Retrofit of the HSE density functional

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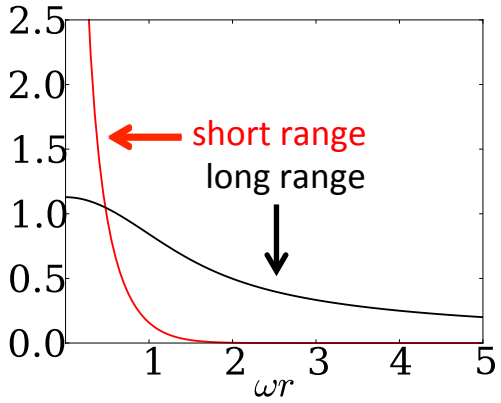
The HSE density functional

(Heyd-Scuseria-Ernzerhof)

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\omega r)}{r}}_{\text{short range (SR)}} + \underbrace{\frac{\mathrm{erf}(\omega r)}{r}}_{\text{long range (LR)}}$$



$$E_{\mathrm{xc}}^{\mathrm{HSE}} = aE_{\mathrm{x}}^{\mathrm{SR-HF}}(\omega) + (1-a)E_{\mathrm{x}}^{\mathrm{SR-PBE}}(\omega) + E_{\mathrm{x}}^{\mathrm{LR-PBE}}(\omega) + E_{\mathrm{c}}^{\mathrm{PBE}}$$

Other DFT functionals as limiting cases:

$$\text{as } a \to 0 \text{ or } \omega \to \infty,\ \mathrm{HSE} \to \mathrm{PBE}$$ (Perdew-Burke-Ernzerhof)

$$\text{as } \omega \to 0,\ \mathrm{HSE} \to \mathrm{PBE0} \qquad (a = 0.25)$$

What can be gained by varying a and ω?

Search in HSE space

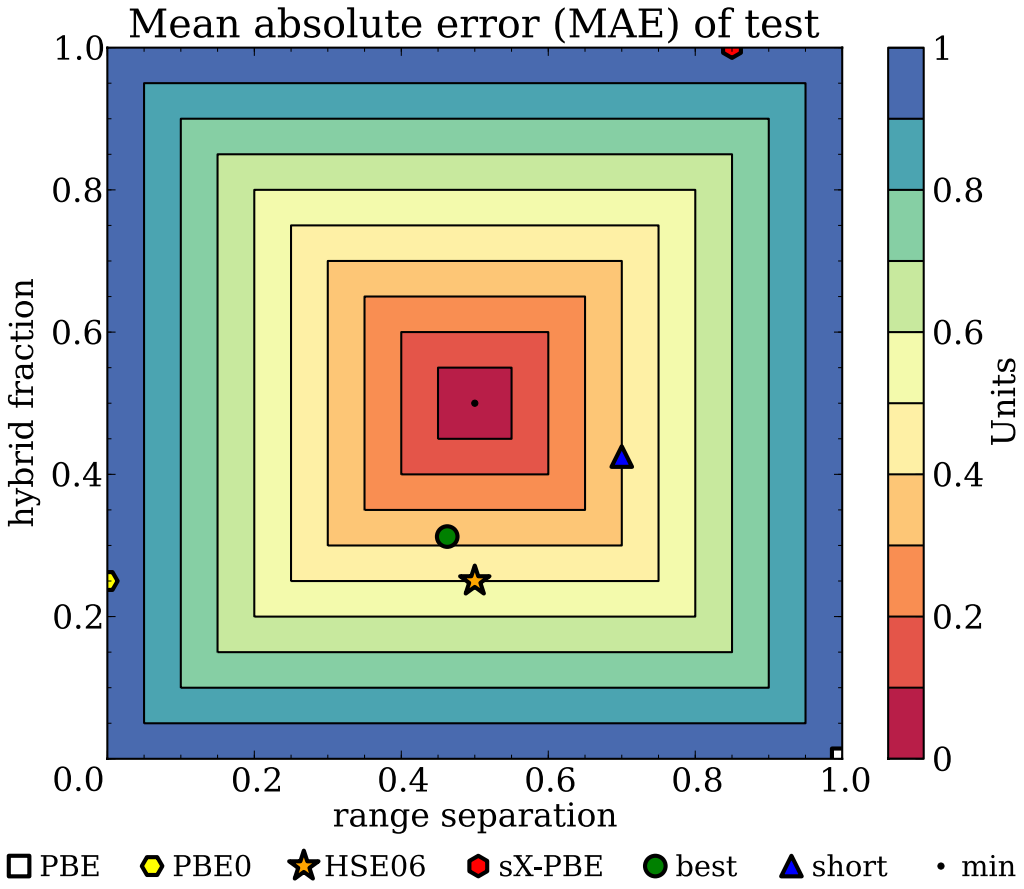
Molecular tests (in Gaussian 09):

G3/99 formation enthalpies (223)
G3/99 ionization potentials (86)
G3/99 electron affinities (58)
T-96R bond lengths (96)
BH42/04 barrier heights (39)

Semiconductor tests (in VASP 5):

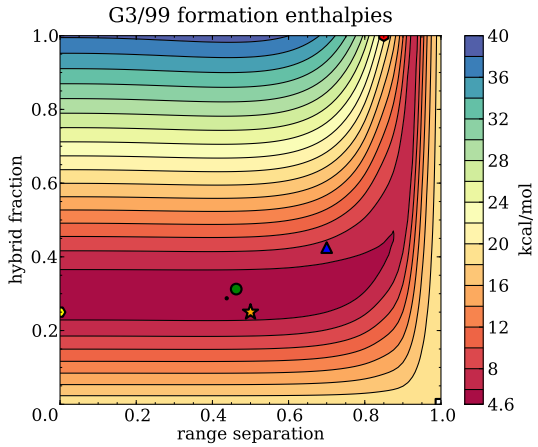
SC40 band gaps (33)
SC40 lattice constants (36)

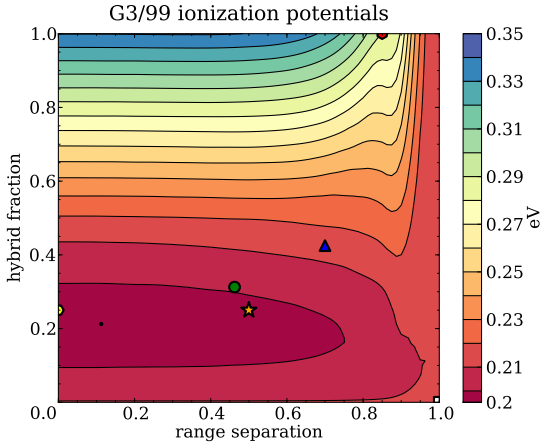
(571 experimental data points)

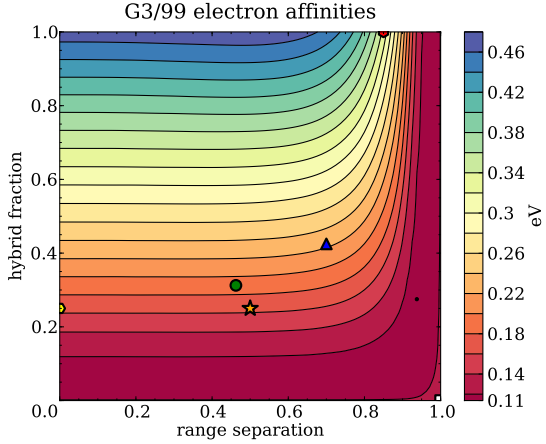


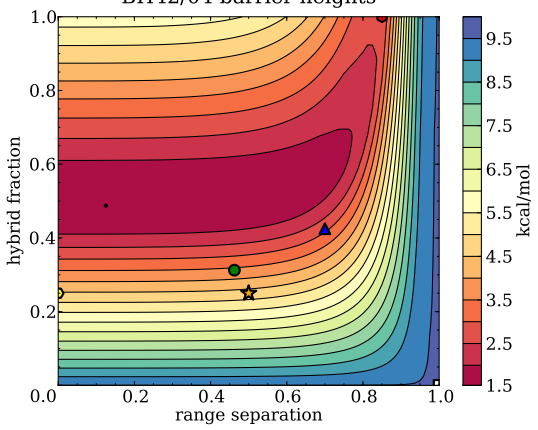
$$\tilde{\omega} = \frac{2}{\pi}\tan^{-1}\left(\frac{\omega}{\omega_{\mathrm{HSE06}}}\right)$$

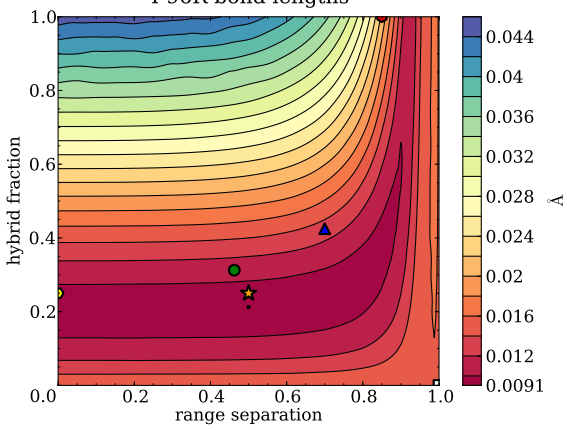
$$\omega \to \infty \text{ as } \tilde{\omega} \to 1$$

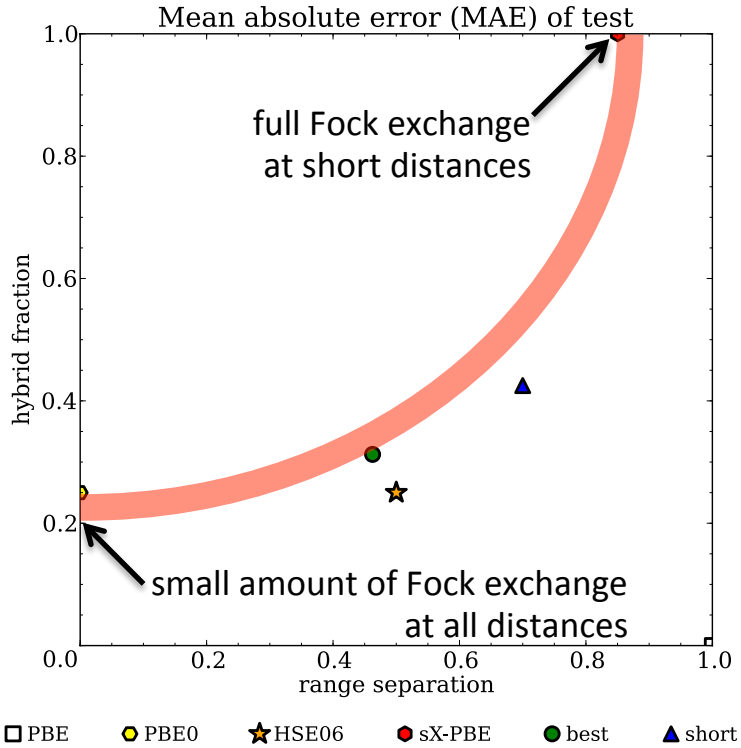


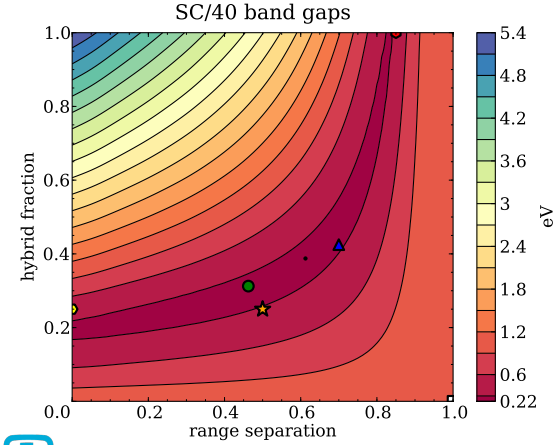


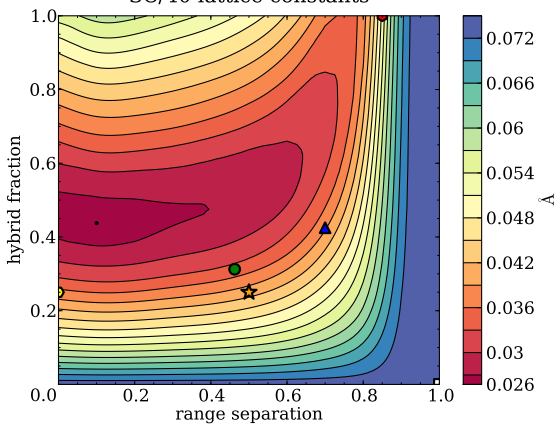






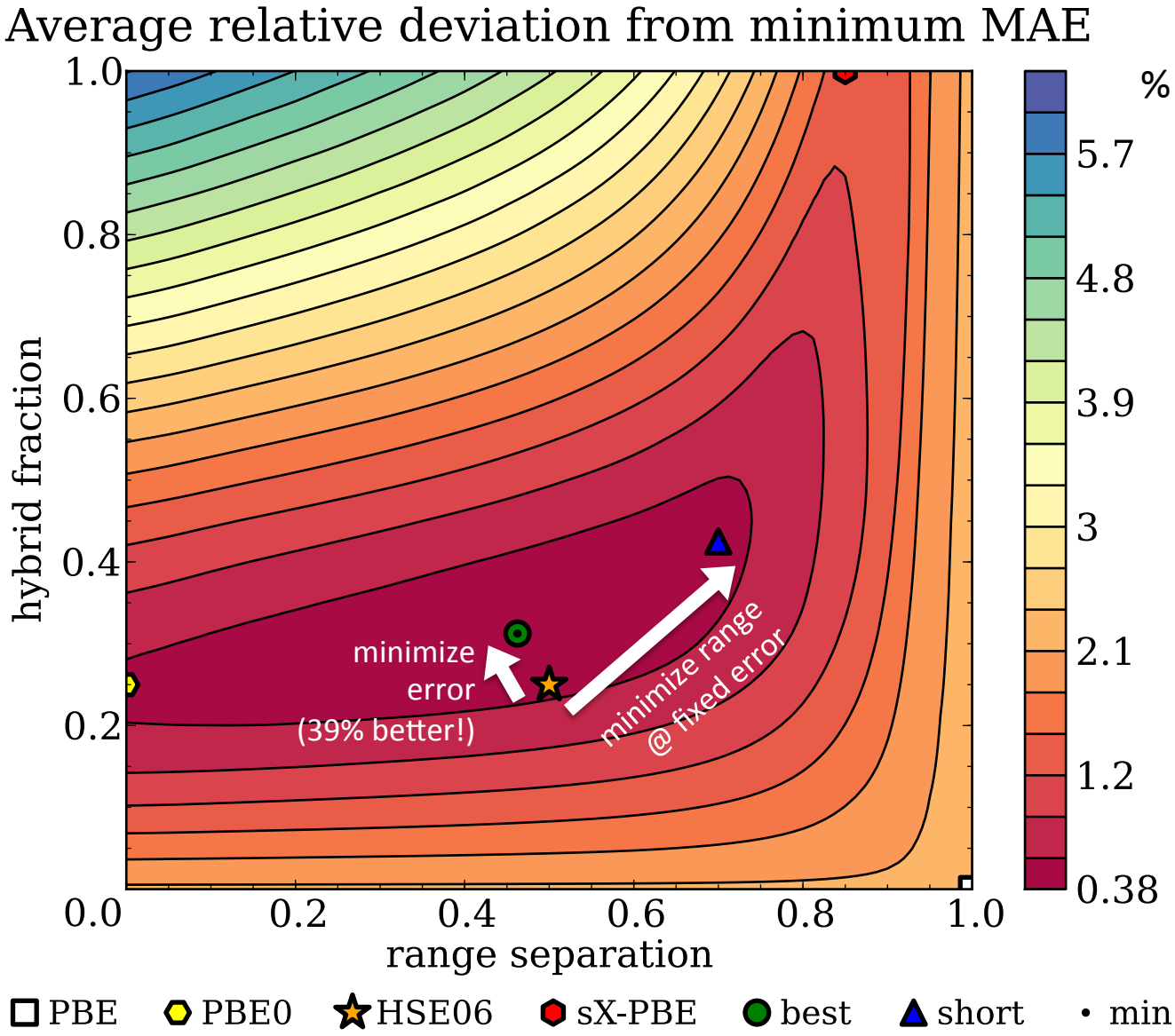






"valley" of similar functionals,
"featureless" exchange!

Balance of accuracy & cost



% of short-range exchange:

$$a_{\text{HSE06}} = 25\%$$
$$a_{\text{best}} = 31\%$$
$$a_{\text{short}} = 43\%$$
$$a_{\text{sX-PBE}} = 100\%$$

Range of Fock exchange:

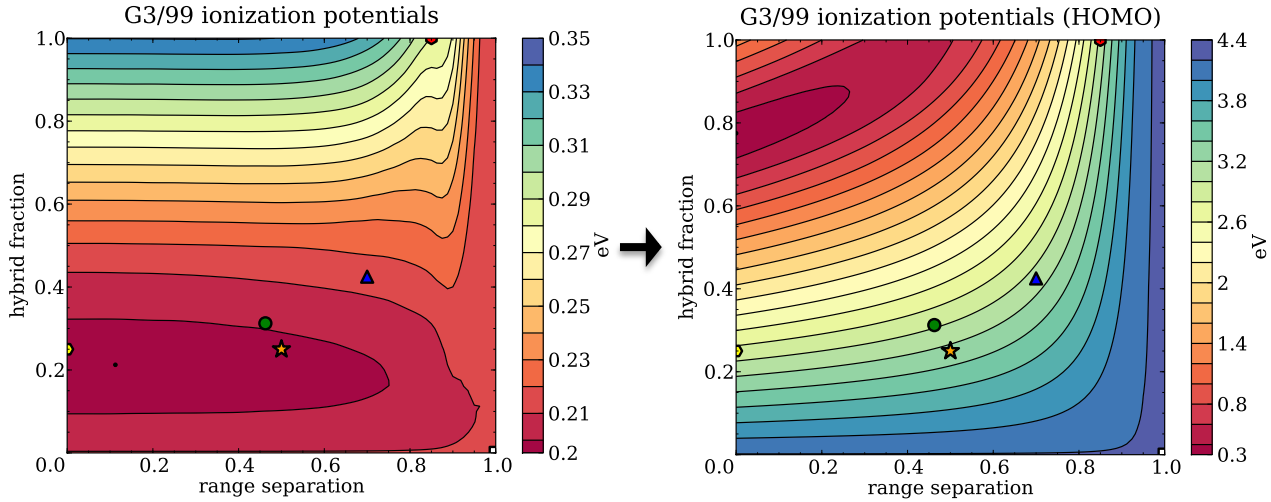
$$\omega^{-1}_{\text{HSE06}} = 4.8\text{Å}$$
$$\omega^{-1}_{\text{best}} = 5.4\text{Å}$$
$$\omega^{-1}_{\text{short}} = 2.5\text{Å}$$
$$\omega^{-1}_{\text{sX-PBE}} = 1.2\text{Å}$$

Quality of Kohn-Sham eigenvalues

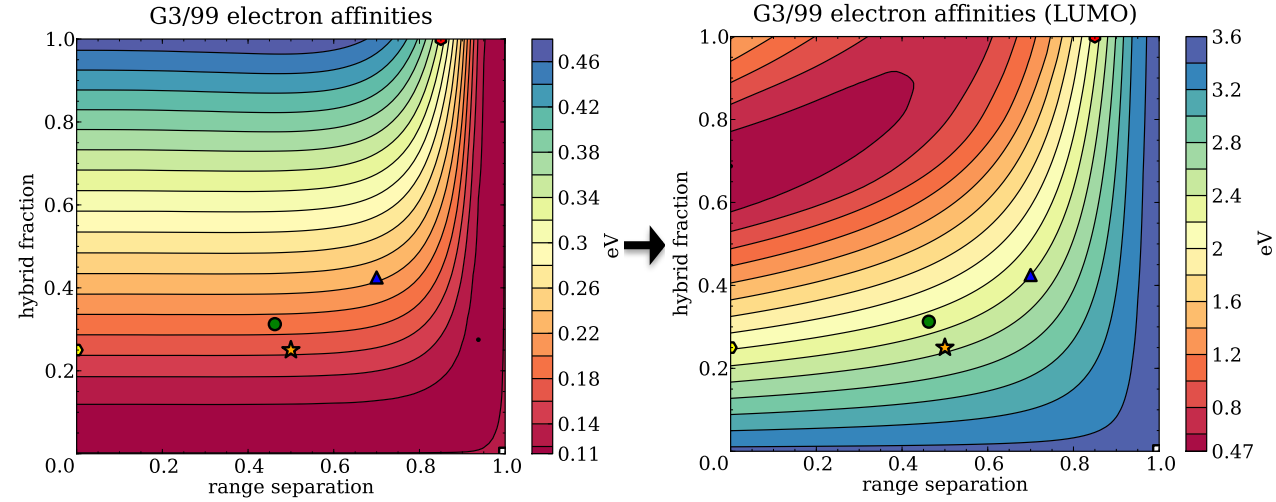
Quasiparticle theory = all eigenvalues are physical excitations

Generalized Kohn-Sham *theory* = just frontier eigenvalues (HOMO & LUMO)

(not necessarily KS *in-practice*!)



Correct KS eigenvalues need more Fock exchange, which is *incompatible* with all other tests!



PBE PBE0 HSE06 sX-PBE best short min

Errors are >2 eV !!!

Large effect on hybridization, alignment, and occupation in composite molecular systems!

[D35.00013 @ 5:18pm]

QP rationalization of KS errors

$$a\frac{1-\mathrm{erf}(\omega r)}{r} \approx \frac{1}{\varepsilon(r)r}$$ screened exchange,

$$\varepsilon(r \to \infty) \to \infty$$

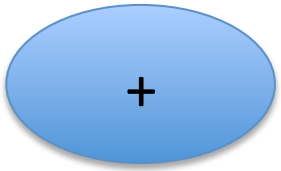
metallic long-range screening

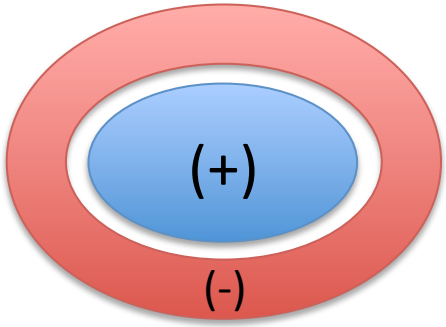
$$aE_{\mathrm{x}}^{\mathrm{SR-HF}}(\omega) \approx -\int \frac{\left|\rho(r,r')\right|^2}{\varepsilon(r-r')\left|r-r'\right|} dr\, dr'$$ screened exchange energy

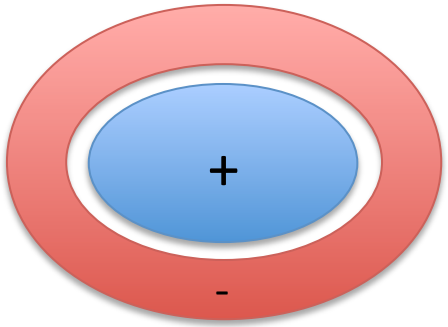
$E_{\mathrm{tot}}^{\mathrm{HSE}}(N-1) - E_{\mathrm{tot}}^{\mathrm{HSE}}(N)$

$-E_{\mathrm{HOMO}}^{\mathrm{HSE}}$

model of error







vacuum doesn't polarize to reduce Hartree energy

vacuum *does* polarize in model screening of Fock exchange

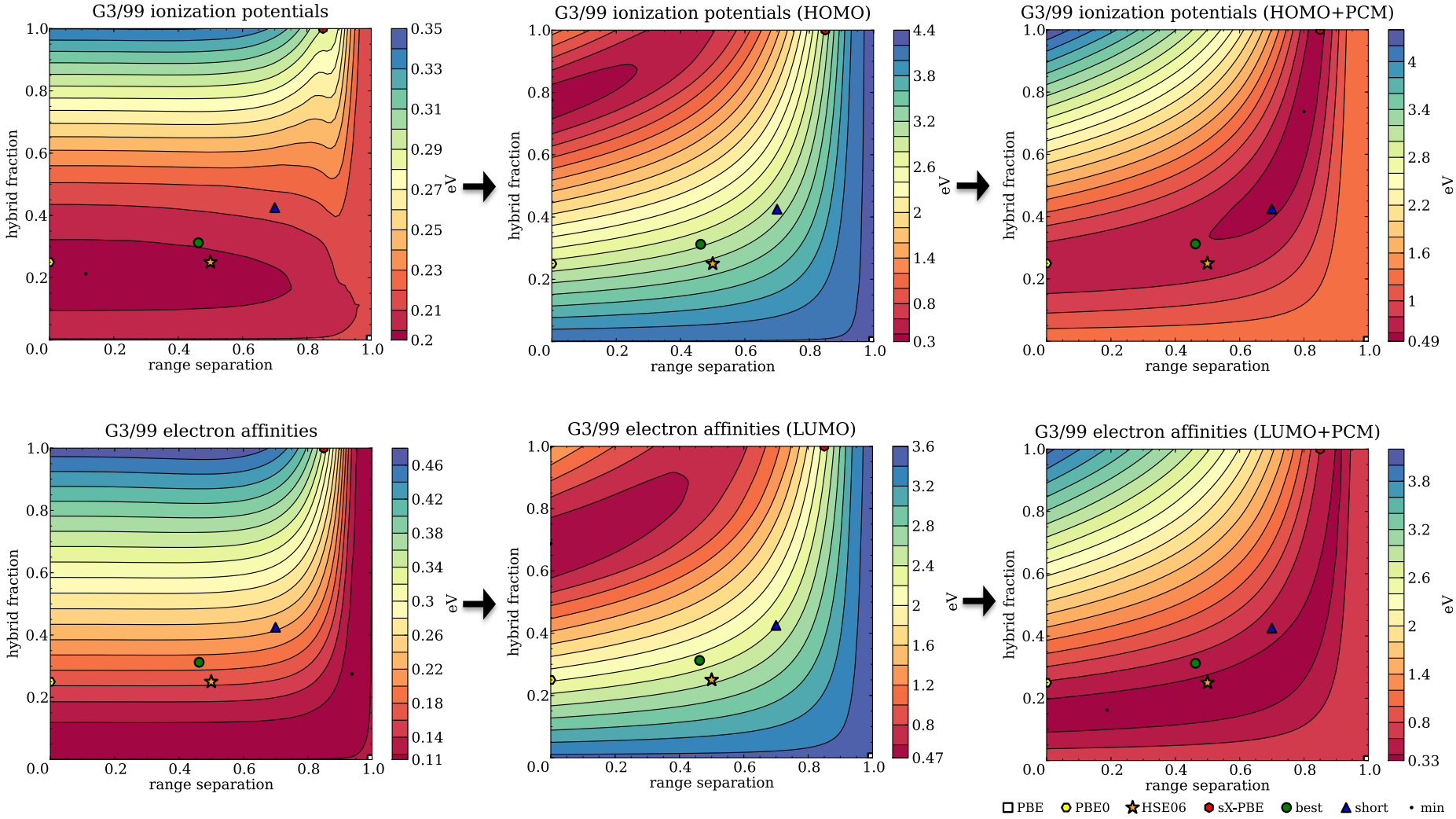
Introduce similar vacuum polarization (PCM) to screen Hartree energy

Screening correction

Quasiparticle theory = all eigenvalues are physical excitations

Generalized Kohn-Sham *theory* = just frontier eigenvalues (HOMO & LUMO)

(not necessarily KS *in-practice*!)



Conclusions

- Improvements to HSE06, just by fine-tuning parameters that define HSE (*either* reduced cost *or* better accuracy).

- Reduction of both cost & error still possible with a new GGA functional compatible with short-range Fock exchange (100% at r=0).

- *Large but conditional* DFT errors remain. We need the physics of inhomogeneous, environment-dependent electronic response and dynamic screening.