

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



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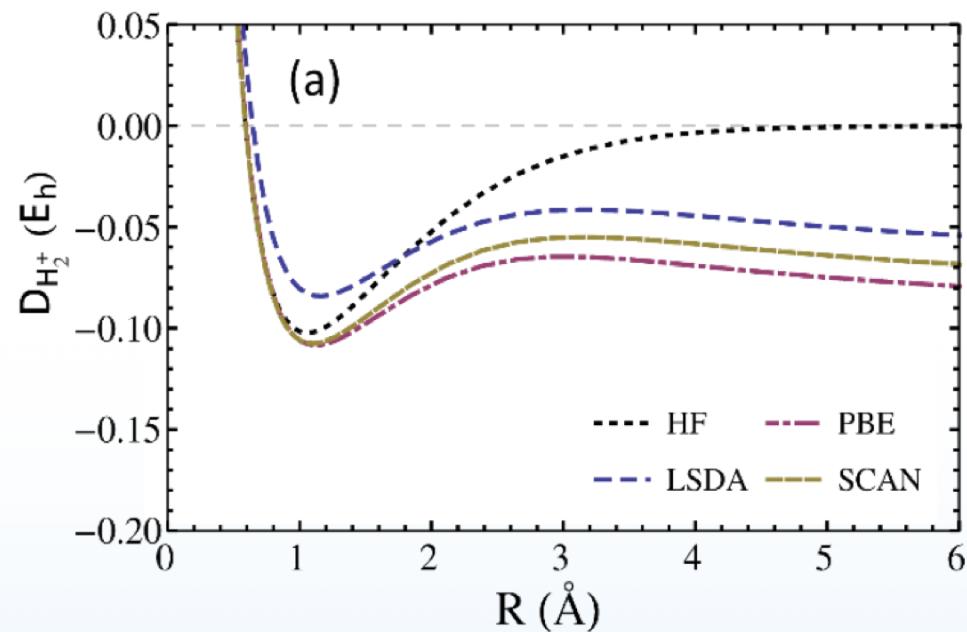
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Self Interaction Error in DFT

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.

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

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

The Gauge Problem

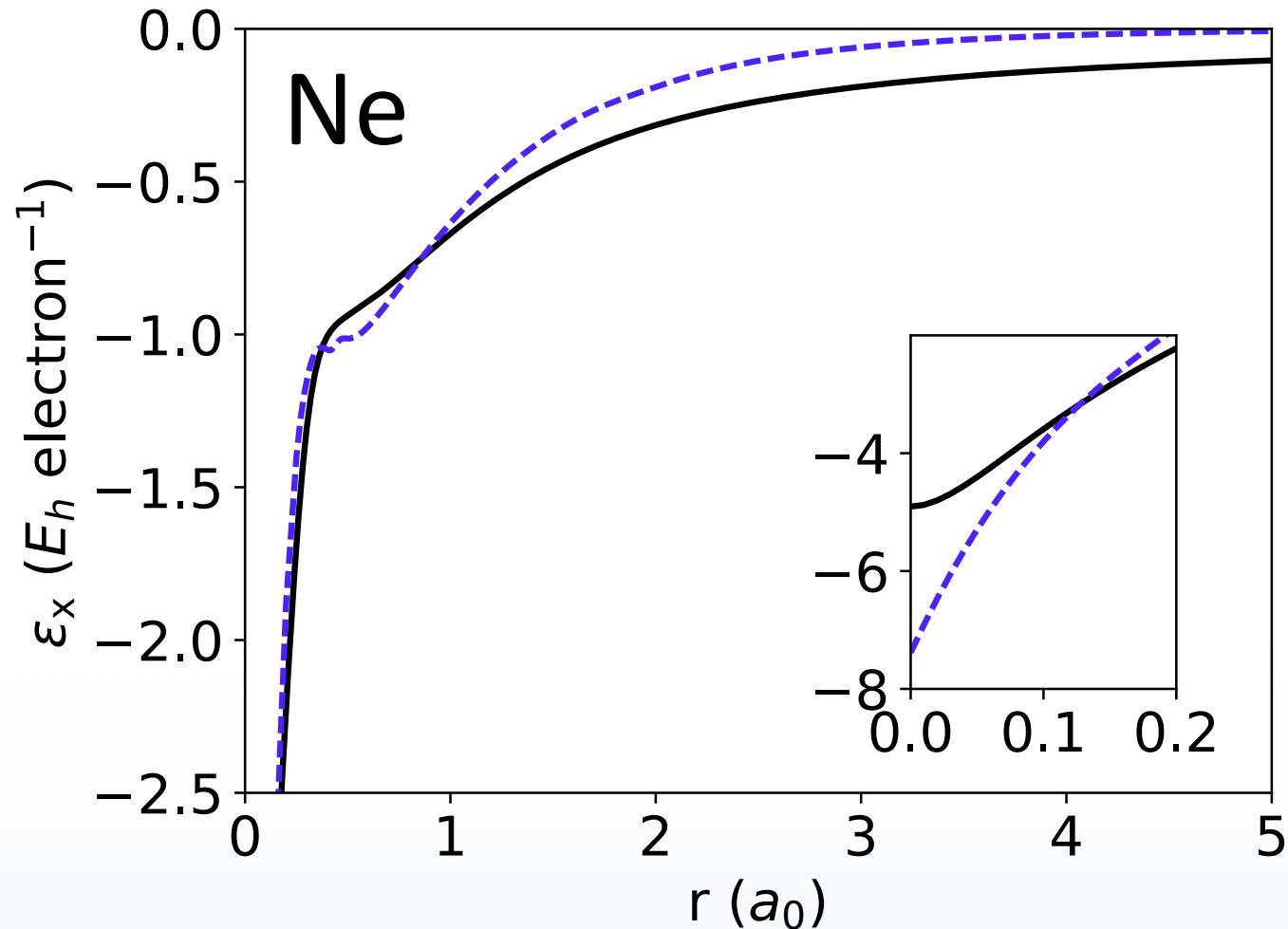
Energy densities are not a well defined quantity.

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

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

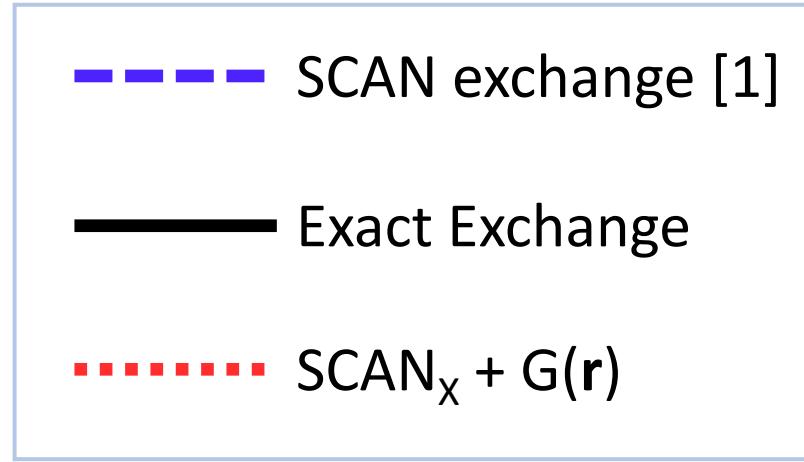
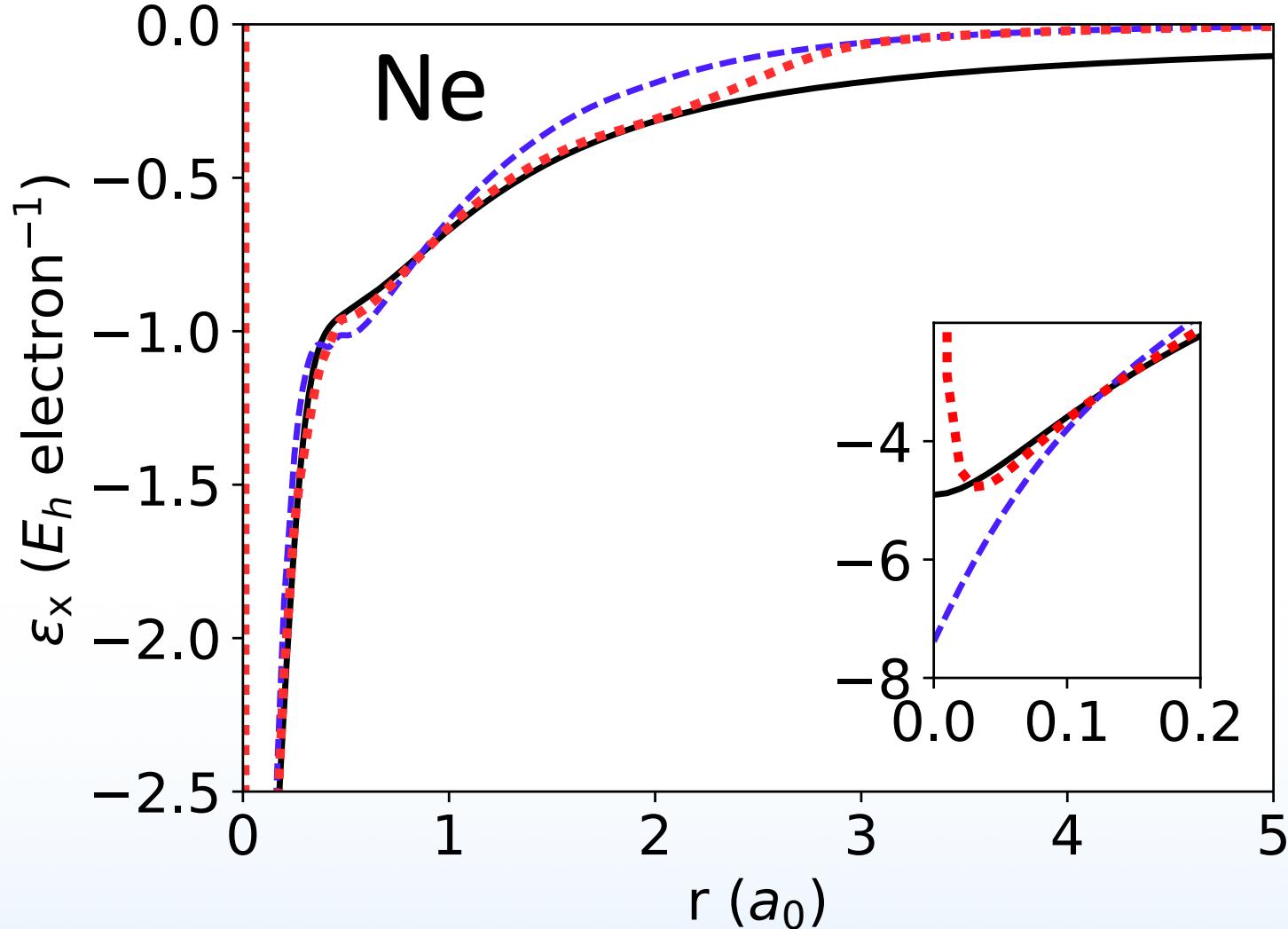
$$G(\mathbf{r}; a, b)$$

Two parameter function of Arbuznikov and Kaupp [1]

Optimised to minimize exchange density difference
in the hydrogen atom.

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

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 minimize 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

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

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

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.



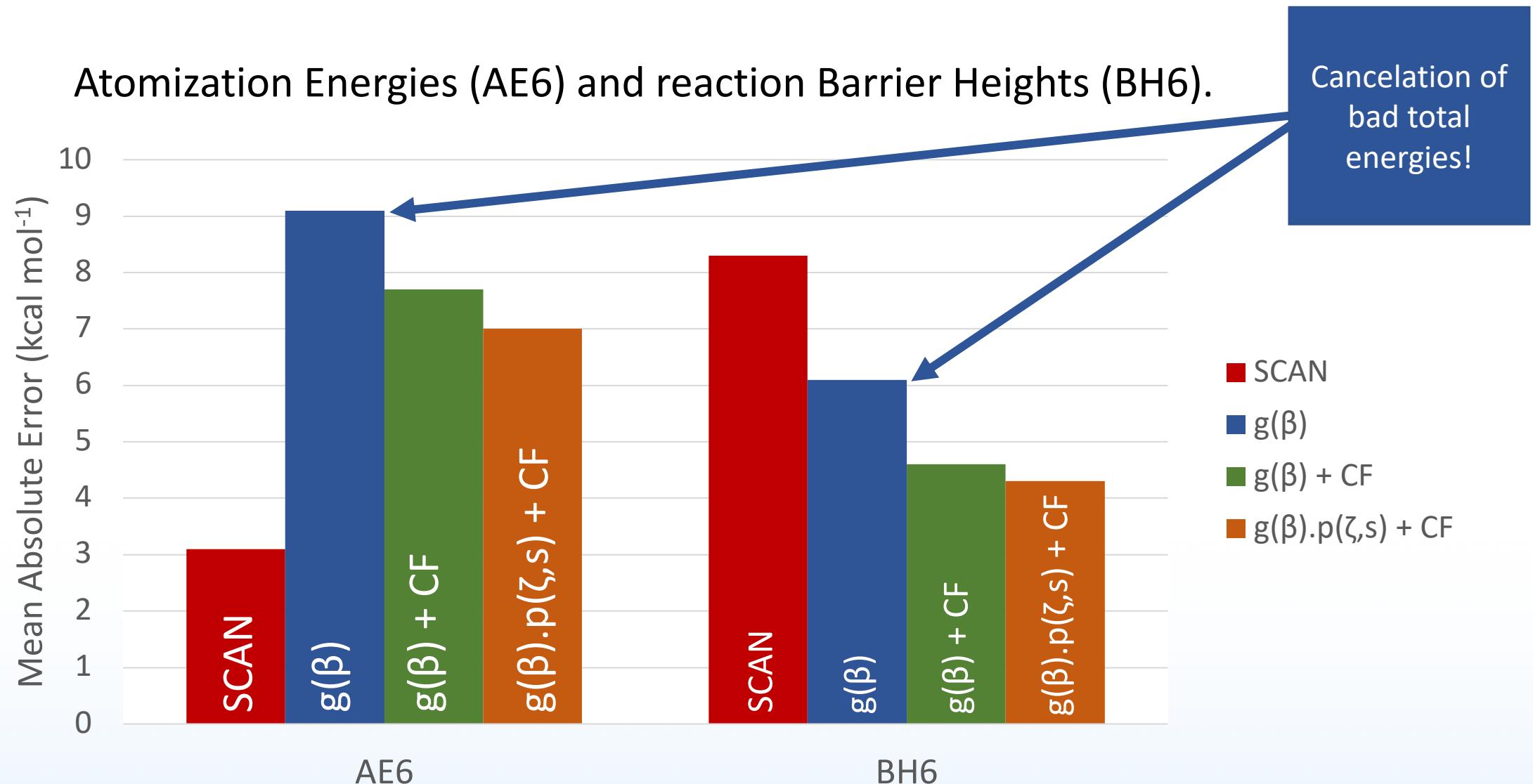
Mixing Function

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

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

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

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.

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