Analysis of the Heyd-Scuseria-Ernzerhof density functional parameter space

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ABSTRACT:
The Heyd-Scuseria-Ernzerhof (HSE) density functionals are popular for their ability to improve the accuracy of standard semilocal functionals such as Perdew-Burke-Ernzerhof (PBE), particularly for semiconductor band gaps. They also have a reduced computational cost compared to hybrid functionals, which results from the restriction of Fock exchange calculations to small inter-electron separations. These functionals are defined by an overall fraction of Fock exchange and a length scale for exchange screening. We systematically examine this two-parameter space to assess the performance of hybrid screened exchange (sX) functionals and to determine a balance between improving accuracy and reducing the screening length, which can further reduce computational costs. Three parameter choices emerge as useful: "sX-PBE" is an approximation to the sX-LDA screened exchange density functionals based on the local density approximation (LDA); "HSE12" minimizes the overall error over all tests performed; and "HSE12s" is a range-minimized functional that matches the overall accuracy of the existing HSE06 parameterization but reduces the Fock exchange length scale by half. Analysis of the error trends over parameter space produces useful guidance for future improvement of density functionals.
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METHODS:
Generalized Kohn-Sham (GKS) theory frees up the Kohn-Sham equations to have a nonlocal potential, such as in Hartree-Fock theory. The two most popular GKS functionals, sX-LDA and HSE, are based on the concept of screened Fock exchange,

$$E_{\rm xc}^{\rm sX-LDA} = E_{\rm sX}(r_{\rm TF}) + E_{\rm x}^{\rm LDA,LR}(r_{\rm TF}) + E_{\rm c}^{\rm LDA}$$
$$E_{\rm xc}^{\rm HSE} = aE_{\rm x}^{\rm HF,SR}(\omega) + (1-a)E_{\rm x}^{\rm PBE,SR}(\omega) + E_{\rm x}^{\rm PBE,LR}(\omega) + E_{\rm c}^{\rm PBE}$$

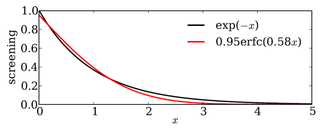
The basic structure of sX-DFT is similar to quasiparticle methods, specifically the Coulomb hole plus screened exchange (COHSEX) form of the self-energy and related total energy expressions,

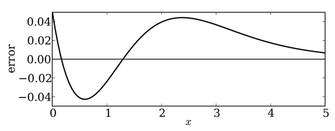
$$\Sigma_{\sigma,\sigma'}^{\rm COHSEX}(\mathbf{r},\mathbf{r}') = -\rho_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}')W_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}') + \frac{1}{2}\delta_{\sigma,\sigma'}\delta(\mathbf{r}-\mathbf{r}')\left(W_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right)$$

$$E_{\rm xc} = \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}d\mathbf{r}'\rho_{\sigma',\sigma}(\mathbf{r}',\mathbf{r})\Sigma_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}')$$ (Galitskii-Migdal formula)

$$E_{\rm x}^{\rm HF,SR}(\omega) = -\frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}d\mathbf{r}'\frac{\mathrm{erfc}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}|\rho_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}')|^2$$
$$E_{\rm sX}(r_{\rm TF}) = -\frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}d\mathbf{r}'\frac{\exp(-|\mathbf{r}-\mathbf{r}'|/r_{\rm TF})}{|\mathbf{r}-\mathbf{r}'|}|\rho_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}')|^2$$

The two screening forms closely approximate each other,
$\exp(-x) \approx 0.95\mathrm{erfc}(0.58x)$





exchange-hole form of semilocal exchange energy,

$$E_{\rm x}^{\rm LR} = \int d\mathbf{r}\rho(\mathbf{r})\int \underbrace{\epsilon_{\rm x}[\rho(\mathbf{r}),R]}_{\text{radial density of exchange energy}}\underbrace{[1-s(R)]}_{\text{screening function}}dR$$

$$E_{\rm x}^{\rm LDA_G,LR} = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{\rm x}^{\rm LDA}[\rho(\mathbf{r})]f\left(\overline{\rho}^{1/3}r_{\rm TF}\right)$$ standard form of sX-LDA

$$E_{\rm x}^{\rm LDA_L,LR} = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{\rm x}^{\rm LDA}[\rho(\mathbf{r})]f\left(\rho(\mathbf{r})^{1/3}r_{\rm TF}\right)$$ correct exchange-hole form

Most significant difference between sX-LDA and HSE:

System-independent ω in HSE, $\omega_{\rm HSE06}$ = 0.208 A^{-1}

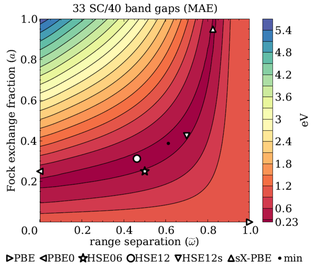
System-dependent $r_{\rm TF}$ in sX-LDA, $r_{\rm TF} = \frac{1}{2}\left(\frac{\pi}{3\bar{\rho}}\right)^{1/6}$ (0.39 A – 0.52 A in semiconductors)

average valence electron density

weak enough variation for a "universal" approximant?

$$\widetilde{\omega} = \frac{2}{\pi}\arctan\left(\frac{\omega}{\omega_{\rm HSE06}}\right)$$

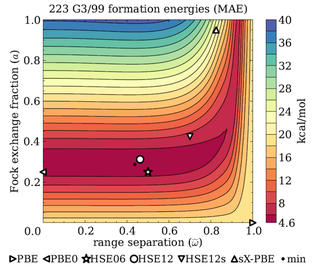
RESULTS:



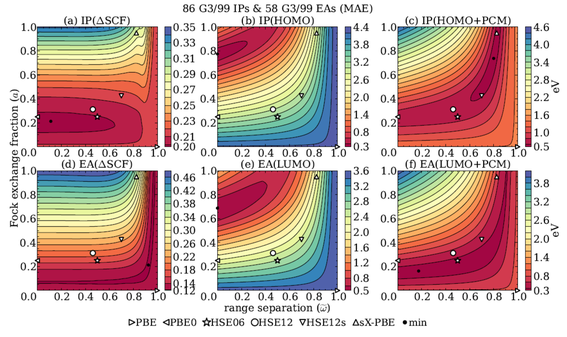
Accurate band gaps within a "valley" of functionals between PBE0 & sX-LDA. Screening can be simply modeled as:

$$W_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}') \approx \frac{\varepsilon_0^{-1} + (1-\varepsilon_0^{-1})\exp(-|\mathbf{r}-\mathbf{r}'|/r_{\rm TF})}{|\mathbf{r}-\mathbf{r}'|}$$

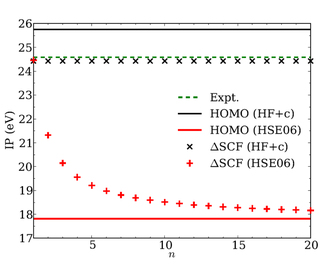
The observed trends come from interpolating between overestimation and underestimation of ε_0^{-1} and $r_{\rm TF}$.



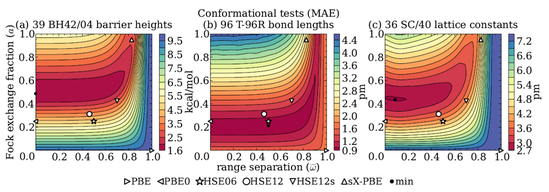
"Valley" of different shape, with less sensitivity for long screening length and increased sensitivity at short screening length. HSE is tuned to near the intersection of good band gaps and formation energies.



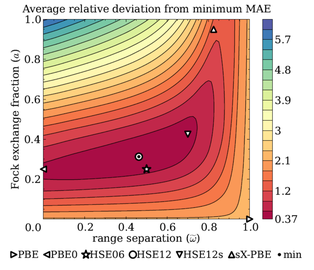
There are large discrepancies between Kohn-Sham eigenvalues and total energy difference estimates of the HOMO & LUMO. The eigenvalue error can be partly corrected by modeling the long-range over-screening of exchange with the polarizable continuum model (PCM).



This example shows the ionization potential of a dilute cluster of *n* helium atoms. Kohn-Sham eigenvalues have large size-consistency errors because of orbital delocalization. HSE is deep in the regime of delocalization error because of overscreening. In this example, the hole uniformly delocalizes over all atoms for HSE and localizes on one atom for Fock exchange plus PBE correlation (HF+c).



Errors in the conformational tests are all quite small.



$$\frac{1}{\#\text{ of tests}}\sum_i^{\rm tests}\left(\frac{\mathrm{MAE}_i(\widetilde{\omega},a)}{\min_{\widetilde{\omega}',a'}\mathrm{MAE}_i(\widetilde{\omega}',a')} - 1\right)$$

To optimize the parameters of an HSE functional, we consider a weighted average of the various tests performed here. There isn't too much frustration between the different tests; they are optimized approximately by a common choice of parameters.

THE FUTURE:
Screened exchange DFT functionals contain a reasonable system-independent model of material screening. Its success relies on the large strength and homogeneity of screening in materials and the relatively modest variations of average valence electron density. The largest failures occur near large regions of vacuum, such as when studying small molecules in the gas phase. Complete screening of the long-range Coulomb interaction is also consistent with the absence of van der Waals energy and forces. Better functionals need a more realistic and system-dependent model of electronic screening of the Coulomb interaction:

An independent-fermion-model density matrix,

$$\rho_{\sigma,\sigma'}(\mathbf{r},\mathbf{r}') = \sum_i f_i\psi_{i,\sigma}(\mathbf{r})\psi_{i,\sigma'}^*(\mathbf{r}')$$

has consistently outperformed orbital-free DFT In terms of accuracy and transferability.

The natural analogy for screening is the independent-fermion-model screened interaction,

$$\chi_{\sigma,\sigma'}^0(\mathbf{r},\mathbf{r}') = \sum_{i,j}\frac{f_i - f_j}{\epsilon_i - \epsilon_j}\psi_{i,\sigma}^*(\mathbf{r})\psi_{j,\sigma}(\mathbf{r})\psi_{j,\sigma'}^*(\mathbf{r}')\psi_{i,\sigma'}(\mathbf{r}')$$
$$W_{\sigma,\sigma'}^{-1}(\mathbf{r},\mathbf{r}') = \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]^{-1} - \chi_{\sigma,\sigma'}^0(\mathbf{r},\mathbf{r}'),$$

compared to the model of HSE: $W_{\sigma,\sigma'}^{\rm HSE}(\mathbf{r},\mathbf{r}') = a\frac{\mathrm{erfc}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$