Supporting information for: Improved accuracy and efficiency in quantum embedding through absolute localization

Xuelan Wen,[†] Daniel S. Graham,[†] Dhabih V. Chulhai,[†,‡] and Jason D. Goodpaster[*,†]

†*Department of Chemistry, University of Minnesota. 207 Pleasant St. SE, Minneapolis MN 55455, USA.*

‡*Current address: Department of Chemistry, University of Indianapolis. 1400 E. Hanna Ave., Indianapolis IN 46227, USA.*

E-mail: jgoodpas@umn.edu

1 Choice of Embedding Strategy

In Figure 2 and Figure 3, the 3rd excited states of chlorodecane and decanol are not included due to the their nature of global excitatoins. Here, we show the embedding results for global excitations. When full-system basis is used the Huzinaga operator converge to the EOM-CCSD results on full system at the ninth carbon; while subsystem basis results are still not converged at the ninth carbon. This is a caveat that absolute localization should not be applied to global excitations and real charge-transfer states.

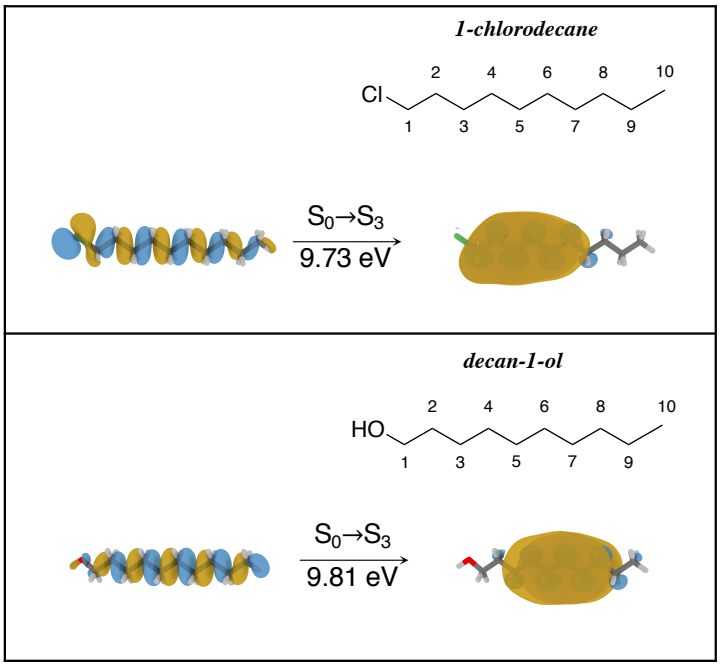


Figure S1: Natural transition orbitals (NTOs) of chlorodecane and decanol on the third singlet excited state. Shown on HONTOs and LUNTOs.

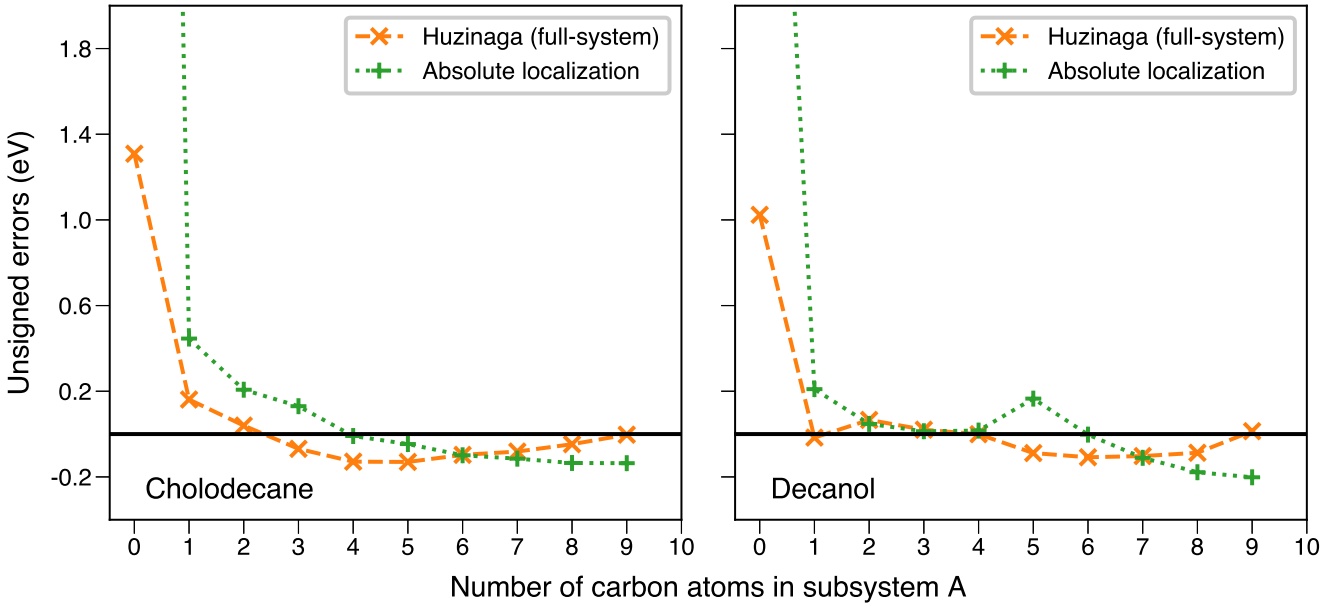


Figure S2: Unsigned errors of vertical excitation energy for the third excited state of chlorodecane and decanol using EOM-CCSD-in-M06. Results are compared to canonical EOM-CCSD.

Table S1: Excitation energies in eV using absolute localization for 1-decene, decanal, decanoic acid, 1-chlorodecane, 1-decanamine, and 1-decanol.

molecule	1- decene			decanal			decanoic acid		
# of C	S1	S2	S3	S1	S2	S3	S1	S2	S3
0	8.843	9.047	9.138	4.222	8.620	10.063	6.326	8.603	9.452
1	8.405	8.600	8.965	4.542	8.717	10.013	6.311	8.811	9.467
2	8.530	8.694	8.892	4.534	8.547	9.440	6.220	8.703	9.415
3	8.475	8.698	8.871	4.561	8.538	9.268	6.243	8.735	9.500
4	8.486	8.727	8.902	4.566	8.548	9.270	6.229	8.743	9.471
5	8.504	8.738	8.908	4.572	8.572	9.331	6.233	8.756	9.479
6	8.512	8.751	8.923	4.572	8.568	9.326	6.228	8.757	9.466
7	8.529	8.754	8.927	4.574	8.579	9.326	6.229	8.764	9.470
8	8.531	8.764	8.939	4.574	8.578	9.327	6.228	8.766	9.466
9				4.576	8.582	9.329	6.229	8.774	9.462

molecules	1-chlorodecane			1-decanaime			1-decanol		
# of C	S1	S2	S3	S1	S2	S3	S1	S2	S3
0	22.758	22.769	23.656	7.581	8.633	13.134	8.453	9.865	14.906
1	8.429	8.648	10.176	6.695	8.025	8.753	7.729	9.540	10.019
2	8.009	8.108	9.937	7.058	8.238	8.790	7.769	9.648	9.857
3	8.103	8.119	9.860	7.052	8.314	8.772	7.750	9.590	9.823
4	7.985	8.008	9.721	7.122	8.373	8.661	7.776	9.492	9.826
5	7.987	7.991	9.683	7.148	8.413	8.717	7.796	9.516	9.975
6	7.972	7.985	9.631	7.170	8.434	8.708	7.804	9.500	9.807
7	7.965	7.982	9.615	7.176	8.443	8.722	7.813	9.495	9.698
8	7.959	7.980	9.595	7.184	8.449	8.719	7.818	9.487	9.631
9	7.956	7.980	9.594	7.185	8.451	8.722	7.822	9.487	9.608
10	7.954	7.978	9.730	7.193	8.455	8.711	7.830	9.474	9.807

Table S2: Excitation energies in eV using Huzinaga operator with full-system basis for 1-decene, decanal, decanoic acid, 1-chlorodecane, 1-decanamine, and 1-decanol.

molecule	1- decene			decanal			decanoic acid		
# of C	S1	S2	S3	S1	S2	S3	S1	S2	S3
0	8.415	8.946	9.078	4.634	8.664	9.196	6.350	8.741	9.593
1	8.400	8.730	8.953	4.570	8.586	8.789	6.245	8.742	9.556
2	8.490	8.726	8.885	4.577	8.577	9.108	6.235	8.745	9.495
3	8.514	8.740	8.901	4.572	8.558	9.249	6.233	8.752	9.465
4	8.522	8.750	8.920	4.573	8.569	9.324	6.229	8.759	9.471
5	8.521	8.755	8.933	4.573	8.580	9.326	6.229	8.765	9.470
6	8.525	8.762	8.934	4.574	8.581	9.332	6.228	8.769	9.471
7	8.540	8.766	8.938	4.575	8.583	9.334	6.228	8.770	9.468
8	8.531	8.764	8.939	4.574	8.582	9.333	6.227	8.774	9.464
9				4.576	8.582	9.329	6.229	8.774	9.462

molecules	1-chlorodecane			1-decanaime			1-decanol		
# of C	S1	S2	S3	S1	S2	S3	S1	S2	S3
0	8.679	8.714	11.039	7.514	8.919	9.981	8.334	10.663	10.833
1	7.967	8.090	9.891	7.107	8.422	8.780	7.765	9.543	9.793
2	7.994	8.020	9.770	7.123	8.861	9.479	7.780	9.628	9.875
3	7.996	8.003	9.661	7.149	8.423	8.730	7.792	9.523	9.830
4	7.973	7.983	9.601	7.167	8.434	8.708	7.806	9.498	9.809
5	7.964	7.982	9.600	7.177	8.442	8.714	7.815	9.494	9.721
6	7.958	7.979	9.633	7.184	8.449	8.720	7.821	9.487	9.701
7	7.954	7.976	9.648	7.187	8.452	8.720	7.823	9.490	9.707
8	7.952	7.975	9.683	7.184	8.449	8.719	7.826	9.486	9.722
9	7.950	7.976	9.727	7.192	8.455	8.715	7.829	9.485	9.823
10	7.954	7.978	9.730	7.193	8.455	8.711	7.830	9.474	9.807

2 Eliminating Spurious Charge-Transfer States in TDDFT

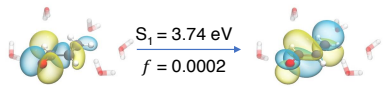
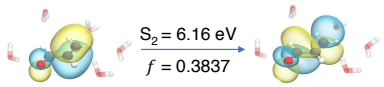
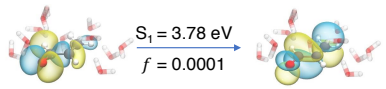
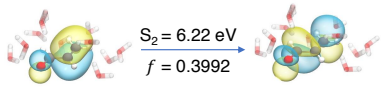
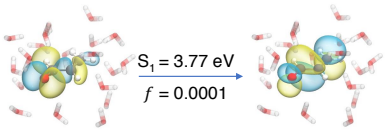
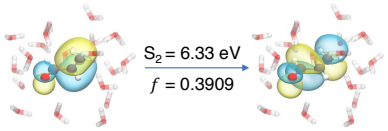
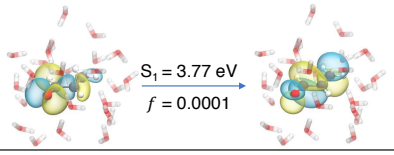
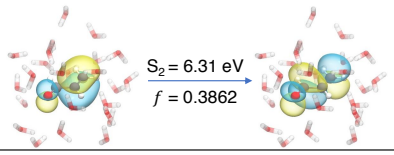
No. water	$n \rightarrow \pi^*$		NTO weight	$\pi \rightarrow \pi^*$		NTO weight
	HONTO	LUNTO		HONTO	LUNTO	
5			1.00			0.96
11			1.00			0.97
19			1.00			0.97
24			1.00			0.97

Figure S3: The HONTOs and LUNTOs for embedded B3LYP/aug-cc-pVDZ calculations for acrolein in different amount of water molecules.

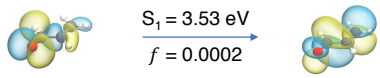
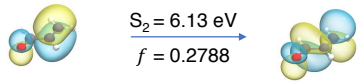
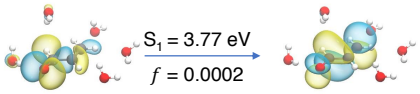
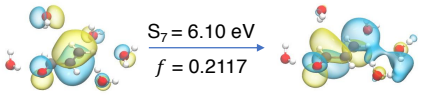
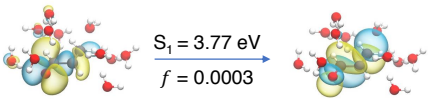
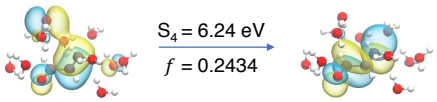
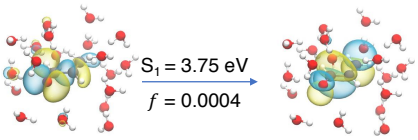
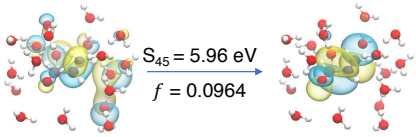
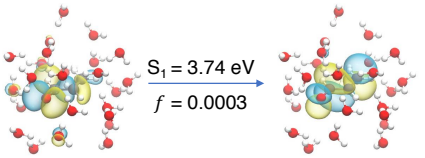
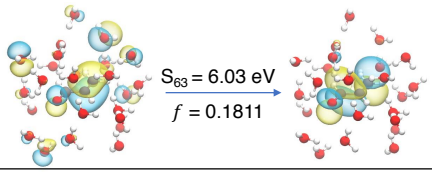
No. water	$n \rightarrow \pi^*$		NTO weight	$\pi \rightarrow \pi^*$		NTO weight
	HONTO	LUNTO		HONTO	LUNTO	
0			1.00			0.74
5			1.00			0.80
11			1.00			0.66
19			1.00			0.71
24			1.00			0.78

Figure S4: The HONTOs and LUNTOs for B3LYP/aug-cc-pVDZ calculations for acrolein in different amount of water molecules.

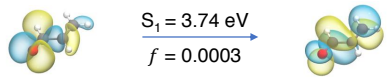
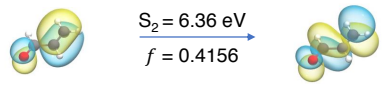
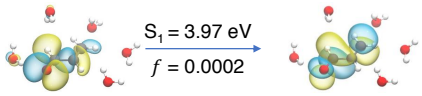
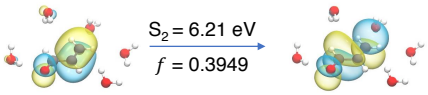
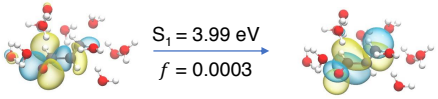
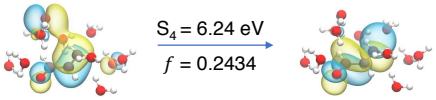
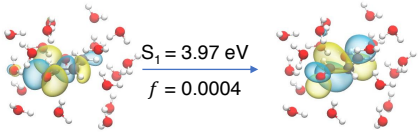
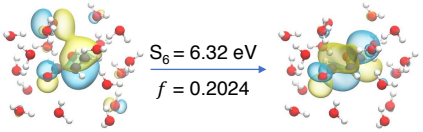
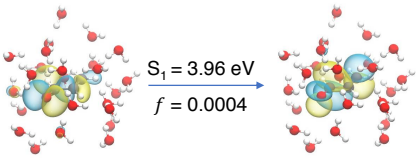
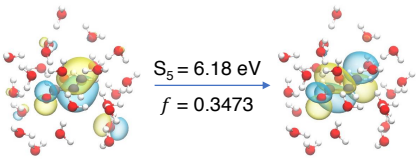
No. water	$n \rightarrow \pi^*$ HONTO	$n \rightarrow \pi^*$ LUNTO	NTO weight	$\pi \rightarrow \pi^*$ HONTO	$\pi \rightarrow \pi^*$ LUNTO	NTO weight
0			1.00			0.94
5			1.00			0.94
11			1.00			0.93
19			1.00			0.66
24			1.00			0.93

Figure S5: The NTO pair with the largest weight for CAM-B3LYP/aug-cc-pVDZ calculations for acrolein in different amount of water molecules.

3 Excitation energies of acrolein + 2 water

Table S3: Excitatin energies in eV of TDHF-in-HF, TDDFT-in-DFT, EOM-CCSD-in-HF, EOM-CCSD-in-DFT compared to canonical TDHF, TDDFT, and EOM-CCSD using the non-relaxed (1) and relaxed (2) scheme, and corresponding correction (3, 4), respectively. All subsystems were described using the monomolecular basis.

Method	Error (kcal/mol)				
	1	2	3	4	full system
TDHF					4.824
TDHF-in-HF	4.774	4.745			
TDDFT					3.776
TDDFT-in-DFT	3.759	3.729			
EOM-CCSD					4.065
EOM-CCSD-in-HF	4.044	4.016	4.093	4.095	
EOM-CCSD-in-DFT	4.050	4.020	4.066	4.067	

4 7HQ

Table S4: Solvent-induced vertical excitation energy shifts $\Delta\omega_{\pi\to\pi^*}$ in cm^{-1} for the lowest $\pi \to \pi^*$ transition in cis-7HQ chromophore. aug-cc-pVDZ basis set is used for all calculations. LDA is used for DFT and TDDFT calculations. Monomer basis is used for all embedding calculations. Complementary to Figure 5.

solvent	ground-state		state-average		supermolecular	
	(a)†	(b)†	(a)†	(b)†	EOM-CCSD	TDLDA
H_2O	-458	-864	-492	-881	-525	-978
NH_3	-647	-1136	-676	-1162	-784	-1380
HCOOH	-577	-1267	-586	-1305	-685	-1620
CH_3OH	-263	-622	-248	-650	-342	-877
$2H_2O$	-1079	-2003	-1089	-2053	-1273	-2564
NH_3-H_2O-H_2O	-1480	-2450	-1464	-2507	-1777	-3061
NH_3-H_2O-NH_3	-1384	-2326	-1381	-2380	-1624	-2823
NH_3-NH_3-H_2O	-1492	-2484	-1505	-2558	-1834	-3083
Mean signed error§	183	-538	175	-582	0	-930

† (a) refers to EOM-CCSD-in-LDA embedding; (b) refers to TDLDA-in-LDA embedding.
§ Mean signed errors are relative to the supermolecular EOM-CCSD results.

5 GFP

Table S5: Excitation energy in eV of the brightest excited state in cluster TDDFT and embedded TDDFT-in-DFT calculations by successively adding the residues in the hydrogen-bond chain from right to left and left to right.

right to left		left to right	
embedded	cluster	embedded	cluster
3.274	3.229	3.274	3.229
3.263	3.225	3.242	3.374
3.260	3.211	3.217	3.114
3.234	3.240	3.193	3.216
3.208	3.069	3.190	3.216
3.175	3.069	3.175	3.069

Table S6: Oscillator strength of the brightest excited state in cluster TDDFT and embedded TDDFT-in-DFT calculations by successively adding the residues in the hydrogen-bond chain from right to left and left to right.

right to left		left to right	
embedded	cluster	embedded	cluster
0.8373	0.5157	0.8373	0.5157
0.8716	0.7177	0.7930	0.6187
0.8712	0.7593	0.8411	0.7665
0.7337	0.5605	0.7082	0.4837
0.6121	0.8350	0.7102	0.4495
0.7409	0.7345	0.7409	0.7345