Supporting Information:

An Embedding Scheme for Constraint-Based Orbital-Optimized Excitations in Molecular and Bulk Environments

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The geometries for the CREST-optimized solvated complexes are available in separate files.

Tables

Table S1: e-COOX with unmodified/non-orthogonal constraint for the S_1 and S_2 excitation energies of isolated uracil and within an explicit hydration shell using a def2-TZVP basis. Brackets denote the corresponding sTDA root of the complete system.

Functional	S_1 ($n \rightarrow \pi^*$)				S_2 ($\pi \rightarrow \pi^*$)			
	Mono.	25 H_2O	50 H_2O	100 H_2O	Mono.	25 H_2O	50 H_2O	100 H_2O
PBE	4.87 [1]	5.48 [8]	5.68 [23]	5.33 [31]	4.45 [3]	5.12 [17]	5.09 [29]	5.31 [56]
B3LYP	5.46 [1]	6.13 [4]	6.22 [7]	5.94 [7]	4.89 [2]	5.76 [3]	5.39 [2]	5.98 [8]
PBE0	5.58 [1]	6.26 [4]	6.35 [4]	6.07 [5]	5.12 [2]	5.80 [1]	5.35 [1]	6.04 [4]
PBEh-3c	6.00 [1]	6.77 [2]	6.87 [2]	6.55 [2]	5.43 [2]	5.84 [1]	5.43 [1]	6.14 [1]

Table S2: Regular COOX (full system) for the S_1 and S_2 excitation energies of isolated uracil and within an explicit hydration shell using a def2-TZVP basis. Brackets denote the corresponding sTDA root of the complete system.

Functional	S_1 ($n \rightarrow \pi^*$)				S_2 ($\pi \rightarrow \pi^*$)			
	Mono.	25 H_2O	50 H_2O	100 H_2O	Mono.	25 H_2O	50 H_2O	100 H_2O
PBE	4.88 [1]	5.10 [8]	5.40 [23]	5.15 [31]	5.17 [3]	5.18 [17]	5.48 [29]	5.29 [56]
B3LYP	5.50 [1]	6.12 [4]	6.35 [7]	5.78 [7]	5.95 [2]	5.86 [3]	5.70 [2]	5.80 [8]
PBE0	5.62 [1]	6.27 [4]	6.50 [4]	6.17 [5]	6.19 [2]	6.02 [1]	5.85 [1]	5.86 [4]
PBEH-3c	6.05 [1]	6.83 [2]	7.19 [2]	6.88 [2]	6.50 [2]	6.28 [1]	6.35 [1]	6.63 [1]

Table S3: sTDA-TDDFT for the S_1 and S_2 excitation energies of isolated uracil and within an explicit hydration shell using a def2-TZVP basis. Brackets denote the corresponding sTDA root of the complete system.

Functional	S_1 ($n \rightarrow \pi^*$)				S_2 ($\pi \rightarrow \pi^*$)			
	Mono.	25 H_2O	50 H_2O	100 H_2O	Mono.	25 H_2O	50 H_2O	100 H_2O
PBE	3.83 [1]	4.43 [8]	4.77 [23]	4.40 [31]	4.77 [3]	4.84 [17]	4.92 [29]	4.68 [56]
B3LYP	4.61 [1]	5.29 [4]	5.57 [7]	5.31 [7]	5.26 [2]	5.18 [3]	5.23 [2]	5.32 [8]
PBE0	4.67 [1]	5.37 [4]	5.66 [4]	5.37 [5]	5.29 [2]	5.18 [1]	5.26 [1]	5.46 [4]
PBEh-3c	4.99 [1]	5.82 [2]	6.17 [2]	5.87 [2]	5.70 [2]	5.58 [1]	5.64 [1]	5.83 [1]

Table S4: e-COOX Q_x/Q_y and B_x/B_y excitation energies [eV] of chlorophyll within an explicit hydration shell using a def2-SVP basis. The label 'n.o.' refers to e-COOX using the unmodified sub-system constraint (non-orthogonal).

Functional	Q_x				Q_y			
	sTDA	COOX	e-COOX [n.o.]	e-COOX	sTDA	COOX	e-COOX [n.o.]	e-COOX
PBE	2.01	1.55	1.47	1.47	2.14	1.61	1.34	1.38
B3LYP	2.16	1.94	1.93	1.94	2.22	1.80	1.71	1.82
PBE0	2.13	2.03	1.98	2.01	2.17	1.91	1.73	1.94
PBEh-3c	2.08	2.01	1.84	2.07	2.01	1.90	1.68	1.90
	B_x				B_y			
	sTDA	COOX	e-COOX [n.o.]	e-COOX	sTDA	COOX	e-COOX [n.o.]	e-COOX
PBE	2.63	1.72	2.04	2.05	2.78	2.00	2.09	2.11
B3LYP	2.98	2.55	2.10	2.06	3.19	2.20	2.06	2.12
PBE0	3.02	2.84*	2.21	2.07	3.25	2.49	2.19	2.26
PBEh-3c	3.44	2.47	1.93	2.15	3.18	2.75	2.39	2.64

*Not converged

Table S5: e-COOX Q_x/Q_y and B_x/B_y excitation energies [eV] of chlorophyll within an explicit solvation shell of acetone using a def2-SVP basis. Brackets denote the corresponding sTDA root of the complete system.

Functional	Q_x				Q_y			
	Mono.	25 Sol.	50 Sol.	100 Sol.	Mono.	25 Sol.	50 Sol.	100 Sol.
PBE	1.74 [3]	1.44 [1]	1.38 [3]	1.48 [3]	1.48 [2]	1.39 [3]	1.38 [6]	1.38 [7]
B3LYP	2.05 [2]	1.92 [1]	1.91 [1]	1.94 [1]	1.83 [1]	1.83 [2]	1.82 [2]	1.82 [2]
PBE0	2.15 [2]	2.01 [1]	1.94 [1]	2.01 [1]	1.96 [1]	1.96 [2]	1.98 [2]	1.94 [2]
PBEh-3c	2.08 [2]	2.05 [2]	2.05 [2]	2.07 [2]	1.92 [1]	1.93 [1]	1.89 [1]	1.90 [1]
	B_x				B_y			
	Mono.	25 Sol.	50 Sol.	100 Sol.	Mono.	25 Sol.	50 Sol.	100 Sol.
PBE	1.68 [9]	2.06 [20]	2.02 [70]	2.05 [73]	2.09 [11]	2.06 [39]	2.13 [93]	2.11 [101]
B3LYP	2.50 [6]	2.12 [7]	2.04 [5]	2.06 [5]	2.39 [7]	2.05 [5]	2.04 [12]	2.12 [9]
PBE0	2.43 [6]	2.13 [7]	2.08 [5]	2.07 [5]	2.72 [7]	2.19 [5]	2.23 [6]	2.26 [7]
PBEh-3c	3.51 [6]	2.34 [6]	2.32 [5]	2.15 [6]	2.75 [7]	2.63 [4]	2.07 [6]	2.64 [4]

Table S6: Excitation energies [eV] of the neutral and anionic forms of GFP obtained with e-COOX for a large QM-region using an embedded constraint constructed from the isolated chromophore in the gas phase.

GFP	Exp.	PBE/TZVP	PBE0/TZVP	B3LYP/TZVP	PBEh-3c
Neutral	3.12	2.37	3.39	3.53	3.48
Anionic	2.59	2.85	3.39	3.16	3.20
Δ	0.53	-0.49	0.00	0.37	0.28

Figures

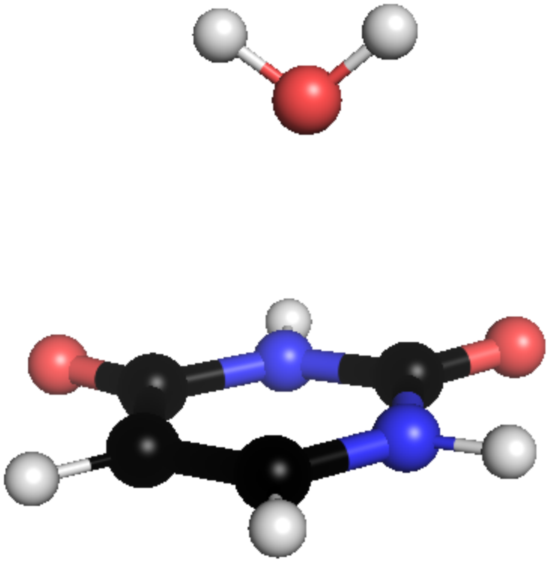

Figure S1: Uracil-water complex at a distance of 3 Å between the oxygen molecule of water and the uracil plane.

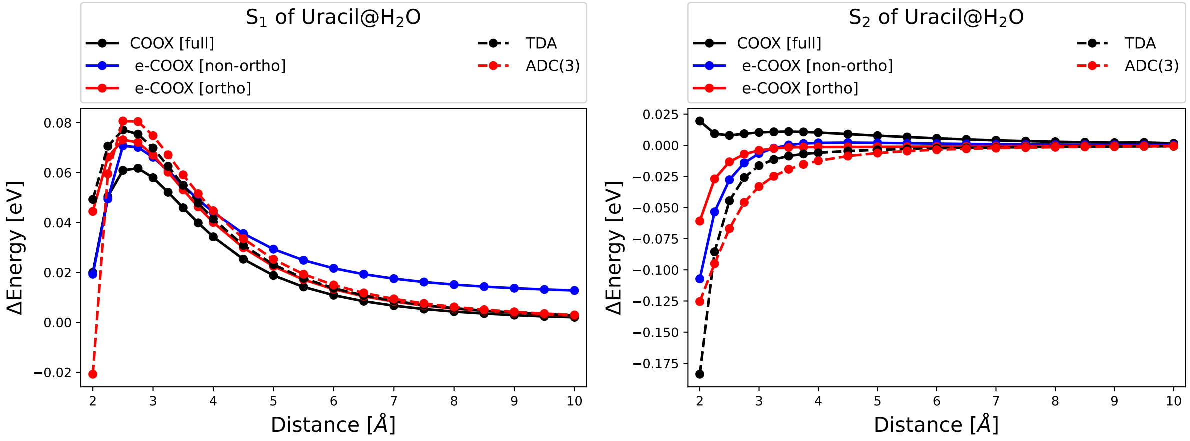

Figure S2: Energy differences [eV] of S_1 ($n \to \pi^*$, left) and S_2 ($\pi \to \pi^*$, right) states of uracil for different distances to a single water molecule. The difference is relative to the excitation energy of the isolated uracil molecule. The results for TDA-TDDFT and ADC(3) are shown compared to **scaled** COOX results obtained from the complete system (full) and the embedded sub-system constraint without (non-ortho) and with reorthogonalization (ortho) using PBE0/def2-TZVP.

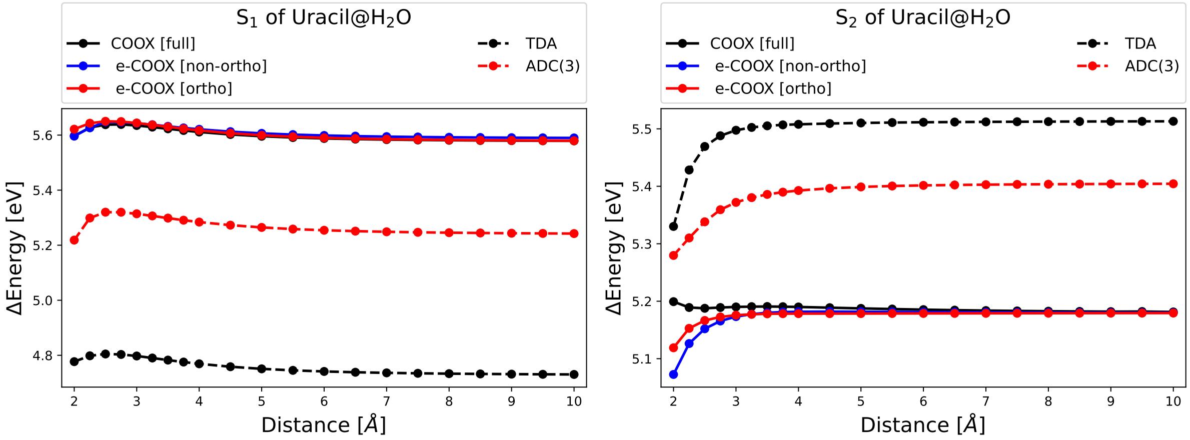

Figure S3: Excitation energies [eV] of S_1 ($n \to \pi^*$, left) and S_2 ($\pi \to \pi^*$, right) states of uracil for different distances to a single water molecule. The results for TDA-TDDFT and ADC(3) are shown compared to **scaled** COOX results obtained from the complete system (full) and the embedded sub-system constraint without (non-ortho) and with reorthogonalization (ortho) using PBE0/def2-TZVP.

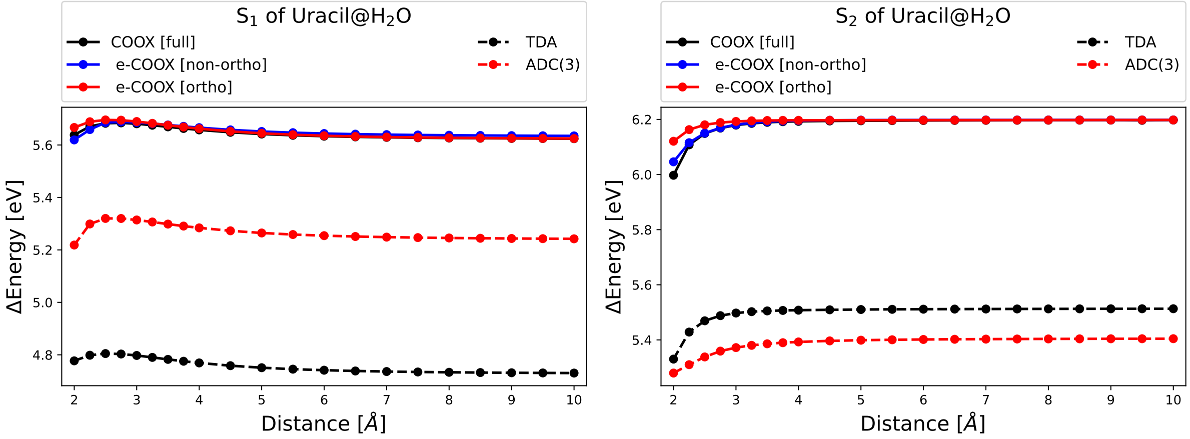

Figure S4: Excitation energies differences [eV] of S$_1$ ($n \rightarrow \pi^*$, left) and S$_2$ ($\pi \rightarrow \pi^*$, right) states of uracil for different distances to a single water molecule. The results for TDA-TDDFT and ADC(3) are shown compared to **unscaled** COOX results obtained from the complete system (full) and the embedded sub-system constraint without (non-ortho) and with reorthogonalization (ortho) using PBE0/def2-TZVP.

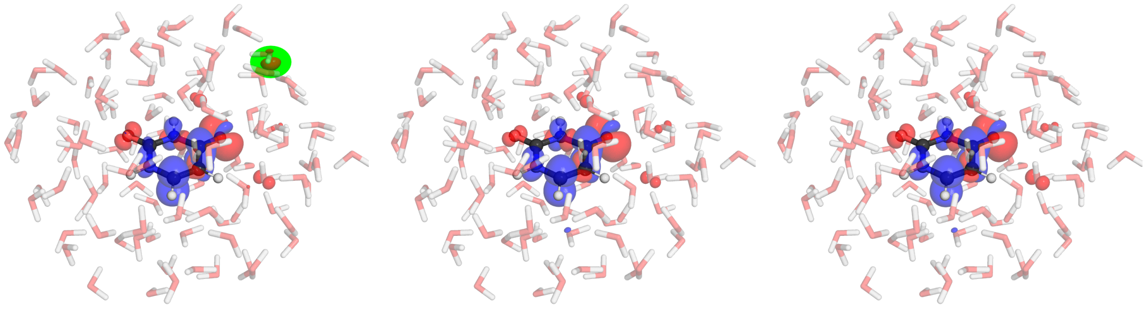

Figure S5: COOX constraint for $n \rightarrow \pi^*$ in Uracil-water complex obtained from the complete system for B3LYP/TZVP (left), PBEh-3c (middle), and BHLYP/TZVP (right). The long-range charge-transfer impact on the constraint potential is highlighted (green).

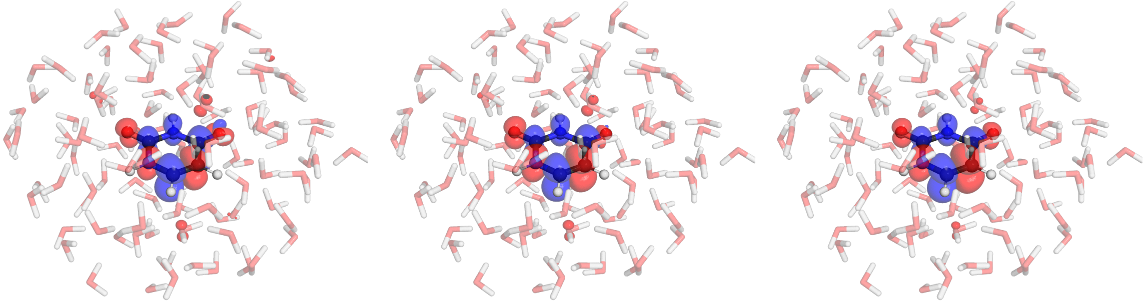

Figure S6: COOX constraint for $\pi \rightarrow \pi^*$ in Uracil-water complex obtained from the complete system for B3LYP/TZVP (left), PBEh-3c (middle), and BHLYP/TZVP (right).

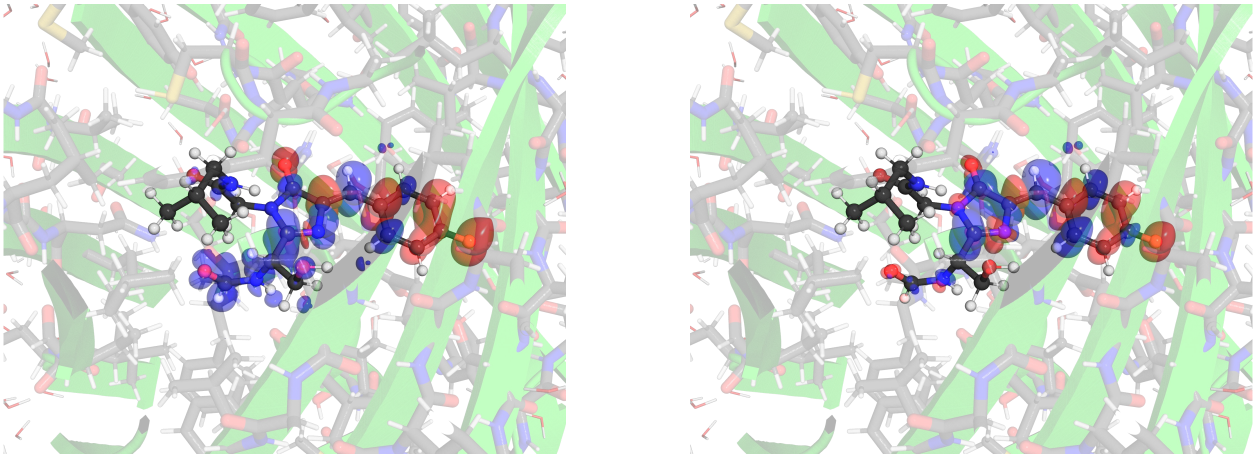

Figure S7: Embedded constraint potential for the chromophore sub-system of the anionic B form of GFP computed with B3LYP/TZVP. Left: Embedding after sub-system TDA calculation in vacuum. Right: Embedding after sub-system TDA calculation with QM/MM treatment of the environment.