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Simulation of electronic structure and excited states of a chlorophyll-A system

Abstract

A system of six chlorophyll-A molecules (Ch-A-6) was studied by quantum chemical modeling methods using density functional theory and its non-local approximations. Theoretical modeling of the spatial structure, electronic levels, distribution of effective charges on atoms and excited states was carried out simultaneously with interpretation of experimental optical absorption spectra of chlorophyll-A in solution with diethyl ether. Analysis of electronic structure and atomic nuclei by Mulliken methods allowed to establish the nature of the bond between chlorophyll-A molecules within the system. The effect of Mg coordinate position in the formation of bands in calculated absorption spectra was studied. According to the calculations, excited states are caused by transitions from within each chlorophyll fragment. Transitions of mixed molecular orbitals can also be detected. A final analysis of non-covalent interactions showed the presence of a high degree of hydrogen bonds and strong Van der Waals interactions.

Keywords: Chlorophyll-A; density functional theory; optical spectroscopy; electronic structure; atomic nuclei.

Simulación de estructura electrónica y estados excitados del sistema molecular clorofila-A

Resumen

Un sistema compuesto por seis moléculas de clorofila-A (Ch-A-6) fue estudiado a partir de métodos de simulación de química cuántica mediante la teoría funcional de la densidad y su aproximación de formano local. La simulación teórica de la estructura espacial, la configuración electrónica y la distribución de cargas efectivas en átomos y en estados excitados se llevaron a cabo simultáneamente con la interpretación de espectros ópticos de clorofila-A en solución con etoxietano. El análisis de la estructura electrónica y de los núcleos atómicos mediante métodos Mulliken permitió establecer la naturaleza del enlace entre las moléculas de clorofila-A dentro del sistema. Se estudió el efecto de la posición del magnesio (Mg) en espectros de absorción simulados. Según los cálculos, los estados excitados son causados por transiciones dentro de cada fragmento de clorofila. También se detectaron otras transiciones entre orbitales moleculares. El análisis de interacciones no covalentes mostró la presencia de un alto grado de enlaces de hidrógeno y fuertes interacciones de Van der Waals.

Palabras clave: clorofila-A; teoría funcional de la densidad; espectroscopia óptica; estructura electrónica; núcleos atómicos.

Simulação da estrutura eletrônica e estados excitados do sistema molecular da clorofila-A

Resumo

Um sistema composto por seis moléculas de clorofila-A (Ch-A-6) foi caracterizado em simulação física quântica usando a teoria do funcional da densidade e sua aproximação não local. A simulação da estrutura espacial, da configuração eletrônica e da distribuição de cargas efetivas nos átomos e nos estados excitados foi realizada simultaneamente, com interpretação dos espectros ópticos da clorofila-A em solução em etoxietano. A análise da estrutura eletrônica e dos núcleos atômicos usando métodos Mulliken permitiu estabelecer a natureza da ligação entre as moléculas de clorofila-A dentro do sistema. O efeito da posição do magnésio (Mg) nos espectros de absorção simulados foi estudado. De acordo com os cálculos, os estados excitados são causados por transições dentro dos fragmentos, outras transições entre orbitais moleculares também foram detectadas. A análise das interações não covalentes mostrou a presença de um alto grau de ligações de hidrogênio e fortes interações de Van der Waals.

Palavras-chave: clorofila-A; teoria do funcional da densidade; espectroscopia óptica; estrutura eletrônica; núcleos atômicos.

Introduction

Chlorophyll-A (Ch-A) is the only pigment in protein structures that is directly involved in photosynthesis [1]. Common structure of Ch-A is composed by a central chlorin ring enclosing a magnesium (Mg) ion with several methyl CH_3 ring substituents connected to a hydrophobic hydrocarbon phytol "tail". These three elements integrate the main areas for absorption of visible radiation. The central chlorin-enclosed Mg is widely believed to heavily influence the absorption abilities of the whole system. The presence of Mg is explained by the heterogeneous biosynthesis of chlorophyll [2], which occurs along the carboxyl pathway by oxidation and chain closure of the propionate substituent [3].

Obtained experimental optical absorption spectra of Ch-A have a complex structure [4]. To connect transitions ground-excited states to their respective fragments and their contributions to the intensity of the bands is almost an impossible task without the use of theoretical methods. Density functional theory (DFT) is one of the most effective methods for calculating electronic structure, excited states and probabilities of transitions from ground state [5–8]. This approach allows one to determine the contribution of each fragment to the intensities of the experimental bands from electronic structure and distribution of Mulliken atomic charges. Additionally, to verify and visualize the non-covalent interactions (van der Waals interactions, hydrogen bonds, and steric clashes) between molecules and molecular fragments, we used the non-covalent interaction index (NCI) based on the reduced density gradient (RDG) of electron density; this topological method has demonstrated great capability and precision on predicting non-covalent interactions and their characteristics [9–12].

In this work, three main structures were calculated and analyzed: the system of six Ch-A fragments (Ch-A-6) (**figure 1A**), two molecules of Ch-A in parallel (**figure 1B**) and perpendicular alignment (**figure 1C**). The main objective of this work was to establish the nature of the bond between Ch-A molecules and their excited states, and to interpret the optical absorption spectra by energy analysis and localization of molecular orbitals (MO). Separate tasks were set to determine and analyze atomic charge, simulated photo-electronic spectra and the effect of coordination of Mg ion in the chlorin ring on the optical absorption spectra for the six-molecule system and individual fragments of Ch-A in order to shed light on long-range order effects (such as characteristic optical spectra that can be measured from passive and active satellite sensors) by analyzing electronic structure and absorbance from excited states.

Methods and approach

Quantum-chemical calculations of the spatial structure, energies (and composition) of MO and distribution of effective atomic charges were performed in the DFT approximation using the program FireFly 8.2.0 [13]. Calculations of 50 excited states and singlet-singlet transitions for all studied compounds were performed in the approximation of non-local density functional theory (TDDFT) using the GAMESS-US (2022 R2) program [14]. For all calculations the hybrid exchange-correlation functional CAM-B3LYP [15] was used, which is a modification of the B3LYP5 functional [16]. The selected functional included long-range corrections and an accurate description of charge transfer processes [17, 18], which allows the calculation of complex systems [18]. The high density of atoms and overall volume of the systems greatly affects calculation time and the choice of basis set requires a compromise between accuracy and time-consumption; therefore, the compact 6-311G basis set [19] was chosen for its well-tested and accurate results for complex systems [20, 21].

Initial structure of the Ch-A molecule was constructed using data from a study into the reaction center of a photo-system [22], regarded as the most accurate analog for experimental absorption spectra of real pigments based on Ch-A; thereafter, the structure was subdivided into several main fragments and calculated separately. For all calculated compounds 50 excited states of singlet-singlet transitions on the TDDFT methods were obtained. Additionally, an analysis of non-covalent interactions and calculation of the smallest density gradient [23] were performed for the system of Ch-A-6 molecules using the program Multiwfn [24].

Results

The initial structure of Ch-A "natural" analog (**figure 1A**) consists of six chlorin rings with phytol chains shortened to a C^7 methyl group; two water molecules coordinating the Ch-A molecules and two extra Ch-A molecules flanking the central system [22]. Structures in **figure 1B** and **1C** demonstrate, respectively, the arrangement of two Ch-A molecules in parallel and perpendicular to each other. Main Ch-A system contains six fragments of Ch-A numerated in **figure 1A**. The acid radical $CH_2CH_2CO_2$- is attached to fragment one (perpendicular to fragment three) and two (perpendicular to fragment four). In fragments three and four, the central Mg ions are connected to water molecules; fragment five (located in the background of **figure 1A**) and six (located in the foreground of **figure 1A**) have histidine (a heterocyclic alpha-amino acid) attached to them. Two subsystems were isolated, each consisting of two molecules with fragments one-three (**figure 1C**) and five-six (**figure 1B**).

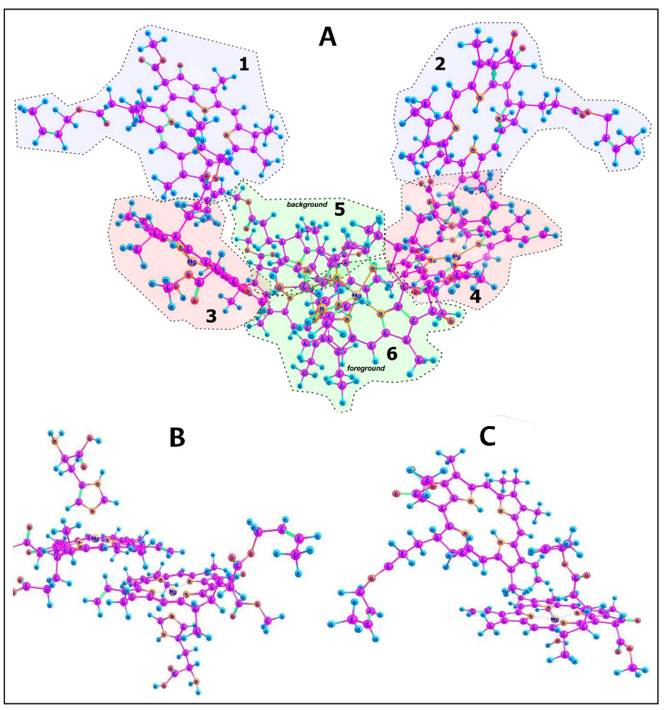

Figure 1. Spatial structure of six molecular chlorophyll-A system (A) and isolated 2-molecular subsystems in parallel (B) and perpendicular (C) configurations.

For all the selected structures energy, localization of MO (**table 1**) and atomic charges (**table 2**) were calculated. In addition, an analysis of the population of the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) interacting in the energy transfer from ground to excited states using theoretical absorption spectra (**figure 2** and **3**) was carried out. The obtained calculated spectra were compared with the experimental spectra of the Ch-A molecule in a diethyl ether solution [25]. The choice of the experimental spectrum in a diethyl ether solution is due to the fact that this solvent is considered "non-polar" (doesn't have donor-acceptor properties), compared to ethanol, acetone, methanol, etc. This allows us to reduce the influence of external variables on the results [26].

Table 1. Energy (eV) and localization (%) of the molecular orbitals (MO) system of six chlorophyll-A molecules (Ch-A-6).

Chlorophyll-A-6 (Ch-A-6)								
N°	MO	ε (eV)	Localization (%)					
			1	2	3	4	5	6
1154	L+9	-0.84	–	100	–	–	–	–
1153	L+8	-0.90	–	–	–	96	–	–
1152	L+7	-0.95	97	–	–	–	–	–
1151	L+6	-0.97	–	–	99	–	–	–
1150	L+5	-1.60	–	–	–	–	21	79
1149	L+4	-1.62	–	–	–	–	80	20
1148	L+3	-1.77	–	99	–	–	–	–
1147	L+2	-1.85	96	–	–	–	–	–
1146	L+1	-1.95	–	–	–	96	–	–
1145	LUMO	-1.97	–	–	99	–	–	–
1144	HOMO	-5.47	–	–	–	–	10	89
1143	H-1	-5.56	–	–	–	–	72	27
1142	H-2	-5.61	–	99	–	–	–	–
1141	H-3	-5.73	–	–	–	–	74	25
1140	H-4	-5.73	99	–	–	–	–	–
1139	H-5	-5.81	–	–	–	–	40	56
1138	H-6	-5.87	–	–	97	–	–	–
1137	H-7	-5.88	–	–	–	94	–	–
1136	H-8	-5.97	–	98	–	–	–	–
1135	H-9	-6.05	54	–	–	45	–	–
1134	H-10	-6.11	46	–	–	54	–	–
1133	H-11	-6.14	–	–	99	–	–	–
1132	H-12	-6.88	–	–	–	–	26	73

N°: Ordinal number of the molecular orbital.
MO: designation of the molecular orbital relative to the HOMO and LUMO, where plus (+) means the next one and the minus sign (-) means the previous one.
ε (eV): energy of the MO measured in eV.
Localization: the relative contribution of each fragment to the MO, expressed as a percentage.

Analysis of electronic structure was focused on both energy and localization of MO in each individual Ch-A molecule (**table 1**). In the system of Ch-A-6, inter molecular mixing of MO (MO numbers: 1144, 1143, 1141, 1139, 1132) is observed only for fragments five and six located parallel to each other; furthermore, in perpendicular configurations no hybridization was observed. The result of calculation of systems composed by two chlorophylls with different mutual arrangements (**table 2**) corroborates a greater mixing of orbitals for fragments of the Ch-A-1 subsystem lying parallel to each other.

The HOMO in the Ch-A-6 system is formed by hybridization of the fragments five and six, in which the fragment six is the predominant contributor. The LUMO is formed by fragment three: with a HOMO-LUMO energy gap of 3.5 eV for the Ch-A-6 system, lower than in the Ch-A-1 and Ch-A-2 systems, which have an energy gap of 0.34 and 0.28 eV respectively. The high density of five lowest unoccupied and twelve highest occupied MO causes high absorption capacity with a relatively narrow energy gap. Based on the results obtained, it can be hypothesized that an increase in the number of Ch-A molecules in the system will increase the density of boundary orbitals with a decrease in the energy gap.

Table 2. Energy (eV) and localization (%) of the molecular orbitals (MO) system of two chlorophyll-A molecules in parallel (Ch-A-1) and perpendicular (Ch-A-2) configurations, with their respective histidine (His#) molecules.

Ch-A-1							Ch-A-2				
N°	MO	ε (eV)	Localization (%)				N°	MO	ε (eV)	Localization (%)	
			1	His1	2	His2				1	2
444	L+7	0.56	100	0	0	0	360	L+5	0.20	3	97
443	L+6	0.48	0	0	0	100	359	L+4	0.10	97	3
442	L+5	0.36	0	0	100	0	358	L+3	-0.95	94	6
441	L+4	0.30	0	100	0	0	357	L+2	-0.98	6	94
440	L+3	-0.46	69	0	31	0	356	L+1	-1.84	96	4
439	L+2	-0.54	33	0	67	0	355	LUMO	-1.95	4	96
438	L+1	-1.40	100	0	0	0	354	HOMO	-5.73	100	0
437	LUMO	-1.46	0	0	100	0	353	H-1	-5.89	0	100
436	HOMO	-5.30	93	0	7	0	352	H-2	-6.06	79	21
435	H-1	-5.41	31	0	69	0	351	H-3	-6.13	22	78
434	H-2	-5.58	28	0	72	0	350	H-4	-7.27	100	0
433	H-3	-5.66	50	0	50	0	349	H-5	-7.45	28	72
432	H-4	-6.69	78	0	22	0	348	H-6	-7.61	43	57
431	H-5	-6.97	56	0	44	0					
430	H-6	-7.21	27	0	73	0					
429	H-7	-7.33	39	0	61	0					
428	H-8	-7.46	100	0	0	0					

N°: ordinal number of the molecular orbital (MO).
MO: designation of the molecular orbital relative to the HOMO and LUMO, where plus (+) means the next one and the minus sign (-) means the previous one.
ε (eV): energy of the MO measured in eV.
Localization: indicates the relative contribution to the MO expressed as a percentage.

As already noted, Ch-A contains a chlorin ring. Chlorin is a composite porphyrin molecule in which two -CH_2 radicals were added. At the same time, porphyrin is a derivative of the dipyrrin molecule consisting of two pyrrole molecules. The molecular orbital energy diagram (**figure 2**) shows correlation between MO from the pyrrole structure to the complete Ch-A structure. Additionally, the energies of the histidine MO are plotted on the diagram to show its participation in the formation of the Ch-A MO. The highest occupied MO of pyrrole (π_2) is retained when transitioning through dipyrrin-porphyrin-chlorin-chlorophyll-A, with destabilization non greater than 1.58 eV. The lowest unoccupied MO of pyrrole (π_4) is also retained during the transition to Ch-A with a high degree of stabilization equal to 4.23 eV. These changes, which have a positive effect on the optical ability of Ch-A, are caused by the increasing density MO near the HOMO-LUMO gap.

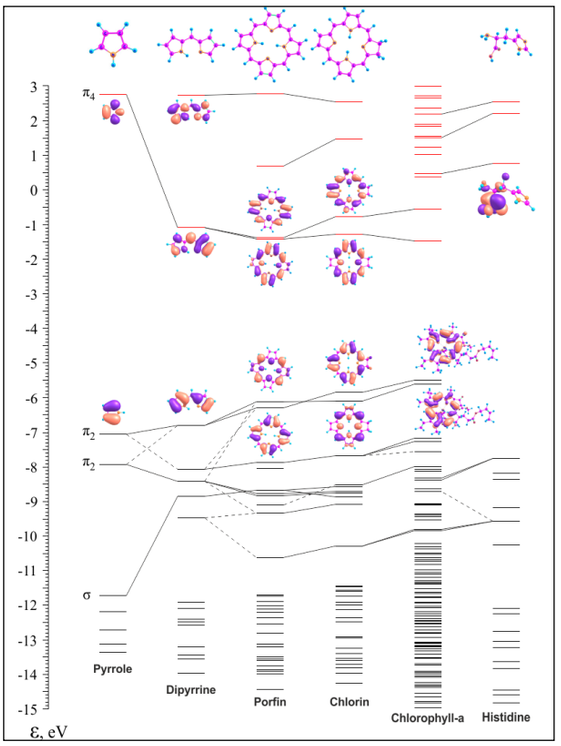

Figure 2. Transitional energy correlation diagram of the chlorophyll-A molecule, its derivatives and components, with occupied molecular orbitals indicated in black and unoccupied molecular orbital in red.

Based on the values of energies and localizations from DFT calculations, theoretical photo electronic spectra (PES) for the Ch-A-6 system and for the Ch-A-1 and the Ch-A-2 subsystems were constructed exhibiting shifts and changes on the MO and their relative intensity when transitioning from a two-molecule system to a six-molecule system. Theoretical photoelectron spectra of all structural molecules of Ch-A (shown in the diagram of **figure 2**) were obtained separately (**figure 3B**).

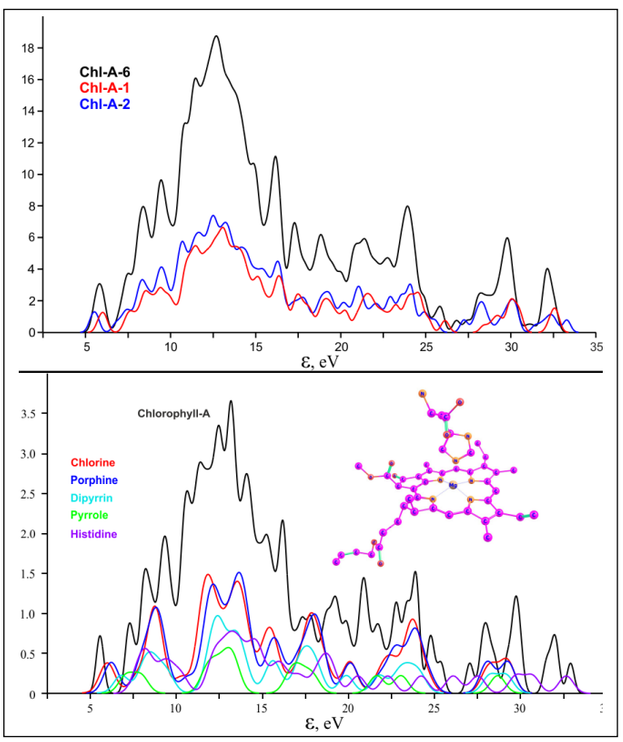

Figure 3. A: Theoretical photoelectron spectra of Ch-A-6 (black line), Ch-A-1 system in parallel configuration (red line) and Ch-A-2 system in perpendicular configuration (blue line) fragments. B: Theoretical photoelectron spectra of Ch-A molecule and derivatives of the pyrrole molecule.

The atomic charges in Mulliken approximation (**table 3**) were obtained by localization of the electron density of molecular orbitals for all three systems. For Ch-A-6, all of the fragments have negative charge; there is a lack of coordination with Mg ion in fragments one and two, so the ion charge value is not given in the table for them. The value of the Mg ion charge differs due to the presence of an additional attached water molecule (H_2O) for three and four fragments; and histidine (His) for fragments five and six. The mutual arrangement of the Ch-A molecules in the system affects the charge distribution.

Table 3. Mulliken atomic charges (a.u.) for system of six chlorophyll-A molecules (Ch-A-6), chlorophyll-a 2-molecule system in parallel configuration (Ch-A-1), chlorophyll-a 2-molecule system in perpendicular configuration (Ch-A-2).

Ch-A-6		Ch-A-1		Ch-A-2	
Fragment	q (a.u.)	Fragment	q (a.u.)	Fragment	q (a.u.)
1	-0.003	1 / Mg	-0.144 / +1.168	1	+0.004
2	-0.014	His1	-0.192	2 / Mg	-0.150 / +1.122
3 / H_2O / Mg	-0.033 / +0.146 / +1.120	2 / Mg	+0.196/ +1.193	H_2O	+0.146
4 / H_2O / Mg	-0.031 / +0.151 / +1.134	His 2	+0.140		
5 / His / Mg	+0.044 / +0.148 / +1.167	-			
6 / His / Mg	+0.037 / +0.144 / +1.195				
Σ	-0.0005	Σ	0	Σ	0

The fragment number is indicated in accordance with **figure 1A.**
q: atomic charge.
Σ: Total charge of the entire system, the total charge of fragments 3-6 includes the charge of the Mg ion.
His: Histidine.

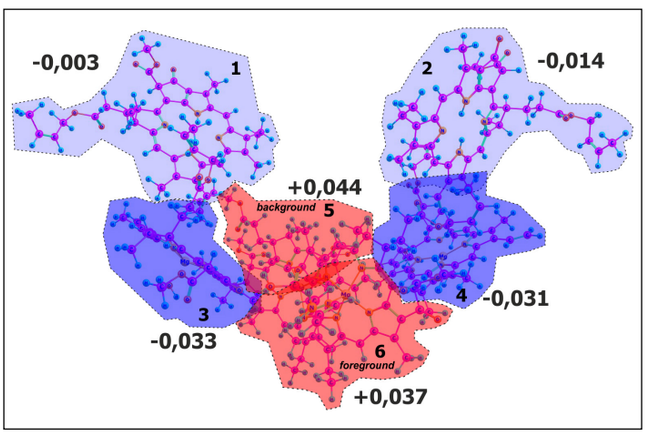

Figure 4. Total charge of fragments in chlorophyll-A six-molecular system; red color indicates positive charge; blue color indicates negative charge.

Total charge of systems Ch-A-6, Ch-A-1 and Ch-A-2 is close to neutral; although, it can be noted that the total charge of fragment one is negative (-0.144), and in fragment two it is positive (+0.196). This indicates a "pulling" of the electron density onto fragment one and of the His molecule from fragment two. Visually, the spatial structure is relatively symmetrical, but the distribution of atomic charges is asymmetrical. In Ch-A-2, the first fragment remains relatively neutral (the electron density is reduced by 0.004 a.u.). The second fragment remains negatively charged, having received a charge from the H_2O molecule. Taking into account the results of the analysis of atomic charge distribution, it can be speculated that, with an in-

crease in the number of Ch-A molecules in the system, the atomic charges are distributed in such a way that the entire system remains neutral, but the fragments will differ in total atomic charge.

By considering atomic charges and their positioning, we can deduce the type of bonding between the fragments (**table 3** and **figure 4**). Fragments one and two are significantly removed from the central position and located perpendicular (respectively) to fragments three and four, attracting an insignificant electron density of about 0.01 a.u. and forming a total negative charge. Fragments three and four have a total negative charge (-0.033 and -0.031 a.u.), while fragments five and six have a positive charge (+0.044 and +0.037 a.u.), indicating a redistribution of electron density drawn to fragments three and four. In **figure 4**, areas with a positive (red) and negative (blue) charge are visually highlighted to clearly demonstrate the distribution of the total charge of the fragments, indicating the ionic nature of the bond between Ch-A molecules in the system.

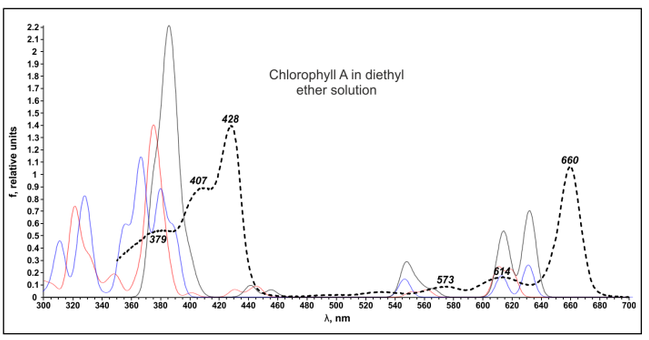

Figure 5. Optical absorption spectra of the calculated chlorophyll-A six-molecular system (Ch-A-6) (gray line), chlorophyll-A 2-molecule system in parallel configuration (red line), chlorophyll-A 2-molecule system in perpendicular configuration (blue line) and the experimental spectrum of chlorophyll-A (black dotted line).

When analyzing the experimental spectrum of Ch-A molecule in a diethyl ether solution (**figure 5**, black dotted line), two groups of maxima can be distinguished: 660, 614, 573 nm (red region) and 428, 407, 379 nm (UV region). The theoretical data (**figure 5**, gray line) for the system of six Ch-A fragments shows that the band with a maximum at 660 nm consists of highly intense transitions 1-5 (**table 4**) to π orbitals within fragments 2-2, 1-1, 6(5)-6(5), 4-4, 3-3. An unambiguous assignment of the bands at 614 and 573 nm is complicated by a high shift of 32 nm caused by the error in the method. Taking into account the calculations of individual Ch-A-1 and Ch-A-2 systems (**table 5**) and the corresponding sequence of transition energies, we can assume that the transition with a maximum at 614 nm refers to the transition within fragments 3-3, and the band at 573 nm corresponds to the transition within the residue 1-1. The transition N° 3 (in **table 4**) stands out from 1144 to 1150 of mixed orbitals of fragments five and six.

Table 4. Calculated singlet-singlet transitions to excited states of the Ch-A-6 molecular system.

Ch-A-6					
N°	E (eV)	λ (nm)	*f*	Transition	Fragments
1	1.954	669.3	0.36	1142-1148	2 - 2
2	1.967	665.4	0.17	1140-1147	1 - 1
3	1.968	665.1	0.28	1144-1150	6, 5 - 6, 5
5	2.016	650.1	0.36	1137-1146	4 - 4
6	2.028	646.4	0.21	1138-1145	3 - 3
11	2.264	600.7	0.11	1133-1145	3 - 3
12	2.268	581.7	0.13	1140-1147	1 - 1
31	3.112	433.4	0.32	1138-1151	3 - 3
34	3.168	426.3	0.31	1135-1146	1, 4 - 4
35	3.179	425.0	0.49	1142-1154	2 - 2
36	3.188	424.0	0.11	1134-1146	1, 4 - 3
39	3.203	422.1	0.53	1132-1150	6, 5 - 6, 5
40	3.230	418.8	1.06	1137-1153	4 - 4
41	3.235	418.3	0.26	1132-1150	6, 5 - 6, 5
44	3.275	413.6	0.22	1132-1149	6, 5 - 5, 6
45	3.306	410.0	0.57	1137-1150	4 - 6, 5
47	3.317	408.8	0.12	1137-1150	4 - 6, 5

E: transition energy in eV.
λ: wavelength in nm.
f: oscillator strength in relative units.
Transition: ordinal number of molecular orbitals between which the transition occurs, the first number indicates the occupied MO, the second, separated by a dash, is the unoccupied MO.
Fragments: numbers of fragments separated by a dash (**figure 1A**) between which the transition occurs are indicated. Transitions with oscillator strength < 0.10 omitted.

The UV-region of the spectrum contains three high-intensity bands with maxima at 428, 407, and 379 nm, which, according to calculations, belong to ten transitions (31-47). About these transitions, the following can be distinguished: mixed transitions 34, 36, 39, 41, 44, 45, 47 and the transition with the highest calculated oscillator strength of 1.06 occurring within fragment 4 (**table 4**, transition N° 40). However, the calculation of the Ch-A-6 system couldn't show the structure of the 407 and 379 nm bands. The calculated individual systems Ch-A-1 and Ch-A-2 (**table 5**) allow us to interpret these bands. In general, the transitions of these two systems are similar, but they are fundamentally different in spatial arrangement, from which it follows that the relative arrangement of Ch-A molecules relative to each other has a little effect on the absorption spectra.

Table 5. Calculated singlet-singlet transitions to excited states of a system of two Ch-A molecules in parallel (Ch-A-1) and perpendicular (Ch-A-2) configuration.

Ch-A-1						Ch-A-2					
N°	E (eV)	λ (nm)	*f*	Transition	Fragments	N°	E (eV)	λ (nm)	*f*	Transition	Fragments
1	1.997	655.9	0.21	436-438	1 - 1	1	1.969	664.7	0.26	354-356	1 - 1
2	2.027	646.5	0.24	435-437	2,1 - 2	2	2.027	646.5	0.18	353-355	2 - 2
3	2.204	597.6	0.06	433-437	1, 2 - 2	4	2.273	580.4	0.13	351-355	2, 1 - 2
10	3.224	419.6	0.26	432-438	1, 2 - 1	7	3.173	425.8	0.24	352-355	1, 2 - 2
11	3.255	415.9	0.20	432-438	1, 2 - 1	8	3.196	423.0	0.33	354-358	1 - 1
12	3.287	412.2	0.76	432-437	1, 2 - 2	9	3.265	414.8	0.82	353-357	2 - 2
13	3.324	408.0	0.78	435-440	2,1 – 1, 2	11	3.374	402.4	0.93	352-358	1, 2 -1
14	3.398	399.9	0.15	435-439	2,1 – 2, 1	12	3.410	398.6	0.29	349-355	2, 1 -2
17	3.539	385.3	0.14	436-439	1 – 2, 1	15	3.495	389.8	0.49	351-357	2, 1 -2
24	3.748	365.8	0.17	436-444	1 - 1	18	3.724	368.0	0.11	348-356	2, 1 - 1
25	3.801	361.2	0.10	428-438	1 - 1	19	3.760	364.7	0.50	354-359	1 - 1
27	3.861	356.2	0.60	433-440	1, 2 – 1, 2	20	3.805	325.8	0.31	350-358	1 - 1
–						23	3.979	311.6	0.45	353-360	2 - 2

E: transition energy (eV). λ: wavelength (nm). *f*: oscillator strength in relative units.
Transition: ordinal number of molecular orbitals between which the transition occurs, the first number indicates the occupied MO. The second is the unoccupied MO.
Fragments: numbers of fragments separated by a dash (**figure 1B**, **1C**) between which the transition occurs are indicated. Transitions with oscillator strength < 0.10 omitted.

The bands at 407 and 379 nm (UV-region of the spectrum) are formed by transitions between fragments three and five, four and six, and five and six. There is no absorption of fragments one and two in this region. The energies of the transitions and their intensities in the theoretical absorption spectra correspond with good accuracy to the experimental spectra of the Ch-A molecule, which allows us to judge the reliability of the results obtained.

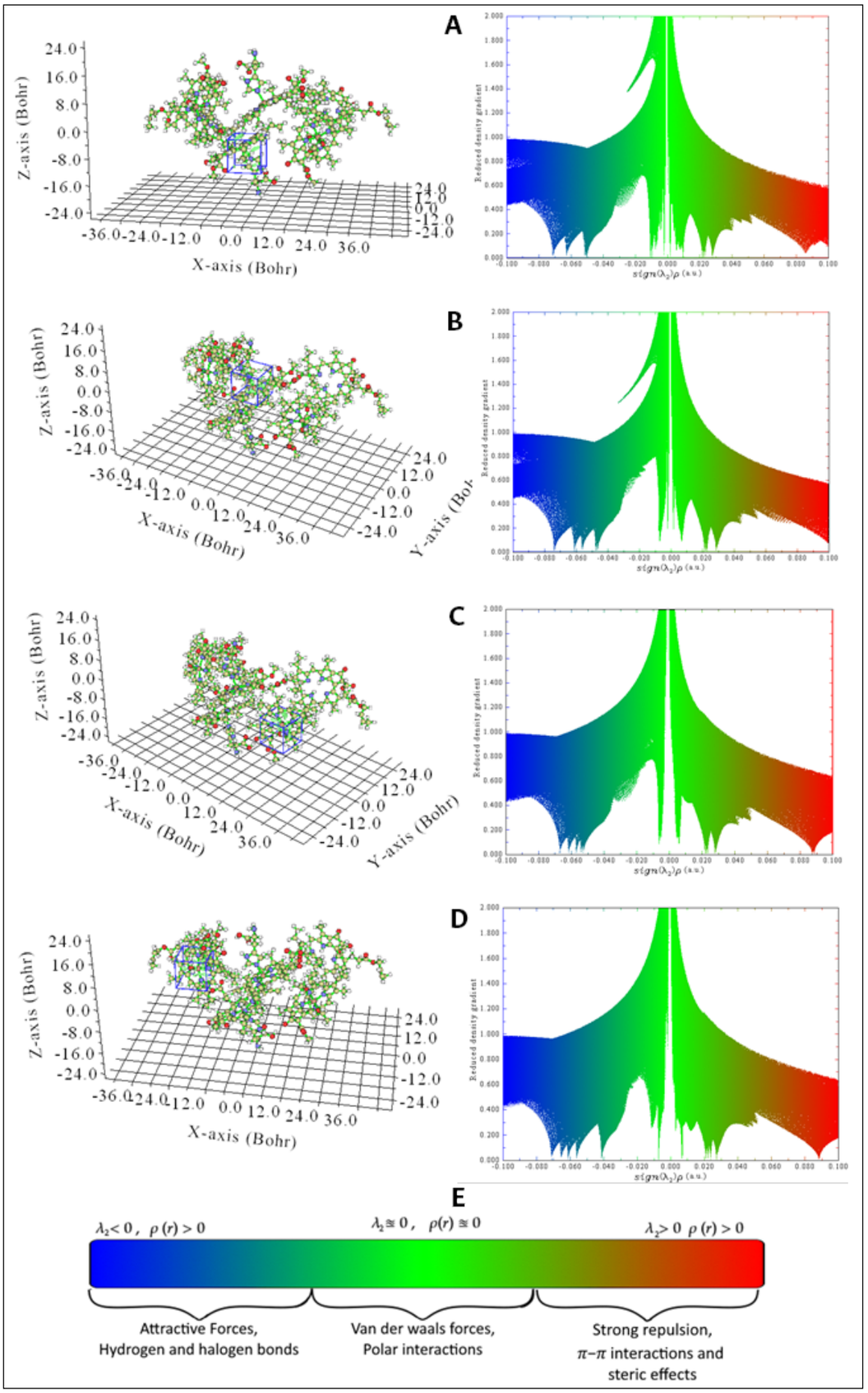

Figure 6. Calculated reduced density gradient (RGD) and data range for (A) first, (B) sixth, (C) third, and (D) forth molecular fragments in chlorophyll-A system; E: Range and correspondence of non-covalent interactions spikes of RDG with their respective electronic density values $\rho(r)$, filtered by attractive or repulsive interaction by the sign of the second eigenvalue of the Hessian of the electron density (sign(λ_2)).

To evaluate non-covalent interactions (NCI), we calculated the reduced density gradient (RDG) around in the Mg coordination regions in a volume of a cube with side of five Bohr with geometrical center in Mg ion (denoted in blue in **figure 6**). As a result, for the fifth and the sixth fragments, an isosurface is observed around the central Mg surrounded by nitrogen atoms, which indicates the presence of a strong attraction in this region (**figure 7C**). For the third and fourth fragments, an attractive region with a hydrogen bond is observed between the central Mg ion and the water molecule, which is reflected in the NCI pattern as "tails" of the gradient touch near sign $(\lambda_2)\ \rho(r) \approx -0.040$ a.u.

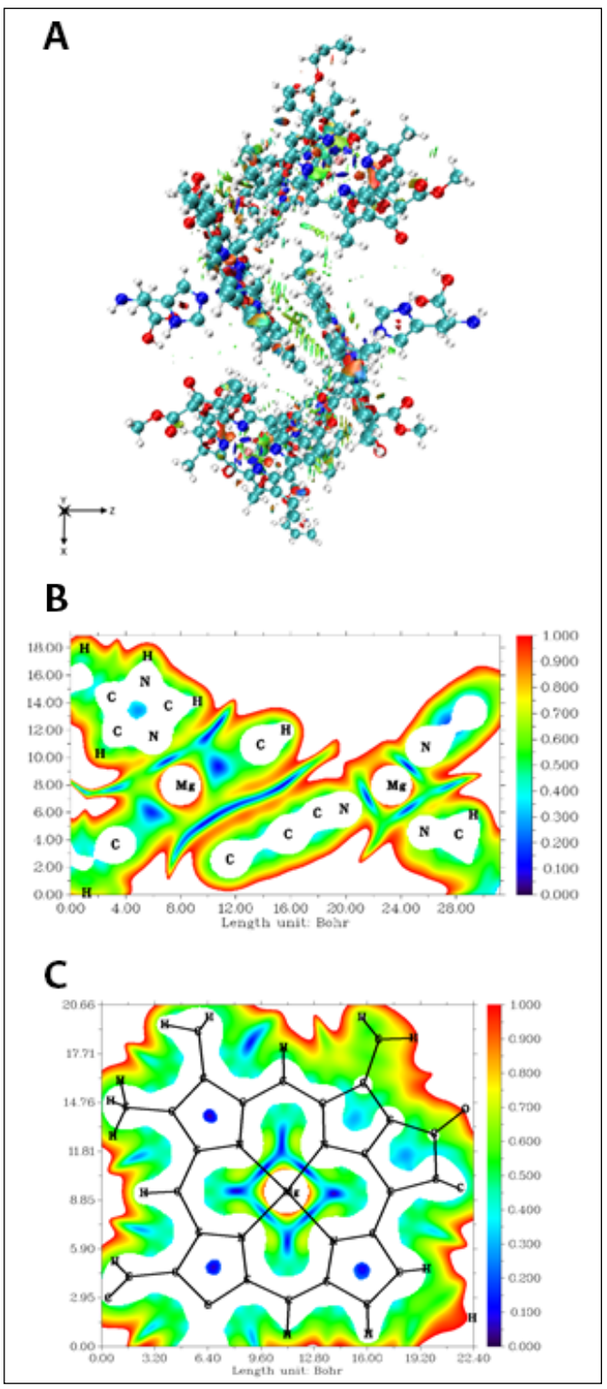

Figure 7. A: Visualization of non-covalent interactions of the system of six chlorophyll-A molecules as isosurfaces (Van-der-Waals interactions demarcated by the color green). B: Reduce density gradient (RDG) in chlorophyll-A system (parallel configuration), sliced perpendicular to interaction, critical values (RDG≈0) correspond to non-covalent interactions (strong Van-der-Waals interactions) between fragments. C: RDG values around the magnesium ion of chlorophyll-A system. White within the plotted area of B and C indicates values of RDG > 1.

For fragments five and six, the isosurface diagram (**figure 7A**) shows critical values within the range 1.400/-0.030 sign$(\lambda_2)\ \rho(r)$ and lower, corresponding to Van der Waals and weak attractive non-covalent interactions. **Figure 7A** shows the visualization of non-covalent interactions as isosurfaces, where blue color is hydrogen and halogen bonds, green is Van der Waals interactions, red is strong repulsion, π-π interactions and steric effects. Van der Waals interactions can be found in the plane between fragments five and six of the system. The high degree of Van der Waals interactions is caused by the chlorin rings of neighboring Ch-A, located near the considered regions. This indicates the presence of polarization of electron shells and the interaction of dipole moments between molecules (**figure 7B**).

Conclusion

Analysis of electron density and atomic charge distribution in the molecular system consisting of six Ch-A molecules showed that fragments interact through ionic bonds. With an increase in the number of Ch-A molecules, the total charge of the entire system remains neutral, and the total charge of the fragments included in the composition is distributed unevenly. Total atomic charge in systems consisting of two Ch-A molecules with different relative positions (Ch-A-1 and Ch-A-2) remains neutral. At the same time, the total charge of chlorin with a methyl group and a phytol "tail" of one fragment in the Ch-A-1 system is negative (-0.144 a.u.), and the second is positive (+0.196 a.u.). The histidine molecules attached to this system have the opposite charge (-0.192 and +0.140 a.u., respectively). The distributions of atomic charges for the system of four Ch-A molecules and two residues (Ch-A-6) indicate a significant redistribution of the atomic charge when several Ch-A molecules appear. The low total atomic charge of the fragments one and two (-0.003 and -0.014 a.u.) derives from the lack of coordination with the Mg ion. This affects insignificantly their participation in the absorption spectra in the UV region. According to the calculations, the coordination of the chlorin ring on the Mg ion causes a significant redistribution of atomic charges, and therefore the electron density which affects the absorption capacity in the UV region of the spectrum. This allows the system consisting of Ch-A to have a high absorption capacity of visible radiation.

The calculation and analysis of the absorption spectra showed transitions from the ground to excited states that occur between mixed molecular orbitals of the nearest Ch-A molecules. Such transitions are carried out with charge transfer (electron density). Thus, the absorption region is formed by transitions not only within one Ch-A, but also between closely located ones.

Theoretical photoelectron spectra were obtained, which clearly show the structure of the valence electron levels involved in the energy transfer. The use of topological methods for analyzing non-covalent interactions (RDG) showed the presence of strong hydrogen bonds and Van der Waals interactions. That indicates the occurrence of polarization between closely located Ch-A molecules and the interaction of the dipole moments of the molecules. For the remains of Ch-A molecules (without Mg coordination), "strong" Van der Waals interactions were not detected.

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References

[1] J. W. Murray, "Photosynthesis: Light and Life", *Biochemist*, vol. 35, no. 5, pp. 4–7, 2013. DOI: https://doi.org/10.1042/BIO03505004

[2] A. Constantin, *Rebeiz Chlorophyll Biosynthesis and Technological Applications*, Springer, 2014.

[3] G. Britton, *The biochemistry of natural pigments*, Cambridge University Press, 1986.

[4] S. M. Petrovic, J. B. Zvezdanović, T. D. Anđelković and D. Z. Marković, "The identification of chlorophyll and its derivatives in the pigment mixtures: HPLC-chromatography, visible and mass spectroscopy studies", *Advanced technologies*, vol. 1, pp. 16–24, 2012.

[5] T. van Mourik, M. Bühl and M. P. Gaigeot, "Density functional theory across chemistry, physics and biology", *Phil. Trans. R. Soc.* A., vol. 372, 2014. DOI: https://doi.org/10.1098/rsta.2012.0488

[6] A. M. Hussein, Y. H. Zaki, S. A. Elroby and A. M. Hassanien, "Optical spectroscopic and DFT/TD-DFT studies on a new synthesized N, S-containing organic heterocyclic", *Physica E: Low-dimensional Systems and Nanostructures*, vol. 153, 2023. DOI: https://doi.org/10.1016/j.physe.2023.115764

[7] M. Vasilescu *et al*., "Optical spectroscopic characteristics and TD-DFT calculations of new pyrrolo[1,2-b]pyridazine derivatives", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 194, no. 2–3, pp. 308–317, 2008. DOI: https://doi.org/10.1016/j.jphotochem.2007.08.029

[8] V.V. Korochentsev *et al*., "Electronic structure of guanidine and its derivatives from X-ray photoelectron spectroscopy and density functional theory studies", *Russian Journal of General Chemistry*, vol. 84, pp. 25–32, 2014. DOI: https://doi.org/10.1134/S1070363214010071

[9] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, "Revealing noncovalent interactions", *Journal of the American Chemical Society*, vol. 132, no. 18, pp. 6498–6506, 2010. DOI: https://doi.org/10.1021/ja100936w

[10] V. Ponnuchamy, A. Sandak and J. Sandak, "Multiscale modelling investigation of wood modification with acetic anhydride", *Physical Chemistry Chemical Physics*, vol. 22, no. 48, pp. 28448-28458, 2020. DOI: https://doi.org/10.1039/d0cp05165a

[11] M. Medimagh *et al*., "Investigations on the non-covalent interactions, drug-likeness, molecular docking and chemical properties of 1,1,4,7,7- pentamethyldiethylenetriammonium trinitrate by density-functional theory", *Journal of King Saud University - Science*, vol. 35, no. 4, 2024. DOI: https://doi.org/10.1016/j.jksus.2023.102645

[12] A. H. Bakheit, R. Al-Salahi and A. A. Al-Majed, "Thermodynamic and Computational (DFT) Study of Non-Covalent Interaction Mechanisms of Charge Transfer Complex of Linagliptin with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and Chloranilic acid (CHA)", *Molecules*, vol. 27, no. 19, 2022. DOI: https://doi.org/10.3390/molecules27196320

[13] A. A. Granovsky, Firefly: computational chemistry program v.8.1, http://classic.chem.msu.su/gran/firefly/index.html

[14] M. W. Schmidt *et al*., "General Atomic and Molecular Electronic Structure System", *Journal Computational Chemistry*, vol. 14, no. 11, pp. 1347–1363, 1993. DOI: https://doi.org/10.1002/jcc.540141112

[15] T. Yanai, D. P. Tew and N. C. Handy, "A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP)", *Chemical Physics Letters*, vol. 393, no. 1–3, pp. 51–57, 2004. DOI: https://doi.org/10.1016/j.cplett.2004.06.011

[16] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior", *Phys. Rev.* A., vol. 38, no. 6, pp. 3098–3100, 1988. DOI: https://doi.org/10.1103/physreva.38.3098

[17] M. Li, J. R. Reimers, M. J. Ford, R. Kobayashi and R. D. Amos, "Accurate prediction of the properties of materials using the CAM-B3LYP density functional", *Journal of Computational Chemistry*, vol. 42, no. 21, pp. 1486–1497, 2021. DOI: https://doi.org/10.1002/jcc.26558

[18] Z. L. Cai, M. J. Crossley, J. R. Reimers, R. Kobayashi and R. D. Amos, "Density Functional Theory for Charge Transfer: The Nature of the N-Bands of Porphyrins and Chlorophylls Revealed through CAM-B3LYP, CASPT2, and SAC-CI Calculations", *The Journal of Physical Chemistry* B, vol. 110, pp. 15624–15632, 2006. DOI: https://doi.org/10.1021/jp063376t

[19] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, "Selfconsistent molecular orbital methods. XX. A basis set for correlated wave functions", *J. Chem. Phys*., vol. 72, no. 1, pp. 650–654, 1980. DOI: https://doi.org/10.1063/1.438955

[20] N. Gelfand, A. Freidzon, V. Vovna, "Theoretical insights into UV–Vis absorption spectra of difluoroboron β-diketonates with an extended π system: An analysis based on DFT and TD-DFT calculations", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 216, pp. 161–172, 2019. DOI: https://doi.org/10.1016/j.saa.2019.02.064

[21] D- Kröner, J. P. Götze, "Modeling of a violaxanthin–chlorophyll b chromophore pair in its LHCII environment using CAM-B3LYP", *Journal of Photochemistry and Photobiology B: Biology*, vol. 109, pp. 12–19, 2012. DOI: https://doi.org/10.1016/j.jphotobiol.2011.12.007

[22] M. A. Kavanagh, J. K. G. Karlsson, J. D. Colburn, L. M. C. Barter and I. R. Gould, "A TDDFT investigation of the Photosystem II reaction center: Insights into the precursors to charge separation", *Proceedings of the National Academy of Sciences*, vol. 117, no. 33, pp. 19705–1971, 2020. DOI: https://doi.org/10.1073/pnas.1922158117

[23] G. Saleh, C. Gatti and L. Lo Presti, "Non-covalent interaction via the reduced density gradient: Independent atom model vs experimental multipolar electron densities", *Computational and Theoretical Chemistry*, vol. 998, pp. 148–163, 2012. DOI: https://doi.org/10.1016/j.comptc.2012.07.014

[24] T. Lu, F. Chen, "Multiwfn: A Multifunctional Wavefunction Analyzer", *Journal of Computational Chemistry*, vol. 33, pp. 580–592, 2012. DOI: https://doi.org/10.1002/jcc.22885

[25] G. R. Seely and J. S. Connolly, "Fluorescence of photosynthetic pigments in vitro", in *Light emission by plants and bacteria*, Academic Press, pp. 99–133, 1986.

[26] S. Jacquemoud and S. Ustin, *Spectroscopy of Leaf Molecules. In Leaf Optical Properties*, Cambridge University Press, 2019.

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