Ab initio modeling of primary processes in photosynthesis : protein induced activation of bacteriochlorophylls for efficient light harvesting and charge separation

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Appendix A

Basis Set and Functional Tests

The Pople's notation is a notation most often used for Gaussian basis sets like 6–311++G(3df,3pd). The 'G' stands for Gaussian-type functions and divides the notation into two parts: functions for occupied atomic orbitals are described before 'G', while high angular momentum functions are given afterwards. '6' denotes that core orbitals are a contraction of six primitive, *i.e.* uncontracted, functions. The next three digits indicate a TZ valence split basis, in which valence orbitals are split into three functions, represented by three, one and one primitives, respectively. First '+' shows that diffuse functions are applied to the heavy atom and the second one informs that the same goes for hydrogens. In the parenthesis polarization functions are given, first for heavy atoms (three d-functions and one f-function) and then for hydrogen (three p-functions and a d-function).

Basis set tests were performed for the reference compounds (TMS, NH_3) in vacuum, using 6-311++G, 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) and analogous double-zeta basis sets together with the 6-31G(d,p) without diffuse functions. The results are collected in Table A.1. Addition of diffuse functions has the largest effect on the nitrogen shielding (8.0 ppm) and influences ^{13}C and ^{1}H chemical shieldings by only 1.2 ppm and 0.6 ppm, respectively. The inclusion of polarization functions has also impor-

	NH_3		TMS	
	N	H	C	H
6-31G(d,p)	255.8	32.0	186.4	31.5
6-31++G	270.7	32.3	189.5	32.3
6-31++G(d,p)	263.8	31.4	187.6	31.4
6-31++G(2d,2p)	265.1	31.4	186.6	31.4
6-31++G(3df,3pd)	262.7	31.4	185.7	31.3
6-311++G	264.2	32.5	184.1	32.5
6-311++G(d,p)	254.8	31.8	178.6	31.7
6-311++G(2d,2p)	255.8	31.7	178.7	31.6
6-311++G(3df,3pd)	256.4	31.4	179.1	31.5

Table A.1: Basis set influence on the DFT/BLYP computed chemical shieldings [ppm] for the reference compounds.

tant effects: When going from the 6-311++G basis to the 6-311++G(d,p) basis, the chemical shieldings change by 9.4 ppm for nitrogen, 5.5 ppm for carbon and 0.8 ppm for hydrogen. Addition of polarization functions in the triple-zeta basis beyond the (d,p) set results in only small changes for all the atoms. Interestingly, the smallest basis set used here, namely 6-31G(d,p), produces values for ^{15}N close to those obtained with larger triple-zeta basis sets. This coincidence, however, may be attributed to a fortuitous error cancelation rather than to the accuracy of this particular basis.

The above-mentioned triple-zeta basis sets were also tested on histidine in all four possible protonation states of its imidazole ring and the results are reported in Table A.3. Similarly to the chemical shieldings of the reference compounds, convergence is essentially reached with the 6-311++G(d,p) basis set. Also in this case the inclusion of (d,p) polarization functions into the 6-311++G basis set has important effects, particularly for the unprotonated ring nitrogens where a chemical shift change of about 30 ppm is observed.

Table A.2 contains the chemical shifts for all the histidines using the B3LYP hybrid functional with the 6-311++G(d,p) basis set. These results show that the choice of this popular functional has a marginal effect on the chemical shifts when compared to BLYP.

	Cationic	Neutral$_\tau$	Neutral$_\pi$	Anionic
C	190.3	185.7	186.7	187.4
Cα	61.1	62.1	61.8	61.4
Cβ	34.9	40.9	32.6	48.1
Cγ	144.5	149.0	132.4	137.5
Cδ	124.0	117.2	135.6	133.4
Cε	135.9	138.6	139.3	154.2
N	47.9	49.2	53.1	36.2
Nπ	209.6	305.9	187.1	290.2
Nτ	186.1	173.8	301.9	290.8
Hδ	7.3	6.9	7.1	6.9
Hε	8.1	7.4	7.4	7.3
Hπ	14.2	–	9.1	–
Hτ	9.1	8.1	–	–
H(–Cα)	3.6	3.3	3.4	3.9
H(–Cβ)	3.2	2.9	2.9	3.4
H(–Cβ)	3.4	3.0	3.0	2.1
H(–N)	1.5	0.9	1.6	0.2
H(–N)	2.2	1.6	1.0	1.5
H(–O)	7.1	5.6	5.8	5.0

Table A.2: Histidine chemical shifts [ppm] in different protonation states calculated with B3LYP/6-311++G(d,p) level of theory. The ^{1}H and ^{13}C chemical shifts are referred to TMS, while the ^{15}N chemical shifts are related to NH_3.

	Cationic				Neutral$_\tau$				Neutral$_\pi$				Anionic			
	B1	B2	B3	B4	B1	B2	B3	B4	B1	B2	B3	B4	B1	B2	B3	B4
C	201.8	190.3	191.3	191.6	196.6	186.5	187.1	187.5	197.2	186.5	187.2	187.4	194.3	185.7	186.4	192.1
Cα	65.4	64.6	64.9	66.0	64.2	63.2	63.3	64.2	64.9	64.8	65.0	65.9	65.8	64.6	64.5	65.9
Cβ	39.7	37.2	37.2	38.2	44.4	42.5	42.0	43.4	34.5	34.3	34.0	35.3	53.3	51.7	51.3	48.9
Cγ	146.2	144.3	143.8	144.9	151.8	148.5	148.7	149.7	133.8	131.6	130.9	131.5	141.0	137.7	138.0	139.3
Cδ	125.4	122.6	121.6	122.6	120.1	117.9	116.8	116.4	137.2	134.5	134.8	135.4	136.4	133.4	133.2	131.0
Cε	135.3	132.9	131.8	132.3	139.4	136.0	135.9	137.3	140.8	137.3	137.0	138.0	159.3	154.0	154.5	154.2
N	60	54	54	53	46	44	44	44	69	62	63	62	48	42	42	51
Nπ	220	212	213	213	331	302	302	302	198	190	190	190	320	293	293	290
Nτ	195	188	188	188	182	175	176	175	332	303	302	302	323	295	294	292
Hδ	7.1	7.2	7.3	7.3	6.7	6.9	6.9	6.9	6.9	7.0	7.1	7.1	6.7	7.0	7.1	6.9
Hε	7.8	8.0	8.1	8.1	7.4	7.4	7.5	7.6	7.3	7.3	7.4	7.4	7.5	7.4	7.5	7.4
Hπ	13.1	14.2	14.9	15.3	–	–	–	–	8.6	8.9	9.2	9.3	–	–	–	–
Hτ	8.5	8.9	9.3	9.4	7.6	8.1	8.4	8.6	–	–	–	–	–	–	–	–
H(–Cα)	3.9	3.7	3.9	3.8	4.2	4.0	4.1	4.1	3.8	3.5	3.6	3.5	4.2	3.9	4.0	4.4
H(–Cβ)	3.4	3.3	3.3	3.3	3.4	3.2	3.2	3.2	3.1	3.0	3.1	3.0	3.7	3.6	3.7	3.7
H(–Cβ)	3.7	3.4	3.5	3.5	2.4	2.3	2.3	2.3	3.2	3.0	3.0	3.0	2.2	2.2	2.2	2.4
H(–N)	1.8	1.7	1.7	1.7	1.4	1.3	1.4	1.5	1.4	1.2	1.3	1.4	1.7	1.7	1.8	0.8
H(–N)	2.5	2.2	2.2	2.3	0.9	0.7	0.7	0.8	2.0	1.8	1.8	1.9	0.6	0.3	0.4	0.5
H(–O)	7.8	7.2	7.4	7.5	6.3	5.8	6.1	6.2	6.4	5.8	6.0	6.2	5.4	4.9	5.2	5.4

Table A.3: Histidine chemical shifts [ppm] in different protonation states calculated with DFT/BLYP and various basis sets. B1, B2, B3 and B4 correspond to 6-311++G, 6-311++G(d,p), 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis set, respectively. The ^{1}H and ^{13}C chemical shifts are referred to TMS, while the ^{15}N chemical shifts to NH_3.