

SUPPLEMENTARY INFORMATION: Optical absorption and electronic spectra of chlorophylls *a* and *b*

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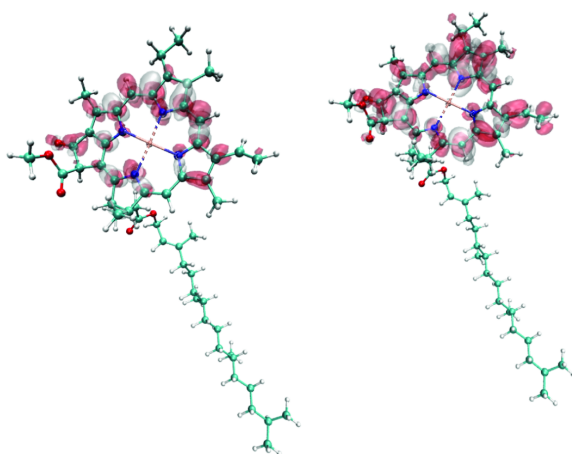


FIG. 1. Addition (red) and depletion (gray) regions of electron charge density in the S_1 (left side) and S_7 excitations (right side) for Chl *a*. A negligible charge transfer character of these excitations is evident from the significant overlap between the above regions. A similar configurations has been obtained for Chl *b*.

Appendix A: Optimized coordinates

Chl *a* optimized coordinate:

C	-24.774304	-13.776933	33.517884
C	-23.350821	-14.179719	33.123816
C	-22.563059	-14.034707	34.288944
C	-23.274793	-13.510300	35.405730
C	-24.663590	-13.266494	35.013283
N	-21.266679	-14.244408	34.564310
C	-21.094752	-13.849660	35.889830
C	-22.355124	-13.379591	36.446352
C	-22.872669	-14.662602	31.910234
N	-21.562861	-15.062152	31.753962
C	-21.401626	-15.594636	30.506391
C	-22.745678	-15.734179	29.801240

C	-23.640099	-14.764456	30.603227
Mg	-19.975279	-14.938580	33.186044
N	-18.504692	-14.767734	34.628563
C	-17.185338	-15.088925	34.455699
C	-16.436076	-14.875701	35.687497
C	-17.344741	-14.386940	36.614575
C	-18.634416	-14.335914	35.932210
C	-23.778458	-13.378763	29.941256
C	-22.461707	-12.619445	29.779903
C	-22.630722	-11.442420	28.845349
O	-21.484090	-10.727475	28.745633
C	-21.560779	-9.650963	27.765696
C	-21.601886	-10.199674	26.374552
C	-20.571930	-10.290733	25.504274
C	-20.786940	-10.948214	24.161024
C	-20.454322	-10.067337	22.945756
C	-20.851225	-10.754474	21.635939
C	-20.360858	-10.083368	20.341049
C	-20.812758	-10.922310	19.131626
C	-20.143044	-10.582971	17.796713
C	-20.633543	-11.490947	16.663950
C	-19.844066	-11.399558	15.346737
C	-20.381770	-12.436509	14.343658
C	-19.510736	-12.663124	13.104396
C	-20.077485	-13.744883	12.179845
C	-19.257180	-14.017947	10.907157
C	-17.855974	-14.549606	11.226245
C	-23.240803	-17.184926	29.891555
C	-20.195844	-16.015392	29.945765
C	-18.910764	-16.010450	30.536027
N	-18.648515	-15.632142	31.825559
C	-17.295057	-15.798015	32.033315
C	-16.671029	-16.304902	30.815793
C	-17.689678	-16.427523	29.874581
C	-17.578580	-16.821888	28.438377
C	-16.634247	-15.558932	33.244330
C	-17.191421	-13.951604	38.049131
C	-15.774796	-13.739682	38.582861
C	-19.841145	-13.906360	36.519343
C	-22.617156	-12.855038	37.819437
O	-25.577571	-12.761692	35.645700
C	-25.667889	-15.003008	33.397153

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O	-25.822895	-15.599156	34.605160
C	-26.591011	-16.806561	34.609911
O	-23.651834	-11.181904	28.230255
O	-26.129703	-15.433585	32.353641
C	-19.180786	-9.785682	25.781780
C	-20.831092	-8.629571	20.231303
C	-19.864264	-9.982658	14.764814
C	-20.003133	-14.993247	9.990564
H	-20.253392	-16.406569	28.920118
H	-15.556284	-15.773979	33.249804
H	-19.800543	-13.579278	37.568145
H	-24.657327	-15.172176	30.782672
H	-22.672503	-15.440666	28.733198
H	-22.530852	-17.886439	29.413322
H	-23.357320	-17.491286	30.950258
H	-24.223571	-17.297440	29.395072
H	-24.483553	-12.749700	30.522984
H	-24.249885	-13.480684	28.940844
H	-21.654210	-13.253459	29.353005
H	-22.064973	-12.258659	30.751382
H	-18.234226	-16.198352	27.798730
H	-16.537998	-16.699172	28.080021
H	-17.866644	-17.880685	28.269915
H	-17.720800	-14.679386	38.703627
H	-17.748093	-12.996984	38.168644
H	-15.812903	-13.257995	39.578427
H	-15.223931	-14.690155	38.709773
H	-15.183065	-13.082365	37.917514
H	-21.982060	-11.975772	38.049858
H	-23.677205	-12.547953	37.896586
H	-22.419351	-13.618948	38.598819
H	-25.212387	-12.984022	32.877253
H	-20.672764	-9.027773	27.972794
H	-22.482925	-9.067599	27.973038
H	-18.968113	-8.856793	25.212771
H	-19.008570	-9.567551	26.850778
H	-18.421739	-10.531125	25.468122
H	-21.841617	-11.286272	24.090514
H	-20.164192	-11.871375	24.110473
H	-19.367721	-9.834992	22.930690
H	-20.981012	-9.096093	23.053128
H	-21.959422	-10.849638	21.598015
H	-20.465045	-11.797068	21.654083
H	-19.245942	-10.084473	20.360567
H	-20.491781	-8.157831	19.289356
H	-21.938217	-8.567327	20.254284
H	-20.444780	-8.003228	21.057621
H	-21.917331	-10.835282	19.025480
H	-20.620274	-11.995029	19.352333
H	-19.040817	-10.687195	17.905126
H	-20.326574	-9.519786	17.537115
H	-21.707448	-11.280500	16.461537
H	-20.599914	-12.544480	17.017918
H	-18.784476	-11.664343	15.571767
H	-19.298762	-9.917433	13.815991
H	-20.902925	-9.654291	14.556519
H	-19.413324	-9.244352	15.454423
H	-21.407517	-12.140109	14.029258

H	-20.501577	-13.409594	14.868060
H	-18.486940	-12.941739	13.433676
H	-19.400770	-11.718179	12.530383
H	-21.109455	-13.455552	11.884796
H	-20.186320	-14.696239	12.747819
H	-19.143553	-13.053681	10.361129
H	-19.447553	-15.176891	9.050583
H	-20.147072	-15.974556	10.486491
H	-21.005399	-14.611315	9.715229
H	-17.285833	-14.762206	10.301288
H	-17.257157	-13.832255	11.818496
H	-17.912521	-15.494652	11.803915
C	-14.968403	-15.161139	35.803837
H	-14.694960	-16.070149	35.232590
H	-14.354628	-14.328245	35.401409
H	-14.651902	-15.336258	36.844592
C	-15.248491	-16.566927	30.650015
H	-14.559908	-15.909470	31.208374
H	-22.582743	-10.616105	26.093960
C	-14.708746	-17.533755	29.876109
H	-13.620337	-17.645858	29.788210
H	-15.327298	-18.267657	29.341402
H	-25.995874	-17.578284	35.130622
H	-27.529586	-16.619758	35.164417
H	-26.814498	-17.111442	33.568382

Chl *b* optimized coordinate:

C	0.037500	-16.656740	4.880760
C	0.710370	-16.163500	6.054890
N	1.972900	-15.778450	5.746540
C	2.155030	-16.007890	4.409020
C	0.945260	-16.570450	3.847270
C	0.148700	-16.108870	7.338270
C	0.721330	-15.615420	8.496150
N	1.947480	-15.053940	8.602120
C	2.121370	-14.584530	9.873760
C	0.840610	-14.664560	10.661090
C	0.058250	-15.700940	9.850720
C	3.326580	-14.074420	10.303240
C	3.740120	-13.598710	11.685100
C	5.213520	-13.081540	11.519260
C	5.577600	-13.396320	10.149580
C	4.463240	-13.958780	9.489580
C	6.594550	-13.304640	9.221070
C	6.030400	-13.836870	8.002770
N	4.718760	-14.225140	8.214370
C	3.653880	-14.761900	12.644330
O	2.627380	-15.206260	13.096140
O	5.854550	-12.522960	12.374060
Mg	3.333800	-15.000000	7.000000
N	4.739660	-14.889000	5.504230
C	4.524500	-15.254190	4.219740
C	5.720180	-15.040920	3.446200
C	6.673450	-14.536560	4.316210
C	6.035400	-14.442220	5.595280
C	6.639430	-13.956600	6.761320
C	7.951220	-12.763070	9.448470
C	0.222660	-17.105530	10.415480

C	0.160150	-13.298550	10.733380
C	-0.092120	-12.629600	9.397270
C	-1.071400	-11.503700	9.551980
O	-1.668980	-11.253400	10.571160
C	3.324780	-15.772350	3.709220
C	8.055890	-14.094090	3.997770
C	8.109320	-12.612230	3.652540
C	0.768920	-16.910290	2.456990
C	0.003310	-17.900360	1.984080
C	-1.376300	-17.087230	4.820850
O	-1.233110	-10.828000	8.410270
C	-2.232030	-9.794080	8.487510
C	-3.596050	-10.358570	8.644500
C	-4.479950	-10.590980	7.665110
C	-4.229010	-10.273480	6.227590
C	-5.802020	-11.217560	7.985600
C	-7.016080	-10.390380	7.580060
C	-8.316810	-11.040370	8.018340
C	-9.592890	-10.409900	7.467760
C	-9.718590	-8.946890	7.856830
C	-10.804800	-11.224580	7.913770
C	-12.114690	-10.882910	7.225890
C	-13.259580	-11.768130	7.687300
C	-14.571900	-11.604920	6.924880
C	-15.122530	-10.193390	7.035990
C	-15.579860	-12.649270	7.399120
C	-16.878780	-12.709890	6.614760
C	-17.778730	-13.849910	7.058670
C	-19.152900	-13.892600	6.396640
C	-20.000000	-15.000000	7.000000
C	-19.063540	-14.050610	4.888290
O	4.865680	-15.281120	12.876910
C	4.916290	-16.422950	13.710790
H	-0.862140	-16.511670	7.438720
H	3.366210	-16.008210	2.639600
H	7.683550	-13.641330	6.687820
H	1.046890	-15.003370	11.691280
H	-1.015710	-15.455810	9.790690
H	-0.219510	-17.862330	9.750710
H	1.289930	-17.349070	10.539130
H	-0.256920	-17.193150	11.401400
H	0.760200	-12.619210	11.362050
H	-0.806990	-13.379460	11.259640
H	-0.521030	-13.323740	8.651200
H	0.832370	-12.248010	8.931370
H	-2.011850	-16.478530	5.482600
H	-1.766730	-16.990800	3.796210
H	-1.508150	-18.139730	5.125010
H	8.454730	-14.684110	3.156640
H	8.723370	-14.304340	4.850570
H	9.135960	-12.287120	3.429530
H	7.484080	-12.395650	2.773540
H	7.729070	-11.998340	4.483080
H	8.179460	-11.925360	8.769440
H	8.026350	-12.398050	10.483870
H	8.730390	-13.528100	9.295550
H	3.101930	-12.793370	12.086590
H	-2.101480	-9.213400	7.565060

H	-1.992920	-9.155890	9.356260
H	-4.756570	-9.355590	5.917830
H	-3.163230	-10.134950	6.003240
H	-4.597220	-11.082190	5.575690
H	-5.848990	-11.428990	9.067000
H	-5.860550	-12.201690	7.480240
H	-7.027660	-10.250430	6.484250
H	-6.919260	-9.381410	8.016330
H	-8.364930	-11.050870	9.123450
H	-8.296710	-12.103680	7.717110
H	-9.539780	-10.464880	6.361870
H	-10.635840	-8.492320	7.455150
H	-9.745030	-8.829090	8.952620
H	-8.879060	-8.344600	7.480390
H	-10.925670	-11.120430	9.008580
H	-10.591450	-12.295760	7.744830
H	-11.989180	-10.983870	6.131810
H	-12.366190	-9.823910	7.403330
H	-13.444140	-11.595580	8.764420
H	-12.941020	-12.823760	7.612110
H	-14.362900	-11.804200	5.854560
H	-16.049410	-10.065820	6.458370
H	-15.348130	-9.936990	8.084310
H	-14.413170	-9.442850	6.658350
H	-15.804530	-12.473590	8.468180
H	-15.099290	-13.643770	7.361910
H	-16.645140	-12.808880	5.539840
H	-17.429390	-11.758130	6.716940
H	-17.916720	-13.787510	8.153350
H	-17.265040	-14.814240	6.883010
H	-19.655680	-12.928680	6.607230
H	-21.013850	-15.016020	6.572530
H	-19.551060	-15.989160	6.813640
H	-20.103390	-14.887070	8.089900
H	-20.063480	-14.103220	4.431920
H	-18.535430	-13.213590	4.409320
H	-18.531620	-14.977270	4.617110
H	1.324970	-16.299030	1.736190
H	-3.837080	-10.656980	9.670370
H	-0.087870	-18.077410	0.911140
H	-0.521290	-18.596060	2.642540
H	5.424190	-17.226650	13.160070
H	5.495060	-16.171820	14.610690
H	3.892850	-16.725800	13.986240
C	5.875330	-15.306280	2.034070
O	5.000290	-15.728470	1.303850
H	6.900090	-15.093470	1.623210

Appendix B: Quadrupole moments

The primitive quadrupole moment tensors of Chl *a* and Chl *b* (in units of ea_0^2) are obtained in the PBE/DPZ level by

SIESTA as follows:

and

$$Q_a = \begin{pmatrix} 141.260 & -30.412 & 79.917 \\ -30.412 & 5.511 & -15.318 \\ 79.917 & -15.318 & 44.732 \end{pmatrix}, \quad (\text{B1})$$

$$Q_b = \begin{pmatrix} 98.5715 & -23.9147 & 41.8340 \\ -23.9147 & 4.8161 & -10.9284 \\ 41.8340 & -10.9284 & 32.0691 \end{pmatrix}. \quad (\text{B2})$$

Hence

$$\text{Tr}[Q_a] = 191.5049, \quad \text{Tr}[Q_b] = 135.4567, \quad (\text{B3})$$

$$q_{b,1} = -0.978, \quad (0.2111, 0.9759, 0.0554), \quad (\text{B7})$$

$$q_{b,2} = 11.903, \quad (-0.4252, 0.0406, 0.9042), \quad (\text{B8})$$

$$q_{b,3} = 124.531, \quad (0.8801, -0.2145, 0.4236). \quad (\text{B9})$$

and the eigenvalues and eigenvectors are obtained, respectively, as

$$q_{a,1} = -2.106, \quad (0.444, 0.729, -0.520), \quad (\text{B4})$$

$$q_{a,2} = 1.067, \quad (-0.258, 0.660, 0.704), \quad (\text{B5})$$

$$q_{a,3} = 192.544, \quad (0.857, -0.178, 0.482), \quad (\text{B6})$$