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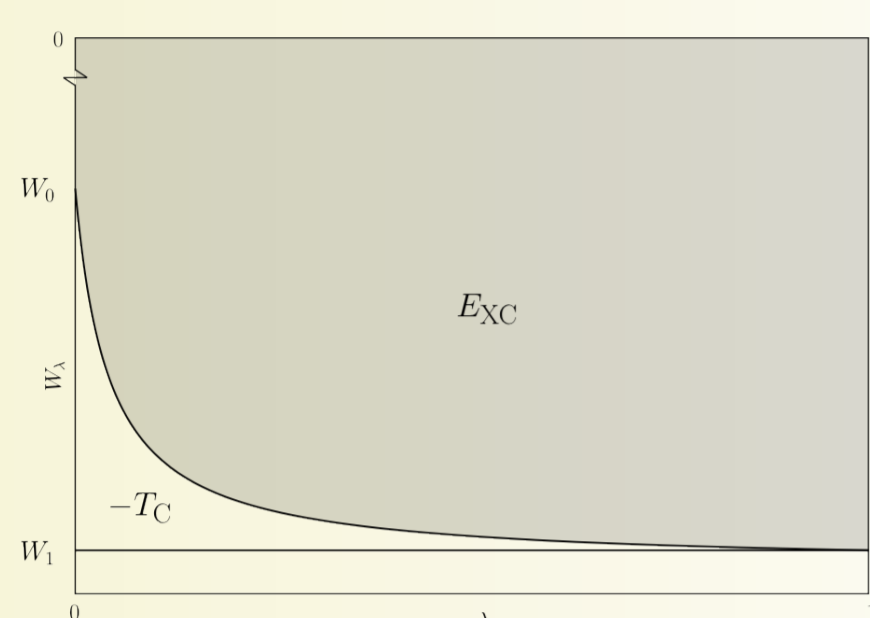
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Introduction

The adiabatic connection formulation¹ of density functional theory^{2,3} allows one to write the exchange–correlation (XC) energy as an integral over an inter-electron coupling strength parameter λ ,

$$E_{XC} = \int_0^1 d\lambda W_\lambda, \text{ where } W_\lambda = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - J, \quad (1)$$

which connects the noninteracting Kohn–Sham system ($\lambda = 0$) to the interacting physical system ($\lambda = 1$). Three known properties of the exact W_λ are



$$W_0 = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle - J = E_X, \quad (2)$$

$$W_1 = \langle \Psi_1 | \hat{V}_{ee} | \Psi_1 \rangle - J = V_{ee} - J, \quad (3)$$

$$W'_0 = 2E_C^{GL2}. \quad (4)$$

Some existing XC functionals approximate the unknown form of W_λ in terms of simple mathematical expressions, typically involving parameters which either exactly or approximately satisfy known properties of W_λ such as those in Eqs. (2)–(4). The Becke half-and-half⁴ and Mori–Sánchez–Cohen–Yang⁵ functionals are two examples where Eq. (2) is satisfied exactly, but which satisfy approximations to Eqs. (3) and (4).

Our Procedure

We have developed a procedure^{6,7} to test the accuracy of approximate W_λ forms. We use FCI calculations to compute exact values of W_0 , W_1 and W'_0 and use them to determine the parameters in the approximate forms, which are used to construct an XC energy through Eq. (1). This data is then combined with other FCI energy components to give the total electronic energy. Any discrepancy between the FCI total energy and the energy from our method is therefore due to the inaccuracies in the form used to model W_λ .

Several computational advantages arise for two-electron systems: $E_X = -1/2J$, which removes the orbital dependence of this expression and E_C^{GL2} reduces to the standard second order Møller–Plesset perturbation theory correlation energy expression E_C^{MP2} which is dependent only on the exact KS orbitals and orbital energies obtained from the FCI density. Furthermore, T_s becomes an explicit functional of the density given by the von Weizsäcker expression T_W . We therefore use

$$W_0 = -J^{FCI}/2, \quad (5)$$

$$W_1 = V_{ee}^{FCI} - J^{FCI}, \quad (6)$$

$$W'_0 = 2E_{C,MP2}^{FCI}, \quad (7)$$

to define the parameters in model forms for W_λ . From these the XC energy is computed via Eq. (1). The total energy is then

$$E = T_W^{FCI} + E_{ne}^{FCI} + J^{FCI} + E_{nn} + E_{XC}^{AC}. \quad (8)$$

Approximate Adiabatic Connection Forms

We consider the following approximate forms

$$\begin{aligned} W_\lambda^{AC1} &= a + \frac{b\lambda}{1+c\lambda} & W_\lambda^{AC5} &= a + \left(\frac{b\lambda}{1+\lambda} \right) + c \left(\frac{\lambda}{1+\lambda} \right)^2 \\ W_\lambda^{AC2} &= a + b\lambda & W_\lambda^{AC6} &= a + b \exp(-c\lambda) \\ W_\lambda^{AC3} &= a + b\lambda + c\lambda^2 & W_\lambda^{AC7} &= a + b \log(1+c\lambda) \\ W_\lambda^{AC4} &= a + \left(\frac{b\lambda}{1+\lambda} \right) & W_\lambda^{AC8} &= a + b \tanh(-c\lambda) \\ & & W_\lambda^{AC9} &= a + b\lambda \exp(-c\lambda), \end{aligned}$$

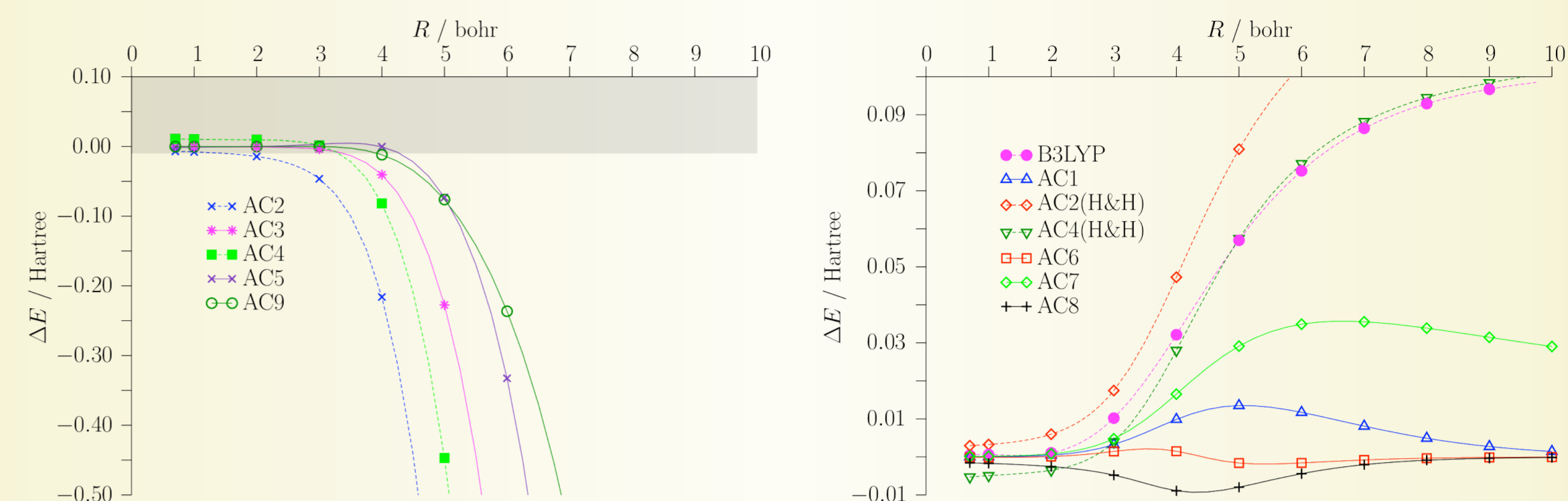
where a , b and c are defined so as to satisfy Eqs. (5)–(7). In the case of the two parameter forms it is possible to define b in two different ways. In the case where b is chosen such that the form satisfies Eq. (6), we denote the results by H&H since this is an exact representation of Becke’s half-and-half functional.

References and Acknowledgements

- This work has been supported by the EPSRC (MJGP studentship), the Norwegian Research Council, Grant No. 171185 (AMT) and the Nuffield Foundation through a science bursary (AMM). The authors thank F. R. Manby and K. Burke for helpful discussions and T. Helgaker for suggesting the basis set scaling approach.
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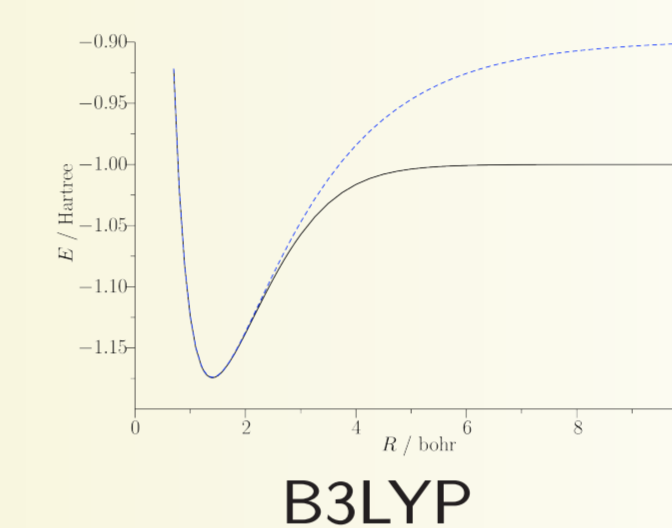
Singlet ground state of H_2

We use the d-aug-cc-pV6Z basis set within a restricted formalism. The plots below present errors in total electronic energies as a function of R .

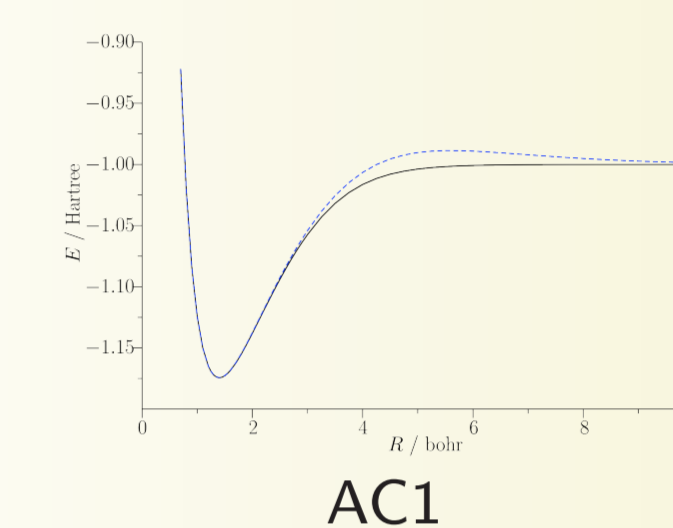


The shaded area on the left hand plot represents the scale of the right hand plot.

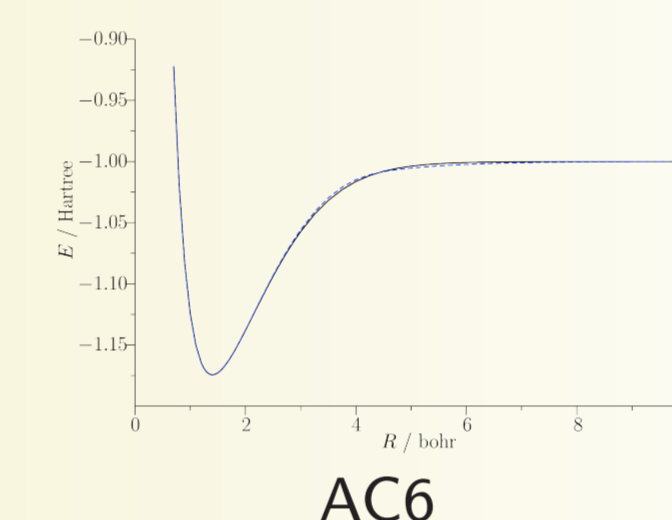
B3LYP⁸ serves as our exemplar XC functional. Its performance is reasonable near equilibrium, becoming significantly poorer as R increases. Several forms diverge as R increases. Those forms which do not diverge perform variably; of particular note are the AC1, AC6 and AC8 forms which are formally exact in the dissociation limit where the divergence of W'_0 is essential to obtain correct behaviour.



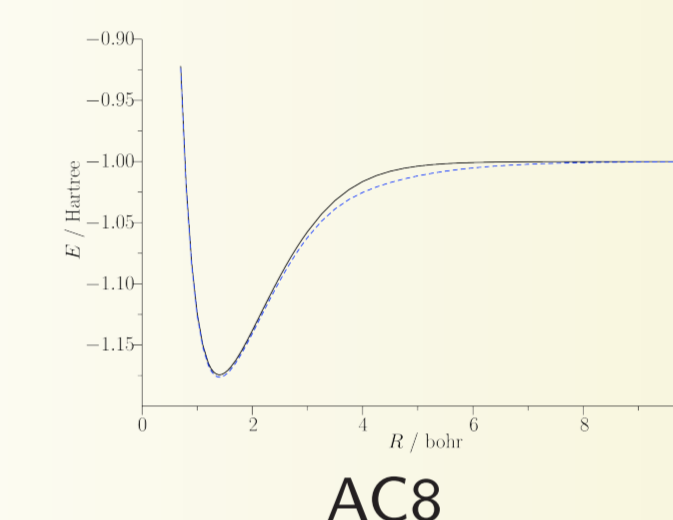
B3LYP



AC1



AC6



AC8

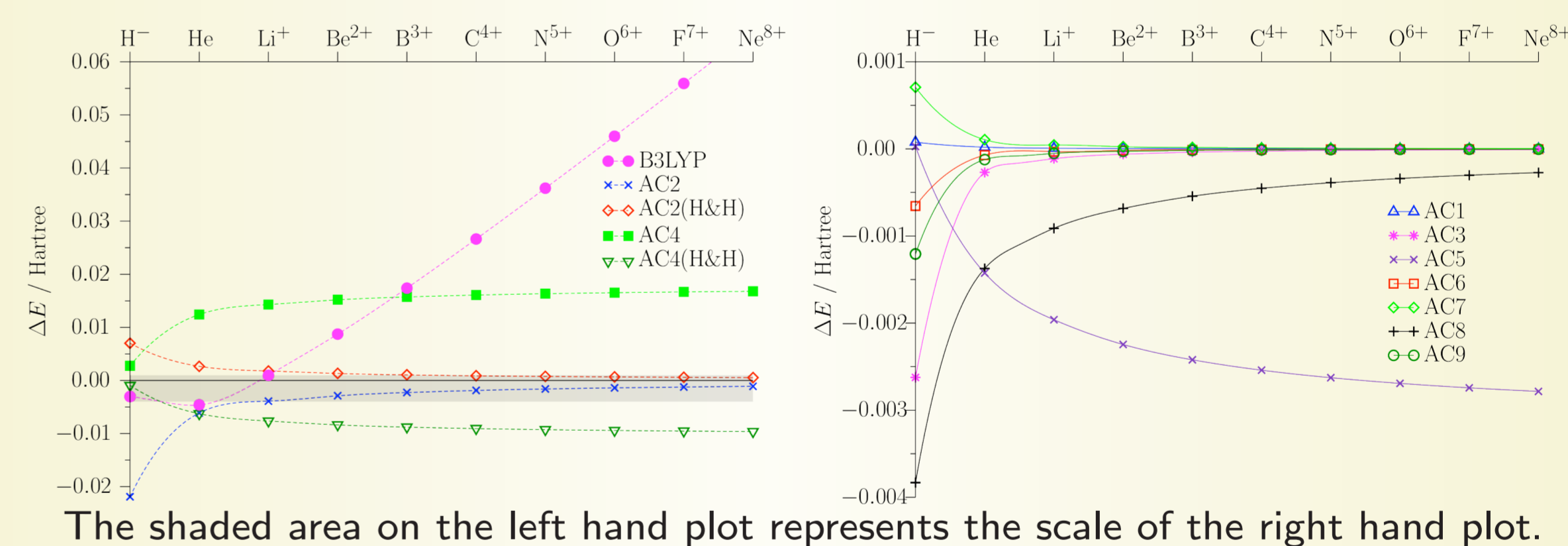
All three of these forms are a significant improvement over B3LYP. AC1 is accurate near equilibrium, however displays an unphysical barrier to dissociation.

AC8 everywhere overestimates the XC energy.

AC6 is most promising, being virtually indistinguishable from FCI on this scale.

He Isoelectronic Series

We use specifically optimised doubly augmented sextuple zeta basis sets for calculations on the He isoelectronic series, considered from H^- to Ne^{8+} .

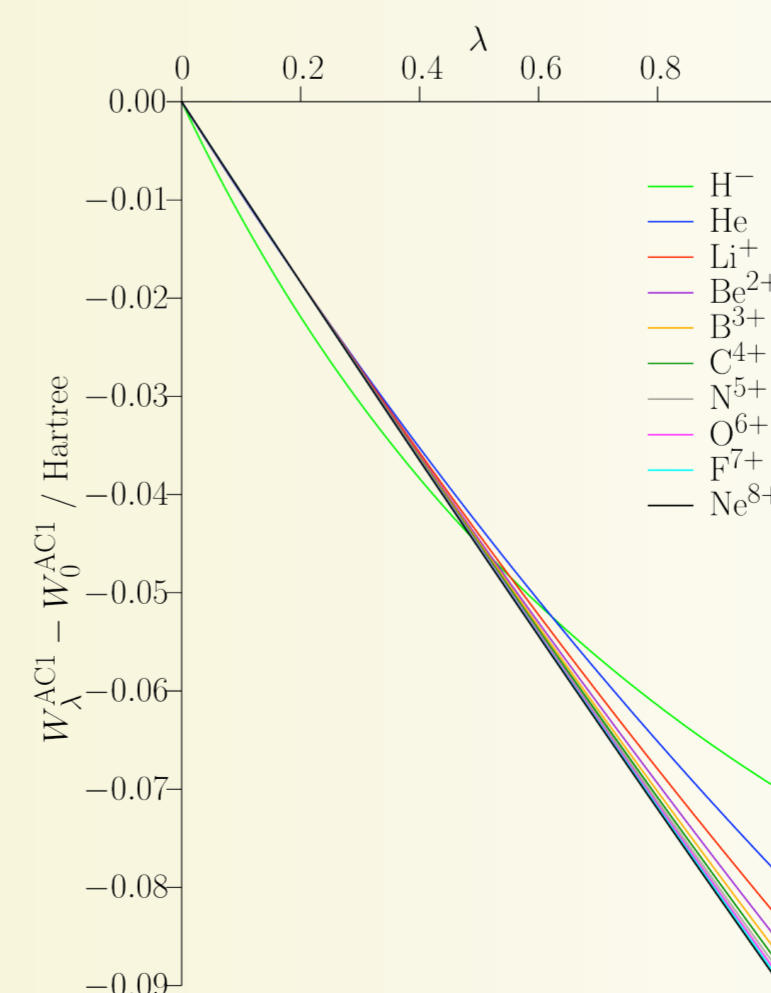


The shaded area on the left hand plot represents the scale of the right hand plot.

The B3LYP error increases significantly with Z . For AC4, AC4(H&H) and AC5, the error also increases with increasing Z ; the remaining forms improve with Z . AC1 has the best overall behaviour, with an error 83,000× smaller than B3LYP for Ne^{8+} while providing the most accurate description of H^- .

Insight can be gained by considering W_λ as $Z \rightarrow \infty$, when the electron–electron interaction can be treated as a small perturbation so the exact W_λ becomes linear;

$$\lim_{Z \rightarrow \infty} W_\lambda = E_X^{FCI} + 2E_{C,GL2}^{FCI} \cdot \lambda \quad (9)$$



Analysis of the behaviour of a , b , and c shows that all of the forms—except AC4, AC4(H&H), and AC5—behave as Eq. (9) as $Z \rightarrow \infty$. The observed improvement in most AC forms with increasing Z therefore simply reflects the approach of this exact, limiting situation. The figure illustrates the increasingly linear behaviour of the AC1 W_λ from H^- to Ne^{8+} .

For full details of this work, see Ref. 7.