

## Research Article

# Computational Nanochemistry Study of the Molecular Structure and Properties of Chlorophyll a

Mónica Alvarado-González,<sup>1</sup> Norma Flores-Holguín,<sup>2</sup> and Daniel Glossman-Mitnik<sup>2</sup>

<sup>1</sup> Centro de Investigación en Alimentación y Desarrollo (CIAD), Avenida Cuarta sur No. 3820, Fracc. Vencedores del Desierto Unidad Delicias, 33089 Delicias, CHIH, Mexico

<sup>2</sup> Laboratorio Virtual NANOCOSMOS, Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, Complejo Industrial Chihuahua, 31109 Chihuahua, CHIH, Mexico

Correspondence should be addressed to Daniel Glossman-Mitnik; [daniel.glossman@cimav.edu.mx](mailto:daniel.glossman@cimav.edu.mx)

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The M06 family of density functionals has been assessed for the calculation of the molecular structure and properties of the chlorophyll a molecule. Besides the determination of the molecular structures, the UV-Vis spectra have been computed using TD-DFT in the presence of a solvent, and the results were compared with the experimental data available. The chemical reactivity descriptors have been calculated through conceptual DFT. The active sites for nucleophilic and electrophilic attacks have been chosen by relating them to the Fukui function indices. A comparison between the descriptors calculated through vertical energy values and those arising from the Koopmans' theorem approximation have been performed in order to check for the validity of the last procedure.

## 1. Introduction

The sun has been shining for some four and half a billion years and is expected to do so for as long again. It is the earth's only truly sustainable source of energy. Photosynthesis, the process by which the energy of sunlight absorbed in the chlorophyll pigments of green plants fixes atmospheric carbon dioxide (CO<sub>2</sub>) to carbohydrates, supplies us directly or indirectly with all our food. The oxygen discarded by plants as part of this process replenishes the atmosphere with the oxygen humans and animals need for survival [1]. Photosynthesis is by far the most spectacular physiological process in plant growth and productivity. Due to this fact, the study of photosynthesis has captivated plant physiologists, botanists, plant biologists, horticulturalists, agronomists, agriculturalists, crop growers, and, most recently, plant molecular and cellular biologists around the world [2].

A fundamental principle of photochemistry—photosynthesis is partly a photochemical reaction—is that, for light to drive a reaction, it must first be absorbed. This means that there must be a pigment, which is any molecule that

absorbs light. Chlorophyll a serves a dual role in oxygenic photosynthesis: in light harvesting as well as in converting energy of absorbed photons to chemical energy [3]. The biological importance of chlorophyll a seems obvious because it is necessary for the photochemistry in oxygenic photosynthetic organisms, with the only known exception of *A. marinus* which utilizes both chlorophyll d and chlorophyll a for the photochemistry [4].

The aim of this work is to test the performance of the M06 family of density functionals [5–7] for the prediction of the infrared (IR) and ultraviolet-visible (UV-vis) spectra, the dipole moment, polarizability, and the chemical reactivity descriptors that arise from conceptual density functional theory (DFT) [8, 9] for the chlorophyll a molecule. A comparison between the descriptors calculated through vertical energy values and those arising from the Koopmans' theorem approximation will be performed in order to check for the validity of the last procedure within DFT. The results will be compared with the empirical evidence available in the literature.

## 2. Theory and Computational Details

All computational studies were performed with the Gaussian 09 [10] series of programs with density functional methods as implemented in the computational package. The equilibrium geometries of the molecules were determined by means of the gradient technique. The force constants and vibrational frequencies were determined by computing analytical frequencies on the stationary points obtained after the optimization to check if there were true minima. The basis sets used in these work were MIDIY, which is the same basis set as MIDI! with a polarization function added to the hydrogen atoms, and the DGDZVP basis set for Mg. The MIDI! basis is a small double-zeta basis with polarization functions on N-F, Si-Cl, Br, and I [11–16].

For the calculation of the molecular structure and properties of the studied systems, we have chosen the hybrid meta-GGA density functionals: M06, M06L, M06-2X, and M06HF [5], which consistently provide satisfactory results for several structural and thermodynamic properties. Solvation energies were computed by the integral equation formalism polarizable continuum model (IEF-PCM) [17], including the UAKS model and methanol as a solvent.

The calculation of the ultraviolet (UV-Vis) spectra of the studied systems has been performed by solving the time-dependent DFT (TD-DFT) equations according to the method implemented in Gaussian 09 [13, 18–20]. The equations have been solved for 10 excited states.

The infrared (IR) and ultraviolet (UV-Vis) spectra were calculated using the SWizard program [21, 22] and visualized with Gabedit [23]. In all cases the displayed spectra show the calculated frequencies and absorption or emission wavelengths.

The highest-occupied molecular orbital (HOMO) and lowest-occupied molecular Orbital (LUMO) were extracted from the calculations and visualized using the Chemcraft Program Revision 1.6 [24].

Within the conceptual framework of DFT [8, 9], the chemical potential  $\mu$ , which measures the escaping tendency of electron from equilibrium is defined as

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi, \quad (1)$$

where  $\chi$  is the electronegativity.

The global hardness  $\eta$  can be seen as the resistance to charge transfer:

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})}. \quad (2)$$

Using a finite difference approximation and Koopmans' theorem [13–16], the above expressions can be written as

$$\begin{aligned} \mu &\approx -\frac{1}{2} (I + A) \approx \frac{1}{2} (\epsilon_L + \epsilon_H), \\ \eta &\approx \frac{1}{2} (I - A) \approx \frac{1}{2} (\epsilon_L - \epsilon_H), \end{aligned} \quad (3)$$

where  $\epsilon_H$  and  $\epsilon_L$  are the energies of the highest occupied and the lowest unoccupied molecular orbitals: HOMO and LUMO, respectively.

The electrophilicity index  $\omega$  represents the stabilization energy of the systems when it gets saturated by electrons coming from the surrounding:

$$\omega = \frac{\mu^2}{2\eta} \approx \frac{(I + A)^2}{2(I - A)} \approx \frac{(\epsilon_L + \epsilon_H)^2}{2(\epsilon_L - \epsilon_H)}. \quad (4)$$

The condensed Fukui functions can also be employed to determine the reactivity of each atom in the molecule. The corresponding condensed functions are given by  $f_k^+ = q_k(N+1) - q_k(N)$  (for nucleophilic attack),  $f_k^- = q_k(N) - q_k(N-1)$  (for electrophilic attack), and  $f_k^0 = [q_k(N+1) - q_k(N-1)]/2$  (for radical attack), where  $q_k$  is the gross charge of atom  $k$  in the molecule.

It is possible to evaluate condensed Fukui functions from single-points calculations directly, without resorting to additional calculations involving the systems with  $N-1$  and  $N+1$  electrons:

$$\begin{aligned} f_k^+ &= \sum_{a \in k} \left[ c_{ai}^2 + c_{ai} \sum_{b \neq a} c_{bi} S_{ab} \right] \quad (\text{where } i = \text{LUMO}), \\ f_k^- &= \sum_{a \in k} \left[ c_{ai}^2 + c_{ai} \sum_{b \neq a} c_{bi} S_{ab} \right] \quad (\text{where } i = \text{HOMO}) \end{aligned} \quad (5)$$

with  $c_{ai}$  being the LCAO coefficients and  $S_{ab}$  the overlap matrix. The condensed Fukui functions are normalized, thus  $\sum_k f_k^+ = 1$  and  $f_k^0 = [f_k^+ + f_k^-]/2$ .

The electrodonating ( $\omega^-$ ) and electroaccepting ( $\omega^+$ ) powers have been defined as [25]:

$$\begin{aligned} \omega^- &= \frac{(3I + A)^2}{16(I - A)}, \\ \omega^+ &= \frac{(I + 3A)^2}{16(I - A)}. \end{aligned} \quad (6)$$

It follows that a larger  $\omega^+$  value corresponds to a better capability of accepting charge, whereas a smaller value of  $\omega^-$  value of a system makes it a better electron donor. In order to compare  $\omega^+$  with  $-\omega^-$ , the following definition of net electrophilicity has been proposed [26]:

$$\Delta\omega^\pm = \omega^+ - (-\omega^-) = \omega^+ + \omega^-, \quad (7)$$

that is, the electroaccepting power relative to the electrodonating power.

Indeed, there exist in the literature many other methods for the computation of the chemical reactivity descriptors considered in this work [27–29].

## 3. Results and Discussion

The molecular structure of chlorophyll a was preoptimized by starting with the readily available PDB structure, and finding

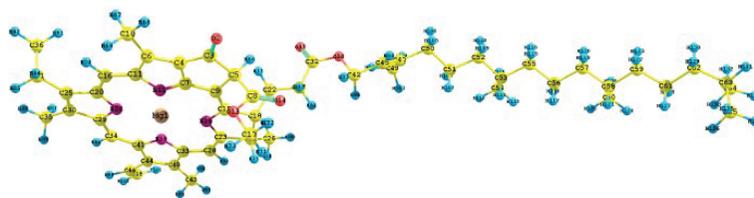


FIGURE 1: Optimized molecular structure of the chlorophyll a molecule.

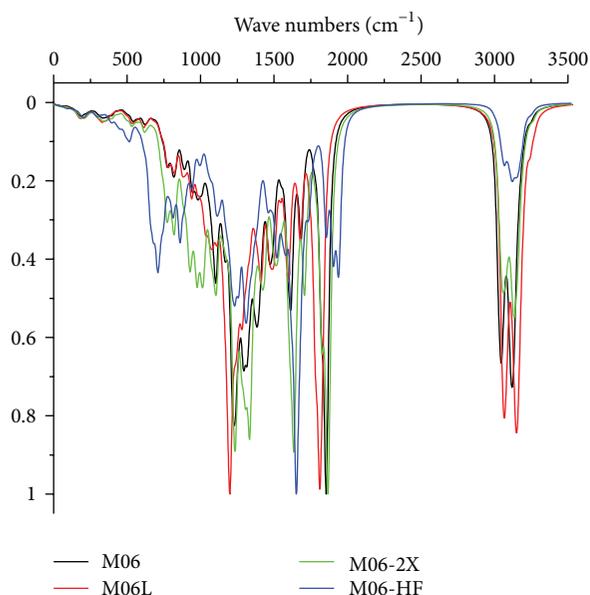


FIGURE 2: Infrared spectra of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets.

the most stable conformer by means of the conformers module of materials studio through a random sampling with molecular mechanics techniques and a consideration of all the torsional angles. The structure of the resulting conformer was then optimized with the M06, M06L, M06-2X, and M06-HF density functionals in conjunction with the MIDIY and DGDZVP basis sets. The optimized molecular structure of the chlorophyll a molecule (with the M06 density functional) is shown in Figure 1, while the bond distances (in Å) and the bond angles (in degrees) calculated with the M06, M06L, M06-2X and M06-HF functionals in conjunction with the MIDIY and DGDZVP basis sets are presented in Tables A.1 and A.2 of the Supplementary Materials available online at <http://dx.doi.org/10.1155/2013/424620>, respectively. It is not the objective of this study to analyze in detail the results predicted by the different functionals for the optimized structure of the chlorophyll a molecule. However, a comparison of the results by superimposing structures reveals that there are not important differences between them. This is not surprising because modern density functionals are able to predict molecular structures with a good degree of accuracy and using low-cost basis sets. These results are an

improvement over those obtained with other low-level older density functionals [30].

The situation is quite different for the prediction of the IR and UV-Vis spectra, and this could be ascribed to the different functional form of the density functionals. The infrared spectra of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets are shown in Figure 2. Indeed, we should note that none of the IR spectra display a frequency value below zero or imaginary, and this means that the structures predicted by all the functionals are a minimum on the potential energy surface. The IR spectrum of chlorophyll a has been measured and elucidated more than 60 years ago [31]. A comparison of the results shown in Figure 2 with those reported in Figure 1 of the mentioned article reveals that the overall shape is more or less the same, with significant differences for the M06-2X and M06-HF spectra. It is well known that calculated Hartree-Fock (HF) IR spectra must be scaled to account for the effects of anharmonicity and correlation. With modern density functionals that explicitly include correlation, this scaling factor is close to 1, and this can be an indication of the goodness of a given functional. For the results presented here, it is remarkable that the M06 and the local M06L predict so well the IR spectrum of chlorophyll a. Notwithstanding, these results should be taken with care because the experimental spectrum in that paper (and also in later works) has been taken from the solid, while the present calculations have been done in the presence of methanol simulated through a polarized continuum method. It should be noticed that a recent work on the estimation of scaling factors for a large number of density functionals have shown that functionals with low percentages of HF exchange tend to predict more accurate frequencies [32].

The molecular dipole moment is perhaps the simplest experimental measure of charge distribution in a molecule. The accuracy of the overall distribution of electrons in a molecule is hard to quantify, since it involves all the multipoles. The polarizability  $\alpha$  contributes to the understanding of the response of the system when the external field is changed, while the number of electrons  $N$  is kept fixed. The polarizability is calculated as the average of the polarizability tensor  $\langle \alpha \rangle = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ .

The molecular dipole moments  $\mu$  (in Debye) and global polarizabilities  $\alpha$  (in Bohr<sup>3</sup>) of the chlorophyll a molecule calculated with the M06, M06L, M06-2X and M06-HF density functionals and the MIDIY and DGDZVP basis sets are shown in Table 1.

TABLE 1: Molecular dipole moments  $\mu$  (in Debye) and global polarizabilities  $\alpha$  (in Bohr<sup>3</sup>) of chlorophyll a calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets.

Property	M06	M06L	M06-2X	M06-HF
$\mu$	5.574	5.498	6.074	7.584
$\alpha$	761.74	786.94	754.28	744.11

The visible part of the electronic absorption spectrum is one of the more fascinating features of chlorophyll molecules [30]. For this reason, there is a great interest in the study of photosynthetic materials for their application in organic solar cells. First, we can refer to a theoretical study of the excited states of chlorophyll a and pheophytin a using a combination of density functional theory and the multireference configuration interaction method (DFT/MRCI) [33]. In a second place, there has been several interesting experimental and theoretical studies on photosynthetic materials: (i) chlorophyll a derivatives with various hydrocarbon ester groups for efficient dye-sensitized solar cells [34]; (ii) natural chlorophyll-related porphyrins and chlorins for dye-sensitized solar cells [35] and (iii) to a significant enhancement in the power-conversion efficiency of chlorophyll cosensitized solar cells by mimicking the principles of natural photosynthetic light-harvesting complexes. Indeed, this is a very enlightening work, but in this study we only want to compare our results with the available experimental data for the absorption spectrum of chlorophyll a in methanol. There is also a recent DFT benchmark calculation on the performance of density-functional-based methods in the description of some biological systems, chlorophyll a among them [36].

The absorption or UV-Vis spectra of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets are presented in Figure 3. The experimental absorption spectrum of chlorophyll a in methanol has been reported [37] and displays the characteristic bands at 432 and 665 nm. All the calculated spectra have the same shape, and it is the same as for the experimental absorption spectrum. However, there is a shift in each one of the spectrum that can be related to the amount of HF exchange that it is included for every density functional considered in this study. The functional form of the M06, M06-2X and M06-HF functionals is the same, with the only difference given by the aforementioned amount of HF exchange. It is evident from the results in Figure 3 that a larger amount of HF exchange included leads to larger shifts of the peaks when compared with the experimental spectrum. Notwithstanding, only the M06L density functional results are able to reproduce the experimental spectrum with a very small error for the blue band (437.4 nm) and of 38 nm for the band belonging to the maximum wavelength (627 nm). The results for the orbital transition assignments for each one of the calculations are given in Tables A3, A4, A5, and A6 of the Supplementary Materials for the interested reader.

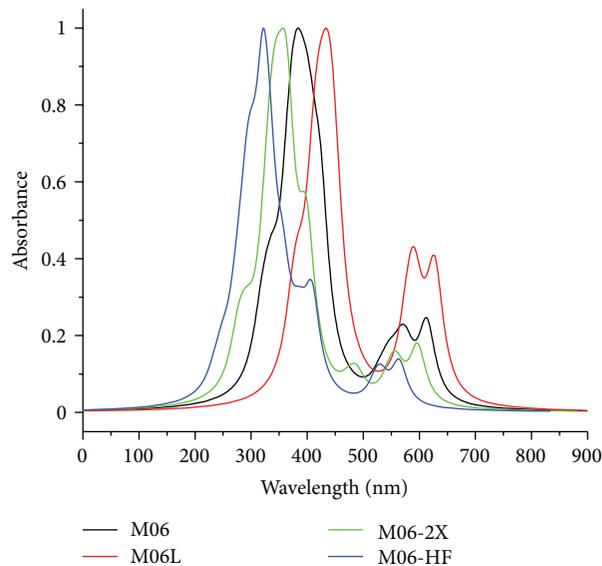


FIGURE 3: Absorption spectra of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets.

The HOMO and LUMO orbitals of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets are shown in Figure 4.

The validity of the Koopmans' theorem within the DFT approximation is controversial. However, it has been shown [38] that although the KS orbitals may differ in shape and energy from the HF orbitals, and the combination of them produces conceptual DFT reactivity descriptors that correlate quite well with the reactivity descriptors obtained through Hartree-Fock calculations. Thus, it is worth to calculate the electronegativity, global hardness, and global electrophilicity for the studied systems using both approximations in order to verify the quality of the procedures.

The HOMO and LUMO orbital energies (in eV), ionization potentials  $I$  and electron affinities  $A$  (in eV), and global electronegativity  $\chi$ , total hardness  $\eta$ , and global electrophilicity  $\omega$  of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets are presented in Table 2. The upper part of the table shows the results derived assuming the validity of Koopmans' theorem, and the lower part shows the results derived from the calculated vertical  $I$  and  $A$ .

The condensed Fukui functions have been calculated using the AOMix molecular analysis program [22, 39] starting from single-point energy calculations. We have presented, discussed, and successfully applied the described procedure in our previous studies on different molecular systems [40–43].

The condensed dual descriptor has been defined as  $\Delta f_k = f_k^+ - f_k^-$  [44, 45]. From the interpretation given to the Fukui function, one can note that the sign of the dual descriptor is very important to characterize the reactivity of a site within a molecule toward a nucleophilic or an electrophilic attack.

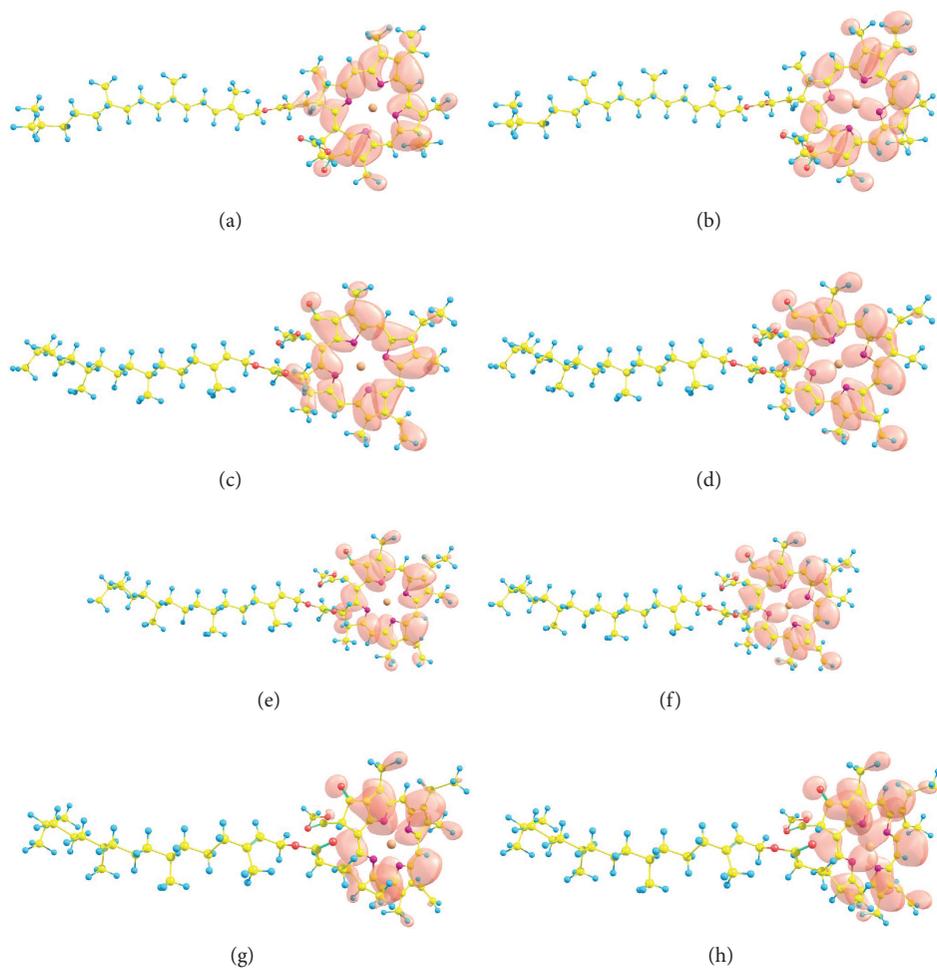


FIGURE 4: HOMO and LUMO orbitals of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets.

TABLE 2: HOMO and LUMO orbital energies (in eV), ionization potentials  $I$  and electron affinities  $A$  (in eV), and global electronegativity  $\chi$ , total hardness  $\eta$ , and global electrophilicity  $\omega$  of chlorophyll a calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets. The upper part of the table shows the results derived assuming the validity of Koopmans' theorem and the lower part shows the results derived from the calculated vertical  $I$  and  $A$ .

Property	M06	M06L	M06-2X	M06-HF
HOMO	5.221	4.680	5.897	7.076
LUMO	2.466	2.989	1.973	0.892
$\chi$	3.8435	3.8344	3.9349	3.9839
$\eta$	2.7550	1.6912	3.9240	6.1840
$\omega$	2.6810	4.3468	1.9729	1.2833
$I$	6.196	6.145	6.361	6.522
$A$	1.442	1.479	0.056	1.453
$\chi$	3.8190	3.8121	3.2084	3.9874
$\eta$	4.7540	4.6660	6.3058	5.0684
$\omega$	1.5339	1.5572	0.8162	1.5685

That is, if  $\Delta f_k > 0$ , then the site is favored for a nucleophilic attack, whereas if  $\Delta f_k < 0$ , then the site may be favored for an electrophilic attack [44–46].

The electrophilic  $f^+$  and nucleophilic  $f^-$  condensed Fukui functions and  $\Delta f$  over the atoms of the chlorophyll a molecule calculated with the M06, M06L, M06-2X and M06-HF density functionals and the MIDIY and DGDZVP basis sets are shown in Table 3. The actual values have been multiplied by 100 for an easier comparison.

The electrodonating ( $\omega^-$ ) and electroaccepting ( $\omega^+$ ) powers and net electrophilicity  $\Delta\omega^\pm$  of the chlorophyll a molecule calculated with the M06, M06L, M06-2X and M06-HF density functionals and the MIDIY and DGDZVP basis sets are presented in Table 4. The upper part of the table shows the results derived assuming the validity of Koopmans' theorem and the lower part shows the results derived from the calculated vertical  $I$  and  $A$ .

The results from Table 4 clearly indicate that chlorophyll a is an electrodonating molecule, with the same result predicted by all the four density functionals considered in this study.

TABLE 3: Electrophilic  $f^+$  and nucleophilic  $f^-$  condensed Fukui functions and  $\Delta f$  over the atoms of the chlorophyll a molecule calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis set. The actual values have been multiplied by 100 for an easier comparison.

Atom	M06			M06L			M06-2X			M06-HF		
	$f^+$	$f^-$	$\Delta f$	$f^+$	$f^-$	$\Delta f$	$f^+$	$f^-$	$\Delta f$	$f^+$	$f^-$	$\Delta f$
1 Mg	0.63	0.04	0.59	0.61	0.05	0.56	0.80	0.03	0.77	1.15	0.07	-0.45
2 O	3.32	1.29	2.03	4.22	1.45	3.77	2.83	1.30	1.53	1.82	1.37	0.45
3 C	2.46	0.26	2.20	2.99	0.32	2.67	2.09	0.22	1.87	1.36	0.16	1.20
4 C	3.97	2.78	1.19	3.97	2.40	1.57	3.88	3.43	0.45	2.88	4.71	-1.83
6 C	9.62	4.74	5.88	10.15	5.45	4.70	9.33	4.29	5.04	8.31	4.32	3.99
7 C	2.46	6.68	-4.22	2.03	6.37	-4.34	2.79	7.00	-4.21	3.16	8.70	-5.54
9 C	4.42	0.83	3.59	4.89	0.90	3.99	3.73	0.95	2.78	1.85	0.73	1.12
11 C	2.89	10.28	-7.39	2.71	9.25	-6.54	2.81	11.62	-8.81	1.83	14.90	-13.07
15 C	1.29	8.03	-6.74	1.34	8.47	-7.13	1.20	7.59	-6.39	0.98	6.66	-5.68
16 C	10.30	0.14	10.16	9.33	0.14	9.19	11.31	0.10	11.21	14.50	0.30	14.20
19 N	7.08	0.16	6.92	7.46	0.18	7.28	6.60	0.12	6.48	5.44	0.10	5.34
20 C	0.52	11.11	-10.59	0.48	9.72	-9.24	0.41	12.70	-12.29	0.01	15.67	-15.66
23 C	2.67	8.08	-5.41	2.77	8.79	-6.02	2.62	6.96	-4.34	2.36	4.59	-2.23
24 N	5.77	0.24	5.53	5.45	0.25	5.20	5.96	0.22	5.74	6.48	0.27	6.21
25 C	1.33	2.17	0.84	1.13	2.14	-0.99	1.73	2.31	-0.58	3.31	1.71	1.60
28 C	4.73	1.69	3.04	4.92	1.84	3.08	4.45	1.27	3.18	4.29	1.37	2.92
29 C	2.29	9.54	-7.25	1.91	8.55	-6.64	2.99	10.49	-7.50	5.46	10.18	-4.72
30 C	0.25	3.62	-3.37	0.23	3.23	-3.00	0.18	3.98	-3.80	0.01	5.22	-5.21
33 C	5.55	6.72	-1.17	5.11	6.98	-1.87	5.96	6.08	-0.12	6.33	0.34	5.99
34 C	7.17	0.64	6.53	6.57	0.60	5.97	7.24	0.62	6.62	6.50	1.49	5.01
40 C	5.65	3.07	-2.58	5.78	2.70	3.08	5.53	2.93	2.60	5.49	2.12	3.37
41 C	4.65	9.53	-4.88	4.04	9.08	-5.04	5.32	9.42	-4.10	6.96	7.60	-0.64
44 C	4.85	1.54	3.31	4.67	2.19	2.48	4.96	1.14	3.82	4.74	0.31	4.43
48 C	2.53	1.07	1.46	3.53	2.13	1.40	1.97	0.62	1.35	1.18	0.13	1.05

TABLE 4: Electrodonating ( $\omega^-$ ) and electroaccepting ( $\omega^+$ ) powers and net electrophilicity  $\Delta\omega^\pm$  of chlorophyll a calculated with the M06, M06L, M06-2X, and M06-HF density functionals and the MIDIY and DGDZVP basis sets. The upper part of the table shows the results derived assuming the validity of Koopmans' theorem, and the lower part shows the results derived from the calculated vertical  $I$  and  $A$ .

Property	M06	M06L	M06-2X	M06-HF
$\omega^-$	7.4560	10.7165	6.1585	4.9450
$\omega^+$	3.6125	6.8821	2.2236	0.9611
$\Delta\omega^\pm$	11.0685	17.5986	8.3821	5.9061
$\omega^-$	5.2745	5.3121	3.6307	5.4474
$\omega^+$	1.4547	1.5000	0.4224	1.4600
$\Delta\omega^\pm$	6.7292	6.8121	4.0531	6.9074

However, only the results obtained through the calculations with the M06 and M06L density functionals are in fairly agreement between those from vertical calculations of  $I$  and  $A$  and those coming from the assumption of the validity of the Koopmans' theorem in DFT.

## 4. Conclusions

From the whole of the results presented in this contribution it has been clearly demonstrated that the sites of interaction of the chlorophyll a molecule can be predicted by using DFT-based reactivity descriptors such as the hardness, softness, and electrophilicity, as well as Fukui function calculations. These descriptors were used in the characterization and successful description of the preferred reactive sites and provide a firm explanation for the reactivity of the chlorophyll a molecule.

The M06 family of density functionals (M06, M06L, M06-2X, and M06-HF) used in the present work leads to the same qualitatively and quantitatively similar description of the chemistry and reactivity of the chlorophyll a molecule, yielding reasonable results. However, for the case of the M06 and M06L functionals, the agreement between the results obtained through energy calculations and those that assume the validity of the Koopmans' theorem is fairly good.

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