

Electronic supplementary information for “Open-ended response theory with polarizable embedding: multiphoton absorption in biomolecular systems”

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This electronic supplementary information (ESI) contains numerical data (excitation energies and multiphoton absorption (MPA) strengths) for the results presented in the figures and text in the main article. All calculations have been done with CAM-B3LYP/6-31+G* using an embedding potential derived from B3LYP/6-31+G* calculations. Unless otherwise specified, calculations are done using the polarizable embedding scheme including the external effective field (EEF) effect, on the medium quantum region (Fig. 1b in the main text), with redistribution of charges (and removal of other parameters) from classical sites that are within 1.4 Å from any quantum-region atom (charges are distributed to all other classical sites).

snapshot	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
small	1	3.47	1.95 (0.50)	626	8.63	19.6
	2	3.46	1.88 (0.48)	698	9.16	34.3
	3	3.44	2.09 (0.53)	1125	10.45	35.8
	4	3.52	2.06 (0.53)	716	10.23	31.1
	5	3.52	1.87 (0.48)	251	9.04	15.1
MAPD			2.9%	76.5%	3.7%	72.0%
medium	1	3.48	1.85 (0.47)	387	7.95	9.8
	2	3.47	1.83 (0.47)	552	8.40	23.3
	3	3.46	2.03 (0.52)	941	10.05	33.6
	4	3.53	1.97 (0.51)	450	9.22	17.4
	5	3.52	1.80 (0.47)	135	8.13	5.7
MAPD			1.6%	16.4%	4.7%	9.6%
large	1	3.49	1.89 (0.48)	355	8.34	9.4
	2	3.47	1.80 (0.46)	441	8.54	21.5
	3	3.47	2.06 (0.52)	899	10.48	33.7
	4	3.54	2.00 (0.52)	410	9.67	16.2
	5	3.52	1.83 (0.47)	101	8.88	7.8

Table S1 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five snapshots with neutral chromophore in protein. The mean absolute percentage deviations (MAPD) are calculated with the large quantum region as reference.

snapshot	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
small	1	2.97	3.06 (0.67)	1418	0.48	56.4
	2	2.95	3.18 (0.69)	839	0.75	66.3
	3	2.96	3.24 (0.70)	960	0.42	66.4
	4	3.03	3.23 (0.72)	1317	0.49	52.5
	5	2.95	3.25 (0.70)	1284	1.40	164.1
MAPD			0.4%	14.6%	98.4%	29.9%
medium	1	3.02	3.01 (0.67)	1533	1.20	49.8
	2	2.98	3.15 (0.69)	995	0.22	77.3
	3	2.98	3.19 (0.70)	1098	0.26	72.3
	4	3.05	3.19 (0.72)	1378	0.78	55.3
	5	3.00	3.22 (0.71)	1412	0.36	84.2
MAPD			1.2%	5.4%	26.6%	4.0%
large	1	3.03	3.03 (0.67)	1580	1.64	46.3
	2	2.99	3.19 (0.70)	1064	0.23	81.5
	3	2.98	3.24 (0.71)	1181	0.39	75.7
	4	3.06	3.23 (0.73)	1444	1.13	54.3
	5	3.01	3.26 (0.72)	1497	0.59	84.8

Table S2 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five snapshots with anionic chromophore in protein. The mean absolute percentage deviations (MAPD) are calculated with the large quantum region as reference.

redist	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
small	1*	3.47	1.87 (0.48)	497	8.32	14.3
	1	3.47	1.96 (0.50)	726	8.97	25.1
	2	3.47	1.96 (0.50)	709	8.92	24.1
	3	3.47	1.96 (0.50)	714	8.91	24.0
	all	3.47	1.95 (0.50)	626	8.63	19.6
PD	1*		-2.4%	-18.8%	-8.1%	-17.8%
	1		1.2%	40.2%	2.4%	65.9%
	2		1.4%	50.9%	2.9%	77.7%
	3		1.5%	56.7%	2.6%	80.6%
	all		3.1%	76.2%	3.5%	108.6%
medium	1*	3.48	1.86 (0.47)	635	6.99	78.1
	1	3.47	1.94 (0.50)	604	8.49	17.2
	2	3.47	1.95 (0.50)	646	8.62	19.4
	3	3.47	1.95 (0.50)	628	8.57	18.6
	all	3.48	1.85 (0.47)	387	7.95	9.8
PD	1*		-3.4%	3.7%	-22.9%	349.4%
	1		0.0%	16.7%	-3.0%	13.7%
	2		0.9%	37.4%	-0.6%	42.8%
	3		0.6%	37.7%	-1.3%	39.7%
	all		-2.1%	8.9%	-4.7%	5.0%
large	1*	3.45	1.92 (0.49)	612	9.06	17.4
	1	3.47	1.94 (0.50)	518	8.76	15.1
	2	3.48	1.93 (0.50)	470	8.67	13.6
	3	3.49	1.93 (0.50)	456	8.68	13.3
	all	3.49	1.89 (0.48)	355	8.34	9.4

Table S3 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five different redistribution schemes using one snapshot with neutral chromophore in protein. The charges on classical sites closer than 1.4 Å from any quantum-region atom have been redistributed to one, two or three of the closest neighboring classical sites, or redistributed to all the other classical sites. The higher-order multipoles and polarizabilities have been redistributed to the closest classical site only in the calculations indicated with 1* and removed in all other cases. The percentage deviations (PD) are relative to the MPA strength calculated for the large quantum region.

redist	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
small	1*	3.00	2.99 (0.66)	1450	0.73	54.1
	1	3.00	3.03 (0.67)	1447	0.64	52.2
	2	3.00	3.03 (0.67)	1451	0.60	57.7
	3	2.99	3.04 (0.67)	1463	0.62	58.1
	all	2.97	3.06 (0.67)	1418	0.48	56.4
PD	1*		-2.4%	-6.9%	-25.1%	-19.5%
	1		-0.4%	-5.6%	-33.8%	-8.2%
	2		-0.7%	-8.1%	-50.2%	9.3%
	3		-0.2%	-8.5%	-56.9%	18.1%
	all		1.2%	-10.3%	-70.5%	21.8%
medium	1*	3.00	2.99 (0.66)	1497	0.62	54.5
	1	2.99	3.06 (0.67)	1461	0.53	60.2
	2	3.00	3.05 (0.67)	1463	0.57	59.7
	3	3.00	3.05 (0.67)	1461	0.56	59.9
	all	3.02	3.01 (0.67)	1533	1.20	49.8
PD	1*		-2.5%	-3.9%	-35.7%	-18.8%
	1		0.4%	-4.6%	-45.7%	5.7%
	2		-0.2%	-7.3%	-52.5%	13.1%
	3		0.4%	-8.6%	-61.2%	21.8%
	all		-0.5%	-3.0%	-26.8%	7.7%
large	1*	2.98	3.07 (0.67)	1558	0.97	67.2
	1	3.01	3.05 (0.67)	1532	0.97	56.9
	2	3.02	3.05 (0.68)	1579	1.21	52.8
	3	3.02	3.04 (0.68)	1599	1.43	49.2
	all	3.03	3.03 (0.67)	1580	1.64	46.3

Table S4 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five different redistribution schemes using one snapshot with anionic chromophore in protein. The charges on classical sites closer than 1.4 Å from any quantum-region atom have been redistributed to one, two or three of the neighboring classical sites, or redistributed to all the other classical sites. The higher-order multipoles and polarizabilities have been redistributed to the closest classical site only in the calculations indicated with 1* and removed in all other cases. The percentage deviations (PD) are relative to the MPA strength calculated for the large quantum region.

snapshot	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
DFT	1	3.60	2.80 (0.74)	687	21.84	19.0
	2	3.61	2.72 (0.72)	697	22.96	28.4
	3	3.62	2.99 (0.80)	789	24.19	22.2
	4	3.63	2.82 (0.75)	767	23.83	29.9
	5	3.63	2.84 (0.76)	971	23.91	61.4
PE-DFT	1	3.48	1.85 (0.47)	387	7.95	9.8
	2	3.47	1.83 (0.47)	552	8.40	23.3
	3	3.46	2.03 (0.52)	941	10.05	33.6
	4	3.53	1.97 (0.51)	450	9.22	17.4
	5	3.52	1.80 (0.47)	135	8.13	5.7

Table S5 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five snapshots of the neutral (medium) quantum region without (DFT) and with (PE-DFT) the protein environment.

snapshot	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)	
DFT	1	3.02	4.73 (1.05)	1098	4.49	171.9
	2	3.00	4.77 (1.05)	966	6.02	471.9
	3	3.03	4.85 (1.08)	1315	6.84	578.1
	4	3.04	4.87 (1.09)	1369	6.30	437.7
	5	3.02	4.74 (1.05)	900	5.72	348.3
PE-DFT	1	3.02	3.01 (0.67)	1533	1.20	49.8
	2	2.98	3.15 (0.69)	995	0.22	77.3
	3	2.98	3.19 (0.70)	1098	0.26	72.3
	4	3.05	3.19 (0.72)	1378	0.78	55.3
	5	3.00	3.22 (0.71)	1412	0.36	84.2

Table S6 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) for five snapshots of the anionic (medium) quantum region without (DFT) and with (PE-DFT) the protein environment.

state	environment	E (eV)	1PA	2PA	3PA (1E+6)	4PA (1E+9)
neutral	vacuum	3.60	2.80 (0.74)	687	21.84	19.0
	EE	3.57	2.63 (0.69)	495	19.07	10.5
	PE(GS)	3.60	2.80 (0.74)	580	19.25	7.7
	PE(-EEF)	3.48	3.39 (0.87)	1235	45.83	89.3
	PE(+EEF)		1.85 (0.47)	387	7.95	9.8
PC	EE		-6.2	-27.9	-12.7	-44.6
	PE(GS)		-0.2	-15.6	-11.8	-59.3
	PE(-EEF)		20.8	79.8	109.9	369.6
	PE(+EEF)		-34.1	-43.6	-63.6	-48.3
anionic	vacuum	3.02	4.73 (1.05)	1098	4.49	171.9
	EE	3.14	4.52 (1.04)	1602	0.54	119.1
	PE(GS)	3.20	4.38 (1.03)	1892	1.14	119.3
	PE(-EEF)	3.02	5.35 (1.19)	4677	5.52	515.1
	PE(+EEF)		3.01 (0.67)	1533	1.20	49.8
PC	EE		-4.4	45.9	-88.1	-30.7
	PE(GS)		-7.3	72.4	-74.6	-30.6
	PE(-EEF)		13.2	326.0	22.9	199.7
	PE(+EEF)		-36.4	39.6	-73.3	-71.0

Table S7 Excitation energies (in eV), one-, two-, three and four-photon absorption strengths (in atomic units), and one-photon oscillator strength (in parentheses, dimensionless) without the protein environment (vacuum), with protein but no polarization (i.e. electrostatic embedding (EE)), with protein but only ground-state polarization [PE(GS)], with protein and full polarization but without effective external field effects [PE(-EEF)], and with protein, full polarization, and effective external field effects [PE(+EEF)] for one snapshot. For each state (neutral and anionic), the calculations were performed with the same (medium) quantum region. The percentage changes (PC) are relative to the MPA strength calculated for the (medium) quantum region in vacuum.