

Utilizing Advanced Kinetic Energy Density Based Ingredients for Novel Local Hybrid Mixing Functions



James W. Furness

Jianwei Sun

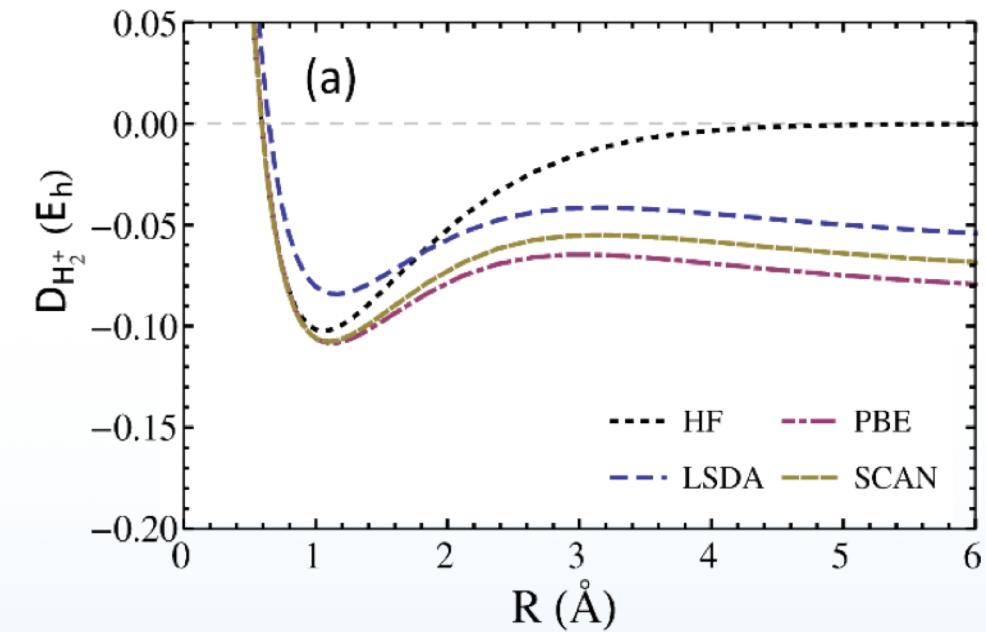
Department of Physics and Engineering Physics
Tulane University

Self Interaction Error in DFAs

Conventional semi-local functionals imperfectly cancel the spurious Coulomb repulsion of an electron with itself.

The canonical example is H_2^+
 SIE drives dissociation energy too low.

Causes delocalisation error in transition metal structures.



Local Hybrid Functionals

A natural extension of the global Hybrid functional.

$$e_x(\mathbf{r}) = a(\mathbf{r})e_x^{\text{Ex.}}(\mathbf{r}) + (1 - a(\mathbf{r}))e_x^{\text{SL}}(\mathbf{r})$$

$$\int e_x^{\text{Ex.}}(\mathbf{r})d\mathbf{r} = E_x^{\text{Ex.}}$$

Burke, K., Cruz, F. G., & Lam, K. C. (1998). *JCP*, **109**, 8161–8167, DOI: 10.1063/1.477479

Jaramillo, J., Scuseria, G. E., & Ernzerhof, M. (2003). *JCP*, **118**, 1068–1073, DOI: 10.1063/1.1528936

The Gauge Problem

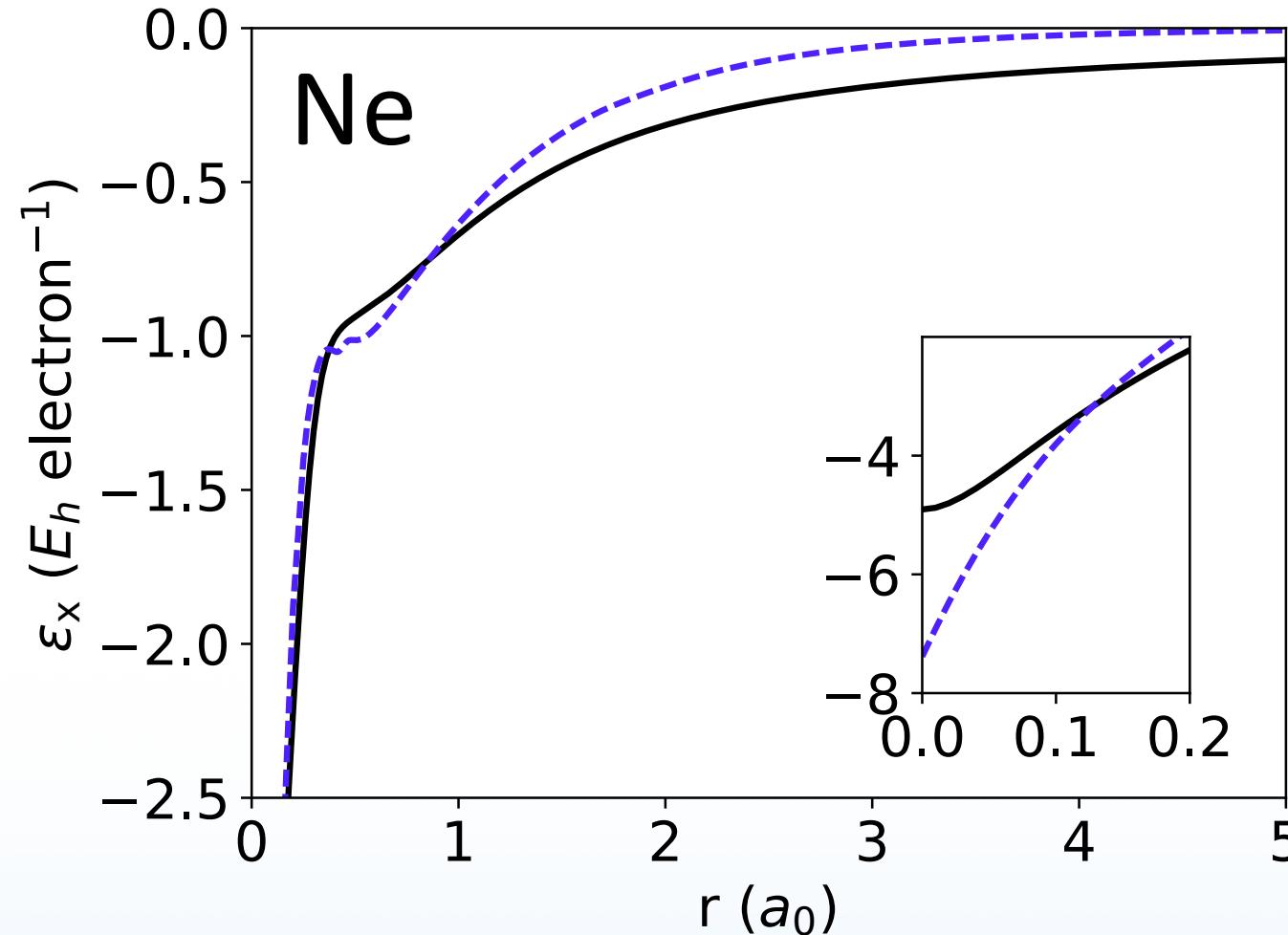
Energy densities are not well defined quantities.

$$\int e_x^{\text{Ex.}}(\mathbf{r}) + G(\mathbf{r}) d\mathbf{r} = E_x^{\text{Ex.}} \quad \text{if} \quad \int G(\mathbf{r}) d\mathbf{r} = 0$$

In a global hybrid functional this integrates out.

This is not the case when a local mixture is used.

The Gauge Problem



----- SCAN exchange [1]
— Exact Exchange

 Exact_x = $-12.108 E_h$
 SCAN_x = $-12.164 E_h$ (0.46% Error)

Gauge Calibration

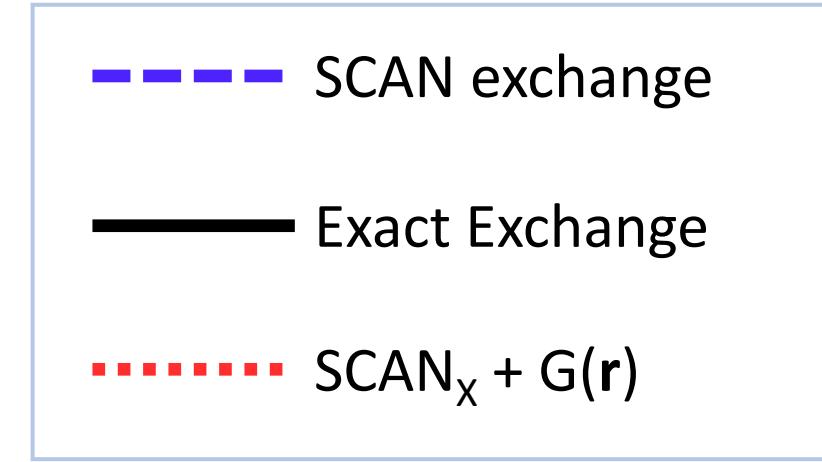
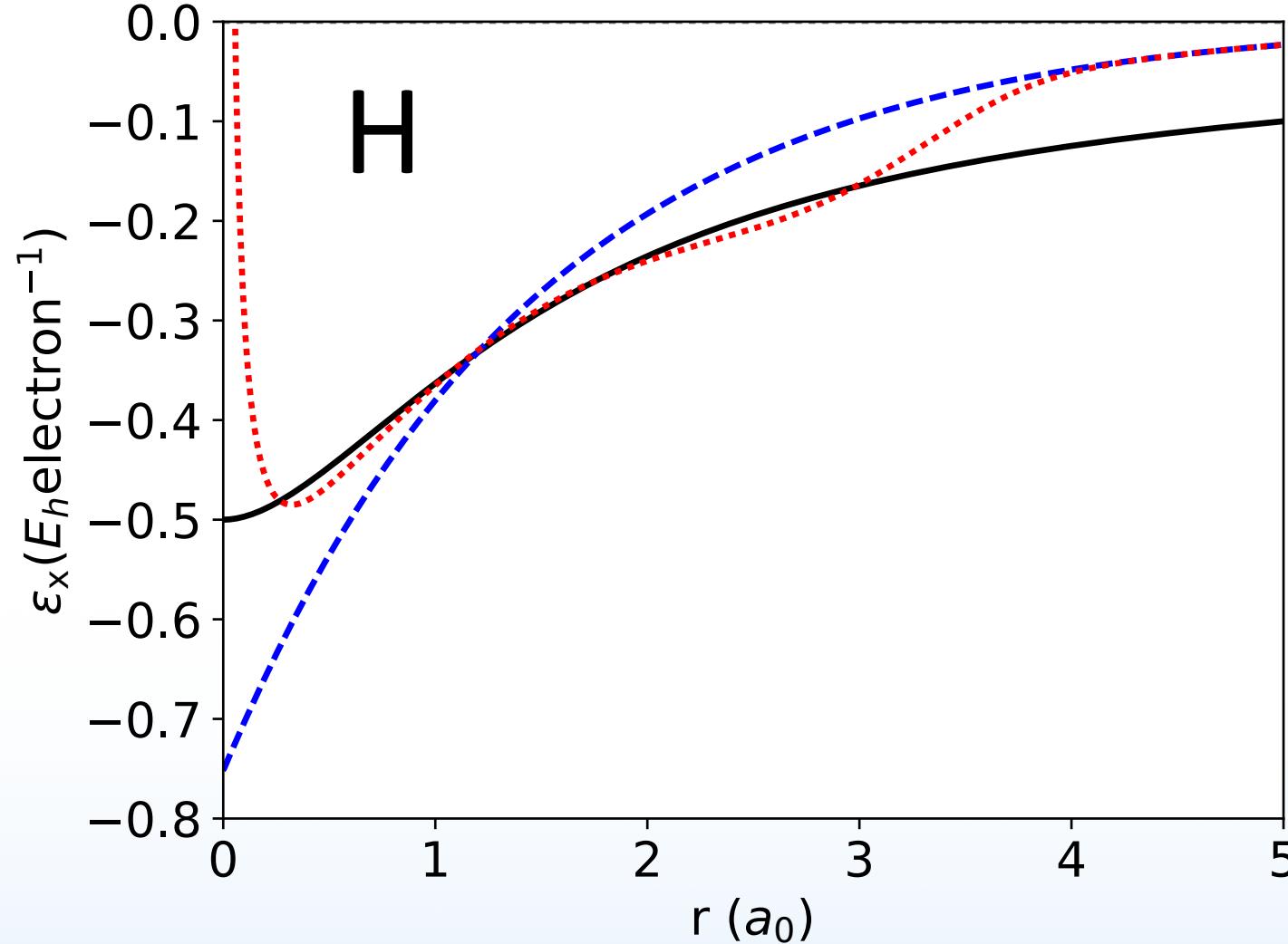
$$G(\mathbf{r}; a, b)$$

Two parameter function of Arbuznikov and Kaupp [1]

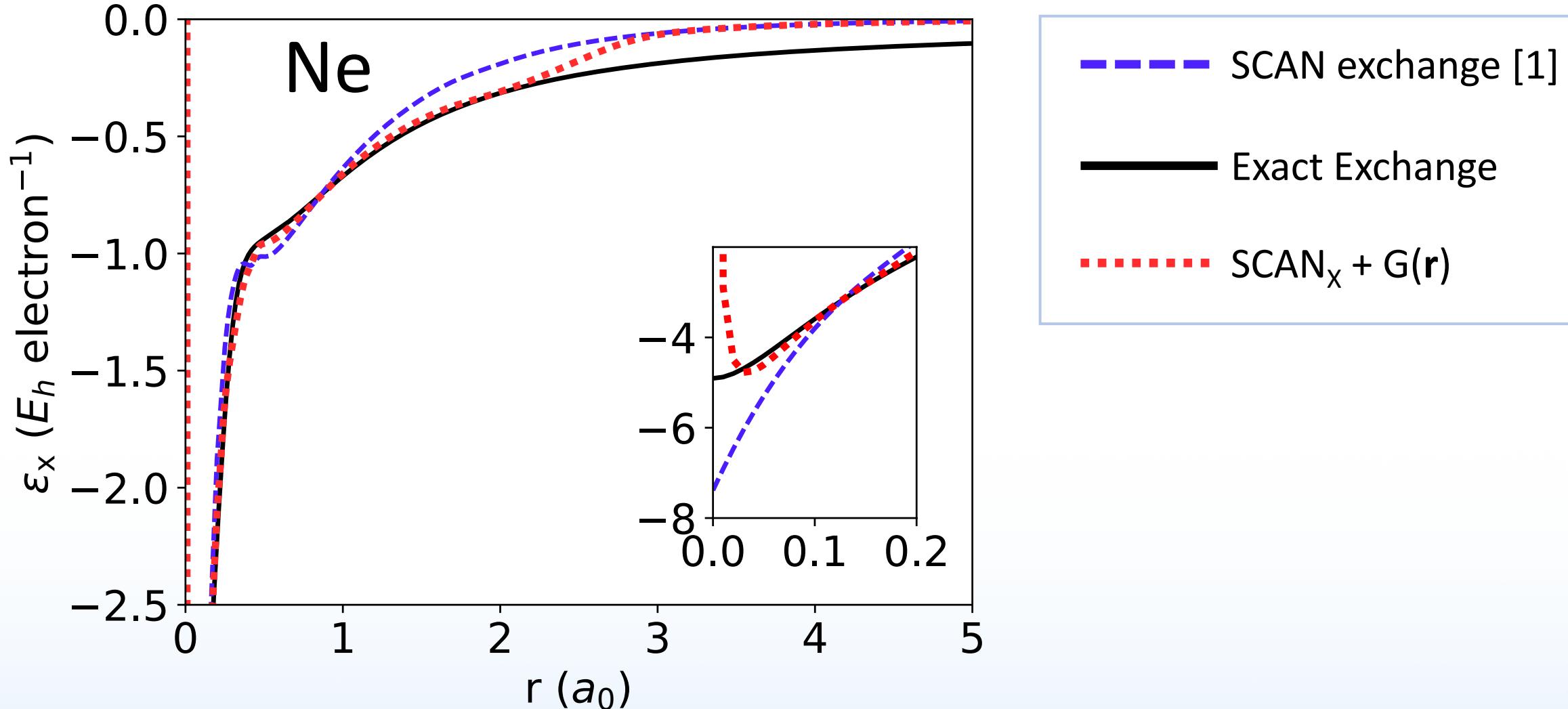
Optimised to minimize exchange density difference
in the hydrogen atom.

$$\Omega = \int |e_x^{\text{Ex.}}(\mathbf{r}) - (e_x^{\text{SCAN}}(\mathbf{r}) + G(\mathbf{r}))| d\mathbf{r}$$

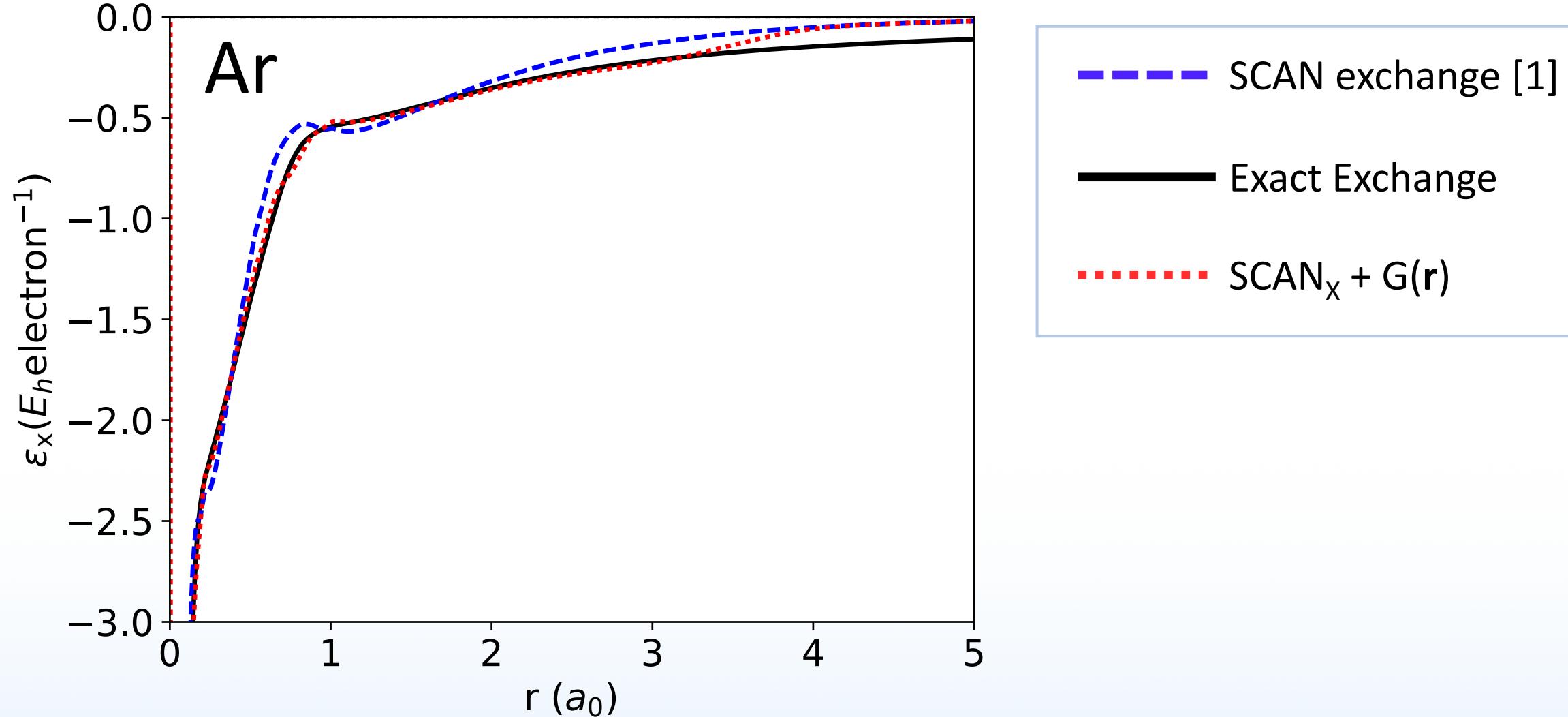
Fitting to Hydrogen



Calibrated Exchange Density



Calibrated Exchange Density



Building a Local Hybrid

We use the SCAN functional as the base semi-local functional and use a local hybrid construction to minimise SIE.

- Improve reaction barrier heights
- Preserve performance around equilibrium distances.

Mixing Function

Existing mixing functions have been built from mGGA quantities,^[1]

$$\tau(\mathbf{r}) = \sum_i^{\text{occ.}} |\nabla \varphi_i(\mathbf{r})|^2$$

$$\tau^W(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})}$$

$$\zeta(\mathbf{r}) = \frac{n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})}{n_\alpha(\mathbf{r}) + n_\beta(\mathbf{r})} \quad s(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3}n(\mathbf{r})} \quad z(\mathbf{r}) = \frac{\tau^W(\mathbf{r})}{\tau(\mathbf{r})}$$

Or more with complicated hyper-GGA ingredients.^[2]

^[1]Theilacker, K., Arbuznikov, A. V., Bahmann, H., Kaupp, M. (2011). *J. Phys. Chem. A* **115**(32). DOI: 10.1021/jp202770c

^[2]Tao, J., Staroverov, V. N., Scuseria, G. E., Perdew, J. P. (2008). *PRA* **77**(1). DOI: PhysRevA.77.012509

The α Iso-orbital Indicator

$$\alpha(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau^W(\mathbf{r})}{\tau^{UEG}(\mathbf{r})}$$

$$\begin{aligned}\tau(\mathbf{r}) &= \sum_i^{\text{occ.}} |\nabla \varphi_i(\mathbf{r})|^2 \\ \tau^W(\mathbf{r}) &= \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})} \\ \tau^{UEG}(\mathbf{r}) &= \frac{3}{10}(3\pi^2)^{\frac{2}{3}} n(\mathbf{r})^{\frac{5}{3}}\end{aligned}$$

Identifies local chemical environment.

Numerically unstable in local-hybrid SCF calculations.

Covalent Bonds $\alpha = 0$

Slowly Varying Density $\alpha \approx 1$

Weak Bonds $\alpha \gg 1$

β Mixing Kernel

$$\beta(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau^{\text{vW}}(\mathbf{r})}{\tau(\mathbf{r}) + \tau^{\text{UEG}}(\mathbf{r})} = \alpha(\mathbf{r}) \cdot \frac{\tau^{\text{UEG}}(\mathbf{r})}{\tau(\mathbf{r}) + \tau^{\text{UEG}}(\mathbf{r})}$$

Better behaved than α , same information.

Covalent Bonds $\beta = 0$

Slowly Varying Density $\beta \approx 0.5$

Weak Bonds $\beta = 1$

Mixing Function Development

- $\beta(\mathbf{r})$ can ensure 1 electron SIE free.
- $s(\mathbf{r})$ gives inhomogeneity information.
- $\zeta(\mathbf{r})$ polarisation maintains 1 electron SIE freedom with $s(\mathbf{r})$ dependence.

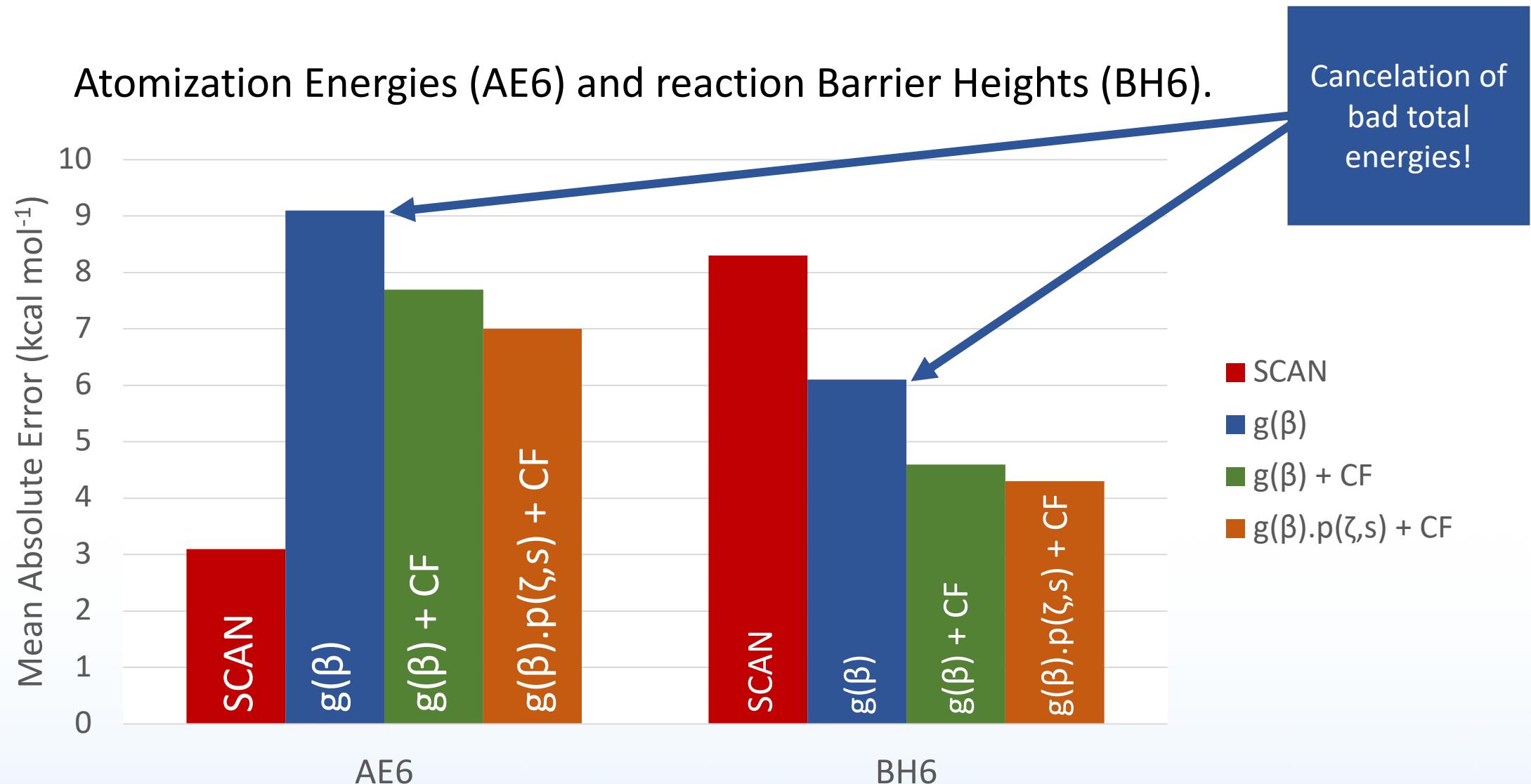
Mixing Function

$$a(\zeta, s, \beta; b, c) = g(\beta; b) \cdot p(\zeta, s; c)$$

$$g(\beta(\mathbf{r}); b) = (1 - 2\beta(\mathbf{r}))^2 \cdot e^{-b\beta^2}$$

$$p(\zeta(\mathbf{r}), s(\mathbf{r}); c) = 1 - \frac{1 - \zeta(\mathbf{r})^2}{c + s(\mathbf{r})^2 + 1}$$

Thermochemical Assessment



Future Goals

Fix broken exact constraints in gauge calibration function.

Incorporate further exact constraints into local hybrid.

Address missing *strong many electron interactions*.

Implement into widely available programs, including plane wave codes for studying transition metal oxides.

Acknowledgements



Cypress

Andy Teale – University of Nottingham

Tom Irons – University of Nottingham



UNITED KINGDOM • CHINA • MALAYSIA



QUEST

www.quest.codes