Effects of histidine ligand on the optical properties of bacteriochlorophyll in LH2

S. Toliautas, R. Tolyte, O. Rancova, J. Sulskus, D. Abramavicius
Department of Theoretical Physics, Faculty of Physics, Vilnius University

Bacteriochlorophyll-ligand pairings are frequently found in photosynthetic pigment-protein complexes responsible for solar light harvesting and delivery to energy processing units. Effects of ligands on the bacteriochlorophyll molecule lead to the range of optical properties suited for conversion of solar energy in varying environmental conditions [1]. Presented study aims to explain the observed spectra of light-harvesting complex II (LH2) by means of theoretical modeling.

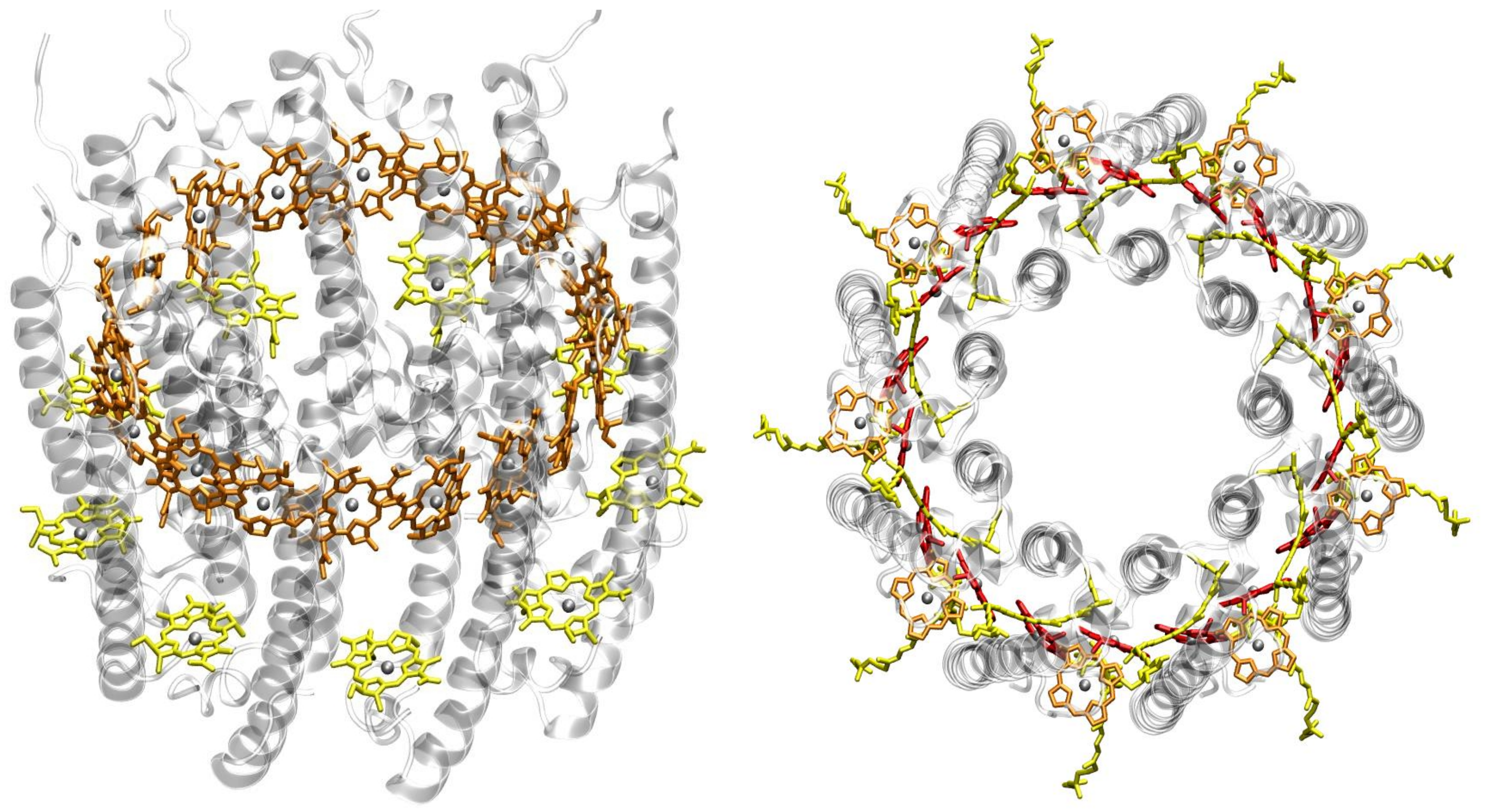

Fig. 1. Light-harvesting complex II (LH2) contains two rings of bacteriochlorophyll-*a* (Bchl-*a*) molecules, commonly referred to as B800 (*yellow*) and B850 (*red*); the numbers correspond to the positions of the respective peaks in the absorption spectrum. The rings are situated between the cylinders formed by two separate chains of polypeptides (*silver*). The denser B850 ring can also be split into B850α and B850β components in relation to the polypeptide chains. The respective chains provide a nearby histidine (His) ligand perpendicular to the principal plane of Bchl-*a*. [*Image source:* commons.wikimedia.org]

$$\hat{H}=\sum_{m} E_m \hat{B}_m^{\dagger} \hat{B}_m + \sum_{m,n}^{m\neq n} V_{mn} \hat{B}_m^{\dagger} \hat{B}_n \qquad E_m = E_0 + \Delta E_m$$

$$\Delta E_m = \frac{1}{\varepsilon_{eff}} \sum_{I=1}^{N} \sum_{k=1}^{M} \sum_{J=1}^{K} \frac{\Delta q_{I,m} \cdot q_{J,k}^{bg}}{|\boldsymbol{r}_{I,m} - \boldsymbol{r}_{J,k}|} \qquad V_{mn} = \frac{1}{\varepsilon_{op}} \sum_{I=1}^{N} \sum_{J=1}^{N} \frac{q_{I,m}^{tr} \cdot q_{J,n}^{tr}}{|\boldsymbol{r}_{I,m} - \boldsymbol{r}_{J,n}|}$$

Table 1. Relative site energies *ΔE* of Bchl-*a* molecules in the B850 ring, calculated using electrostatic model of the Frenkel exciton Hamiltonian [2] (*above*) and assigning different charges to the nearby *β-his* molecule. Neither automatic assignment of protons to the structure of LH2 [3] nor the corrections based on various studies reproduce the known value of (B850α – B850β) ≈ 300 cm^{-1}, as long as histidines of both polypeptide chains are kept neutral. However, making *β-his* negatively charged gives qualitatively correct results.

automatic (β-his neutral)		***corrected (β-his neutral)***		***corrected (β-his negative)***	
ΔE(B850α), cm^{-1}	**ΔE(B850β), cm^{-1}**	**ΔE(B850α), cm^{-1}**	**ΔE(B850β), cm^{-1}**	**ΔE(B850α), cm^{-1}**	**ΔE(B850β), cm^{-1}**
-196.2	38.3	-66.9	63.9	161.2	-106.5
-197.7	50.1	-53.6	61.8	159.2	-123.5
-152.9	94.9	-60.7	58.1	159.3	-126.2
-196.2	38.3	-66.9	63.9	161.2	-106.5
-197.7	50.1	-53.6	61.8	159.2	-123.5
-152.9	94.9	-60.7	58.1	159.3	-126.2
-196.2	38.3	-66.9	63.9	161.2	-106.5
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-152.9	94.9	-60.7	58.1	159.3	-126.2

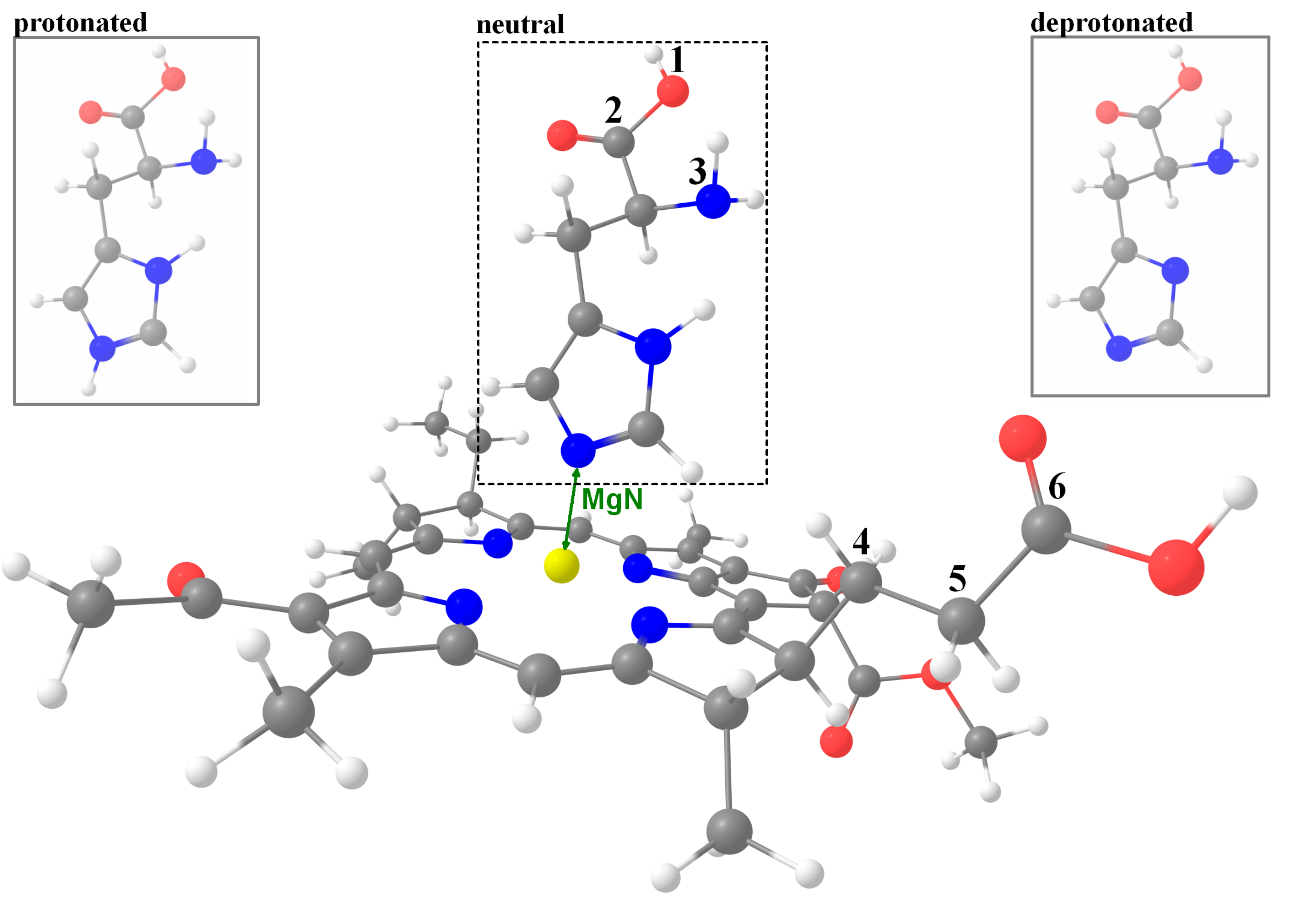

Fig. 2. Molecular structure of bacteriochlorophyll-*a* (Bchl-*a*) – histidine (His) complex in LH2, based on crystallographic data from Protein Data Bank (ID: 2FKW [2]). MgN denotes distance between the histidine ligand (*framed*) and the center of Bchl-*a* (2.12 Å in PDB, 2.16 Å after structure optimization). Numbers 1-6 mark the atoms whose positions are fixed to simulate protein-induced geometric constraints. Different forms of the ligand are shown in insets.

A time-dependent density functional theory (TDDFT) modeling of bacteriochlorophyll-*a* (Bchl-*a*) – histidine (His) complexes containing neutral and deprotonated (negatively charged) forms of His is performed using B3LYP functional and 6-311G(d,p) basis set in order to determine electronic excitation properties of chlorophylls in light-harvesting complex II (LH2).

Initial structure of the complex is based on the reported structure [3] of chlorophyll-ligand pair with the smallest distance between the two groups. Positioning of Bchl-*a* and His groups is then varied to simulate the protein environment and its possible changes ("breathing" of the protein) (Fig. 2).

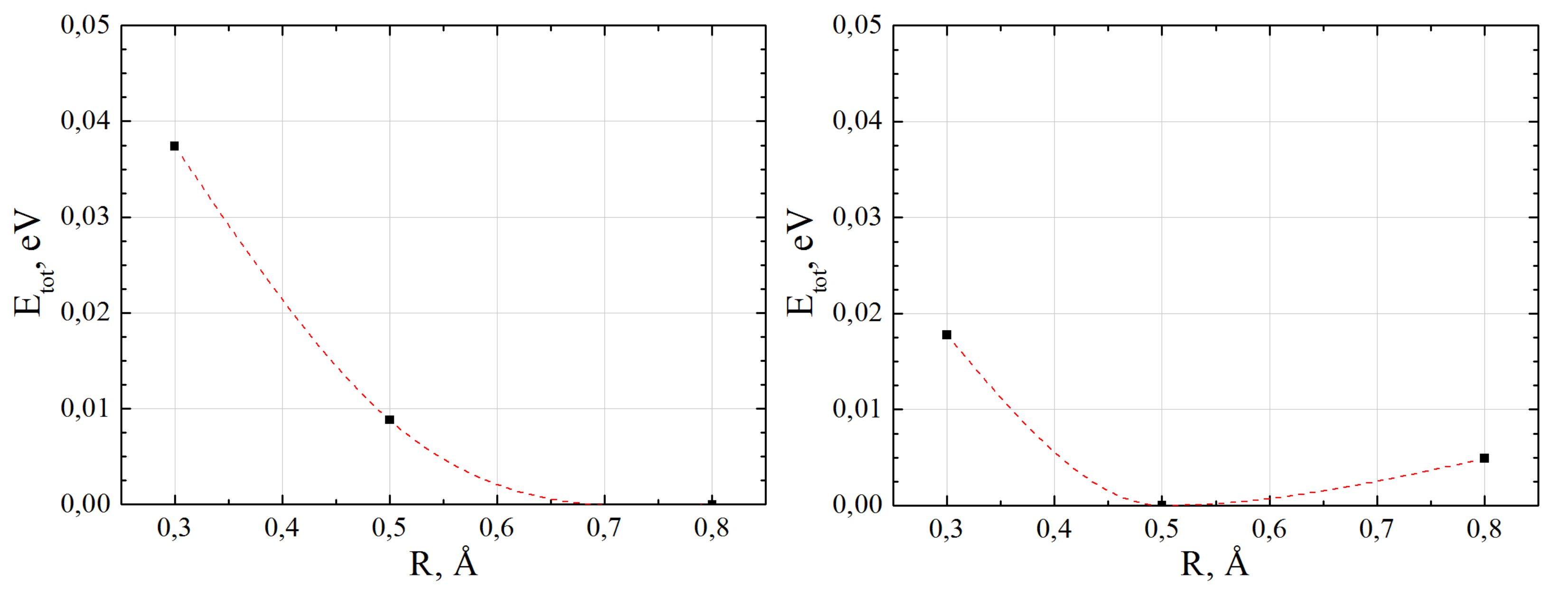

Fig. 3. Change in total energy of the Bchl-*a* – His complex with neutral ligand (*left*) and deprotonated ligand (*right*) during the "breathing" of the LH2. *R* is the change in distance between the two sites linked to the surrounding protein (numbers 1-3 and 4-6 in Fig. 2). Complexes with different forms of His assume slightly different molecular structure.

Table 2. Distance between the histidine ligand and the center of the Bchl-*a* molecule during the "breathing" of the LH2. In a complex containing deprotonated form of His, Mg-N length is smaller and very close to the distance between *bcl1601* and *β-his30* reported in [3]. *R* is the change in distance between the two protein-linked sites. Values corresponding to the minimal total energy of the respective structures are highlighted in bold.

with neutral His		***with deprotonated His***	
R, Å	***r* (Mg-N), Å**	**R, Å**	***r* (Mg-N), Å**
0.3	2.215	0.3	2.088
0.5	2.223	**0.5**	**2.127**
0.8	**2.255**	0.8	2.139

Table 3. Wavelength of the lowest electronic excitation calculated for different kinds of Bchl-*a* – His complexes. *R* is the change in distance between the two protein-linked sites.

separate Bchl-a		827.0 nm	
with neutral His		***with deprotonated His***	
R, Å	**λ (S_0-S_1), nm**	**R, Å**	**λ (S_0-S_1), nm**
0.3	835.0	0.3	839.4
0.5	838.3	**0.5**	**838.4**
0.8	**836.7**	0.8	844.8

Table 4. Partial charges of the structural groups (e^- units) for different kinds of Bchl-*a* – His complexes. Total charge is equal to 0 for the case of neutral ligand and -1 for deprotonated ligand. In both cases, Bchl-*a* group becomes partially negatively charged.

separate Bchl-a	***with neutral His***		***with deprotonated His***	
	Bchl-a	***His***	***Bchl-a***	***His***
0.000	-0.183	0.183	-0.435	-0.565

Conclusions

- In the case of deprotonated form of His the obtained value of the Mg-N distance between the Bchl-*a* and the ligand (2.127 Å) agrees very well with the recent crystallographic data of the LH2.
- Presence of the ligand decreases the energy of the lowest excitation by 10 nm, while the "breathing" of the external structure in the range of thermal fluctuations results in additional differences of about 5 nm.
- Modeling results show the partial electronic charge redistribution from histidine to Bchl-*a* for both forms of the ligand.

Acknowledgments

The public access supercomputer from the High Performance Computing Center (HPCC) [4] of the Lithuanian National Center of Physical and Technology Sciences (NCPTS) at Physics Faculty of Vilnius University was used. Calculations were carried out using electronic structure modeling packages *Gaussian09* [5] and *GAMESS* [6].

References

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