Adiabatic Connection Forms in DFT

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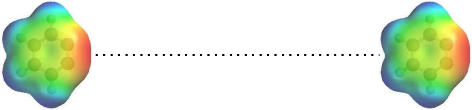
Department of Chemistry

The Adiabatic Connection

$$\hat{H}_\lambda = -\frac{1}{2}\sum_i \nabla_i^2 + \lambda \hat{V}_{\mathrm{ee}} + \sum_i v_\lambda(\mathbf{r}_i)$$



$\lambda = 0$, *Non-interacting*

$\lambda = 1$, *Interacting system*

$$\begin{aligned} E_{\mathrm{XC}} &= \int_0^1 W_\lambda \, d\lambda \\ W_\lambda &= \langle \psi_\lambda | \hat{V}_{\mathrm{ee}} | \psi_\lambda \rangle - J \end{aligned}$$

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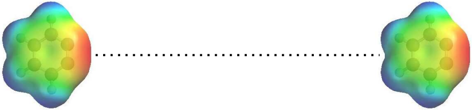

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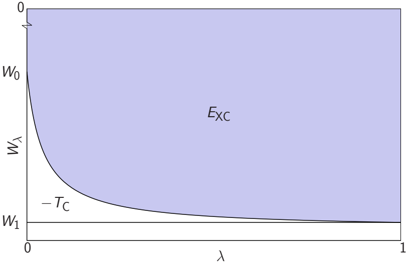
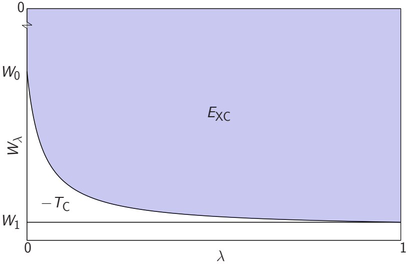


Exact Properties



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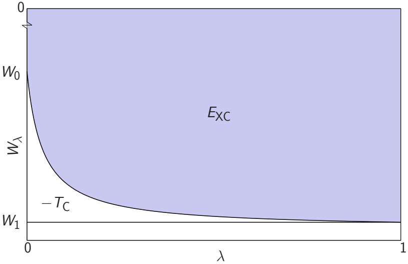
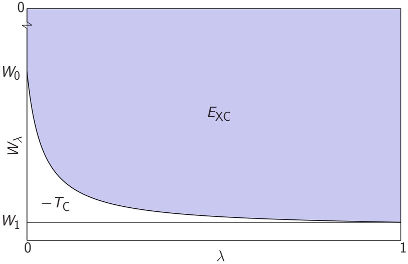


$$W_\lambda = \langle \psi_\lambda | \hat{V}_{ee} | \psi_\lambda \rangle - J$$

$$W_0 = \langle \psi_0 | \hat{V}_{ee} | \psi_0 \rangle - J = J + E_X - J = E_X$$

Exact Properties



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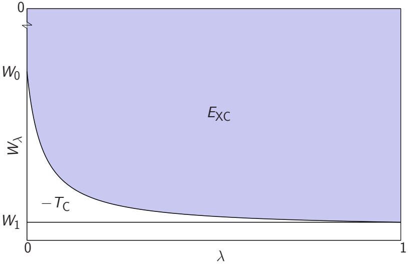
Exact Properties



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$$\left.\frac{\partial W_\lambda}{\partial\lambda}\right|_{\lambda=0} = 2E_{C,GL2} = -\frac{1}{2}\sum_{i,j,\alpha,\beta}\frac{|(\alpha i|\beta j)-(\alpha j|\beta i)|^2}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_i-\varepsilon_j} - 2\sum_{i,\alpha}\frac{\langle\phi_i|v_X - v_X^{NL}|\phi_\alpha\rangle^2}{\varepsilon_\alpha-\varepsilon_i}$$

Functional Development ...

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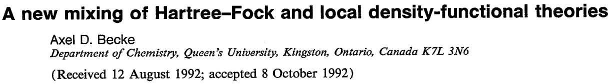

A new mixing of Hartree–Fock and local density-functional theories

Axel D. Becke
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 12 August 1992; accepted 8 October 1992)

$$W_\lambda = a + b\lambda \qquad E_{\mathrm{XC}} = a + \frac{b}{2} \qquad \textbf{H\&H} \rightarrow \textbf{B3LYP}$$

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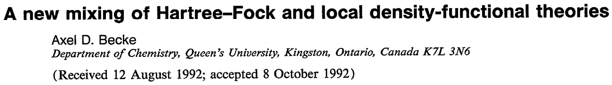

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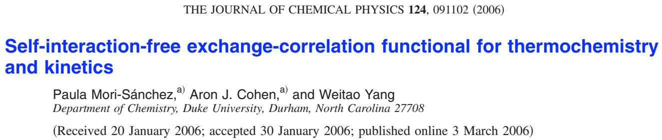

THE JOURNAL OF CHEMICAL PHYSICS **124**, 091102 (2006)

Self-interaction-free exchange-correlation functional for thermochemistry and kinetics

Paula Mori-Sánchez,[a] Aron J. Cohen,[a] and Weitao Yang
Department of Chemistry, Duke University, Durham, North Carolina 27708

(Received 20 January 2006; accepted 30 January 2006; published online 3 March 2006)

$$W_\lambda = a + \frac{b\lambda}{1 + c\lambda} \qquad E_{XC} = a + \frac{b}{c}\left(1 - \frac{\log_e(1+c)}{c}\right) \qquad \textbf{MCY}$$

(Ernzerhof, CPL **263** 499 (1996))

$$W_\lambda = a + \frac{b\lambda}{1 + c\lambda}$$

Choice of a, b, c ....

$$a = W_0 = E_X$$

$$b = \left.\frac{\partial W_\lambda}{\partial \lambda}\right|_{\lambda=0}$$

c chosen to reproduce BLYP W_λ at some λ

$\longrightarrow$ MCY1 (1e SI free)

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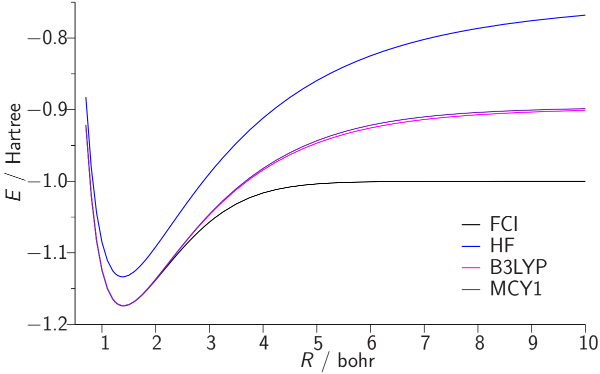
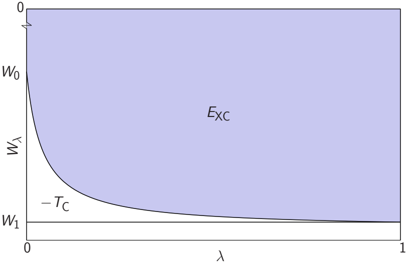
PE curve of H_2 in RKS – static correlation / fractional spins



Why poor? Mathematical form or approximate parameters?

How well does it perform when all three parameters are determined so as to reproduce exact properties of the adiabatic connection?

Strategy - determine accurate properties using Full CI



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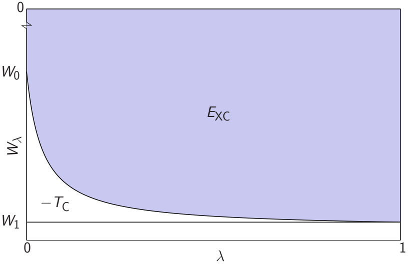

$$W_0^{\mathrm{FCI}} = E_{\mathrm{X}}^{\mathrm{FCI}} = -\frac{1}{2} J^{\mathrm{FCI}}$$

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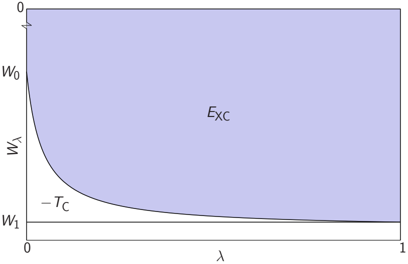

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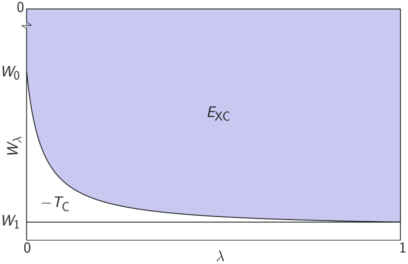

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... evaluated using 'exact' KS orbitals [Wu & Yang, JCP **118** 2498 (2003)]

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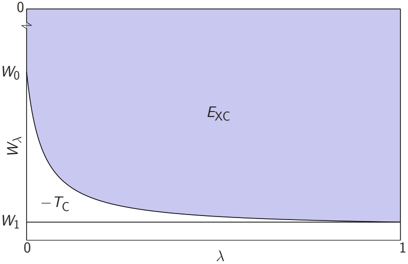

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Then choose *a*, *b*, *c* to reproduce these three quantities exactly.

$$E_{\mathrm{XC}} = E_{\mathrm{XC}}(a, b, c) = a + (b/c)\left(1 - \frac{\log_e(1+c)}{c}\right)$$

$$\Big\downarrow$$

$$E = T_s^{\mathrm{FCI}} + V_{\mathrm{ne}}^{\mathrm{FCI}} + J^{\mathrm{FCI}} + V_{\mathrm{nn}} + E_{\mathrm{XC}}$$

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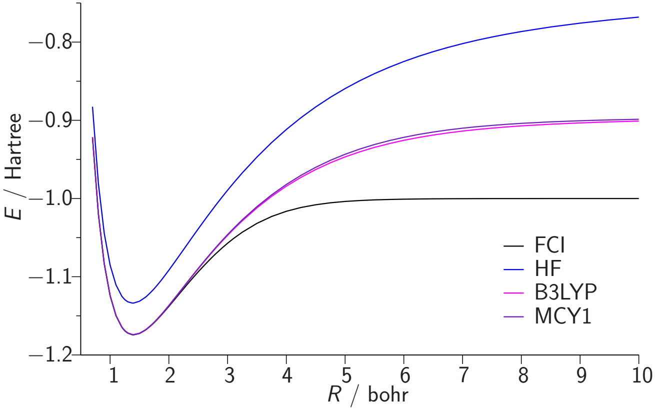
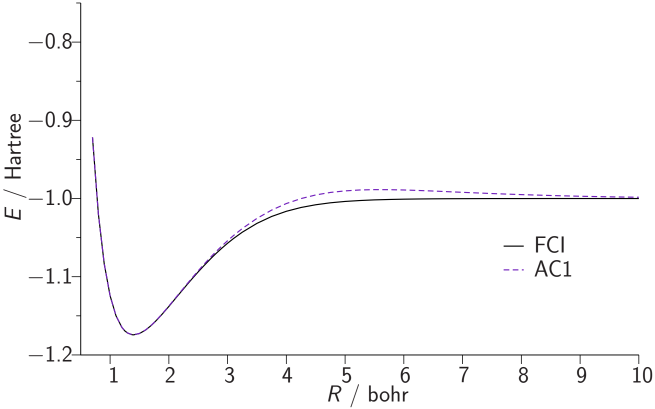
$$\Big\downarrow$$

$$E = T_s^{\mathrm{FCI}} + V_{\mathrm{ne}}^{\mathrm{FCI}} + J^{\mathrm{FCI}} + V_{\mathrm{nn}} + E_{\mathrm{XC}}$$

Discrepancy from FCI quantifies ability of AC form to describe H2 dissociation

Denote results **AC1**


−0.8
−0.9
−1.0
−1.1
−1.2
E / Hartree
1
2
3
4
5
6
7
8
9
10
R / bohr
FCI
HF
B3LYP
MCY1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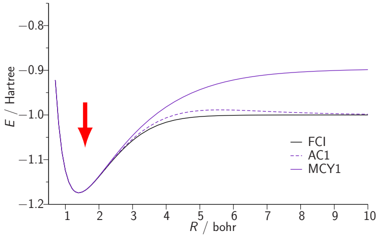
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2
3
4
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6
7
8
9
10
R / bohr
FCI
AC1
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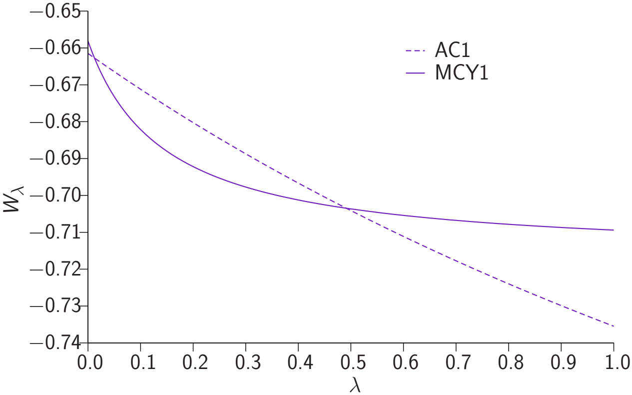
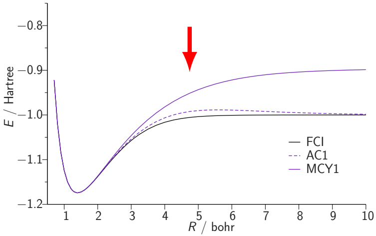
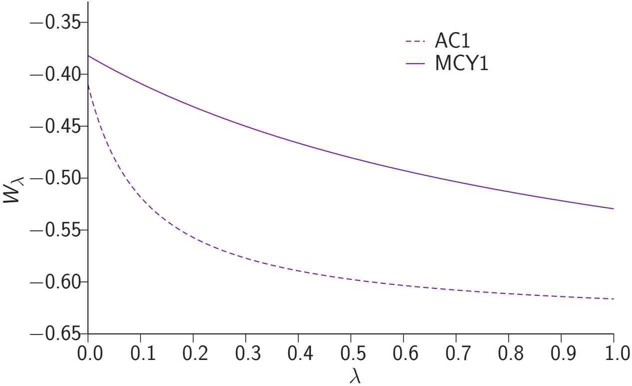
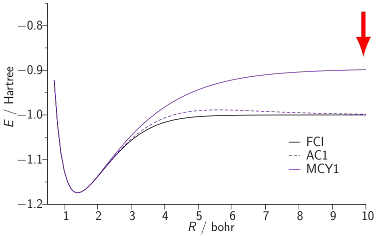

W_λ
−0.65
−0.66
−0.67
−0.68
−0.69
−0.70
−0.71
−0.72
−0.73
−0.74
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
λ
AC1
MCY1


E / Hartree
−0.8
−0.9
−1.0
−1.1
−1.2
1
2
3
4
5
6
7
8
9
10
R / bohr
FCI
AC1
MCY1


W_λ
−0.35
−0.40
−0.45
−0.50
−0.55
−0.60
−0.65
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
λ
AC1
MCY1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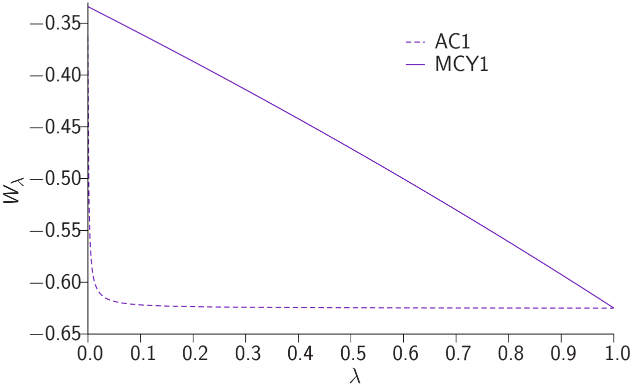
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W_λ
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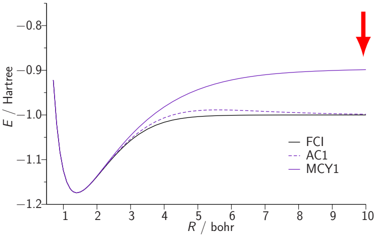
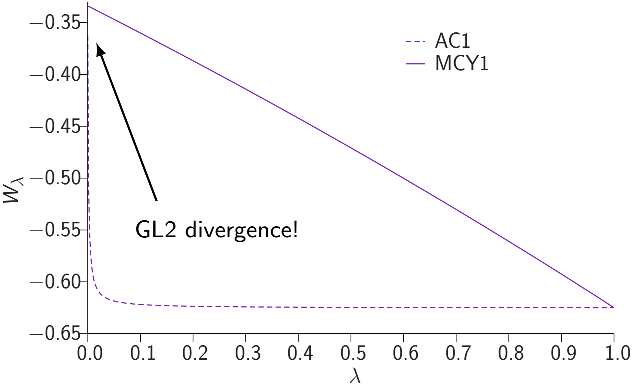
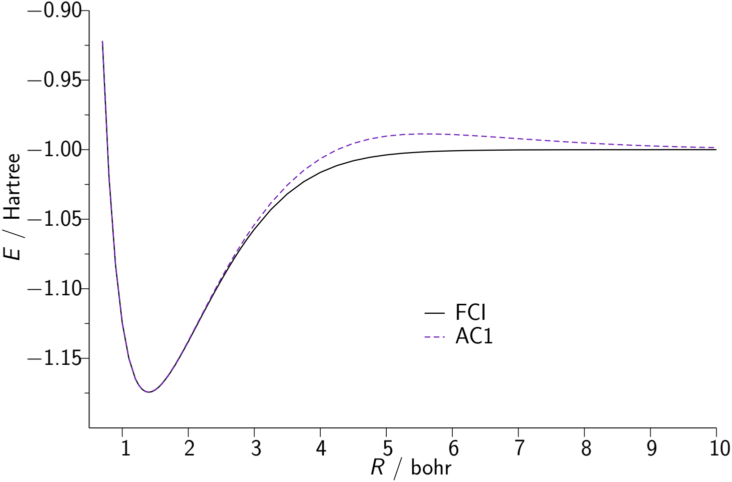




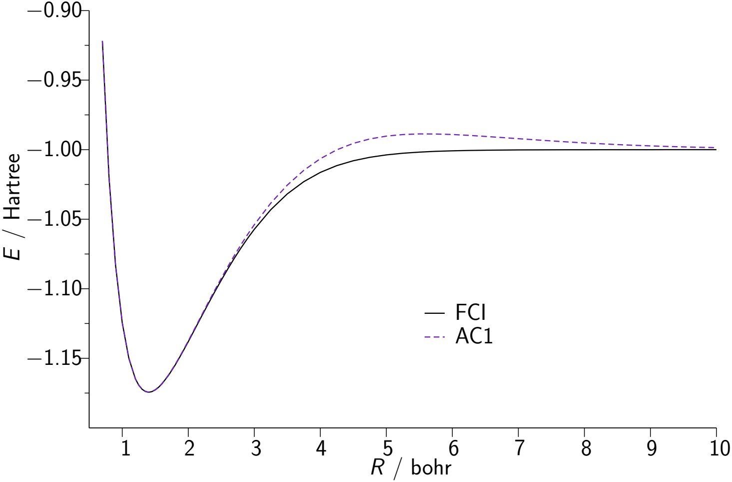
GL2 divergence!

$$W_\lambda^{\mathrm{AC1}} = a + \frac{b\lambda}{1 + c\lambda}$$



$$W_\lambda^{\text{AC1}} = a + \frac{b\lambda}{1 + c\lambda}$$

$$W_\lambda^{\text{AC6}} = a + b \exp(-c\lambda)$$



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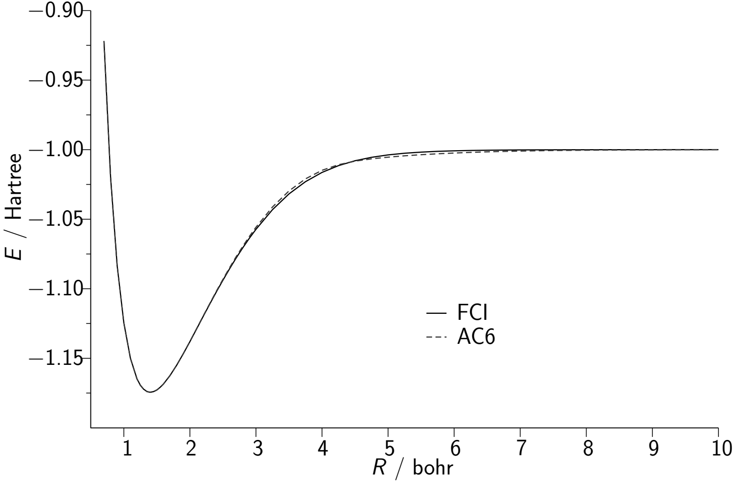

Other 2 electron systems? He-isoelectronic series!

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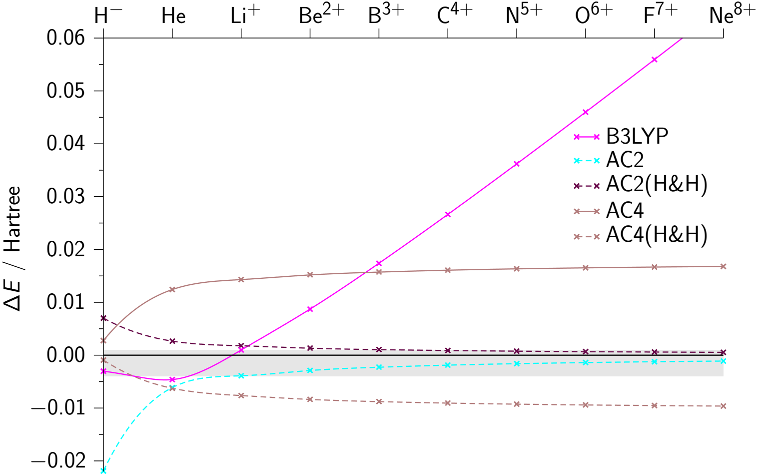

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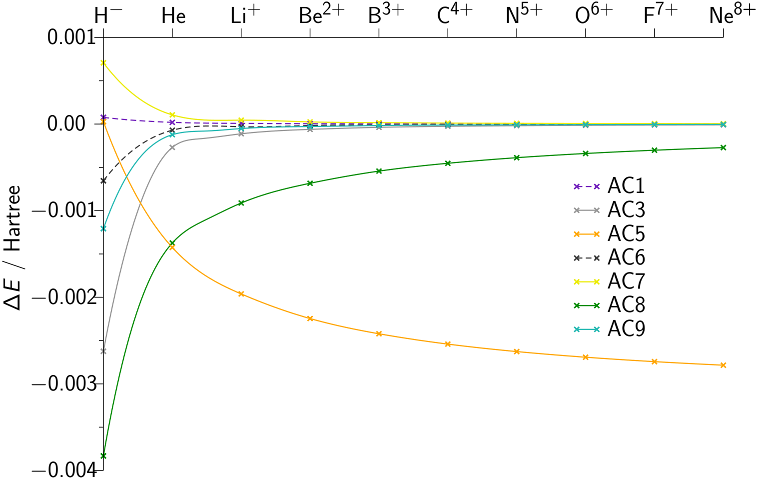


Why do most improve, but three get worse from H^- to Ne^{8+}?
How do we achieve such high accuracy for large Z?

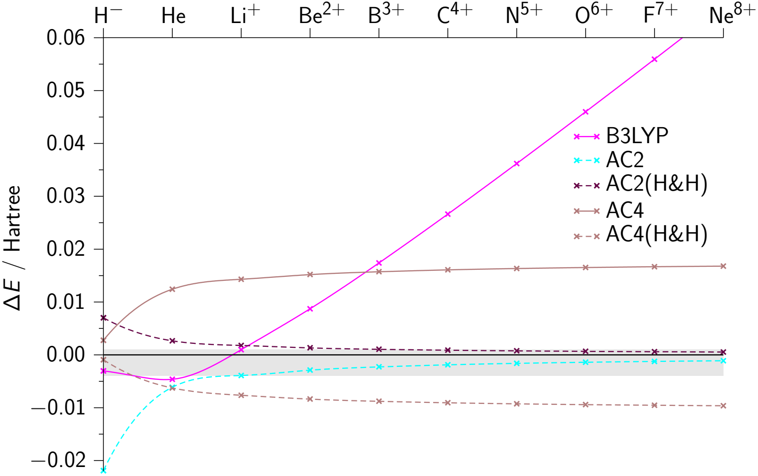
Why do most improve, but three get worse from $H^-$to Ne^{8+}?
How do we achieve such high accuracy for large Z?

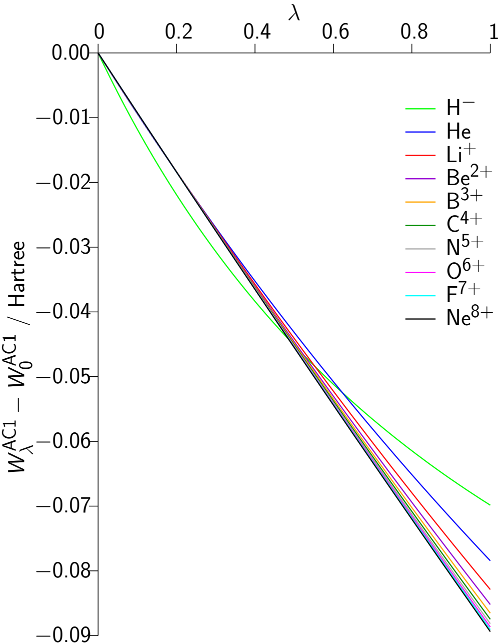
In the $Z \to \infty$ high-density limit, the exact AC is linear

$$W_\lambda = E_X + 2E_{C,GL2}\lambda \qquad (E_{XC} = E_X + E_{C,GL2})$$

As $Z \to \infty$, most of the AC forms exactly reproduce this.

But, three of the forms do *not* behave in this manner. They are the forms that become less accurate from $H^-$to Ne^{8+}.


H$^-$
He
Li$^+$
Be^{2+}
B^{3+}
C^{4+}
N^{5+}
O^{6+}
F^{7+}
Ne^{8+}
0.06
0.05
0.04
0.03
0.02
0.01
0.00
−0.01
−0.02
ΔE / Hartree
B3LYP
AC2
AC2(H&H)
AC4
AC4(H&H)


λ
0
0.2
0.4
0.6
0.8
1
0.00
−0.01
−0.02
−0.03
−0.04
−0.05
−0.06
−0.07
−0.08
−0.09
$W_\lambda^{\mathrm{AC1}} - W_0^{\mathrm{AC1}}$ / Hartree
H^-
He
Li^+
Be^{2+}
B^{3+}
C^{4+}
N^{5+}
O^{6+}
F^{7+}
Ne^{8+}

Conclusions

J. Chem. Phys. **126** 244104 (2007)
J. Chem. Phys. **129** 064105 (2008)

- Illustration of how accurate Ψ can provide insight into DFT
- Simple AC forms can be very accurate for 2e systems, when exact input data provided
- Key role of GL2 energy in H_2 ($R \to \infty$) and He-series ($Z \to \infty$)

Acknowledgments

Michael Peach

Andy Teale

EPSRC