Supplemental Material: Radicals in aqueous solution: Assessment of density-corrected SCAN functional

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FIG. S1. Absolute errors (kcal/mol) in interaction (upper panel) and binding energies (lower panel) calculated for the neutral water cluster subset of the BEGDB data set using r2SCAN, DC-r2SCAN, r2SCAN-D3, and DC-r2SCAN-D3 with respect to the CCSD(T)/CBS reference values.

I. VALIDATION OF IMPLEMENTATION

A. Neutral water clusters

Following the example of Dasgupta et al.¹, we performed r2SCAN and (ADMM accelerated) DC-r2SCAN simulations of the neutral water cluster subset of the BEGDB database². The energy calculations were performed with correlation-consistent cc-GRB-X (X = D,T,Q) basis sets, enhanced with augmentation functions. For the D3 dispersion correction³ we used the scaling parameters 1.0, 1.324, and 0.0 for s6, sr6, s8, respectively.

We show in Figure S1 the absolute errors in interaction (upper panel) and binding (lower panel) energies associated with the four r2SCAN-based methods relative to the CCSD(T)/CBS reference values⁴. The errors are for entire clusters, not per molecule.

In Figure S2 we show the r2SCAN errors relative to the CCSD(T) reference values for the



FIG. S2. Absolute errors $(E_{r2SCAN} - E_{CCSD(T)}, E_{r2SCAN@LDA} - E_{CCSD(T)}, and E_{DC-r2SCAN} - E_{r2SCAN@LDA})$ in interaction energies calculated for the water clusters of the BEGDB data set.

BEGDB clusters $(E_{r2SCAN} - E_{CCSD(T)})$ with the errors associated with SCAN calculations carried out using the LDA density $(E_{r2SCAN@LDA} - E_{CCSD(T)})$. We also show the density sensitivity, that is, the difference between the DC-r2SCAN and r2SCAN@LDA results $(E_{r2SCAN@HF} - E_{r2SCAN@LDA})$.

in Figure S3, we show the absolute and per monomer basis-set superposition error in interaction energies for the neutral water clusters up until the pentamer. The BSSE calculations have been performed with the BSSE module in CP2K.

The mean absolute error (MAE) of the binding energy per monomer relative to the CCSD(T)/CBS reference binding energy for the neutral water clusters are reported in Table I cc-GRB-X (X = D,T,Q) basis sets.

TABLE I. Mean absolute error (kcal/mol) of binding energies per monomer for the neutral water cluster subset of the BEGDB database with cc-GRB-X (X = D,T,Q) basis sets.

MAE (kcal/mol)	cc-GRB-D	cc-GRB-T	cc-GRB-Q
r2SCAN	4.96	1.34	0.72
DC-r2SCAN	4.25	0.61	0.06

In Table II we plot the MAEs of the interaction energies for the neutral water cluster subset of the BEGDB database with and without the D3 dispersion correction³. The addition of the D3 dispersion correction deteriorates the interaction energies of both r2SCAN and DC-r2SCAN, reproducing the result by Dasgupta et al.⁵



FIG. S3. Absolute basis-set superposition errors (BSSE) and BSSE per monomer in interaction energies calculate for the neutral water cluster subset of the BEGDB database using r2SCAN/(ccGRB-Q + aug-cc-Q).

TABLE II. Mean absolute error (kcal/mol) of the interaction energies for BEGDB water cluster with and without D3 dispersion correction.

MAE (kcal/mol)	no D3	D3
SCAN	4.19	5.96
DC-SCAN	0.37	1.61

II. GEOMETRY OPTIMIZATION OF RADICAL CATION CLUSTERS

In order to verify the minimum structures of the $[CH_3S \therefore CH_3SH]^+$ and $[HS \therefore SH_2]^+$ clusters in the gas phase, we performed geometry optimizations with r2SCAN and DC-r2SCAN of these structures, by using the BFGS algorithm. The structures were considered converged to the corresponding thresholds (given in bracelets) of the following criteria: maximum geometry change $(8.0 \times 10^{-5} a_0)$, maximum nuclear gradient component $(6.0 \times 10^{-6} Ha a_0^{-1})$, root-mean-square (RMS) of geometry change $(4.0 \times 10^{-5} a_0)$ and RMS of nuclear gradient $(3.0 \times 10^{-5} Ha a_0^{-1})$. The geometry optimizations were performed with TZV2P-MOLOPT-SCAN-GTH basis sets, and GTH-SCAN pseudopotentials.

A. Scaling Benchmark

Scaling benchmarks were performed to assess the performance of the ADMM accelerated DC-DFT implementation using an increasing number of water molecules from 32 to 1024. The bench-



FIG. S4. Relative execution time, expressed in percentages of total runtime, spent in each of the most relevant sections of the DC-DFT algorithm: ground state (blue), DC-DFT energy functional (maroon), linear response solver (dark pink), and response forces (pink).

marks were conducted on two HPE Cray EX nodes part of the Eiger@Alps supercomputer at the Swiss National Supercomputing Centre (CSCS). Each node consisted of two 64-core AMD EPYC[™] 7742 CPUs, with 256 GB of RAM per node. The calculations used parallelization based on the Message Passing Interface (MPI) with 256 tasks and 1 thread.

Instead of examining the scaling of the total execution time with respect to system size, the percentage of the total time by segments of the code as a function of system size was analyzed and are presented in Figure S4. The ground state calculation, indicated in blue, consistently accounted for approximately 60% of the cost of a DC-DFT calculation, primarily attributed to the computation of electron repulsion integrals (ERIs). This was found to be the rate-limiting step in the calculations.

The density correction, shown in red-ish colors, accounted for the remaining 40%. The MObased linear response solver, represented in magenta, accounted for about 25% of the time spent on the DC-DFT calculation. The remainder was dedicated to the evaluation of the kernel contribution to the response force, where derivative electron repulsion integrals (DERIs) needed to be



FIG. S5. Deviation of instantaneous conserved energy to the moving average conserved energy with a window of 1 ps.

calculated.

III. MD SIMULATIONS OF SOLVATED SYSTEMS

A. Energy conservation

Figure S5 illustrates the time evolution of the relative conserved energy, which is calculated as the deviation of the instantaneous conserved energy from the average conserved energy over a rolling window of 1 ps. The fluctuations in the relative conserved energy are reported in Table III as the standard deviation normalized per molecule and per picosecond.

	r2SCAN I	DC-r2SCAN	
H ₂ O	0.09	0.24	
•OH	0.08	1.31	
•SH	0.09	2.53	
$[CH_3S \therefore CH_3SH]^+$	0.19	0.96	
$[{\rm HS}\mathrel{.\dot{}} {\rm SH}_2]^+$	0.09	1.67	

TABLE III. Conservation of total energy (µHa/molecule/ps)



FIG. S6. Temperature evolution (K) of (left panels) r2SCAN and (right panels) DC-r2SCAN production NVT simulations for solvated hydroxyl and sulfanyl radical, and solvated cation clusters $[CH_3S \therefore CH_3SH]^+$ and $[HS \therefore SH_2]^+$. Dotted black lines indicate mean temperature.



FIG. S7. RDF of solvent O–O in solution with [•]OH for (solid red) r2SCAN and (dashed blue) DC-r2SCAN.

B. Temperature evolution

C. Solvent structure of solvated hydroxyl radical

In Figure S7 we show the radial distribution function between the solvent oxygen atoms in the solvated hydroxyl radical system. The positions and intensities of the first minimum and maximum are reported in Table IV. The results indicate that both r2SCAN and DC-r2SCAN reproduce the experimental RDF of liquid water at ambient conditions. The solvent avoids entering a glassy state or elevated first solvation shell peak that would indicate overstructuring of the liquid phase.⁶ This behavior confirms our choice of performing the r2SCAN calculations at 350 K to reproduce liquid water.

TABLE IV. Positions and intensities of the first maximum (r_1, g_1) , first minimum (r_2, g_2) , and coordination number (n_{OO}) from the solvent oxygen-oxygen RDF in the solvated hydroxyl radical system are compared among r2SCAN, DC-r2SCAN, and experimental values of pure liquid water⁷.

SCAN DC-SCAN Experimental ⁷					
r_1 (Å)	2.81	2.84	2.80		
g_1	2.69	2.51	2.57		
r_2 (Å)	3.44	3.50	3.45		
<i>8</i> 2	0.81	0.91	0.84		
$n_{\rm OO}$	4.32	4.37	4.31		

D. Solvated hydroxyl radical

1. Dipole moment distribution



FIG. S8. Dipole moment distribution of the solvated hydroxyl radical.

E. Solvated sulfanyl radical

1. Distribution of the number of hydrogen bonds



FIG. S9. Distribution of the number of hydrogen bonds between solvent and the sulfanyl radical.

2. Mulliken charge analysis



FIG. S10. Distribution of Mulliken charge population on •SH in solution.

3. Dipole moment distribution



FIG. S11. Dipole moment distribution of the solvated sulfanyl radical.

F. $[CH_3S \therefore CH_3SH]^+$

1. Hydrogen bond angle distribution

In Figure S12, we show the hydrogen bond angle distribution when the distance criterion is met. A strong peak at 164° can be observed for the r^2 SCAN functional, which suggests a preferred and consistent bonding orientation between the solute and solvent. This observation is in agreement with the stronger acceptor hydrogen bond network shown in the (S*–H) RDF for r^2 SCAN. On the other hand, the absence of well-defined peaks in favor of a more uniform distribution in the hydrogen bond angle distribution with DC- r^2 SCAN implies a lack of specific preferred bonding orientations. The uniform distribution suggests that hydrogen bonds can form at a wide range of angles, resulting in a more diverse and flexible hydrogen bonding network between the solute and solvent.



FIG. S12. Hydrogen bond angle distribution involving the (left panel) CH_3S moiety and the (right panel) SH moiety of the $[CH_3S \therefore CH_3SH]^+$ cluster.

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