

Ab-Initio Calculation of Chlorophyll-b UV-Vis Absorbance Spectra using Gaussian 09 Based Density Functional Theory (DFT)

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ABSTRACT

In this study, the optimization structure and the UV-Vis spectra of a chlorophyll-b molecule are observed under ground state condition using the density functional theory and the time dependent density functional theory. The optimization of a chlorophyll-b molecule is done using several basis sets and it is found that the cc-pVDZ basis set is the most suitable basis set since it gives the most minimum energy. There are two structures of chlorophyll-b constructed, one is having phytol chain perpendicular with main group while the other one is having phytol chain parallel with main group. The two structures in chlorophyll are given the similar result, the difference only at the direction of curvature at chain. This happens because the optimized structure must calculate whole system and the SCF must be achieved. Furthermore, as UV-Vis absorbance spectra is calculated, the two maximum peaks are observed at 448 nm and 590 nm.

Keywords: excitation, chlorophyll-b, orbital, transition

1. INTRODUCTION

Solar cells have played role as an alternative energy concern. Incident Photon to Electron Conversion Efficiency (IPCE) from solar cell is one of the main problem. Theoretically, the highest IPCE in solar cell is around 33%, so not all of the energy from solar cell is converted to electricity. Plant or organic material has high IPCE, for example perovskite. Although perovskite solar cell still do not have the best efficiency due to conversion energy, there is an alternative organic material such as chlorophyll-b which can be used as a light harvesting active layer in solar cell. Chlorophyll has been well known as molecule that is used in the experimental and theoretical studies [1]-[6]. The advantage of utilizing chlorophyll is having low cost production and does not damage nature. Another thing is that the chlorophyll will give good IPCE.

Since, the efficiency very depends on how much light energy convert to electricity, the absorption of light energy is important. Therefore, in this study the energy absorption particularly at the peaks of UV-Vis spectra, as it is know that energy absorption depends at the peaks in UV-Vis spectra, from chlorophyll is investigated.

The UV-Vis Spectra from single molecule chlorophyll-b will be observed to get the maximum peak. Furthermore, this research will be a reference for further investigation on how to harvest energy from organic material such as chlorophyll.

2. THEORY

2.1. The Structure of Chlorophyll-b

Chlorophyll-b is an organic material and one of the most abundant pigments on organism which

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responsible for trapping the light energy. It has chemical formulation $C_{55}H_{70}O_6N_4Mg$ which have porphyrin-like ring with magnesium ion is located in its center and hydrophobic hydrocarbon tail. Therefore, the total of number of atoms that we consider in this work is 136 atoms. These number comes from 55 carbon, 70 hydrogen, 6 oxygen, 4 nitrogen, and 1 magnesium atom. Since chlorophyll-b has the aldehyde group then it has a difference characteristic compared with other chlorophyll.

The energy level of Chlorophyll-b can be observed from its HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Un-occupied Molecular Orbital). Determination of the Chlorophyll-b spectra relies on 4-orbital model suggested by Gouterman [5]. The Gouterman's theory only considers the two highest HOMO and two lowest LUMO. So far, the electronic spectra of chlorophyll is restricted in semi-empirical approaches [5].

2.2. Molecular Orbital

Molecular orbitals (MO) are constructed from atomic orbitals (AO). Therefore, we can derives the wave function from the electron using this equation [7],

$$\psi_j(\vec{r}, t) = \sum_{i=1}^n c_{ij} \chi_i \quad 1$$

The part of molecular orbitals symbolized by wave function ψ_j as summarized from the total n constituent orbital of atom χ_i . In the chemical process, molecular orbitals are constructed from combination of atomic orbitals through the hybridization process. This process happens when the electron from every atomic orbitals interacts with other orbital and construct chemical bonding. Hence, this bonding will affect the molecular structure.

2.3. Basis Set

Gaussian 09 molecule orbitals are constructed by defining the basis set. The Basis set will define the electron as a wave function. Furthermore, the basis set is differentiated by the quantity of primitive and contracted function of them. There are many kinds of basis sets [8]-[9], such as:

1. *Fixed size* basis set
2. *Split valence* basis set
3. *Corelation-consistent* basis set
4. *Efective core potential* basis set

2.4. Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD DFT)

Density Functional Theory (DFT) is one of accurate method for computing many body system problems which is approach through electronic structure based on quantum mechanics [10]-[11]. This method is based on Kohn-Sham approximation to solve the Schrödinger equation.

The Kohn Sham equation for formulation the Time Dependent Density Functional Theory is shown as this equation [12],

$$i \frac{\partial}{\partial t} \Psi_i(\vec{r}, t) = \left(-\frac{1}{2} \nabla_i^2 + \vartheta(\vec{r}, t) + \int d^3r' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + \frac{\delta A_{xc}[\rho]}{\delta \rho(\vec{r}, t)} \right) \Psi_i(\vec{r}, t) = \hat{F}^{KS} \Psi(\vec{r}, t) \quad 2$$

where,

$$\rho(\vec{r}, t) = \rho_s(\vec{r}, t) = \sum_i^N |\Psi_i(\vec{r}, t)|^2 \quad 3$$

The TD-DFT (Time Dependent Density Functional Theory) was calculated through linear responses from DFT equation. Using perturbation potential $v(\vec{r}, t)$ as oscillation potential of electrical field $v_l(\vec{r}, t) = E_z \cos wt$ as an assumption. The potential given at $t = t_0$. So the external potential can be written as,

$$v_{ext}(\vec{r}, t) = v_0(\vec{r}) + v_l(\vec{r}, t) = \begin{cases} v_0(\vec{r}), & t \leq t_0 \\ v_0(\vec{r}) + E_z \cos wt, & t > t_0 \end{cases} \quad 4$$

where $v_0(\vec{r})$ is Coulomb potential between electron and nuclei interactions.

$$v_0(\vec{r}) = - \sum_K^N \frac{Z_K}{|\vec{R}_K - \vec{r}|} \quad 5$$

The value of $\rho(\vec{r}, t)$ is obtained from differential of $\rho_0(\vec{r})$. Therefore, the particle with interaction can be written as,

$$\rho(\vec{r}, t) - \rho_0(\vec{r}) \approx \rho_l(\vec{r}, t) = \int dt' \int d\vec{r}' \chi(\vec{r}, t, \vec{r}', t') v_l(\vec{r}', t') \quad 6$$

with response function interaction is,

$$\chi(\vec{r}, t, \vec{r}', t') = \left. \frac{\delta \rho(\vec{r}, t)}{\delta v_{ext}(\vec{r}', t')} \right|_{v_0} \quad 7$$

For particle without interaction is,

$$\chi \rho_l(\vec{r}, t) = \int dt' \int d\vec{r}' \chi(\vec{r}, t, \vec{r}', t') v_{s,l}(\vec{r}', t') \quad 8$$

With response function interaction is,

$$\chi(\vec{r}, t, \vec{r}', t') = \left. \frac{\delta\rho(\vec{r}, t)}{\delta v_{ext}(\vec{r}', t)} \right|_{v_0[\rho_0]} \quad 9$$

Response function from system with interaction showed as transition energy from system.

2.5. Calculation Methods

The computer cluster used in this research was SUPERMICRO blade server with the model of SBE-720E-R75. The cluster contains 1 main node and 19 compute nodes, which each node has 2 processors of Intel Xeon X5650, ECC type RAM with capacity of 8 GB, 1 TB HDD capacity for main node, and 150 GB HDD capacity for each of compute nodes. The operating system used in this cluster was Rocks version 7.0 with the codename Manzanita.

The calculations in this research is conducted using Gaussian 09, developed by John Pople in 1970 [13]-[14]. Single molecule chlorophyll-b is calculated using B3LYP method with several basis sets (6-31G(d), LANL2DZ, cc-pVDZ, and cc-pVTZ). Basis set is used to optimize the geometry of chlorophyll-b until the best of optimize parameter result is achieved.

The initial structure of single molecule of Chlorophyll-b is obtained from PubChem with the total number of atom is 136 [17]. The Chlorophyll-b structure is then modified using AVOGADRO (An Advance Semantic Chemical Editor, Visualization, and Analysis Platform) [15]-[16], as depicted in figure 1.

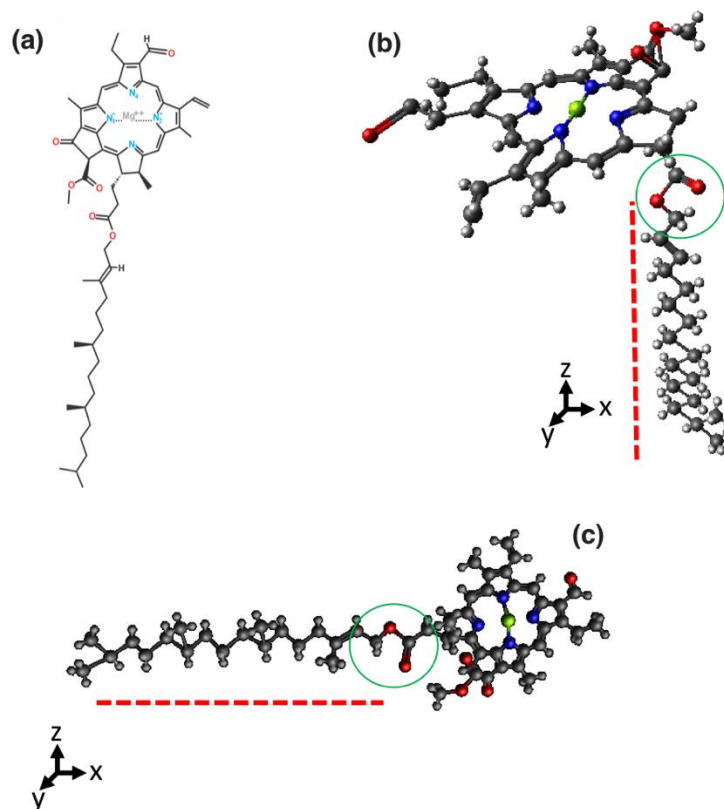


Figure 1. Chlorophyll-b structure (a) from PubChem, (b) Model 1: modification design of chlorophyll-b at $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail perpendicular with Porphyrin-like ring, (c) Model 2: modification design of chlorophyll-b at $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail parallel with Porphyrin-like ring.

3. Result and Discussion

3.1. Optimization Result

Optimization process is done by using Gaussian 09 with B3LYP (Becke, three-parameter, Lee-Yang-Parr) for Model 1 (Fig. 1.b). This process is used to calculate the length of the bonds between atoms in molecules. Chlorophyll-b has two Mg-N bonding with the same length. The Mg-N bond length becomes one of parameter that is used for optimization. The optimization result is shown in figure 2.

Table 1, shows that basis set affects the bond length of N-Mg. It is shows that using basis set 6-31G(d) gives difference bond length between DFT calculation and reference at around 0.07 Å to 0.08 Å. Calculation using basis set LANL2DZ has a closer result to references around 0.06 Å, because LANL2DZ calculates every AO in a system using Effective Core Potential (ECP). ECP will define every charges when the calculation is started and hence makes the density function calculation more precisely. Whereas, calculation using the correlation consistent basis set (cc-pVDZ and cc-pVTZ) with correlation consistent polarized function gives unchanged polarization during the calculation. Since unchanged polarization occurred, hence, the calculation much faster and the results are more accurate. From table 1 we can conclude that the cc-pVDZ and cc-pVTZ are a suitable basis set for the chlorophyll-b in this study.

Table 1. Bond length for several basis set compared with references [18]-[19].

Bonding	Bond length (Å)					
	References [18]-[19]	Initial	Basis sets			
			6-31G(d)	LANL2DZ	cc-pVDZ	cc-pVTZ
N ₁ -Mg	1.95	2.329	2.020	2.014	2.020	2.012
N ₂ -Mg	1.95	2.270	2.033	2.029	2.034	2.025
N ₃ -Mg	1.95	2.749	2.153	2.150	2.153	2.148
N ₄ -Mg	1.95	3.000	2.098	2.087	2.098	1.090
C=O	1.21	7.951	1.228	1.265	1.227	1.222
O-H	0.98	1.032	1.109	1.105	1.117	1.105
C=C	1.34	2.262	1.396	1.408	1.398	1.391
C-C	1.54	2.253	1.453	1.448	1.455	1.450
C=N	1.30	2.202	1.385	1.407	1.380	1.381
C-N	1.32	1.893	1.357	1.376	1.359	1.351

Table 2. Stationary energy for chlorophyll-b using several basis set in Gaussian 09.

Basis set	Maximum Force	RMS Force	Maximum Displacement	RMS Displacement	Predicted Change in Energy
6-31G(d)	0.000009	0.000002	0.005593	0.000898	-3.372x10 ⁻⁸
LANL2DZ	0.000010	0.000001	0.004191	0.000888	-3.477x10 ⁻⁸
cc-pVDZ	0.000005	0.000001	0.000886	0.000178	-3.372x10 ⁻⁹
cc-pVTZ	0.000019	0.000003	0.000755	0.000188	-2.256x10 ⁻⁸
Threshold	0.000450	0.000300	0.001800	0.001200	

Table 2, shows the smallest maximum force achieved when using cc-pVTZ basis sets, in other hand the smallest maximum displacement achieved when using cc-pVTZ followed by cc-PVDZ. In this study, the cc-pVDZ and cc-pVTZ basis sets are suitable basis set for calculation. Furthermore, Self Consistence Field (SCF) is also one of another parameter for obtaining good result. The SCF energy and CPU time are shown in Table 3.

Table 3. SCF energy and CPU time for several basis set.

Basis set	SCF energy (Hartree)	SCF energy (eV)	CPU time
6-31G(d)	-3008.66392372	-81869.945855763	1d 11h 27m 23.1s
LANL2DZ	-2808.97507741	-76436.133555722	1d 16h 04m 54.7s
cc-pVDZ	-3008.81014942	-81873.924861210	5d 21h 45m 01.2s
cc-pVTZ	-3009.66124500	-81897.084360184	<i>not enough memory</i>

The chlorophyll-b is considered quite big molecules with a lot of interatomic interactions. The methyl group (CH₃) which appear at the hydrophobic hydrocarbon tail have many weak interactions between each other to maintain its structures. Interaction in porphyrin-like ring, in addition, is also considered complicated. Furthermore, the cc-PVTZ basis set is based on the extrapolation techniques, which take in into account the valence and core electron correlation. To this end, based on those condition the wave number and density that are generated during the calculation becomes large. In this regard, the number of functions also increases double than that cc-PVDZ basis set. From Table 3, calculation using cc-pVTZ basis set resulting unfinished calculation due to insufficient memory of hardware (more detailed hardware specification refers to section 2.6).

From Table 2 and 3 we can conclude that the best basis set in this study is cc-pVDZ. Even though another basis set such as LANL2DZ, cc-pVTZ, and 6-31G(d) basis sets have their own advantages, but after considering several parameters listed in Table 1, 2 and 3, the best basis set is still cc-pVDZ.

Figure 2 and figure 3 are the optimized structure of chlorophyll- b using several basis set. It shows that the CH₂CH₂COO-Phytyl tail of chlorophyll- b is curved. From figure 2 and figure 3, we obtain that using several different basis sets makes the CH₂CH₂COO-Phytyl tail generally curved. This happens because the CH₂CH₂COO-Phytyl tail has C=C and C=O bonding, which will make the tail curved, as indicated by the red dashed line. Furthermore, after considering the results from several optimization parameters, LANL2DZ and cc-PVDZ basis sets will be used for calculating the UV-Vis spectra.

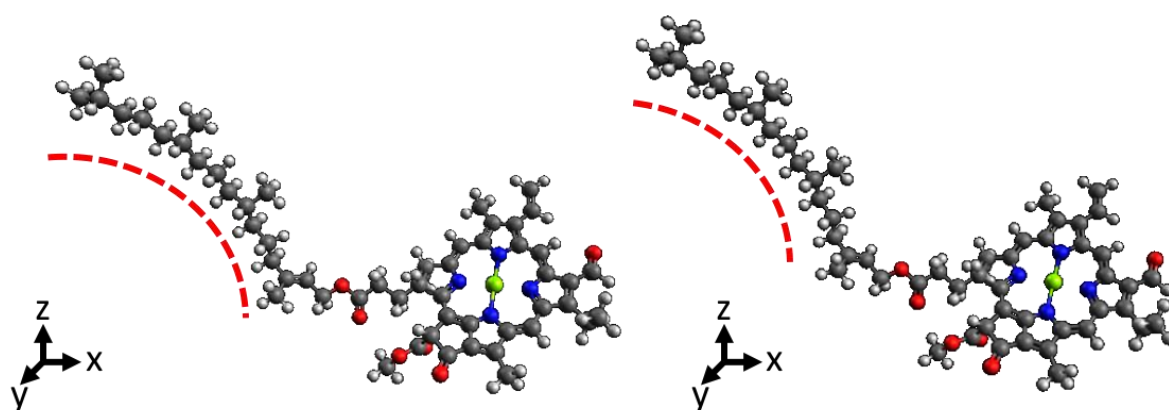


Figure 2. Visualization results of chlorophyll-b from optimization process using 6-31G(d) basis set (left) and LANL2DZ basis set (right).

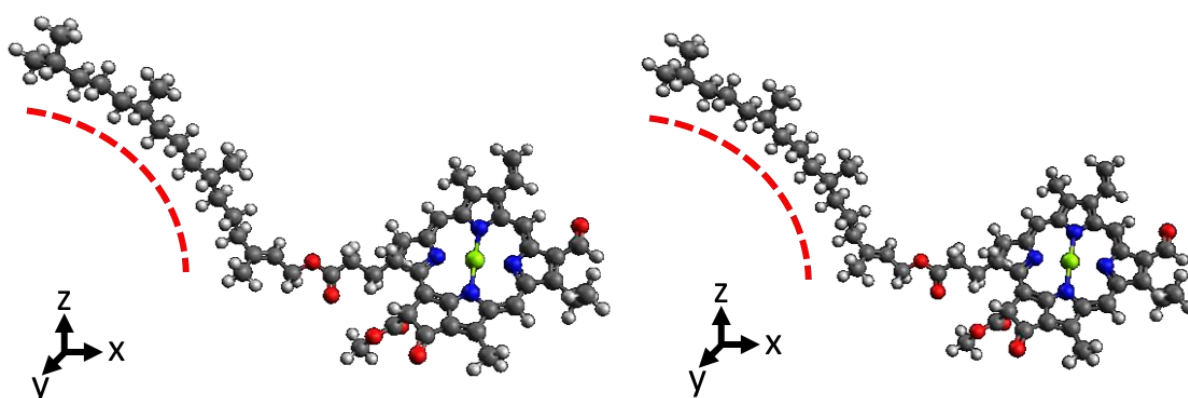


Figure 3. Visualization results of chlorophyll-b from optimization process using cc-pVDZ basis set (left) and cc-pVTZ basis set (right).

3.2. Correlation between the difference of CH₂CH₂COO-Phytyl tail in optimization result

The Position of CH₂CH₂COO-Phytyl in molecule model 1 (figure 1.b) will influence the optimization result which was shown in the figure 3 and 4. It is shown by the CH₂CH₂COO-Phytyl tail curved that make it different from the initial configuration. Therefore, the configuration of the chlorophyll-b in initial model 1 (figure 1.b.) and model 2 (figure 1.c.) will influence the calculation results. Table 4 and table 5 shows the SCF energy and bond length from different initial configuration of chlorophyll-b using 2 basis sets (LANL2DZ and cc-pVDZ),

Table 4. Difference of SCF energy from 2 models of chlorophyll-b using LANL2DZ and cc-pVDZ basis sets.

	Basis	SCF energy (Hartree)	SCF energy (eV)	CPU time
Model 1	LANL2DZ	-2808.97507741	-76436.133555722	1d 16h 04m 54.7s
Model 2	LANL2DZ	-2808.97483817	-76436.127045668	2d 11h 30m 40.8s

Model 1	cc-pVDZ	-3008.81014942	-81873.924861210	5d 21h 45m 01.2s
Model 2	cc-pVDZ	-3008.81109123	-81873.950489175	3d 15h 41m 16.1s

Table 5. Bond length in chlorophyll-b for model 1 and model 2 using LANL2DZ and cc-pVDZ basis sets.

Bonding	Bond length (Å)				
	References [18]-[19]	Basis set used in Model 1		Basis set used in Model 2	
		LANL2DZ	cc-pVDZ	LANL2DZ	cc-pVDZ
N ₁ -Mg	1.95	2.014	2.020	2.017	2.019
N ₂ -Mg	1.95	2.029	2.034	2.028	2.03
N ₃ -Mg	1.95	2.150	2.153	2.148	2.156
N ₄ -Mg	1.95	2.087	2.098	2.086	2.097
C=O	1.21	1.265	1.227	1.096	1.228
C=C	1.34	1.408	1.398	1.411	1.402
C-C	1.54	1.448	1.455	1.470	1.461
C=N	1.30	1.407	1.380	1.405	1.384
C-N	1.32	1.376	1.359	1.375	1.357

Table 4 and table 5 shows no significant differences between model 1 and model 2. Basis set LANL2DZ used in model 2 gives lower energy than model 1. This difference is due to initial configuration of chlorophyll-b molecule, particularly CH₂CH₂COO-Phytol tail in model 2, affect the main group and then it will generate molecular orbitals and total energy of chlorophyll-b bigger than others. The cc-pVDZ basis set used in model 2 has bigger energy than model 1. Hence, the position of the tail, in this case, will generate the molecular orbital fewer, which is does not interact with the main group.

On figures 4 and 5, we can see some differences in CH₂CH₂COO-Phytol chain. Figure 5 shows the position of CH₂CH₂COO-Phytol chain in model 1 (figure 4.a) in which the direction of the curvature approaching the main group (CH₂-CH₃ bonding) in the middle of the chain. Whereas in model 2 (figure 4.b), directions of the CH₂CH₂COO-Phytol curvature move as it left the main group and lift the atoms at the end of the CH₂CH₂COO-Phytol chain. Overall, the LANL2DZ basis set makes the position of CH₂CH₂COO-Phytol chain chlorophyll-b molecule model perpendicular to the main group.

Figure 5 shows the result of the using cc-pVDZ basis set. The results of model 1 are similar to that of model 1 (figure 5.a) of LANL2DZ basis. However, it has a significant difference with model 2 (figure 5.b) for the cc-pVDZ basis set. The position of CH₂CH₂COO-Phytol in cc-pVDZ model 2 is under the main group (does not affect the main group when defining the molecular orbital) and it has a similar curvature direction with model 2 (figure 4.b) of a LANL2DZ basis set.

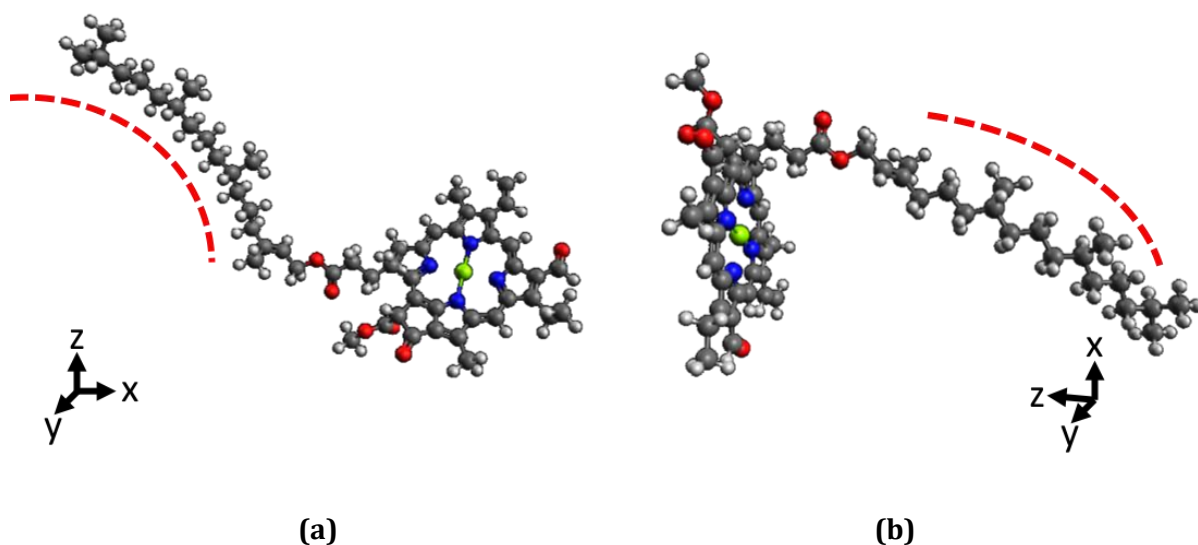


Figure 4. Visualization result from 2 models of chlorophyll-b with LANL2DZ basis set resulted (a) from model 1, (b) from model 2.

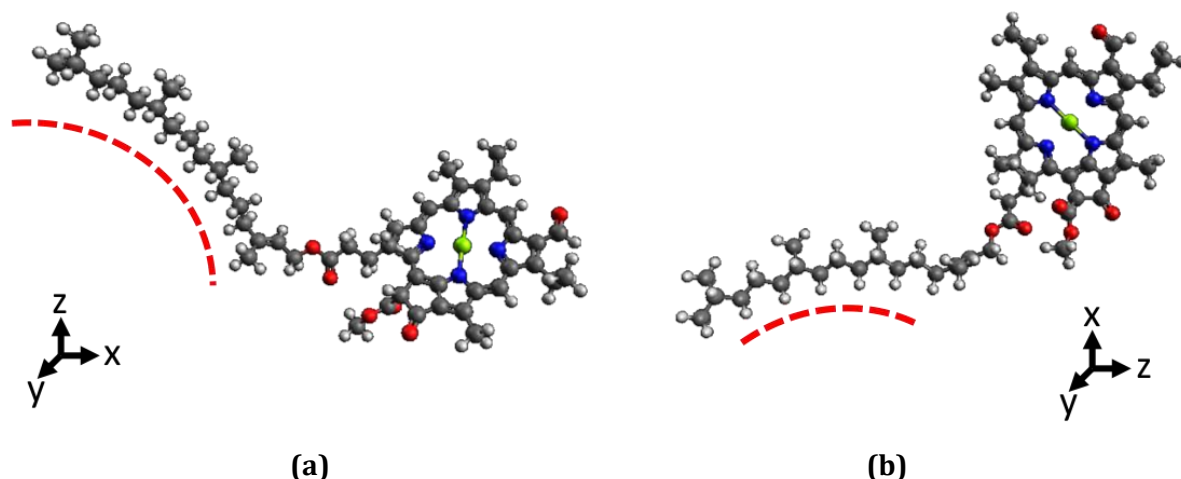


Figure 5. Visualization result from 2 models of chlorophyll-b with cc-pVDZ basis set resulted (a) from model 1, (b) from model 2.

The interaction between the hydrophobic hydrocarbon tail and porphyrin-like ring in the chlorophyll-b molecule interact through ether group (C-O-C bond). The angle of the C-O-C bond is reduced from $\sim 120^\circ$ into $\sim 109^\circ$ after optimization, which make the interaction between hydrocarbon tail and porphyrin-like ring become stronger yield to the curving the hydrocarbon tail. Moreover, the curvature of the hydrocarbon tail is also due to the C-C and C=C bonds relaxation. Initially, the bond length of the C-C and C=C is 1.529 \AA and 1.352 \AA , respectively. Upon relaxation, the bond length will reduce $\sim 0.2 \text{ \AA}$ yield to suppressed the hydrocarbon tail (which is indicated by the dashed curved line). Therefore, compared to the Fig.1(c) and (b) we can see the difference between the shape of the tail, which is initially flat and perpendicular to the porphyrin ring becomes curved after optimization.

The result of optimization using LANL2DZ and cc-pVDZ basis set showed a slight difference. Visualization of the optimization shows that the molecule of chlorophyll-b has the shape of CH₂CH₂COO-Phytyl chain curved. However, the comparison of bond lengths, SCF energy, and visualization result from chlorophyll-b makes the model 2 (figure 5.b) using cc-pVDZ basis set more suitable for the chlorophyll-b molecule in this research.

3.3. Molecular Orbitals

3.3.1. Molecular orbital of chlorophyll-b with LANL2DZ basis set

The LANL2DZ basis set gives the number as many as 773 orbital molecular orbital. There are 239 pieces of HOMO and 534 pieces of LUMO that resulted from Gaussian. Each condition has an orbital energies ranging from -522.37 eV to 209.297 eV. Figure 6 shows the shape visualization of the four molecular orbitals of chlorophyll-b using LANL2DZ basis set. Orbital molecules of chlorophyll-b are mostly located in the main group. Hence, it will make the electrons in Mg-N bonding will greatly affect the calculation results. Only few molecular orbitals that exist on the tail will participate in the determination of UV-Vis spectrum. Based on the results, the difference between HOMO and LUMO energy is 2.498 eV. This difference will be the basic theory for the calculation of chlorophyll-b absorbance spectrum. Therefore, electron needs energy more than 2.498 eV to move from HOMO orbital towards LUMO, likewise its energy to move from another orbital.

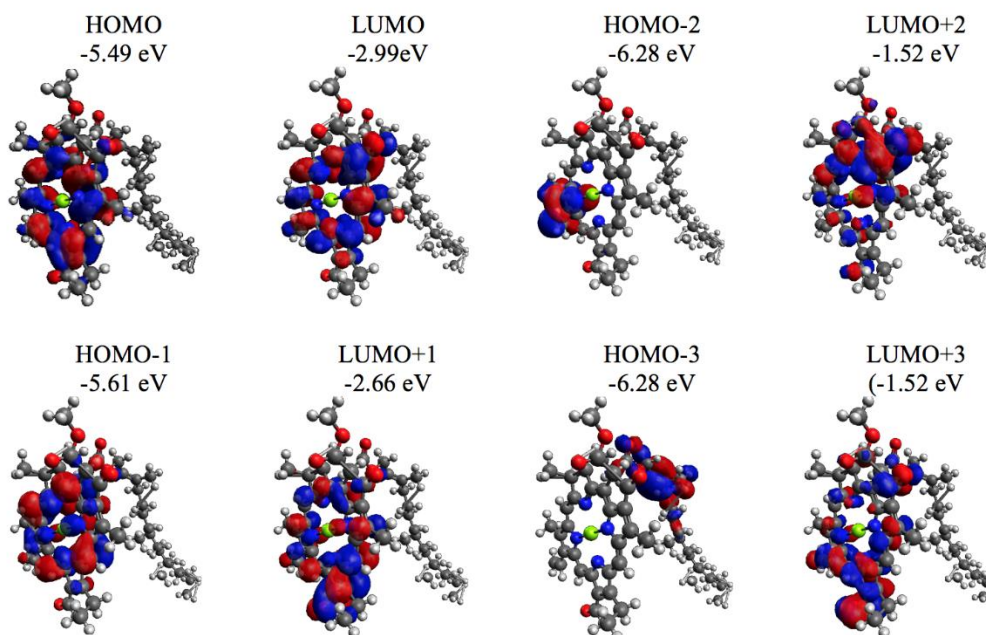


Figure 6. Orbital molecules shape of chlorophyll-b using LANL2DZ basis set from HOMO to HOMO-3 and from LUMO to LUMO+3.

3.3.2. Molecular orbital using cc-pVDZ basis set

The cc-pVDZ basis set gives the different results in determining the molecular orbitals of chlorophyll-b. The number of molecular orbitals using this basis set is 1278 pieces. The energy

range starts from -1272.842 eV until 71.062 eV . We obtained 244 and 1034 occupied orbital and unoccupied orbitals.

In figure 7, we can see only few orbital of chlorophyll-b molecules that will influence the determination of UV-Vis spectrum. Figure 7 also shows the similar result when using LANL2DZ basis set, that the orbital molecules mostly at the main group. Although, there are differences in the number and the shape of the molecular orbitals the differences are constituted by a wave function which is created by the basis set used.

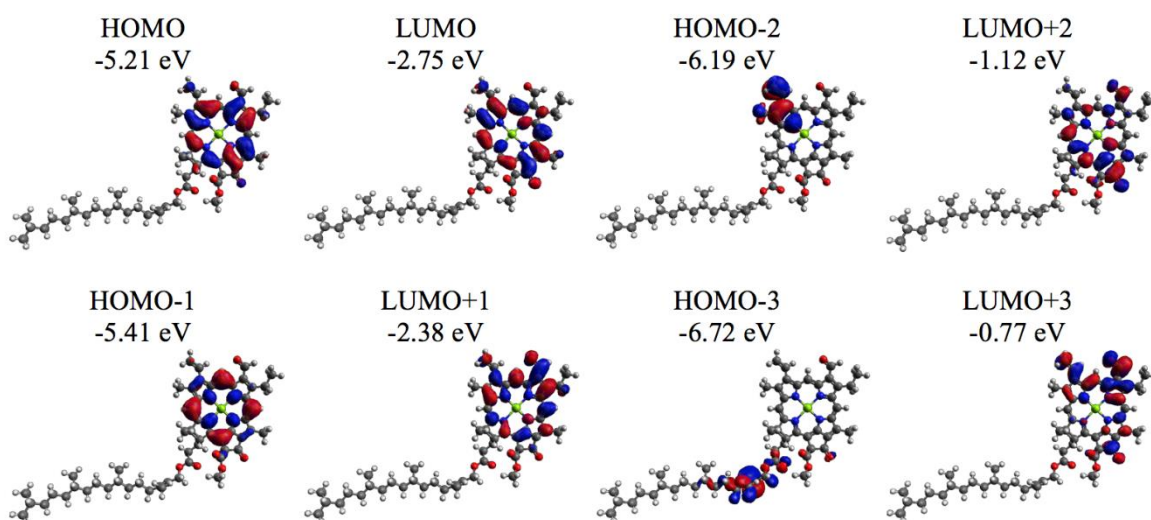


Figure 7. Orbital molecules shape of chlorophyll-b using cc-pVDZ basis set from HOMO to HOMO-3 and from LUMO to LUMO+3.

The molecular orbital shape of chlorophyll-b almost has similarities with LANL2DZ basis set. Significant differences can be seen in each orbital energy molecule present. The cc-pVDZ basis set gives the HOMO energy of -5.21 eV, whereas if the basis set LANL2DZ is used, the HOMO energy is -5.49 eV. There is differences about 0.29 eV between two basis sets. This difference is due to the characteristics of each molecular orbital in determining the amount of available wave function.

In addition to the energy differences, there are other factors that have an important role in determining the absorbance spectrum of chlorophyll-b, such as the flexibility of electrons movement in a molecule. Hence, the selection of the basis set is very important. For example, LANL2DZ is good for optimization, but not for UV-Vis Spectra calculation. Therefore, to get more simple and accurate calculation the selection of larger basis set is used to cover the shortage of available wave function.

3.4. UV-Vis Absorbance Spectrum

After performing the optimization, the next step is to determine the absorbance spectrum of the molecule. Results, which is issued by Gaussian output file, will show the excitation energy (in nanometers) and the strength of the oscillation (in oscillator strength), along with details about other information. To construct the UV-Vis Spectra curves, Stephens et al. [20] explains how to

make the results of plot the absorbance spectrum from the power and strength of the dipole oscillation. Construction of the UV-Vis absorbance spectra from gaussian output use equation in reference no 20 (see equation 10)

$$\varepsilon_i(\tilde{\nu}) = \varepsilon_i^{max} \exp \left[- \left(\frac{\tilde{\nu} - \tilde{\nu}_i}{\sigma} \right)^2 \right] \quad 10$$

where $\tilde{\nu}_i$ is the excitation energy (in wave number), ε_i^{max} is maximum value of ε_i at maximum band, and σ is deviation standard (in wave number) usually is 0.4 eV, but in this research we used 0.06 eV.

In other to obtain UV-Vis spectrum of chlorophyll-b, Comar et al. [21] used spinach leaves as a subject of experiment. The results showed that the highest UV-Vis absorbance appears at a wavelength of 454 nm [21], this is known as Soret band peak. Besides, there was also a dominant absorbance at 643 nm, which is known as a Q-band peak [21].

In this calculation, better result of UV-Vis spectra is obtained using 10 excitation state for LANL2DZ and cc-pVDZ basis sets, because it is sufficient to shows the all the minimum peak in spectrum. The LANL2DZ basis set provides strong oscillation force at 447 nm, 451 nm, 466 nm, and 590 nm. Meanwhile, with cc-pVDZ basis set, the large oscillation force appears at 446 nm, 463 nm, and 598 nm. The absorbance spectrum of chlorophyll-b molecules can be seen in the figure 8.

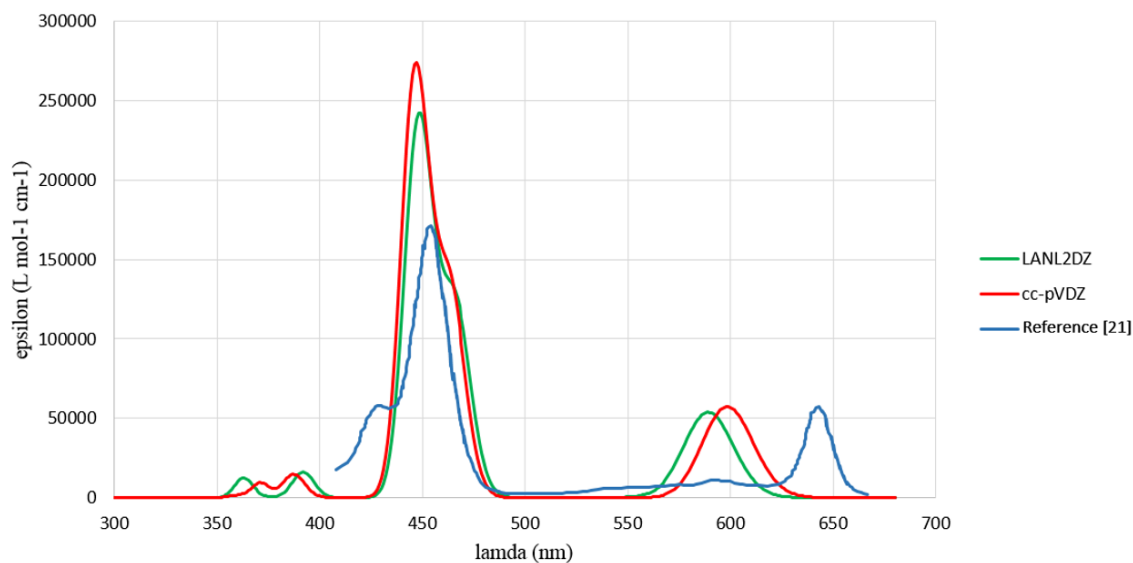


Figure 8. Absorbance spectrum from chlorophyll-b using LANL2DZ and cc-pVDZ basis sets compared to reference [21].

Figure 8 corresponds to the UV-Vis spectrum of optimized chlorophyll-b. The UV-Vis Spectra from the calculation is compared with the experimental research from Comar et al. [21]. We observed similar blue shifted peaks in the Soret and Q-bands as reported by Bevilacqua, et al. [22] We found that the calculated Soret and Q-band peaks are 448 and 590 nm, respectively. The largest blue shifted can clearly see at the Q-band, which is shifted ~53 nm, while the Soret band is only shifted ~6 nm from the reported experimental value.

Our calculated Soret and Q-bands is higher than previous reported value by Bevilacqua, which is 25-40 nm larger. The difference in the wavenumber is due to the the basis set. In this work, we showed that the LANL2DZ and cc-pVDZ basis sets are overestimate the absolute values of the wavelength. These overestimation values are consistent with the nature of LANL2DZ and cc-pVDZ basis sets itself, which is the generation of wavefunction in the calculation becomes more exaggerated. Furthermore, our calculation indicates the importance of the basis set selection in the large molecules calculations.

Based on the results, there is no difference between LANL2DZ and cc-pVDZ spectrum results of chlorophyll-b molecules. The results using cc-pVDZ and LANL2DZ basis sets are matched because the wave function coefficients used in the calculation are just slightly different. This indicates that larger basis set do not affect the spectra, but it will give better UV-Vis spectra result.

The calculation result in Q-Band shows that there is indeed a peak at 590 nm (2.10 eV), while based on the Comar et al. [21]. Result, the Q-band peak appears at a wavelength 643 nm (1.93 eV). There is the energy difference of 53 nm (0.1732 eV) in the Q-band which can be seen as negligible in molecular system. The energy difference is caused by the use of TD-DFT theory in calculations which will always provide a shift at around 0.1-0.2 eV (red shifted) [23]. However, using a larger basis set is the best solution, but the consequence is smaller excitation energy would be obtained. Mostly, the DFT is not able to describe the asymptotic behaviour at long distance, because the energy HOMO is generally small at the DFT (Koopmans' Theorem not fulfilled) [5]. The difference in wavelength is also caused by the coefficient of the wave function and the power oscillations that arise in the calculation. Until now, there still has not been many studies that use chlorophyll-b to calculate an absorbance spectrum. Most research provides little explanation of how to modelling the actual chlorophyll-b. Hence, to modelling the real chlorophyll-b molecule was very difficult. Gaussian will provide the results in accordance with possessed, if using one of model chlorophyll-b then the calculation basis set will define the molecular orbitals of the molecule and then will calculate the excitation state appears. So, it can be said that the determination of molecular orbital calculations is very important in the absorbance spectrum. The results of the specific absorbance (epsilon) with cc-pVDZ and LANL2DZ basis sets are not different specific absorbance. This is due to the strength of oscillation is not different from that of the Soret band and Q-band. However, there is a considerable difference with the specific absorbance of the chlorophyll-b from experiment. At Soret band, there is a difference, which is much against specific absorbance, is caused by the difference in the number of interactions of electron transitions in the main group. While the Q-band far, there is no difference between the specific absorbance reference to the calculation results. This is because almost all of the interaction of electrons occurs at the tail group chlorophyll-b. Hence, the spectrum of chlorophyll-b obtained in the calculations are similar to the reference. Besides, the specific absorbance difference is also influenced by the environment.

4. Conclusion

From the results it can be concluded that the shape of the molecule chlorophyll-b is not same as that of the early models which were made in this research. Geometrically can be observed on a CH₂CH₂COO-Phytyl chain curve. This curved chain is caused by intermolecular forces that form a strong bond enough to pull all the atoms bonding.

Basis set has a huge influence on the results of the optimization. Basically, energy and bond lengths in the molecule are quite different. Bigger basis set will make the optimization result

parameter better. Those parameters are indicated by small stationary energy, constant SCF energy, and short CPU time. In this research, the suitable basis sets are LANL2DZ and cc-pVDZ.

The use of different models give quite different optimization result parameters. This difference is done by moving $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain perpendicular to the main group (model 1) and parallel to the main group (model 2). The difference result occurs only in the direction of the curvature $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain. Furthermore, there is no fundamental difference between the length of an existing bond in a molecule and SCF energy in model 1 and model 2.

The maximum absorbance in this calculation is obtained at a wavelength of 448 nm and 590 nm. However, the experimental result shows the absorbance peak wavelengths occurred at 454 nm and 643 nm. There is a difference in UV-Vis spectrum from the calculation, especially for the Q-band. This difference appeared because the possible structure of a single molecule chlorophyll-b which has not been verified. However, this difference is acceptable due to the DFT which is used. The output of the Gaussian calculation shows that the excitation indeed occurs at a wavelength of 590 nm, and it is the Q-band. Hence, the UV-Vis spectrum of Gaussian calculation in this research not entirely wrong. This is because the Gaussian only will define the molecular orbitals in accordance with the initial models were used.

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