MC–srDFT

Triplet Response and meta-GGAs

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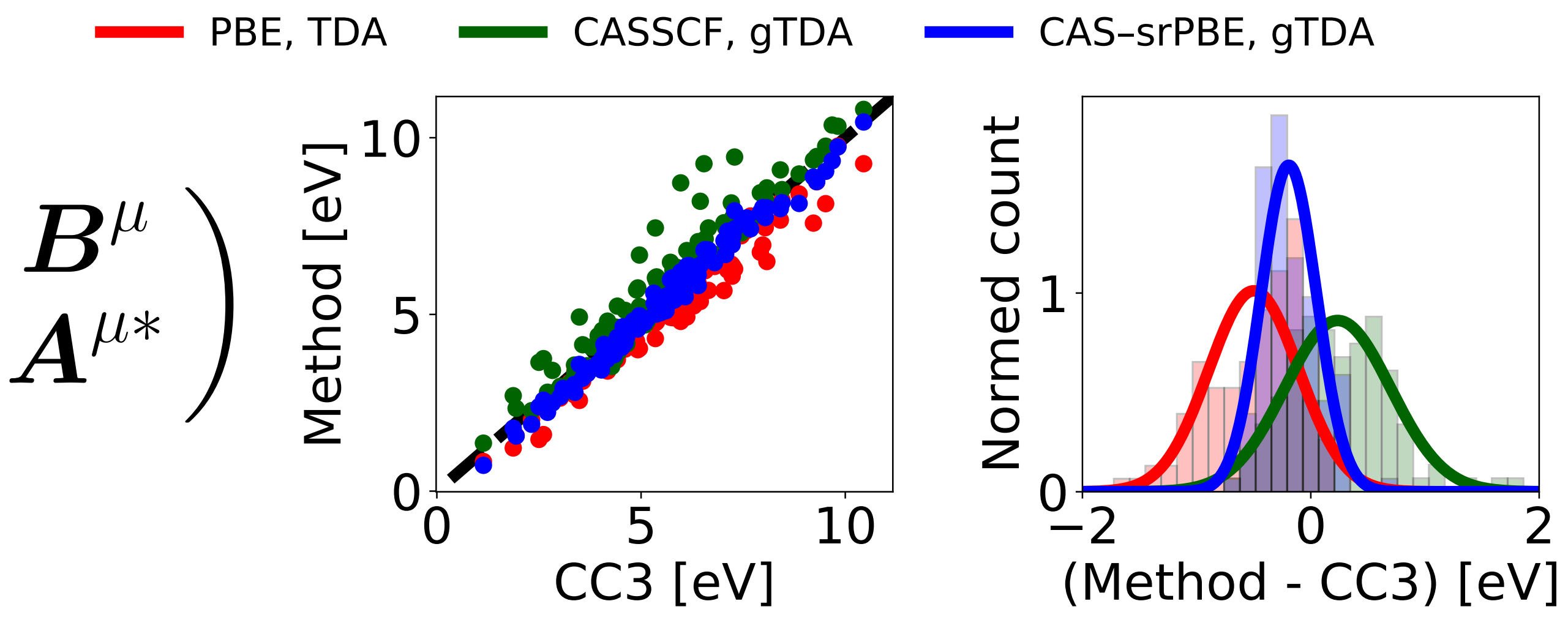
$$\begin{pmatrix} \boldsymbol{A}^{\mu} & \boldsymbol{B}^{\mu} \\ \boldsymbol{B}^{\mu *} & \boldsymbol{A}^{\mu *} \end{pmatrix}$$



Conclusions

The hybrid range-separated MC–srDFT model have been extended to include triplet response, and to utilize srTPSS. Calculated triplet excitation energies with srDFT are significantly more accurate when compared to DFT. The MAD of HF–srLDA is 0.22 eV using TDA. The accuracy is comparable to CC2. Short-range meta-GGAs need more work, and srSCAN will be investigated in the future.

The MC–srDFT model

The MC–srDFT model is a range-separated hybrid of multi-configurational wave function theory and density functional theory. The electron-electron interaction operator is split into a long-range and short-range operator:

$$\frac{1}{r} \rightarrow \underbrace{\frac{\operatorname{erf}(\mu r)}{r}}_{\text{long-range}} + \underbrace{\frac{1-\operatorname{erf}(\mu r)}{r}}_{\text{short-range}} \qquad (1)$$

with the range-separation parameter μ. The split of the electron-electron interaction operator can be seen in figure 1 for different values of μ. A value of around $\mu = 0.4\ \text{a.u.}^{-1}$ has been found to be a good choice.[1,2]

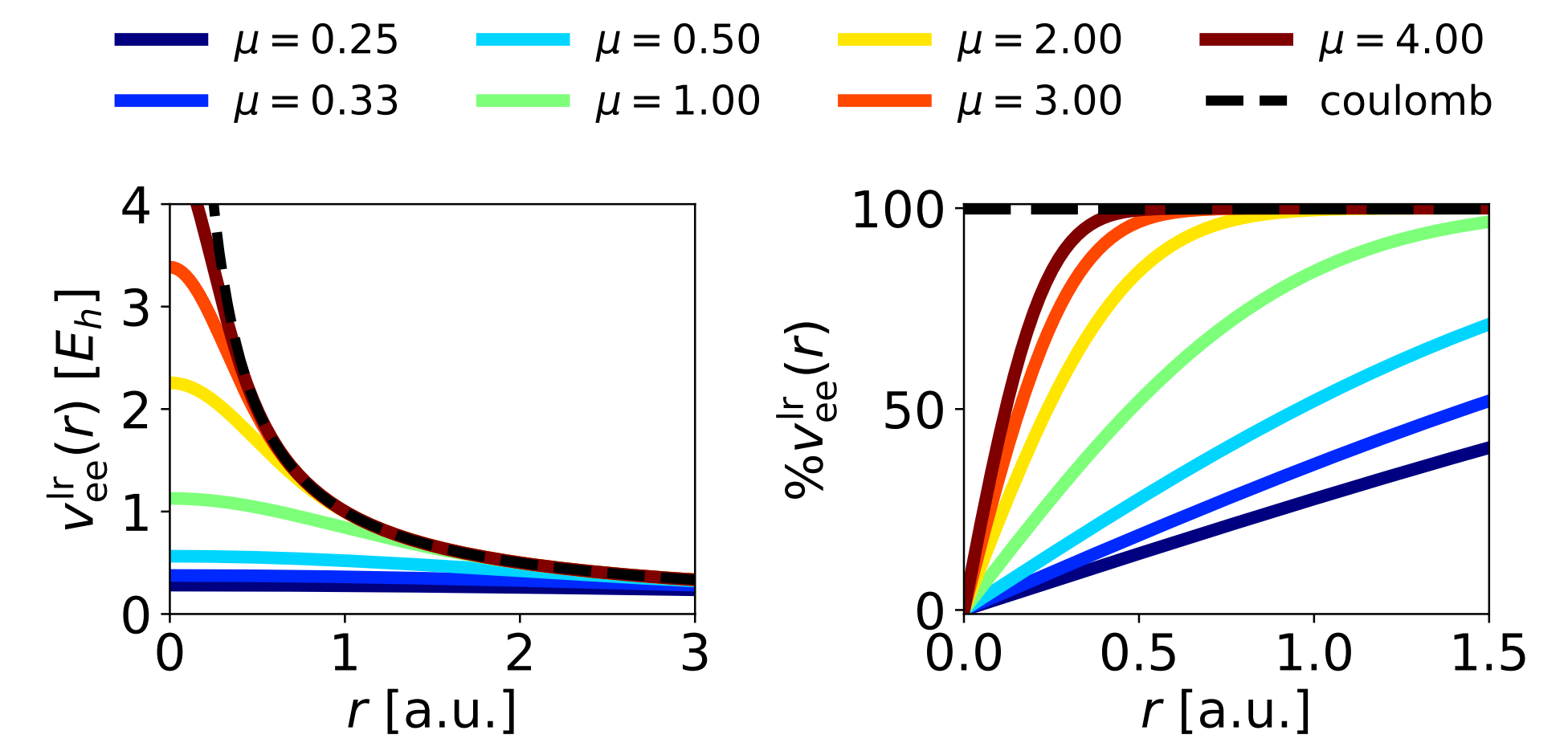


Figure 1: The long-range part of the electron-electron interaction using the error function.

The wave function part is handled by modified integrals, whereas tailored DFT functionals need to be constructed for the srDFT part. This ensures no double counting of the electron-electron interaction. The energy becomes simply a sum of long-range and short-range energies:

$$\begin{aligned} E\left(\boldsymbol{\lambda}\right) = {} & \left\langle \Psi\left(\boldsymbol{\lambda}\right) \middle| \hat{H}^{\mathrm{lr},\mu} \middle| \Psi\left(\boldsymbol{\lambda}\right) \right\rangle \\ & + E_{\mathrm{H}}^{\mathrm{sr},\mu}\left[\rho_C\left(\boldsymbol{r},\boldsymbol{\lambda}\right)\right] + E_{\mathrm{xc}}^{\mathrm{sr},\mu}\left[\boldsymbol{\xi}\left(\boldsymbol{r},\boldsymbol{\lambda}\right)\right], \end{aligned} \qquad (2)$$

with the density and density related quantities being constructed from the wave function. The energy can be minimized fully variationally in the wave function parameters.

This makes the MC–srDFT model useful for calculation of response properties.

MC–srDFT Linear Response

In the framework of linear response the matrix equation to be solved is very similar to that of DFT and MCSCF, and was derived for singlet response by Fromager et. al.[3]

$$\left(\boldsymbol{E}^{[2],\mu} - \omega \boldsymbol{S}^{[2],\mu}\right) \Lambda\left(\omega\right) = i\boldsymbol{V}_{x}^{[1],\mu} \qquad (3)$$

With the electronic Hessian being expressed as a matrix of two different blocks as is known from TD-DFT and MCSCF linear response.

$$\boldsymbol{E}^{[2],\mu} = \begin{pmatrix} \boldsymbol{A}^{\mu} & \boldsymbol{B}^{\mu} \\ \boldsymbol{B}^{\mu *} & \boldsymbol{A}^{\mu *} \end{pmatrix} \qquad (4)$$

The Tamm-Dancoff approximation (TDA) is setting $B^{\mu} = 0$. Due to the expression of the energy within the MC–srDFT model in eq. (2) the Hessian is simply the sum of a long-range and a short-range contribution:

$$\boldsymbol{E}^{[2],\mu} = \boldsymbol{E}^{[2],\mathrm{lr}} + \boldsymbol{E}^{[2],\mathrm{sr}} \qquad (5)$$

Triplet Excitation Energies

The performance of the MC–srDFT to calculate triplet excitation energies is benchmarked against CC3 triplet excitation energies.[4,5] This concatenated benchmark set consists of 33 molecules and 111 triplet excitation energies.

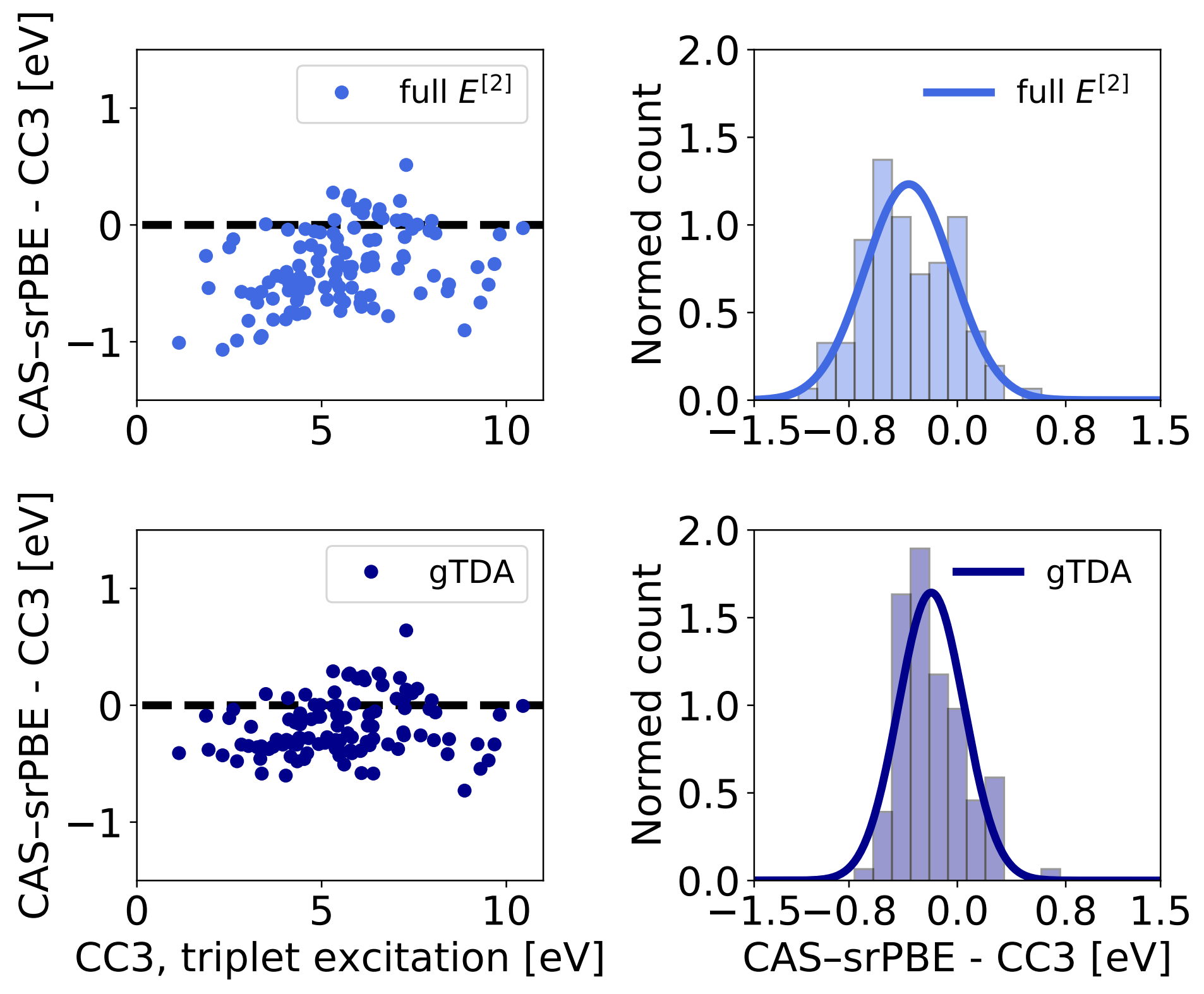


Figure 2: The difference in calculated triplet excitation energies between CAS–srPBE and CC3.

As can be seen in figure 2 using TDA is important especially for low lying triplet excitations. This is due to near triplet instabilities from Hartree-Fock and DFT.

When using gTDA, CAS–srDFT can be seen to give a consistent accuracy over a wide range of triplet excitation energies (between 0 eV and 10 eV).

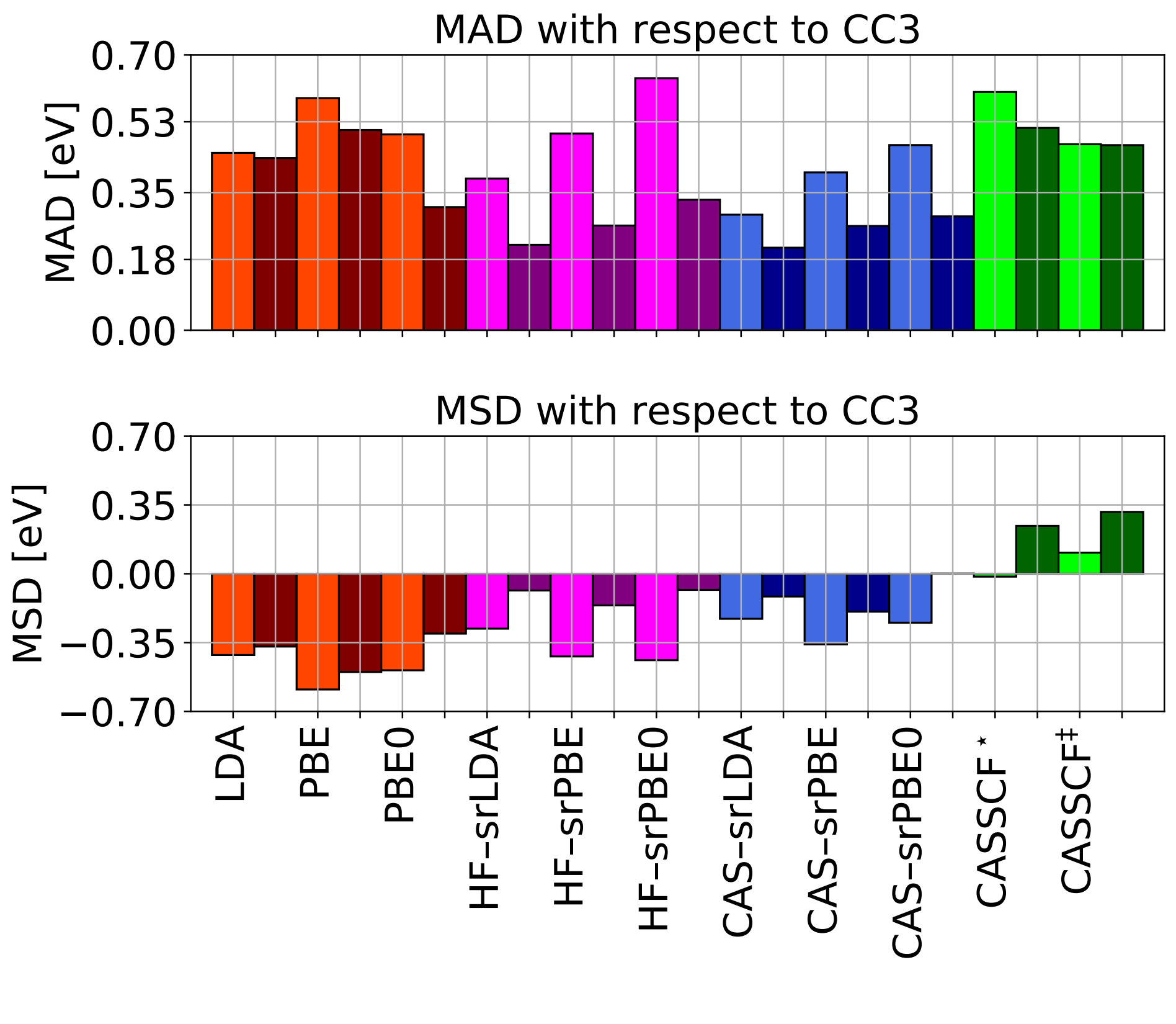


Figure 3: The Mean Absolute Deviation (MAD) and Mean Signed Deviation (MSD) for calculated triplet excitation energies for a set of methods compared to CC3. $*$ indicates the CAS is the same as used in CAS–srDFT. ‡ indicates a CAS tuned for CASSCF was used.

Three different short-range functionals benchmarked for this set of triplet excitation energies. In figure 3 it can clearly be seen that srDFT outperforms the conventional DFT functionals, but that TDA should be used for calculation of triplet excitation energies. Surprisingly srLDA is the better performing sr–functional for this particular benchmark. HF–srDFT and MC–srDFT are performing very similarly, this can be expected because of the molecules in the benchmark set, due to very little multi-configurational character.

Method	MAD [eV]	MSD [eV]	σ [eV]
LDA	0.48	-0.40	0.50
HF–srLDA	0.21	0.04	0.29
CAS–srLDA	0.17	0.00	0.22
PBE	0.49	-0.47	0.40
HF–srPBE	0.23	-0.01	0.30
CAS–srPBE	0.18	-0.04	0.22
PBE0	0.24	-0.21	0.21
HF–srPBE0	0.33	0.09	0.41
CAS–srPBE0	0.28	0.11	0.33
CASSCF	0.73	0.53	0.91

Table 1: Statistical data for a subset of the triplet excitation energies, picked on basis of static-correlation for the molecules.

In Table 1 statistical data for a subset of the benchmark set can be seen. Molecules with increased static correlation are picked.

The use of multiple configurations can be seen to be increasingly important for this subset.

Short-Range meta-GGAs

A short-range version of the TPPS meta-GGA functional has been developed by Goll et. al.[6]

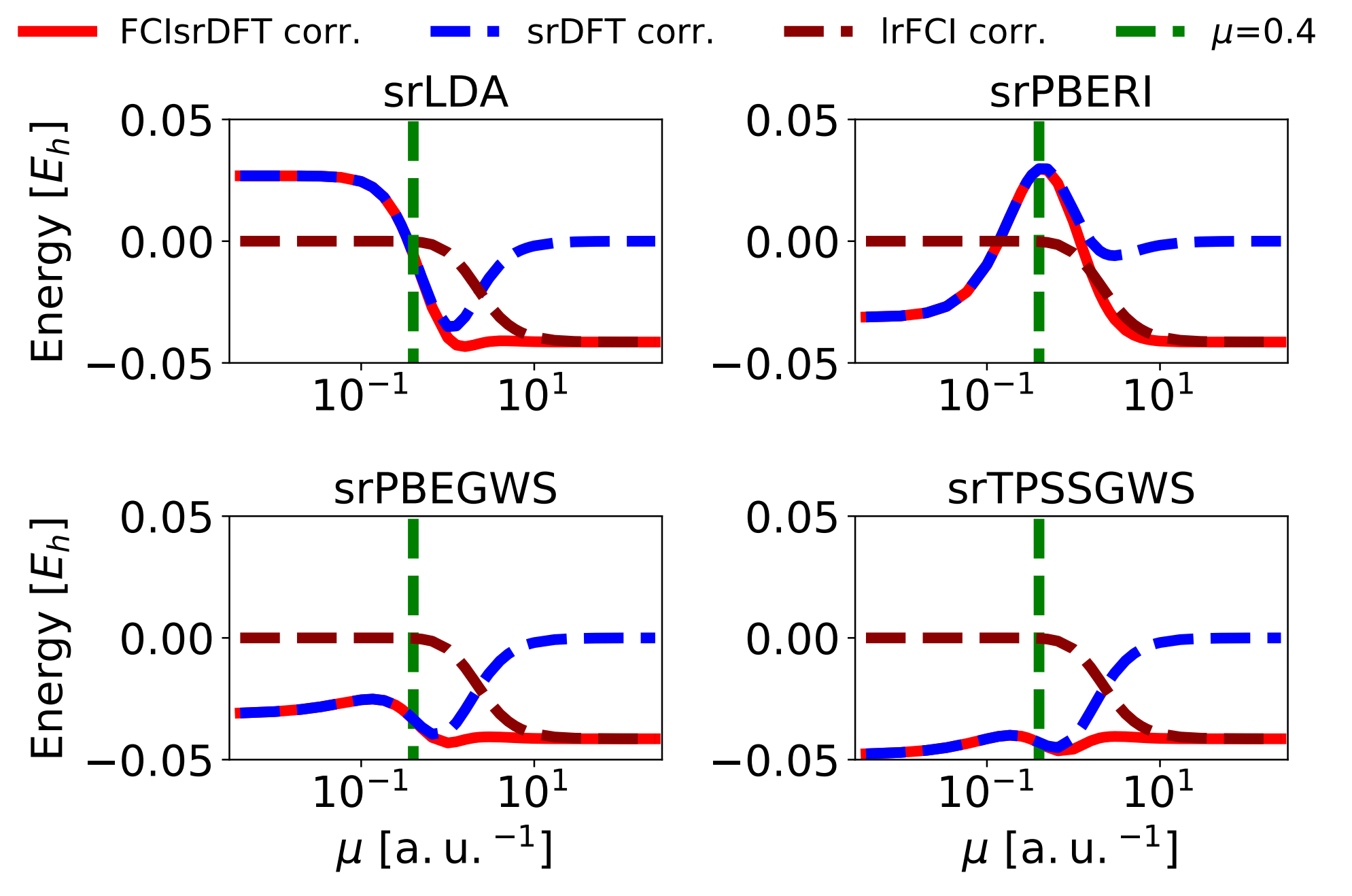


Figure 4: The correlation energy decomposed into long-range and short-range using FCI–srDFT for a range of μ values on the Helium atom.

A well designed short-range functional will make the energy constant of FCI–srDFT over a wide range of μ values. Figure 4 shows how different sr–functionals behave with respect to μ for FCI–srDFT. Here srTPSS looks promising.

Method	MAD [eV]	MSD [eV]	σ [eV]
TPSS	0.42	-0.41	0.33
HF–srTPSS	0.27	-0.15	0.28
CAS–srTPSS	0.27	-0.19	0.25

Table 2: Statistical quantities for the calculation of triplet excitation energies using (sr)TPSS using the CC3 benchmark set. Using TDA.

As can be seen in Table 2, srTPSS is also a clear improvement to conventional TPSS for the calculation of triplet excitation energies. But the performance is very close to that of srPBE.

References

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