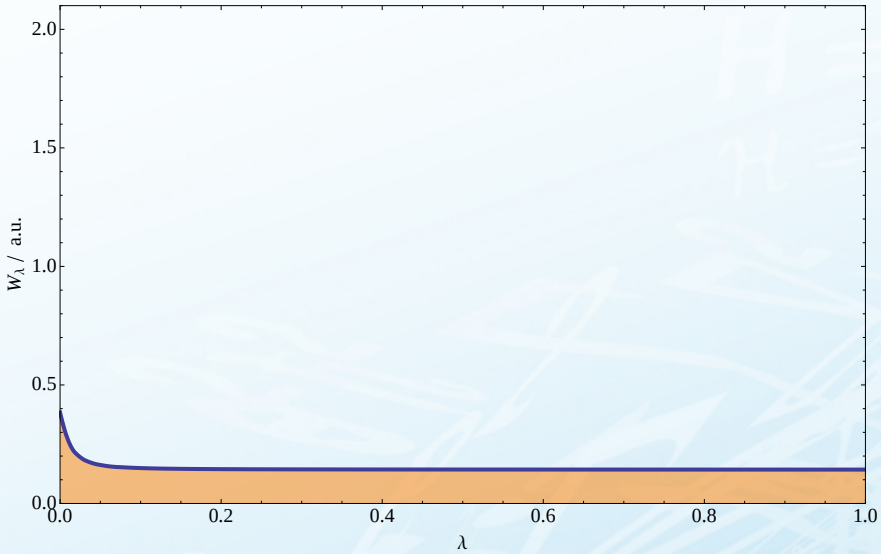

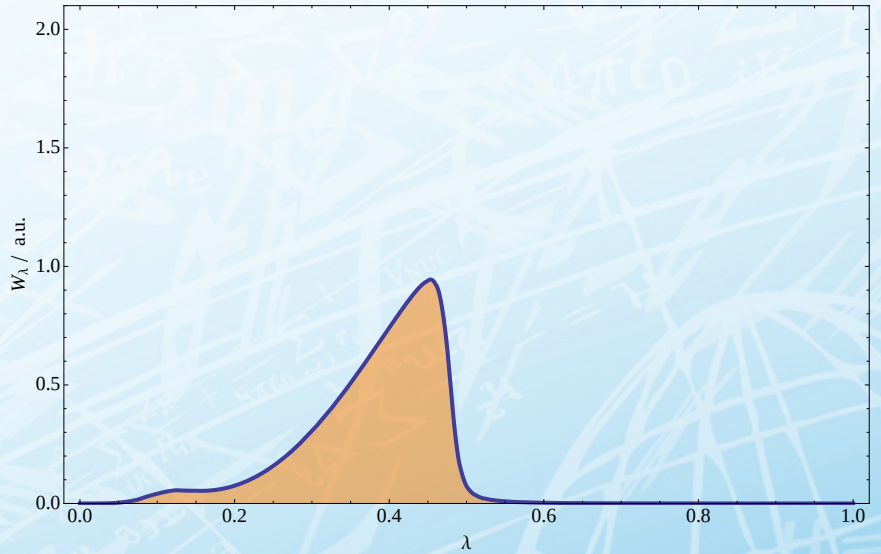

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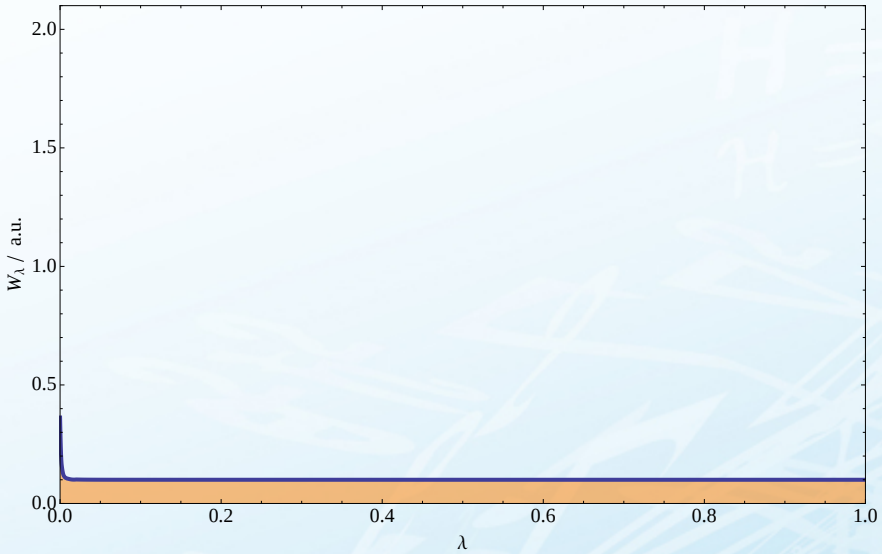
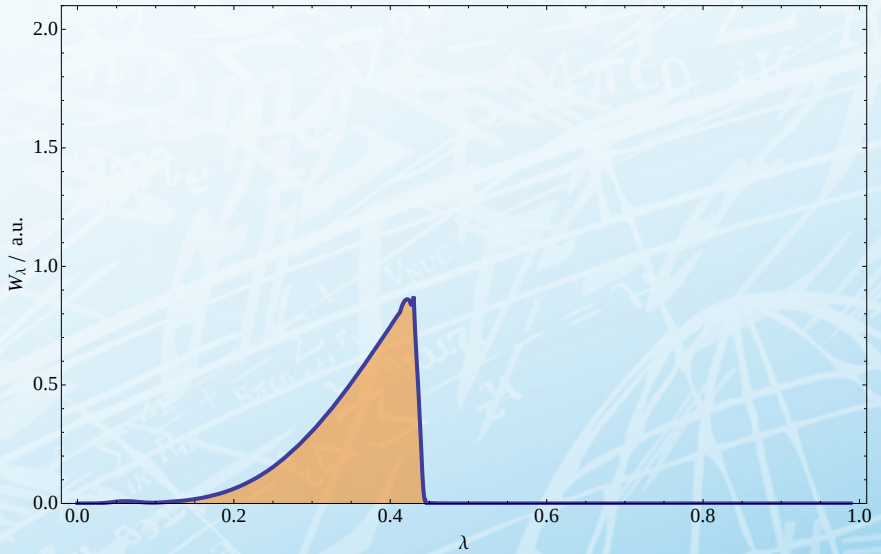
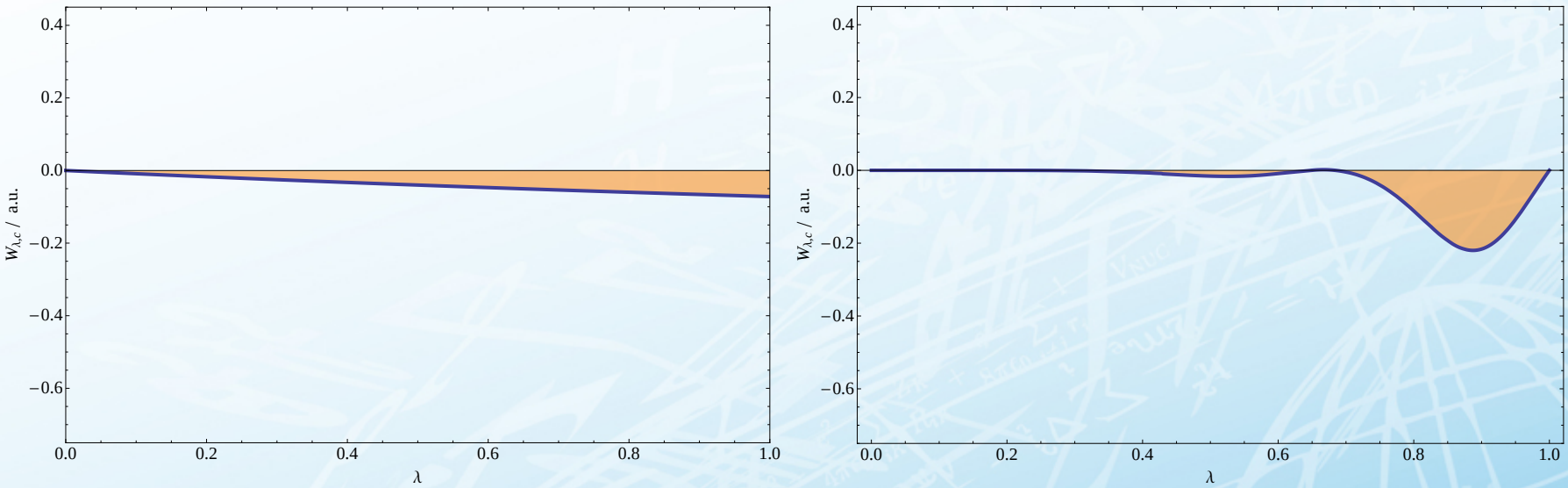
  - at full separation, all total interactions are interatomic
- $R = 10.0$ bohr





Range-dependent AC: Correlation-only, dissociating H_2

- Standard 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-dependent erf–gau curve on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 0.7$ bohr



- Static correlation is an all range effect

Range-dependent AC: Correlation-only, dissociating H_2

- Standard curve on the left
  - it undergoes the same transition from a sloped to horizontal curve
  - this reflects the transition from dynamical to static correlation
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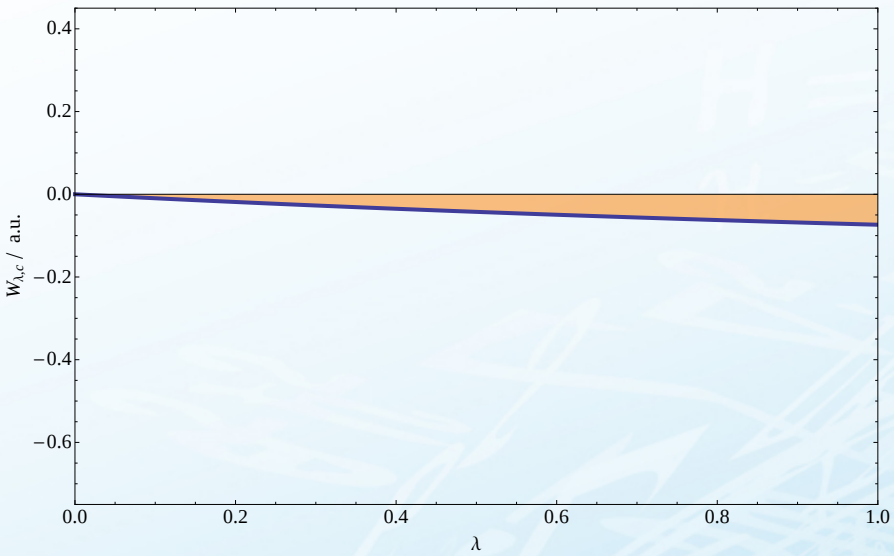
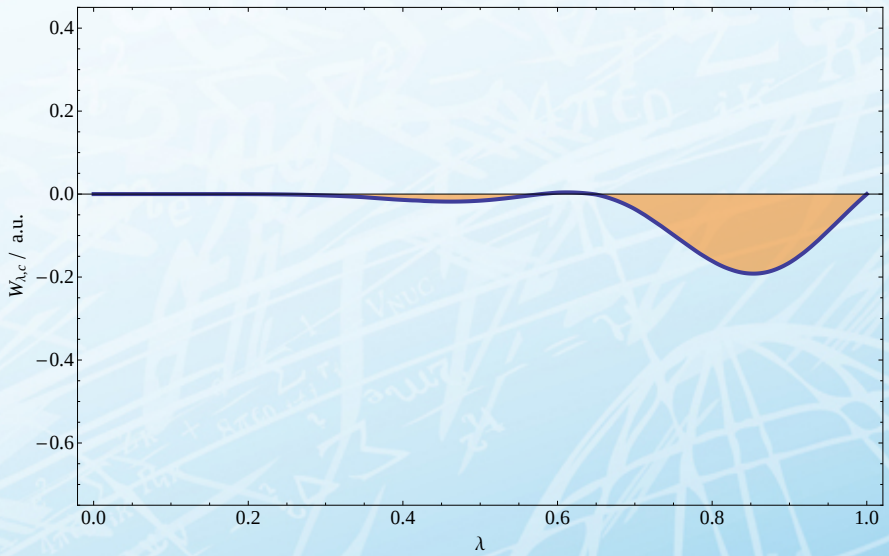
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 1.4$ bohr

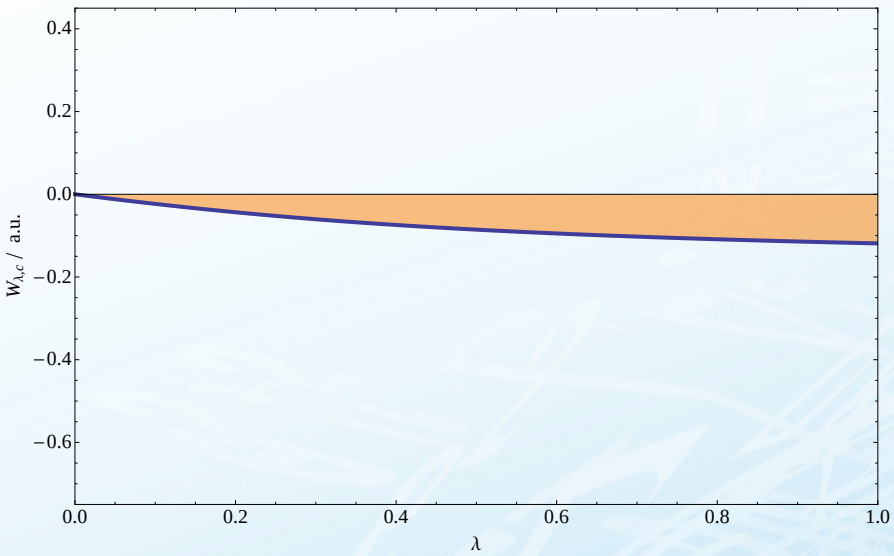


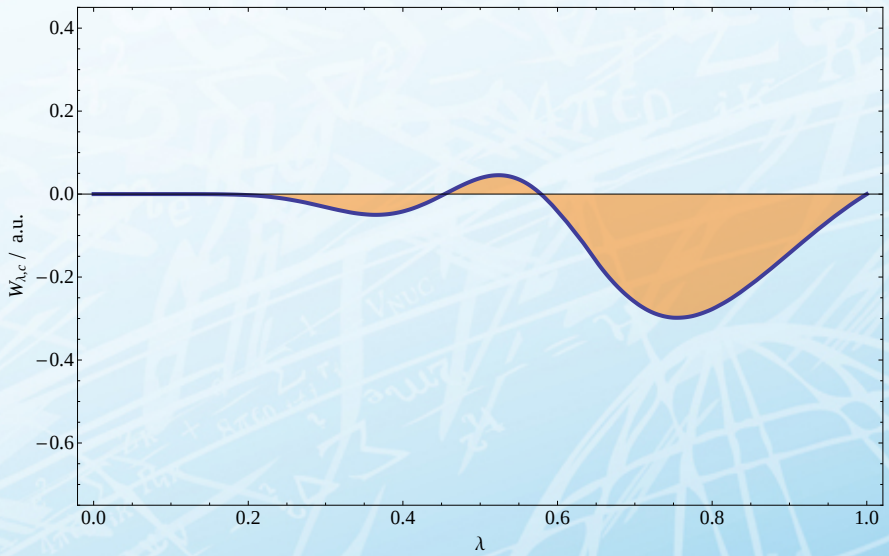


- Static correlation is an all range effect

Range-dependent AC: Correlation-only, dissociating H_2

- Standard 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-dependent erf–gau curve on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 3.0$ bohr

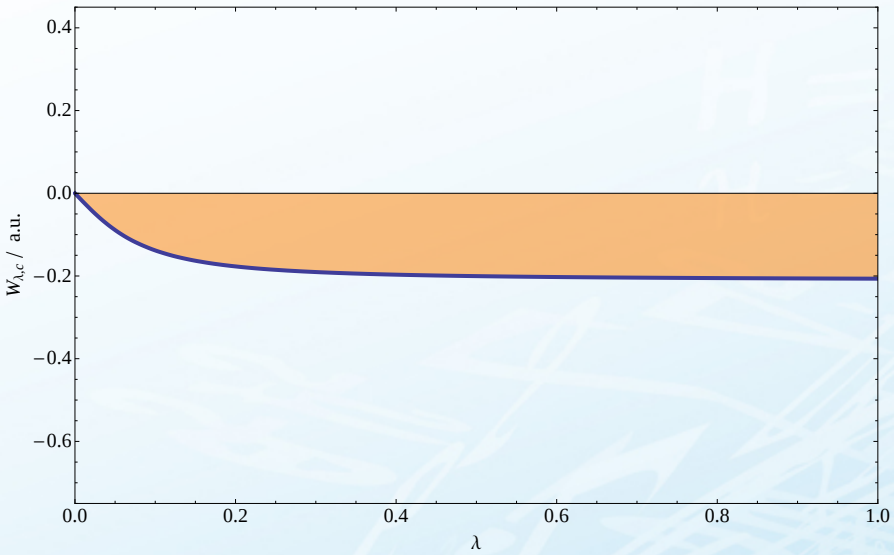


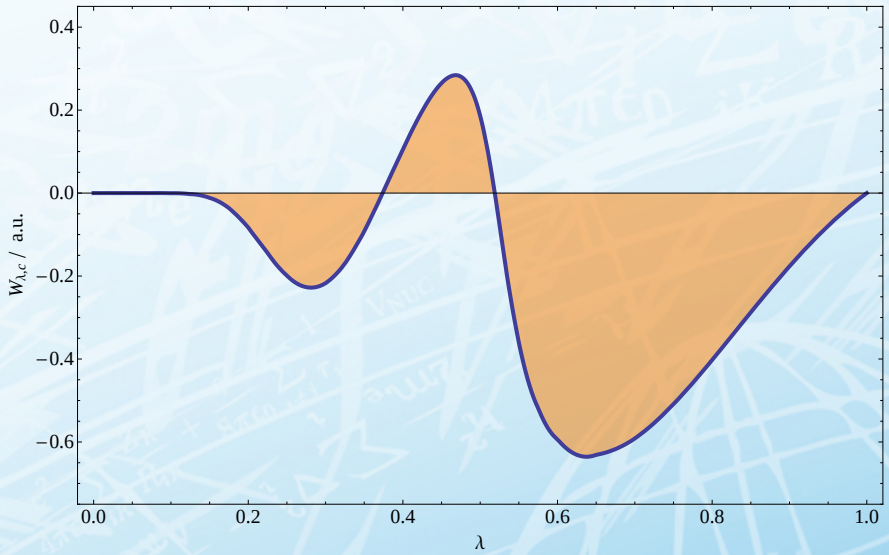


- Static correlation is an all range effect

Range-dependent AC: Correlation-only, dissociating H_2

- Standard 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-dependent erf–gau curve on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 5.0$ bohr

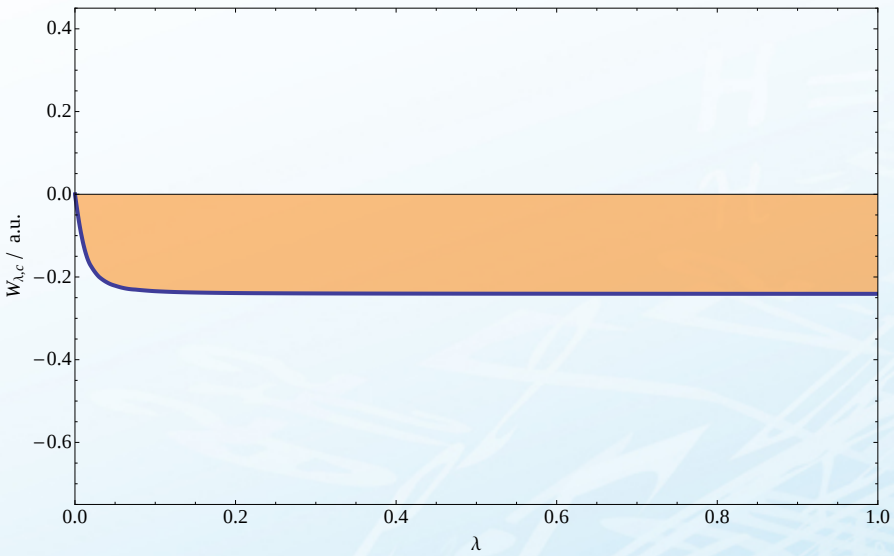


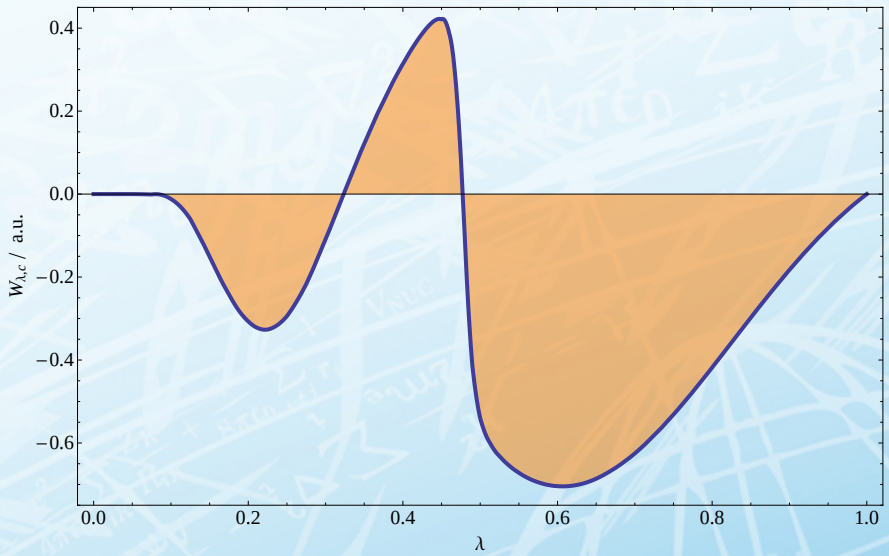


- Static correlation is an all range effect

Range-dependent AC: Correlation-only, dissociating H_2

- Standard 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-dependent erf–gau curve on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 7.0$ bohr

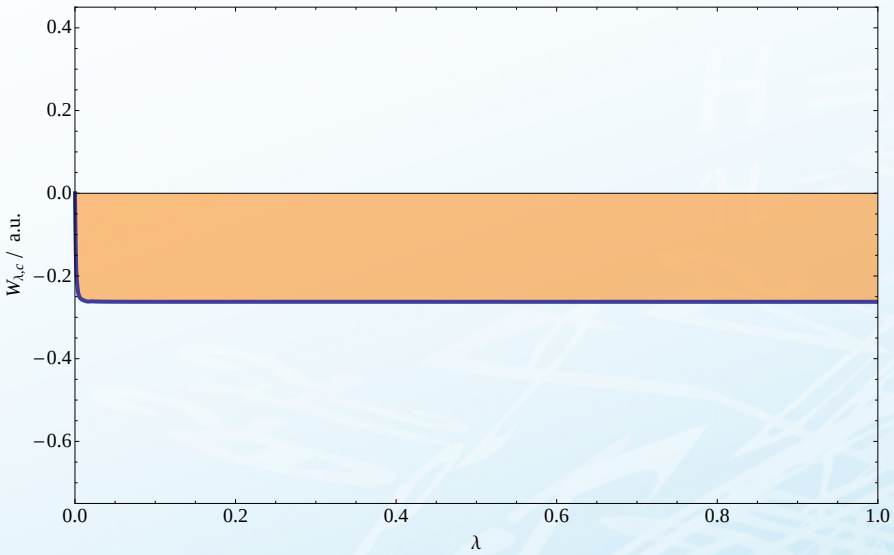


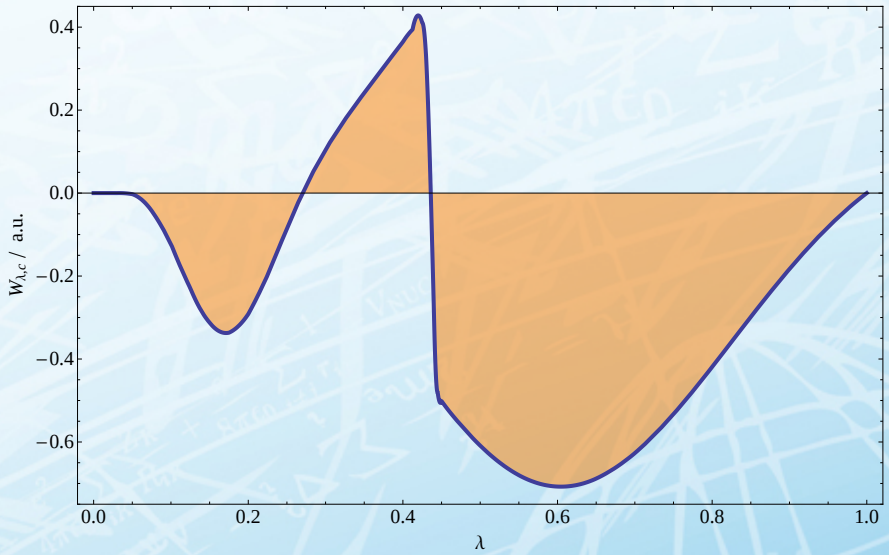


- Static correlation is an all range effect

Range-dependent AC: Correlation-only, dissociating H_2

- Standard 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-dependent erf–gau curve on the right
  - at short bond distance, the interactions are predominantly short-ranged
  - at long distances, short- and long-ranged interactions partially cancel
  - $R = 10.0$ bohr





- Static correlation is an all range effect

Modelling the Adiabatic Connection

- We now return to considering the linear AC
- Modelling of ACs can provide a constructive route to new functionals
- A prominent model is the interaction strength interpolation (ISI) of Seidl *et al.*
- This model makes use of simple density functionals for the coefficients $\mathcal{W}_\infty$ and $\mathcal{W}'_\infty$ in the asymptotic expansion $\mathcal{W}_\lambda[\rho] \rightarrow \mathcal{W}_\infty[\rho] + \mathcal{W}'_\infty[\rho]\lambda^{-1/2} (\lambda \rightarrow \infty)$
- Using these functionals an interpolation between the weak and strongly interacting limits is setup

$$\mathcal{W}_\lambda^{\mathrm{ISI}} = \mathcal{W}_\infty + \frac{X}{\sqrt{1+Y}+Z}$$

where

$$X = \frac{xy^2}{z^2}, \qquad Y = \frac{x^2y^2}{z^4}, \quad Z = \frac{xy^2}{z^3} - 1$$
$$x = -2\mathcal{W}'_0, \quad y = \mathcal{W}'_\infty, \quad z = \mathcal{W}_0 - \mathcal{W}_\infty$$

with

$$\mathcal{W}^{\mathrm{PC}}_{\mathrm{xc},\infty}[\rho] = \int \left[A\rho^{4/3}(\mathbf{r}) + B\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} \right] \mathrm{d}\mathbf{r} \qquad A = -\frac{9}{10}\left(\frac{4\pi}{3}\right)^{1/3} \quad B = \frac{3}{350}\left(\frac{3}{4\pi}\right)^{1/3}$$

$$\mathcal{W}'^{\mathrm{PC}}_{\mathrm{xc},\infty}[\rho] = \int \left[C\rho^{3/2}(\mathbf{r}) + D\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{7/6}(\mathbf{r})} \right] \mathrm{d}\mathbf{r} \qquad C = \frac{1}{2}(3\pi)^{1/2} \quad D_0 = \frac{1}{40}\left(\frac{3}{4\pi}\right)^{1/6}$$

- For the coefficient D several possibilities have been suggested and the quality of the results obtained is very sensitive to this choice
- Seidl, Perdew and Kurth, PRA **62**, 012502 (2000)

Modelling the Adiabatic Connection

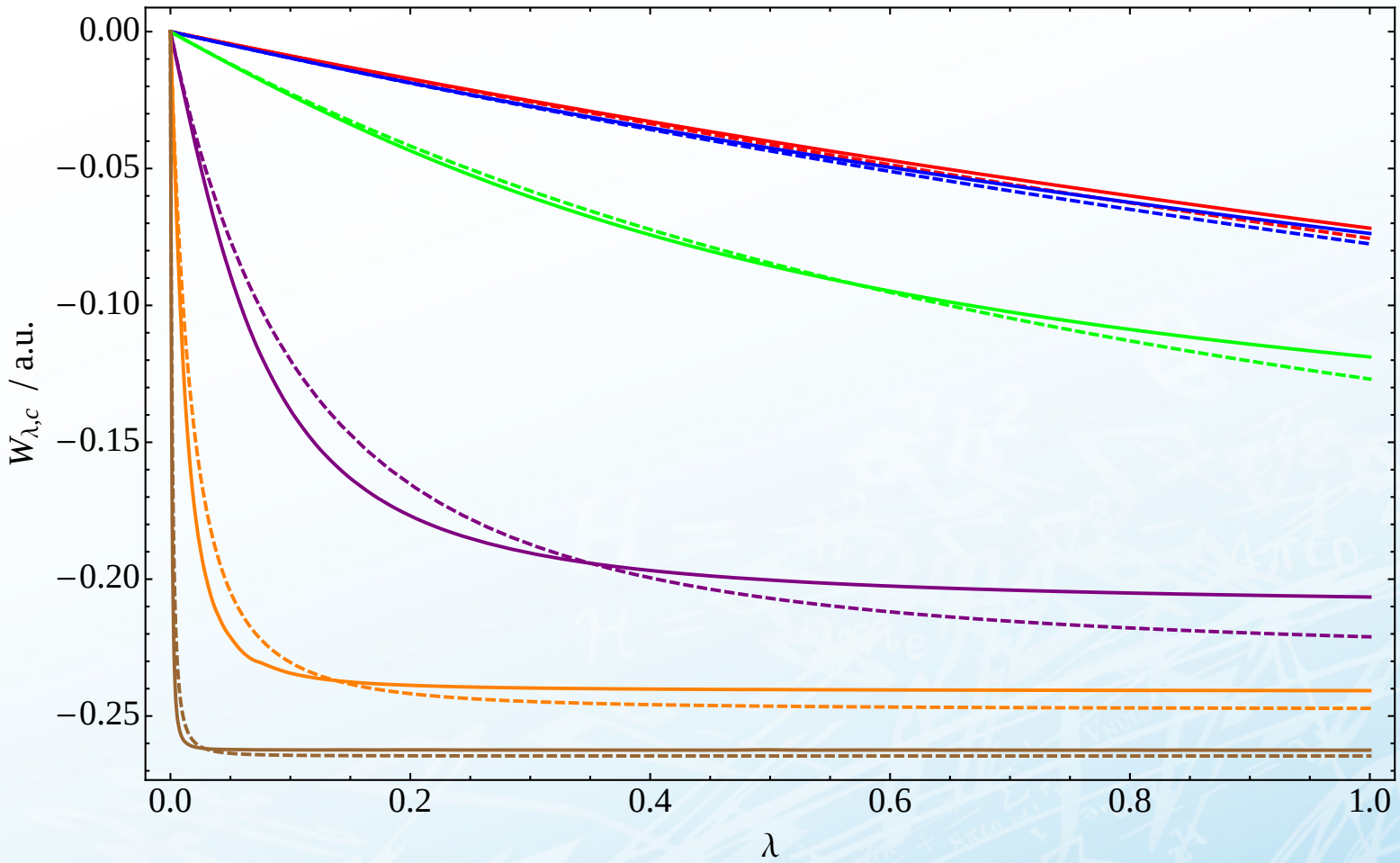
- Recently we have used our approach for the calculation of accurate ACs to guide the construction of models for the AC
- By considering the λ dependence of the correlation energies in second order perturbation theory and a simple CI model we obtained the forms

$$\mathcal{W}_{\mathrm{D}}(\lambda) = \frac{as\lambda(4a + s\lambda)}{(2a + s\lambda)^2}$$

$$\mathcal{W}_{\mathrm{CI}}(\lambda) = -\frac{1+\sqrt{5}}{4}a - \frac{4\left(2+\sqrt{5}\right)a^2 + 5\left(3+\sqrt{5}\right)as\lambda}{2\sqrt{8\left(7+3\sqrt{5}\right)a^2 + 16\left(2+\sqrt{5}\right)as\lambda + 10\left(3+\sqrt{5}\right)s^2\lambda^2}}$$

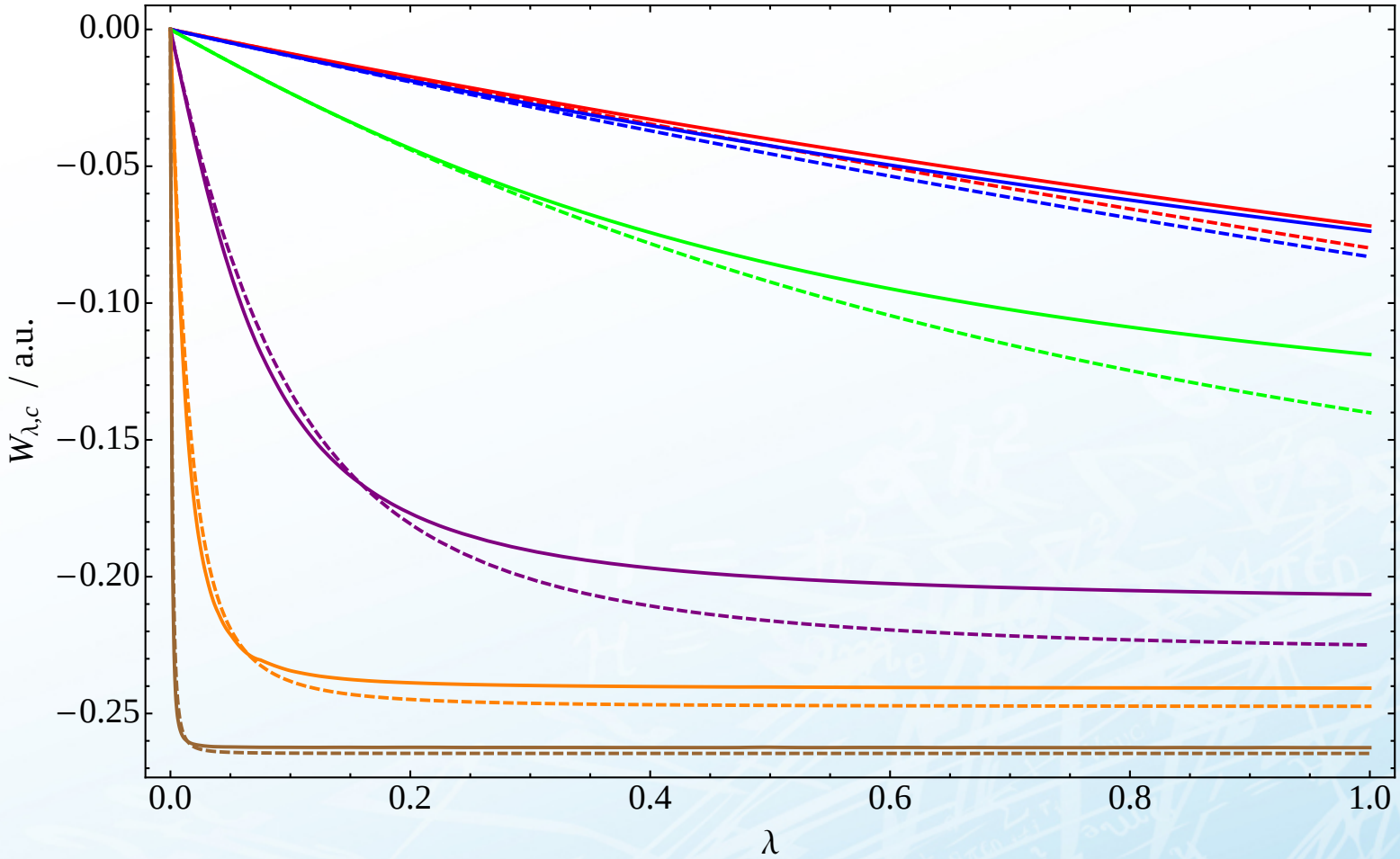
- Here the parameter a is the asymptotic value $\mathcal{W}_{\mathrm{c},\infty}$ and s the initial slope of the AC $(2E_{\mathrm{c}}^{\mathrm{GL2}})$
- Using the functional $\mathcal{W}_{\mathrm{xc},\infty}^{\mathrm{PC}}[\rho] - E_{\mathrm{x}}[\varphi^{\mathrm{KS}}]$ for the asymptotic value and $2E_{\mathrm{c}}^{\mathrm{GL2}}[\varphi^{\mathrm{KS}}]$ for the initial slope a model for the AC is obtained in terms of the density and Kohn–Sham orbitals only
- Teale, Coriani, Helgaker, JCP, *submitted* (2010)

Modelling the Adiabatic Connection



- The model $\mathcal{W}_{\mathrm{D}}(\lambda)$ gives a surprisingly good description of static correlation in H_2.

Modelling the Adiabatic Connection



- The model $\mathcal{W}_{\mathrm{Cl}}(\lambda)$ gives a slightly too negative correlation energy - both models seem to hint that the approximate $\mathcal{W}^{\mathrm{PC}}_{\mathrm{xc},\infty}[\rho] - E_{\mathrm{x}}[\varphi^{\mathrm{KS}}]$ may be slightly too negative

Modelling the Adiabatic Connection

- Integration of these models between $\lambda = 0$ and $\lambda = 1$ yields correlation energy functionals

$$E_c^{\text{D Model}} = \frac{as}{2a + s}$$

$$E_c^{\text{CI Model}} = \frac{4a^2 + \left(\sqrt{5} - 1\right) as + a\sqrt{16a^2 + 8\left(\sqrt{5} - 1\right) as - 10\left(\sqrt{5} - 3\right) s^2}}{2(\sqrt{5} - 3)s}$$

- These functionals
  - are suitable for addition to orbital dependent exchange
  - avoid error cancellation between exchange and correlation components
  - correspond to AC models that have the correct $\lambda = 0$ point and slope at $\lambda = 0$ and have a finite asymptotic value
  - do not use $\mathcal{W}'_\infty$ in their construction
  - have scaling of N^5 owing to the use of the exact slope
- Approximations to the slope are under investigation...

Summary

- Calculation of $F_\lambda[\rho]$ and the AC Integrand
  - Performed the Lieb functional maximization at different coupling strengths
  - Decomposed the universal functional into T_s, J, E_x and E_c
  - Represented these as adiabatic connection integrands
- The Adiabatic Connection and RPA
  - Discussed preliminary results obtained for the RPA and dRPA ACs
  - Compared these with more accurate results from wavefunction methodologies
  - Highlighted the shortcomings of a typical GGA functional
- Range-Dependent Adiabatic Connections
  - Examined generalized range-dependent ACs (Erf and Erf-Gau)
  - Discussed the description of static correlation in these ACs
- Modelling the Adiabatic Connection
  - Discussed some recent results for modelling the AC in terms of ρ and φ^{KS} only

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