Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supporting Information:

Combining low-cost electronic structure theory and low-cost parallel computing architecture

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Contents

1 Implementation details and element availability

To check the method implementation in this work, we control the energies and gradients against the corresponding ORCA and TURBOMOLE implementations. We consider the energy as equivalent, when the absolute difference in electronic energies $E_{\text{elec.}}$ is smaller than the threshold defined in Equation 1. For the gradients $d\mathbf{X}$, we take the absolute difference between two quantum chemical programs and average over the number of atoms N_{atoms} in that molecule, see Equation 2. This measure $\Delta d\mathbf{X}$ is averaged over the Cartesian coordinates x, y, z, then computed and compared to a threshold, see Equation 3.

$$|E_{\text{elec.,TC}} - E_{\text{elec.,ORCA,TM}}| \leq 2 \cdot 10^{-4} \text{ Eh} \tag{1}$$

$$\sum_{\alpha}^{\alpha \in (x,y,z)} \frac{\Delta d\mathbf{X}^{\alpha}}{3} \leq 1 \cdot 10^{-4} \text{ atomic units} \tag{2}$$

$$\text{where: } \Delta d\mathbf{X} = \sum_{i=0}^{N_{\text{atoms}}} |d\mathbf{X}_{i,\text{TC}} - d\mathbf{X}_{i,\text{ORCA,TM}}| \cdot \frac{1}{N_{\text{atoms}}} \tag{3}$$

2 Comparing the price/performance aspect of GPU models

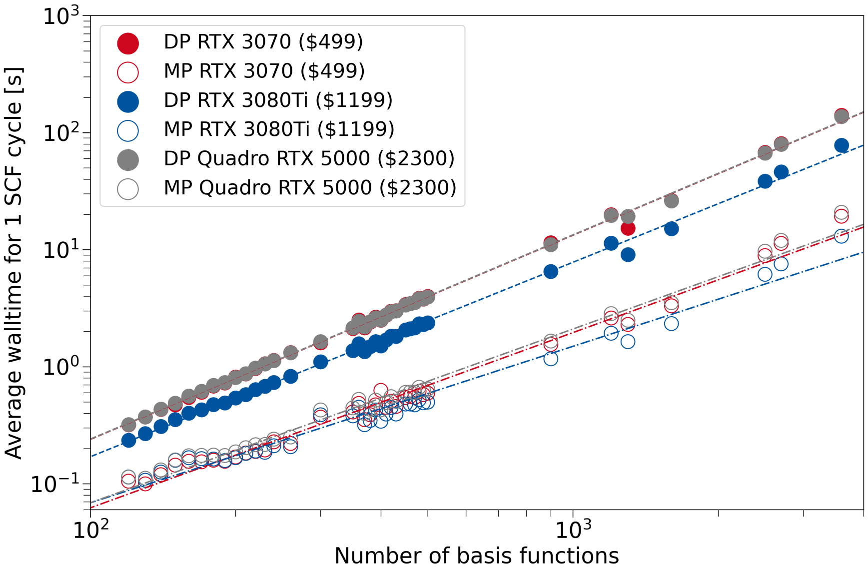

Figure S1: Average wall time for 1 SCF cycle for the composite method HF-3c as a function of the number of basis set functions. For TeraChem, the mixed precision (MP) and double precision (DP) computation schemes are compared for different GPU models. The indicated prices are MSRP according to Ref. S1.

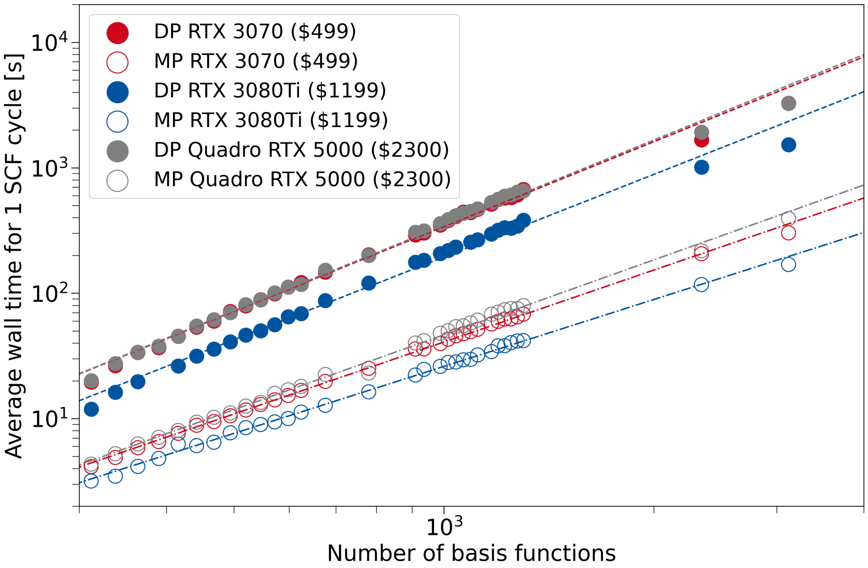

Figure S2: Average wall time for 1 SCF cycle for the composite method ωB97X-3c as a function of the number of basis set functions. For TeraChem, the mixed precision (MP) and double precision (DP) computation schemes are compared for different GPU models. The indicated prices are MSRP according to Ref. S1.

3 Benchmarking 3c methods for their use with FOMO-*hh*-TDA

Statistical measures:

- x_i denotes the computed/sample value
- r_i denotes the reference value
- n denotes the sample size
- Mean deviation (MD) : $\mathrm{MD} = \frac{\sum_i^n x_i - r_i}{n}$
- Mean absolute deviation (MAD) : $\mathrm{MAD} = \frac{\sum_i^n |x_i - r_i|}{n}$
- Root mean square deviation (RMSD) : $\mathrm{RMSD} = \sqrt{\frac{\sum_i^n (x_i - r_i)^2}{n}}$
- Bessel corrected standard deviation (STD) : $\mathrm{STD} = \sqrt{\frac{\sum_i^n (x_i - r_i - \mathrm{MD})^2}{n-1}}$

3.1 Intermolecular charge-transfer excitations set

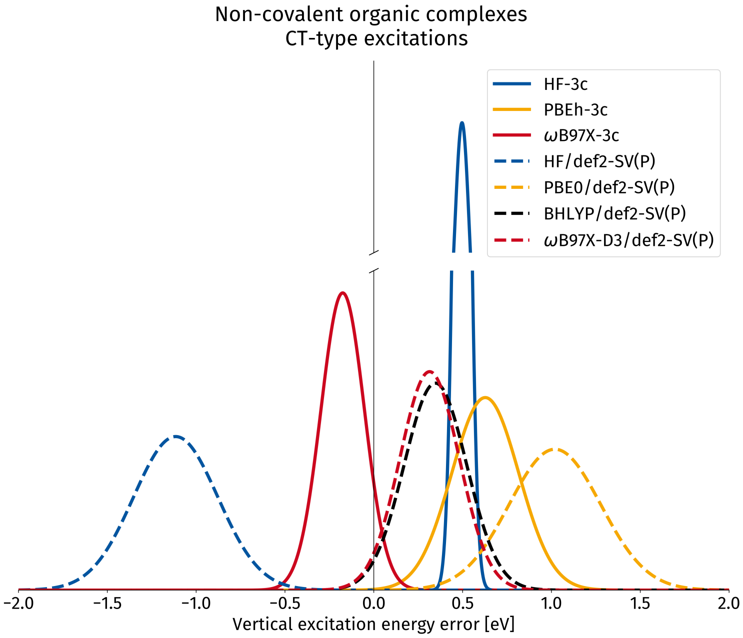

Figure S3: Gaussian error distribution functions for *hh*-TDA with different density functional approximations in the calculation of vertical excitation energies. Comparing the implemented 3c methods with their parent methods with the spherical def2-SV(P) basis set. BHLYP/def2-SV(P) is added as it is one of the best performing density functionals in the original publication.[S2,S3] The centers of the Gaussians correspond to the mean deviation (MD), whereas the width of the Gaussian corresponds to the standard deviation (SD), both in eV. This subset contains molecules with dipole-allowed intermolecular CT character.

Table S1: Vertical excitations computed with FOMO-*hh*-TDA for different organic complexes with intermolecular charge-transfer type excitations (set taken from Ref. S2). Only 3c-methods implemented in this work are shown. The values are given in eV.

	Reference	hh-TDA-HF-3c	hh-TDA-PBEh-3c	hh-TDA-wB97X-3c
CA-diphenylene	2.81	3.29	3.67	2.78
CA-hexamathylbenzene	2.87	3.38	3.54	2.62
TCNE-benzene	3.78	4.31	4.34	3.75
TCNE-diphenylene	2.28	2.82	3.08	2.10
TCNE-hexamathylbenzene	2.36	2.84	2.70	2.03
TCNE-o-xylene	3.17	3.60	3.71	2.95
MD	-	0.50	0.63	-0.17
MAD	-	0.50	0.63	0.17
RMSD	-	0.50	0.65	0.21
STD	-	0.04	0.19	0.12
MAX	-	0.54	0.86	-0.02

3.2 Push-pull-type set

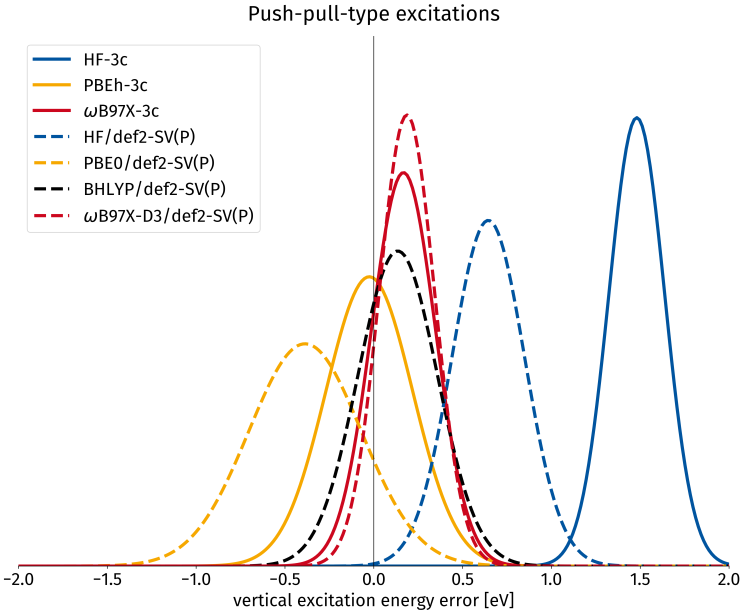

Figure S4: Gaussian error distribution functions for *hh*-TDA with different density functional approximations in the calculation of vertical excitation energies. Comparing the implemented 3c methods with their parent methods with the spherical def2-SV(P) basis set. BHLYP/def2-SV(P) is added as it is one of the best performing density functionals in the original publication.[S2,S3] The centers of the Gaussians correspond to the mean deviation (MD), whereas the width of the Gaussian corresponds to the standard deviation (SD), both in eV. This subset contains molecules with push-pull type intramolecular excitations.

Table S2: Vertical excitations computed with FOMO-*hh*-TDA for different molecules with push-pull type excitations (set taken from Ref. S4,S5). Only 3c-methods implemented in this work are shown. The values are given in eV.

	Reference	hh-TDA-HF-3c	hh-TDA-PBEh-3c	hh-TDA-wB97X-3c
bcf	4.10	5.41	4.41	4.49
Coumarin	3.69	5.16	3.96	4.07
DANS	3.42	4.74	3.25	3.43
DCS	3.56	5.03	3.31	3.57
S0904	3.81	5.42	3.67	3.87
S2127	3.66	5.37	3.49	3.82
MD	-	1.48	-0.03	0.17
MAD	-	1.48	0.22	0.17
RMSD	-	1.49	0.22	0.23
STD	-	0.16	0.24	0.18
MAX	-	1.71	0.31	0.39

3.3 Local excitation set

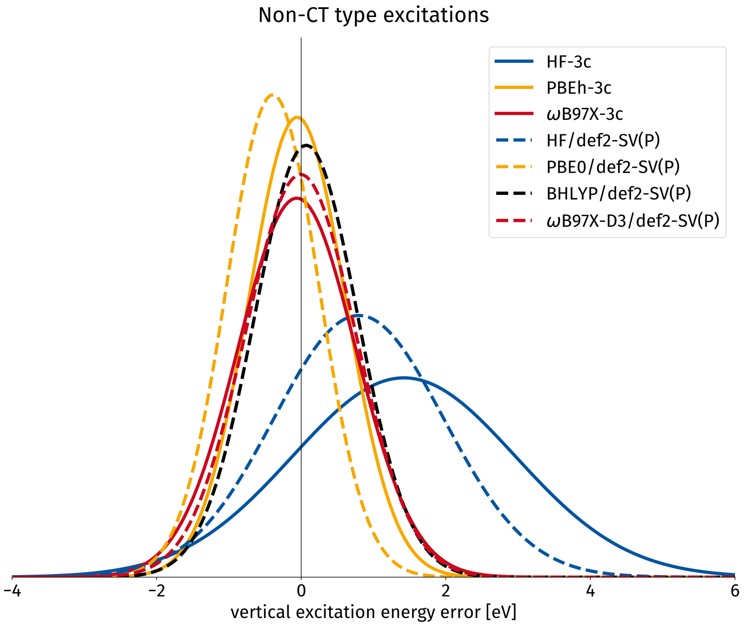

Figure S5: Gaussian error distribution functions for *hh*-TDA with different density functional approximations in the calculation of vertical excitation energies. Comparing the implemented 3c methods with their parent methods with the spherical def2-SV(P) basis set. BHLYP/def2-SV(P) is added as it is one of the best performing density functionals in the original publication.[S2] The centers of the Gaussians correspond to the mean deviation (MD), whereas the width of the Gaussian corresponds to the standard deviation (SD), both in eV. This subset has excitations with local excitation character.

Table S3: Vertical excitations computed with FOMO-*hh*-TDA for different molecules with local excitation (set taken from Ref. S5). Only 3c-methods implemented in this work are shown. The values are given in eV.

	Reference	hh-TDA-HF-3c	hh-TDA-PBEh-3c	hh-TDA-wB97X-3c
acenapthen	3.65	4.75	3.01	3.33
bisthiophen	4.48	6.47	4.15	4.24
cf3cooh	5.95	6.15	6.49	6.37
cpropenon	4.42	0.74	2.06	1.86
dithiacyclohexan	4.52	5.30	4.90	4.31
Ethene	7.80	10.70	7.10	6.45
fluoroisochinolin	4.50	7.30	4.85	4.96
Furan	6.32	9.67	6.32	6.09
hcsoh	3.57	3.06	3.44	4.97
hexatriyne	4.85	5.54	4.10	4.28
mepc2h4	6.53	8.83	6.87	6.22
p2h4	6.25	8.59	7.04	5.54
proflavin	3.54	5.32	3.47	3.59
purine	4.69	6.33	4.80	4.96
S0491	2.70	3.48	3.03	3.24
S2084	2.37	3.29	2.59	3.02
S2153	3.48	5.00	3.50	3.71
S2408	3.64	5.39	3.86	4.12
sacharin	4.91	6.36	5.26	5.00
si4h8	5.22	7.70	5.01	5.31
silabenzen	4.23	7.49	4.59	4.74
MD	-	1.42	-0.06	-0.06
MAD	-	1.82	0.44	0.56
RMSD	-	2.07	0.65	0.79
STD	-	1.54	0.67	0.81
MAX	-	3.35	0.79	1.40

References

(S1) `https://www.techpowerup.com/`, (last accessed: 21.11.2023).

(S2) Bannwarth, C.; Yu, J. K.; Hohenstein, E. G.; Martínez, T. J. *J. Chem. Phys.* **2020**, *153*, 024110.

(S3) Yu, J. K.; Bannwarth, C.; Hohenstein, E. G.; Martínez, T. J. *J. Chem. Theory Comput.* **2020**, *16*, 5499–5511.

(S4) Risthaus, T.; Hansen, A.; Grimme, S. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14408–14419.

(S5) Grimme, S.; Bannwarth, C. *J. Chem. Phys.* **2016**, *145*, 054103.