

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 optimisation 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 optimisation 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 the main group while the other one is having phytol chain parallel with the main group. The two structures in chlorophyll are given similar results; the difference only at the direction of curvature at chain. This happens because the optimised 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 an important role as an alternative energy source. However, Incident Photon to Electron Conversion Efficiency (IPCE) from solar cell is one of the main problems that requires attention. 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 higher IPCE, for example perovskite. Perovskite solar cell still does not have the best efficiency due to energy conversion, but 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 utilising chlorophyll is its low-cost production and lesser nature damage. Another thing is that the chlorophyll will give good IPCE.

Since the efficiency is depending highly on how much light energy conversion to electricity, the absorption of light energy is important. Therefore, in this study, the energy absorption, particularly at the peaks of UV-Vis spectra from chlorophyll is investigated.

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

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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 responsible for trapping the light energy. It has chemical formulation of $C_{55}H_{70}O_6N_4Mg$ which has porphyrin-like ring with magnesium ion located in its centre and hydrophobic hydrocarbon tail. Therefore, the total of number of atoms that is considered 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, it has a different 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 Orbitals

Molecular orbitals (MO) are constructed from atomic orbitals (AO). Therefore, the wave function can be derived from the electron using Eq. 1 [7],

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

The part of molecular orbitals symbolised by wave function ψ_j as summarised 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 hybridisation process. This process happens when the electron from every atomic orbital 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 the accurate methods for computing many body system problems 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 formulating the Time Dependent Density Functional Theory is shown as in Eq. 2 [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 the DFT equation, assuming perturbation potential $v(\vec{r}, t)$ as oscillation potential of electrical field $v_l(\vec{r}, t) = E_z \cos wt$. 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,

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

For particle without interaction,

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

with response function interaction,

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

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 the capacity of 8 GB, 1 TB HDD capacity for main node, and 150 GB HDD capacity for each compute nodes. The operating system used in this cluster was Rocks version 7.0 with the codename Manzanita.

The calculations in this research are 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 optimise the geometry of chlorophyll-b until the best optimised parameter result is achieved.

The initial structure of single molecule of Chlorophyll-b is obtained from PubChem with the total number of atoms 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 Fig. 1.

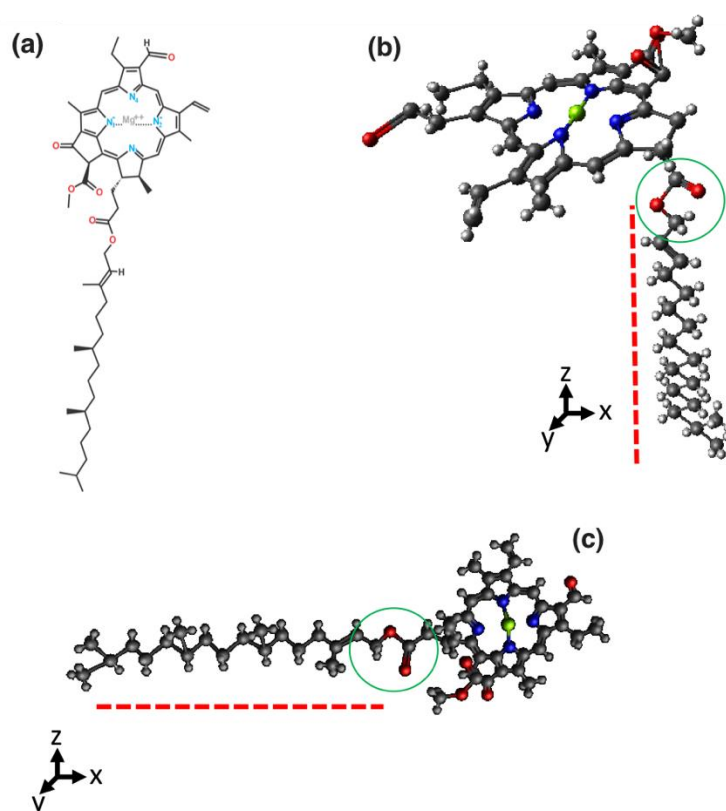


Figure 1. Chlorophyll-b structure (a) from PubChem, (b) Model 1: modification design of chlorophyll-b at $\text{CH}_2\text{CH}_2\text{COO}$ -Phytol tail perpendicular with Porphyrin-like ring, (c) Model 2: modification design of chlorophyll-b at $\text{CH}_2\text{CH}_2\text{COO}$ -Phytol tail parallel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

3. Results and Discussion

3.1. Optimisation Result

Optimisation 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 the parameters that is used for optimisation. The optimisation results are shown in Fig. 2.

Table 1 shows that basis set affects the bond length of N-Mg. It shows that using basis set 6-31G(d) gives different bond length between DFT calculation and references 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 the system using Effective Core Potential (ECP). ECP will define every charges when the calculation is started and hence makes the density function calculation more precise. 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, the calculation is faster and the results are more accurate. From Table 1, we can conclude that the cc-pVDZ and cc-pVTZ are the suitable basis sets 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. On the other hand, the smallest maximum displacement achieved when using cc-pVTZ followed by cc-PVDZ. Apart from that, Self Consistence Field (SCF) is also other parameters that can be considered for obtaining good results. 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 | not enough memory |

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 in maintaining its structures. Interaction in porphyrin-like ring, in addition, is also considered as complicated. Furthermore, the cc-PVTZ basis set is based on the extrapolation techniques, which take into account the valence and core electron correlation. To

this end, based on these conditions, the wave number and density that are generated during the calculations are larger. In this regard, the number of functions also doubles 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 can be referred to Section 2.5).

From Table 2 and 3, we can conclude that the best basis set in this study is cc-pVDZ, considering several parameters as listed in the tables. Even though other basis sets such as LANL2DZ, cc-pVTZ, and 6-31G(d) have their own advantages, results shown in the tables are supporting this.

Fig. 2 and 3 are the optimised structure of chlorophyll- b using several basis set. It shows that the $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail of chlorophyll- b is curved. From these figures, we observed that in general, using several different basis sets makes the $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail curved. This happens because the $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail has C=C and C=O bonding, which will make the tail curved, as indicated by the red dashed line. After considering the results from several optimisation parameters, LANL2DZ and cc-pVDZ basis sets will be used for calculating the UV-Vis spectra.

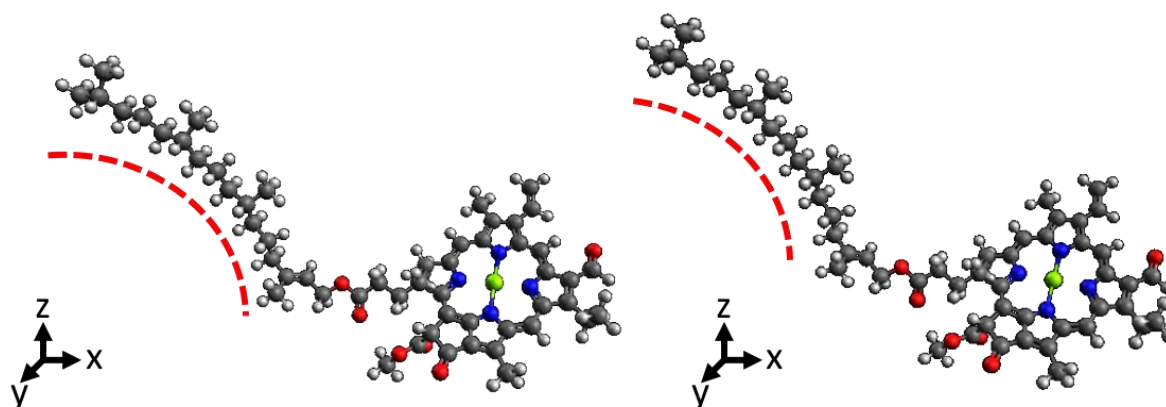


Figure 2. Visualization results of chlorophyll-b from optimisation process using 6-31G(d) basis set (left) and LANL2DZ basis set (right).

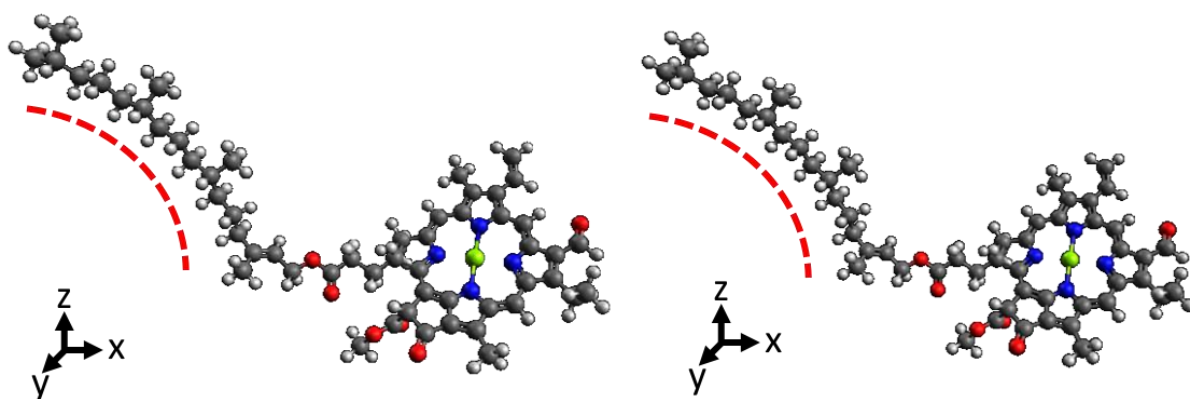


Figure 3. Visualization results of chlorophyll-b from optimisation process using cc-pVDZ basis set (left) and cc-pVTZ basis set (right).

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

The position of CH₂CH₂COO-Phytyl in molecule Model 1 (Fig 1(b)) will influence the optimisation results shown in Fig. 3 and 4. It is shown by the curvy CH₂CH₂COO-Phytyl tail which differ from the initial configuration. Therefore, the configuration of the chlorophyll-b in initial Model 1 (Fig. 1(b)) and Model 2 (Fig. 1(c)) will influence the calculation results. Table 4 and 5 show 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 5 show 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 the initial configuration of chlorophyll-b molecule, particularly $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl tail in Model 2, affecting the main group and then 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 fewer molecular orbital, which does not interact with the main group.

In Fig. 4 and 5, we can see some differences in $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain. Fig. 5 shows the position of $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain in Model 1 (Fig. 4(a)) in which the direction of the curvature approaching the main group ($\text{CH}_2\text{-CH}_3$ bonding) in the middle of the chain. Whereas in Model 2 (Fig. 4(b)), the directions of the $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl curvature move as it left the main group and lift the atoms at the end of the $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain. Overall, the LANL2DZ basis set makes the position of $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain chlorophyll-b molecule model perpendicular to the main group.

Fig. 5 shows the result using cc-pVDZ basis set. The results of Model 1 (Fig. 5(a)) are similar to that of Model 1 of LANL2DZ basis. However, it has a significant difference with Model 2 (Fig. 5(b)) for the cc-pVDZ basis set. The position of $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl 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 of LANL2DZ basis set (Fig. 4(b)).

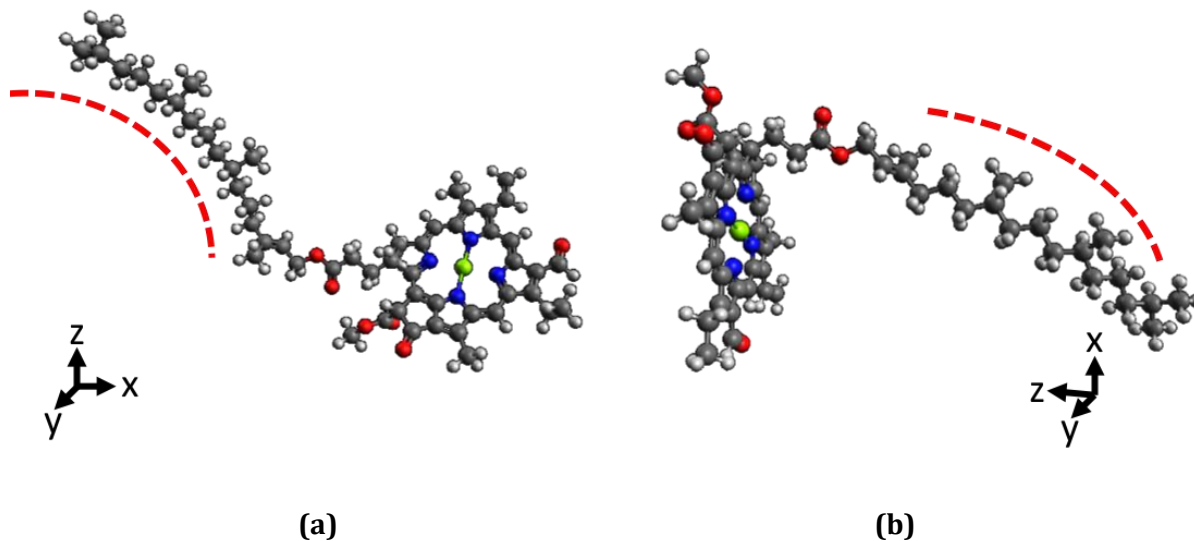


Figure 4. Visualization result from 2 models of chlorophyll-b with LANL2DZ basis set resulted (a) from Model 1, (b) from Model 2.

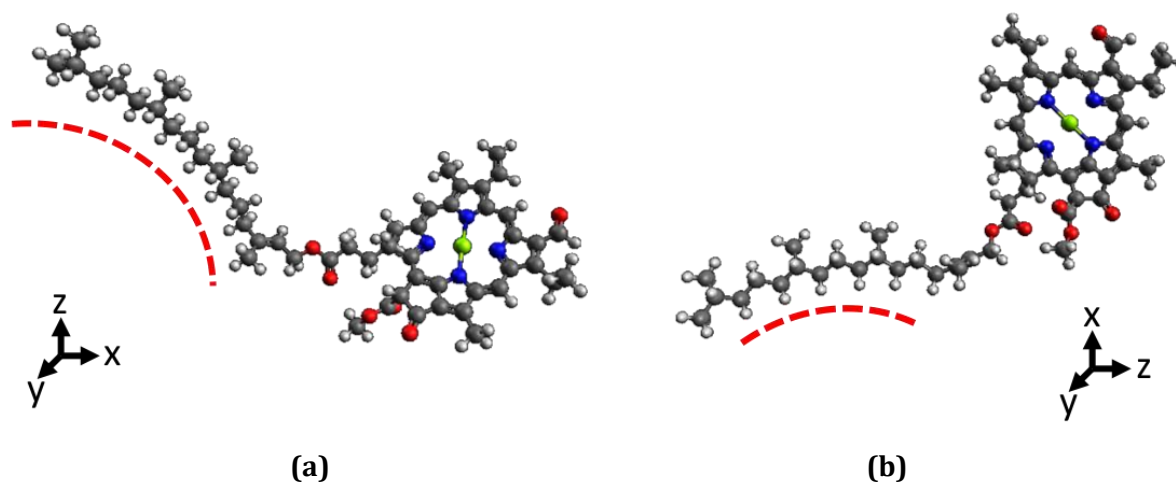


Figure 5. Visualization result from 2 models of chlorophyll-b with cc-pVDZ basis set resulted (a) from Model 1, (b) from Model 2.

The interaction between the hydrophobic hydrocarbon tail and porphyrin-like ring in the chlorophyll-b molecule is through the 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 optimisation, which makes the interaction between hydrocarbon tail and porphyrin-like ring stronger, yielding 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 is reducing $\sim 0.2 \text{ \AA}$ yielding to a suppressed hydrocarbon tail (which is indicated by the dashed curved line). Therefore, compared to Fig. 1(c) and (b), we can see the difference in the shape of the tail, which is initially flat and perpendicular to the porphyrin ring, and becomes curved after optimisation.

The result of optimisation using LANL2DZ and cc-pVDZ basis set shows a slight difference. Visualization of the optimisation shows that the molecule of chlorophyll-b has the curve shape of $\text{CH}_2\text{CH}_2\text{COO}$ -Phytyl chain. However, the comparison of bond lengths, SCF energy, and visualization result from chlorophyll-b makes Model 2 (Fig. 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 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 . Fig. 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 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.

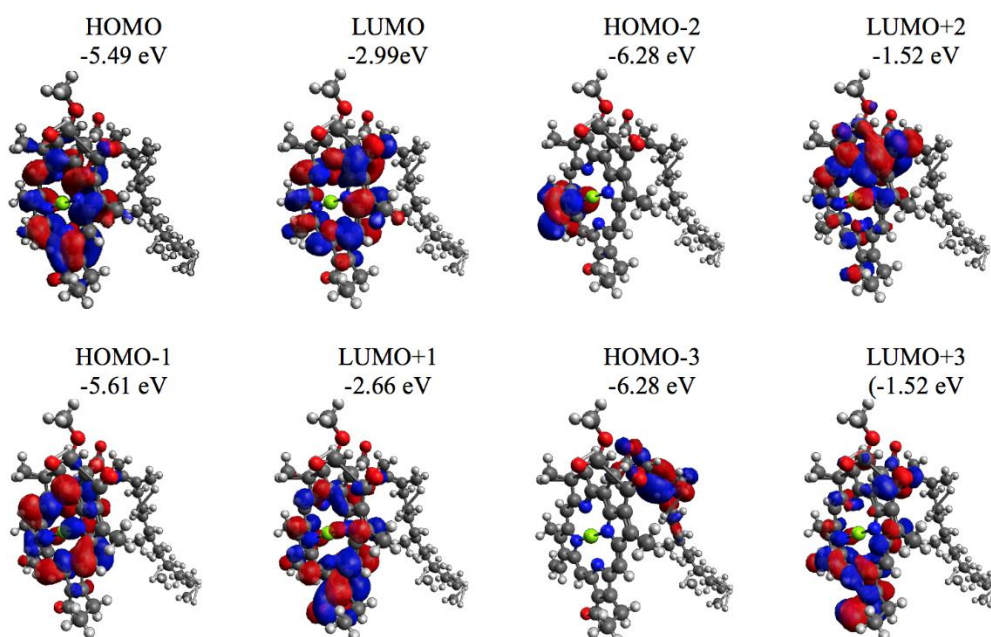


Figure 6. Orbital molecules shape of chlorophyll-b using LANL2DZ basis set from HOMO to HOMO-3 and from LUMO to LUMO+3.

3.3.2. Molecular orbital using cc-pVDZ basis set

The cc-pVDZ basis set gives 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 respectively.

From Fig. 7, we can see only few orbitals of chlorophyll-b molecules that will influence the determination of UV-Vis spectrum. It also shows similar results 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.

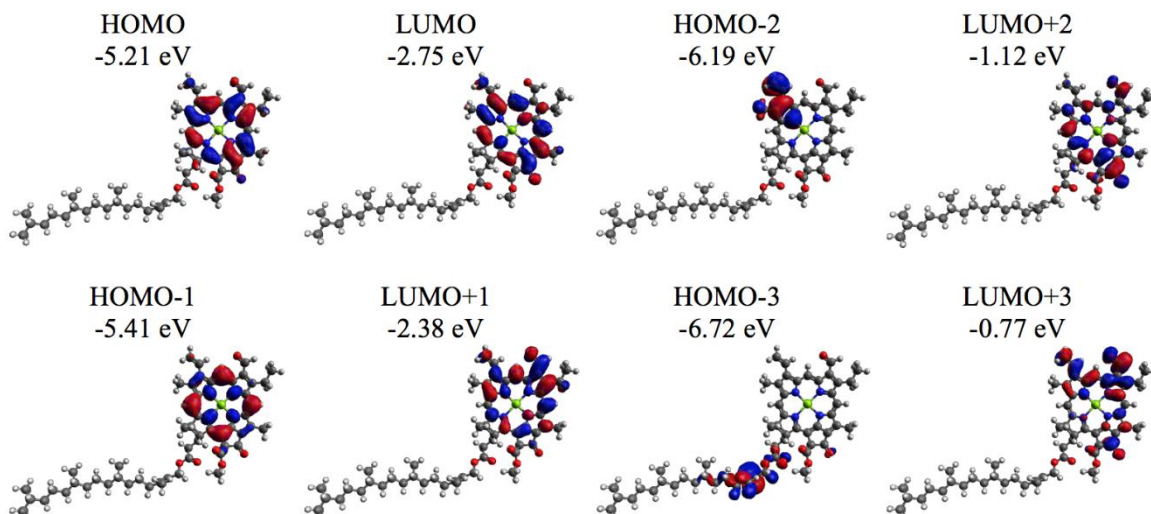


Figure 7. Orbital molecules shape of chlorophyll-b using cc-pVDZ basis set from HOMO to HOMO-3 and from LUMO to LUMO+3.

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 a difference about 0.29 eV between these two basis sets. This 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 important factors 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 optimisation, but not for UV-Vis Spectra calculation. Therefore, to get simpler and accurate results, 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 optimisation, the next step is to determine the absorbance spectrum of the molecule. The results, which are issued by the Gaussian output file, will show the excitation energy (in nanometers) and the strength of the oscillation (in oscillator strength), along with other information. To construct the UV-Vis Spectra curves, Stephens et al. [20] explains how to make the results of absorbance spectrum from the power and strength of the dipole oscillation. Construction of the UV-Vis absorbance spectra from Gaussian output use Eq. 10 [20],

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

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) which usually equals to 0.4 eV (but in this research, we used 0.06 eV).

In order 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], which 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 all the minimum peaks 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 Fig. 8.

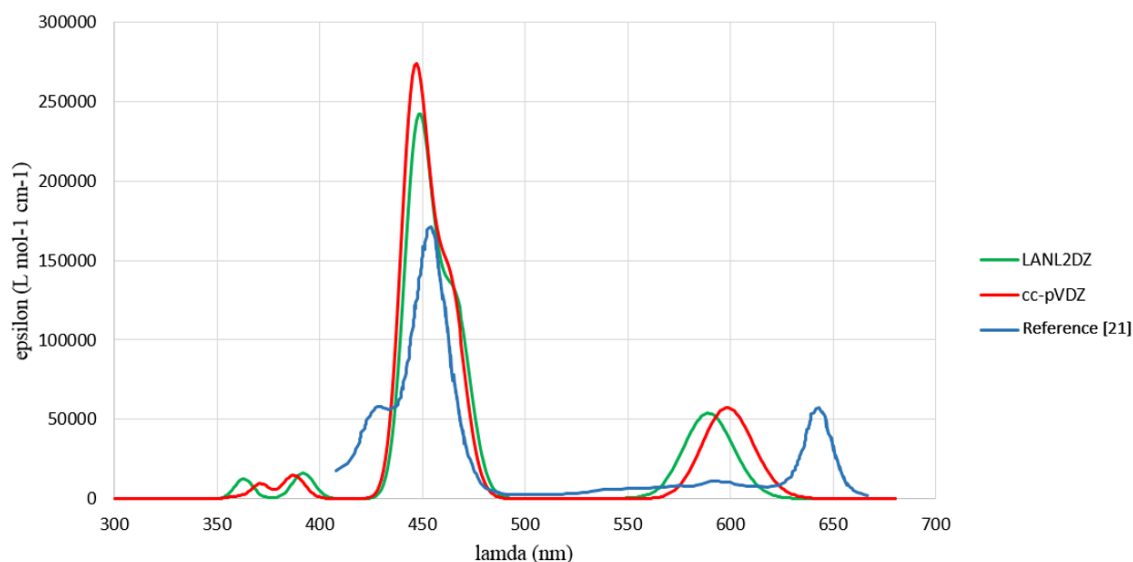


Figure 8. Absorbance spectrum from chlorophyll-b using LANL2DZ and cc-pVDZ basis sets compared to reference [21].

Fig. 8 corresponds to the UV-Vis spectrum of optimised chlorophyll-b. The UV-Vis Spectra from the calculation is compared with the experimental results from Comar et al. [21]. We observed similar blue shift 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 shift 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 25-40 nm higher than previous reported values by Bevilacqua. 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 overestimating the absolute values of the wavelength. These overestimation values are consistent with the nature of LANL2DZ and cc-pVDZ basis sets itself, which resulting 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 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), based on Comar et al. [21]. Result of the Q-band peak appears at a wavelength 643 nm (1.93 eV). There is 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 shift) [23]. However, using a larger basis set is the best solution, but the consequence of smaller excitation energy would be obtained. Mostly,

the DFT is not able to describe the asymptotic behaviour at long distance, because the HOMO energy 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 in calculating absorbance spectrum. Most researches provide little explanation on how to model the actual chlorophyll-b. Hence, to model the real chlorophyll-b molecule is very difficult. Gaussian will provide the results in accordance with the possessed. If using chlorophyll-b model, then the calculation basis set will define the molecular orbitals of the molecule and then will calculate the appeared excitation state. 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. 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. At Soret band, there is a difference, which is much against specific absorbance, which caused by the difference in the number of interactions of electron transitions in the main group. While for the Q-band, there is no difference between the specific absorbance reference with the calculation results. This is because almost all of the interaction of electrons occurs at the tail group of chlorophyll-b. Hence, the spectrum of chlorophyll-b obtained in the calculations are similar to the reference. Apart from that, 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 the same as that of the early models which were made in this research. The changes can be observed geometrically on the CH₂CH₂COO-Phytyl chain curve. This curved chain is caused by intermolecular forces that forms a strong bond, enough to pull all the atoms bonding.

Basis set has a huge influence on the results of the optimisation. Basically, energy and bond lengths in the molecule are quite different. Bigger basis set will make the optimisation result parameter better. Those parameters are indicated by smaller stationary energy, constant SCF energy, and shorter CPU time. In this research, the suitable basis sets are LANL2DZ and cc-pVDZ.

The use of different models give quite different optimisation results. This difference is the movement of CH₂CH₂COO-Phytyl chain perpendicular to the main group (Model 1) and parallel to the main group (Model 2). The differences of results occur only in the direction of the curvature CH₂CH₂COO-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 results 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 usage of DFT. 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 is not entirely wrong. This is because the Gaussian will only define the molecular orbitals in accordance with the initial models used.

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