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## Hybrid DFT

- Incorporating exact exchange enhances DFT, especially in alleviating self-interaction error, correcting asymptotic of XC potential, etc.
- In fact, Hybrid DFT functionals are widely used compared to local and semilocal functionals.
- Further, Hybrid functionals can be broadly classified into global and range-separated hybrid functionals depending on whether the exact exchange is applied globally or applied to a certain range in the real space.
- Unlike local and semilocal functionals, due to the non-locality, directly computing the exchange-correlation potential corresponding to hybrid functionals is not possible.
- Recent Progress in Inverse Kohn-Sham methods has facilitated computing XC potential from the electron densities.
- In the present work, we have analyzed the XC potential computed using the Wu-Yang inverse Kohn Sham method of 155 hybrid DFT functionals.
- We found direct correlations between the XC potential, Ionization potential, and the long-range Hartree Fock coefficient.
- The study uncovers crucial factors that could help improve hybrid DFT functionals.

## Work Summary

- We studied 155 hybrid DFT functionals available in Libxc library.
- We used FCI and CCSD(T) data to quantify errors.
- We analyzed the most important quantities, such as Total Energy, Electron Density, Ionization Potential, and Exchange-Correlation Potential.
- Five systems were considered at the FCI level. 16 systems were considered at the CCSD(T) level.
- And importantly, we computed the functional-driven and density-driven errors of these functionals.

## Methodology

We quantify errors in electron densities and exchange-correlation potential, which are represented in the 3-Dimensional DFT grid as.

$$\Delta v_{xc} = \frac{\|\delta v_{xc}\|_{L_2}}{\|v_{xc}^{\text{ref}}\|_{L_2}}, \quad \Delta \rho = \frac{\|\delta \rho\|_{L_2}}{\|\rho^{\text{ref}}\|_{L_2}} \quad (1)$$

To emphasize the core and valence region in the 3D XC potential, we define  $\Delta \rho^{\text{ref}} v_{xc}$ . Rapid decaying behavior of the  $\rho$  diminishes the asymptotics and predominantly presents the core and valence region

$$\Delta \rho^{\text{ref}} v_{xc} = \frac{\|\rho^{\text{ref}} \delta v_{xc}\|_{L_2}}{\|\rho^{\text{ref}} v_{xc}^{\text{ref}}\|_{L_2}} \quad (2)$$

Errors for Total Energy and IP are computed as

$$\Delta E_t = \frac{|E^{\text{ref}} - E|}{|E^{\text{ref}}|}, \quad \Delta IP = \frac{|IP^{\text{ref}} - IP|}{|IP^{\text{ref}}|} \quad (3)$$

Further, we compute Density Driven(DD) and Functional Driven(FD) Errors using WFT densities and Total energies.

$$\Delta E_t^{DD} = \frac{|E[\rho^{\text{ref}}] - E[\rho]|}{|E^{\text{ref}}|} \quad (4)$$

$$\Delta E_t^{FD} = \frac{|E^{\text{ref}}[\rho^{\text{ref}}] - E[\rho^{\text{ref}}]|}{|E^{\text{ref}}|}, \quad (5)$$

## Systems Considered

Systems considered at the level of Full CI.

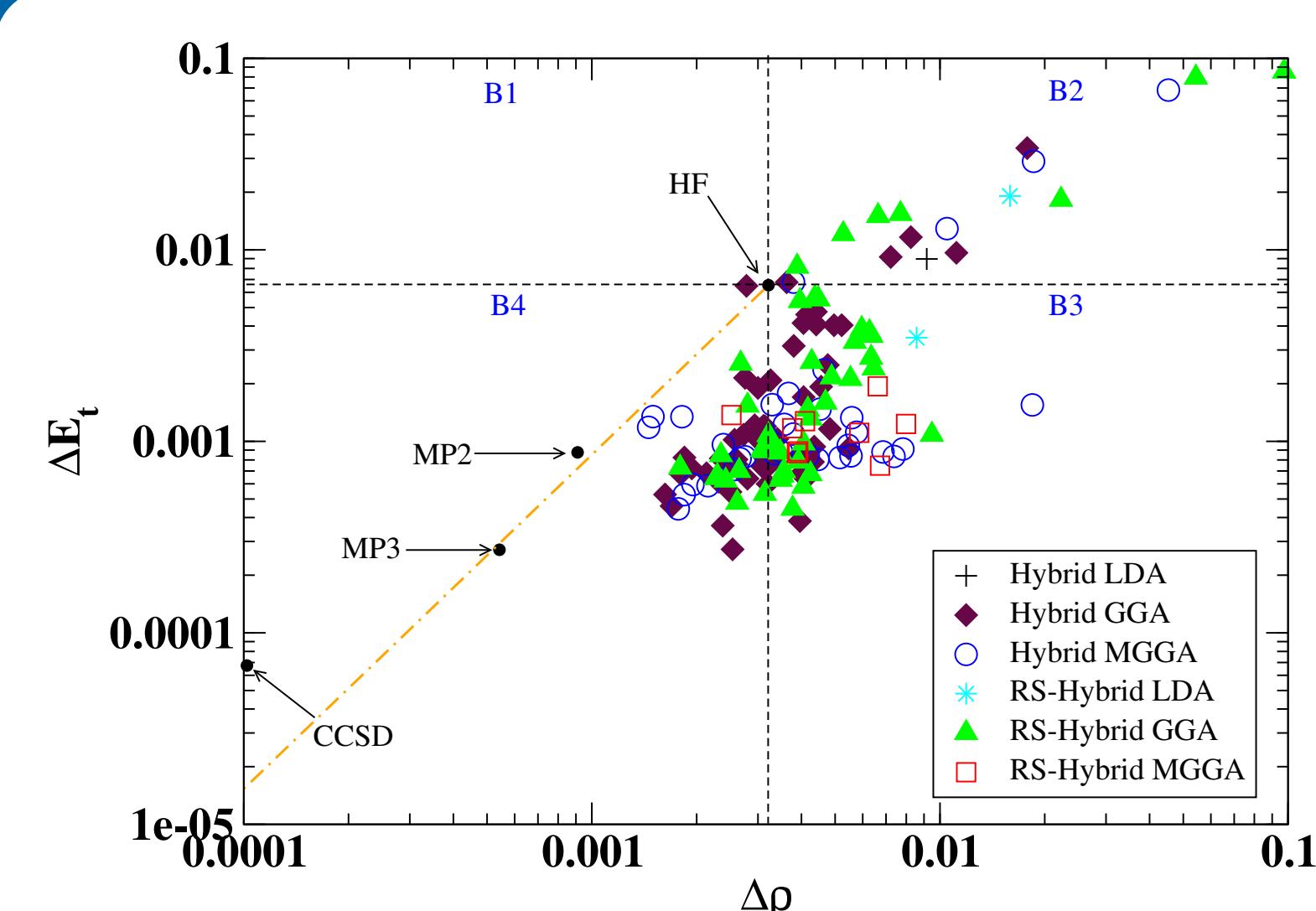
He, Be, H<sub>2</sub>, He<sub>2</sub>, LiH

Systems considered at the level of CCSD(T)

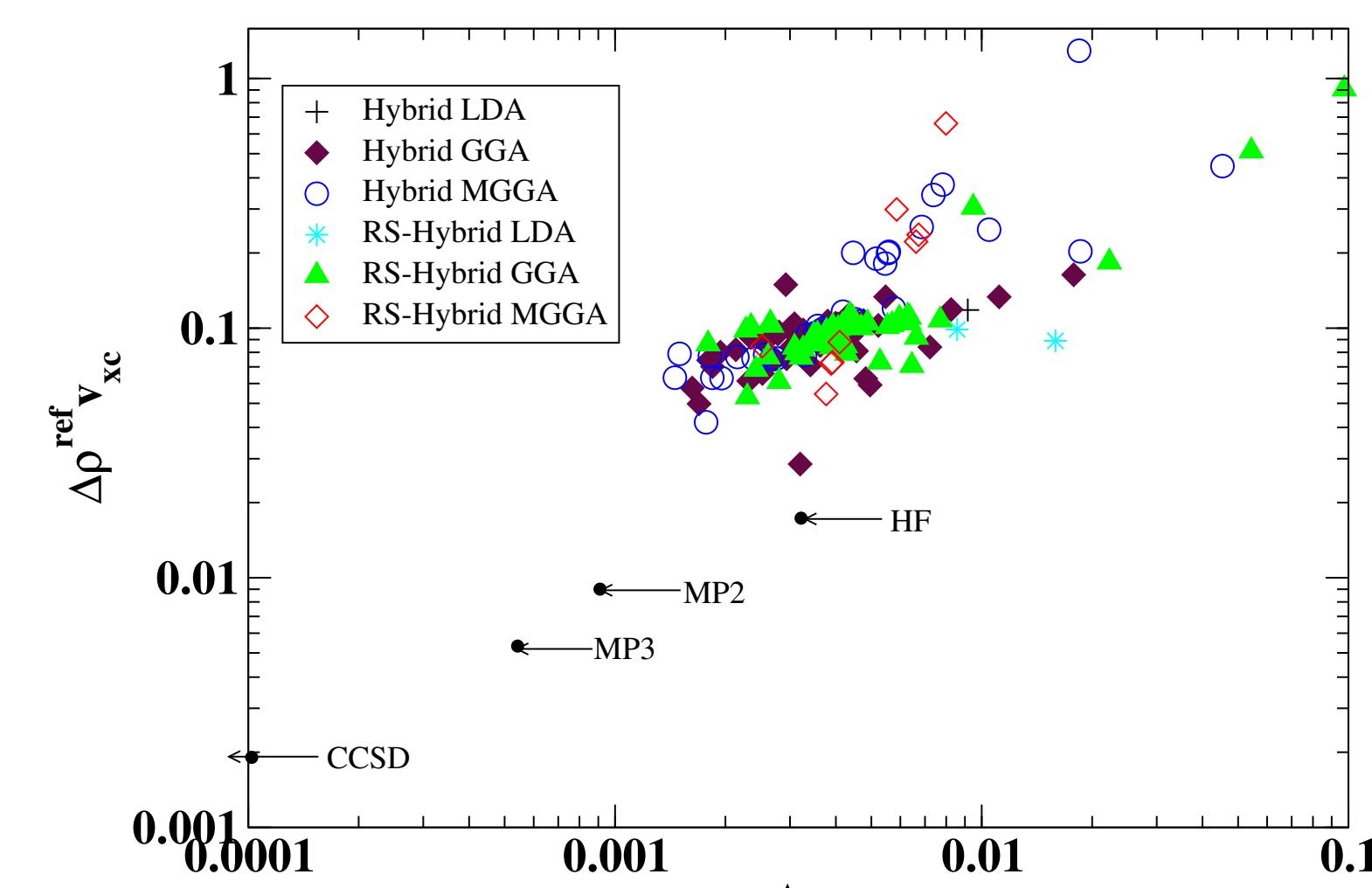
Ar, Be, C<sub>2</sub>H<sub>6</sub>, Cl<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, HCl,

He, He<sub>2</sub>, HF, Mg, N<sub>2</sub>, Ne, Ne<sub>2</sub>, NH<sub>3</sub>,

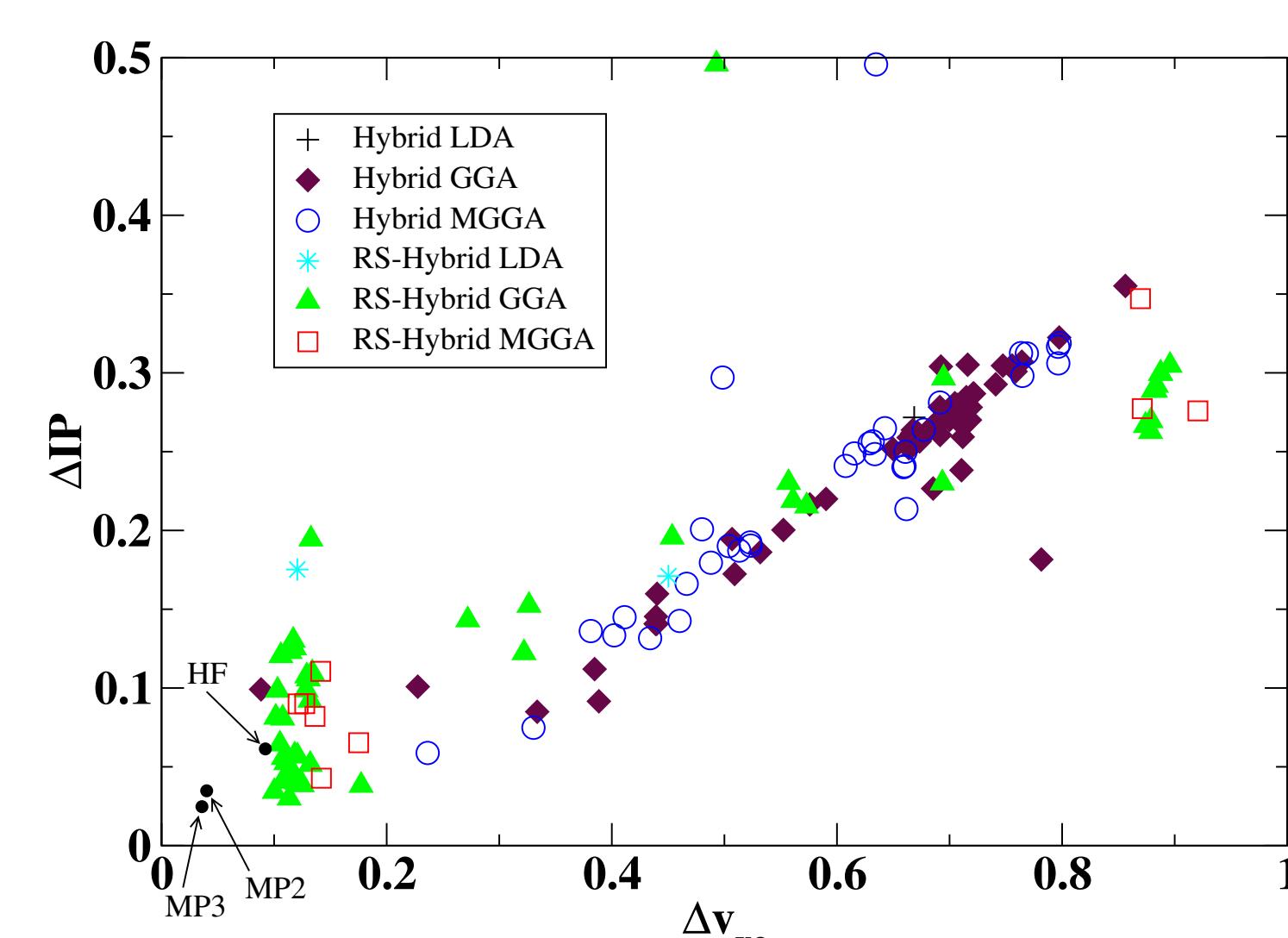
## Error Correlation Plots



Correlation plot for  $\Delta \rho$  vs  $\Delta E_t$ . Most functionals perform better than HF for Energy and on par with HF but not better than MP2 for density.



Analysing the core of XC potential, we observe that none of the hybrid functionals can perform even better than HF.



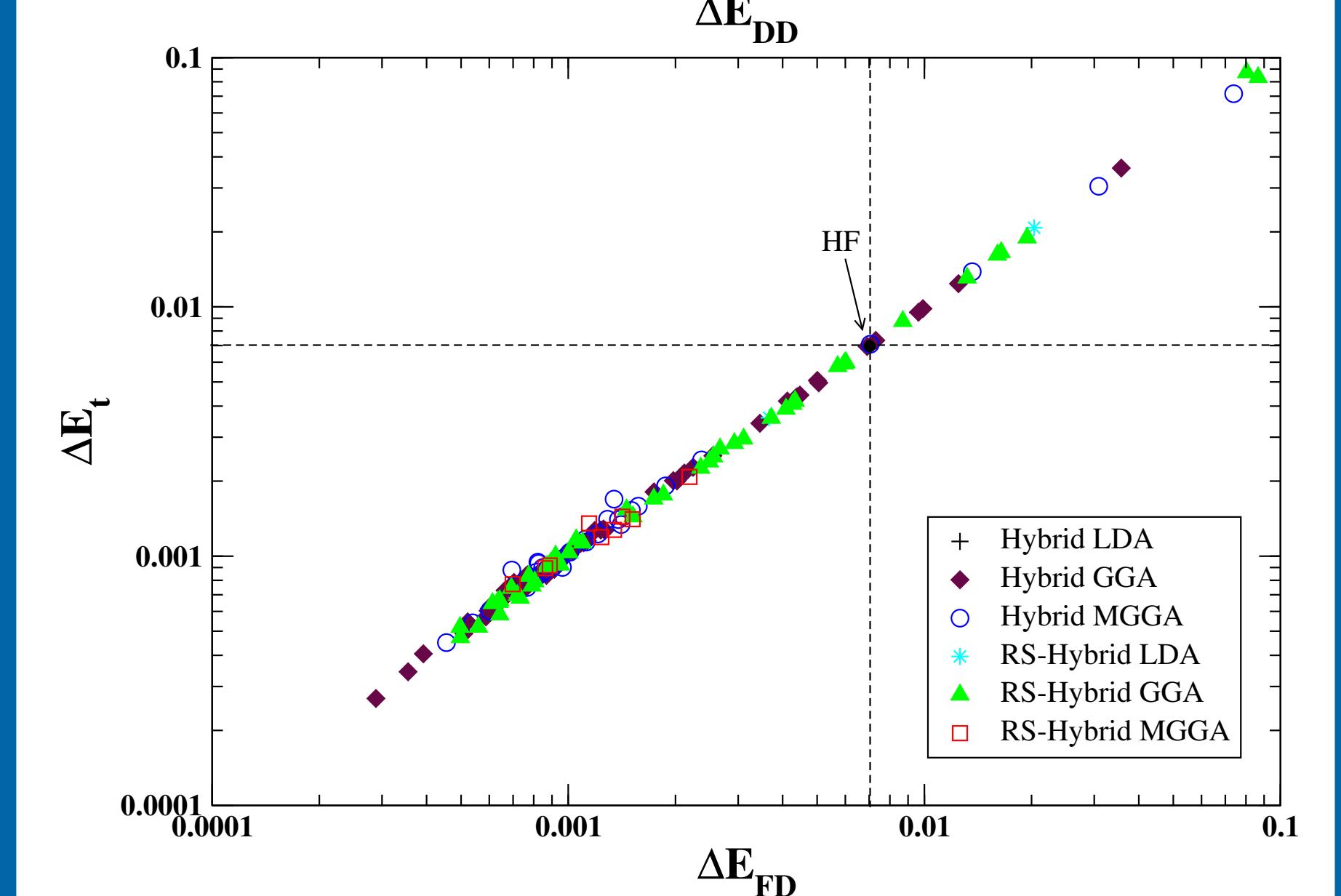
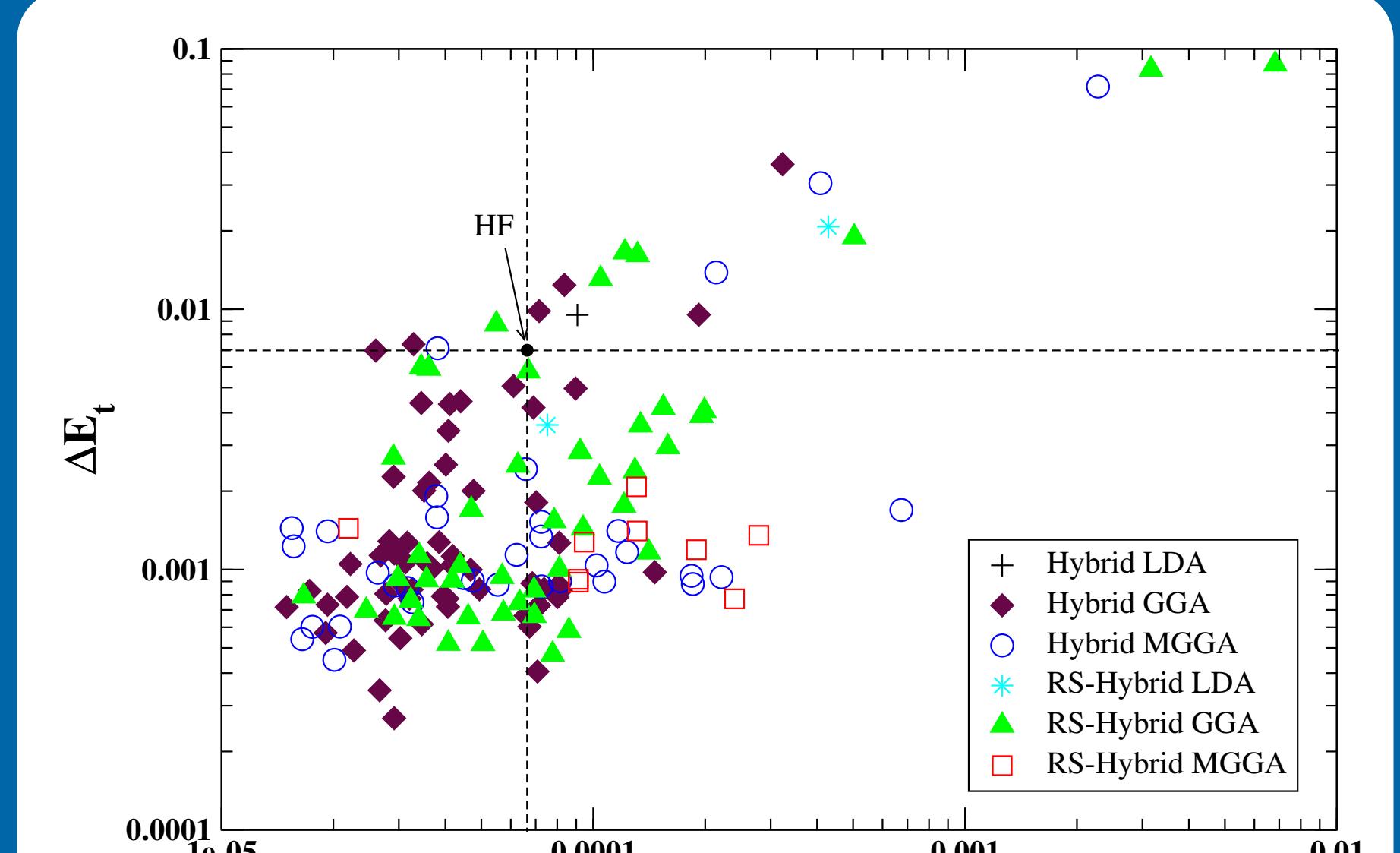
The direct correlation between the quality of XC potential and IP(negative of HOMO) is presented above. Range-Separated hybrids and meta-gga type hybrid functionals dominate the low error region. It is also important to note that most functionals are below the accuracy of HF for  $\Delta IP$  and  $\Delta V_{xc}$  error.

## Acknowledgements

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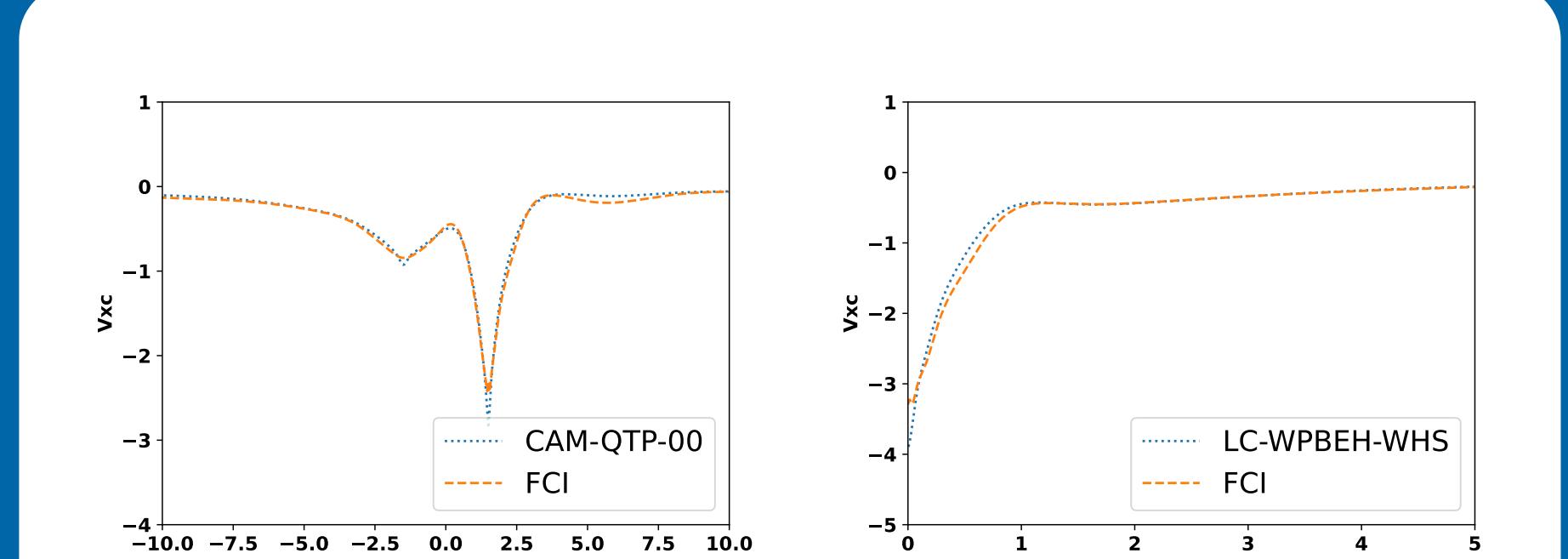
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## Density and Functional Driven Errors



Correlation plot between  $\Delta E_{DD}$  - The Density Driven Error vs the error in total energy (Top). Correlation plot between the  $\Delta E_{FD}$  - The Functional Driven Error vs the error in total energy (Bottom).

## XC Potentials



The exchange-correlation potential computed for LiH and Be using the Wu-Yang method.

## Conclusions

- The work primarily introduces a methodology to vet density functionals considering XC potential and density on a grid using reference from WFT.
- The analysis indicates that a vast majority of functionals performs better for total energy and density whereas performs poor for quantities such as XC potential, Ionization potential. It is vital to note that the performance of XC potential in the core region is below than that of the Hartree-Fock theory.
- Functional-driven error dominates the density-driven error, which is another crucial area where the attention of XC functional developers is deemed necessary.

## References

- V.B. Kumar, S.Śmiga, I. Grabowski. In Review 2024..
- S.Śmiga, L.A. Constantin, *The Journal of Physical Chemistry A* 2020, 124(27).
- B. Kanungo, Paul. S. Zimmerman and V. Gavini, *The Journal of Physical Chemistry Letters*, 2021, 50.
- A Singh, V. B. Kumar, I. Grabowski and S. Śmiga , *Advances in Quantum Chemistry* 2023, 93.