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ORIGINAL PAPER

Optimally tuned functionals improving the description of optical and electronic properties of the phthalocyanine molecule

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Abstract By means of Density functional theory and time-dependent density functional theory calculations, we present a comprehensive investigation on the influence of different functional schemes on electronic and optical properties of the phthalocyanine molecule. By carrying out our own tuning on the OT-LC-BLYP/6-31G(d,p) functional, we show that such a procedure is fundamental to accurately match experimental results. We compare our results to several others available in the literature, including the B3LYP/6-31+G(d,p) set, which is commonly portrayed as the best combination in order to obtain a good description of the band gap. The results obtained here present not only significant improvement of the optical properties from the conventional BLYP, but we can also objectively report an improvement of our tuned functional when compared to the current benchmark of the literature as far as optical properties are concerned. Particularly, by means of this approach, it was possible to achieve a good agreement between the theoretical and experimental optical gap as well as the positioning of the main peaks in the absorption spectrum. Our results thus suggest that correcting the long-range term on exchange term of the Coulomb operator, by means of a tuning procedure, is a good option to accurately describe properties of the phthalocyanine molecule.

Keywords DFT · UV-Vis · Phthalocyanine molecule · Optical gap · Excited states · Oscillator strength

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Introduction

In the beginning of the last century, an interesting organic semiconductor was casually discovered by Imperial Chemical Industries [1, 2]. This system, latter refereed as phthalocyanine (PC), presented interesting features such as photoluminescence, a strong absorption in the ultraviolet and visible portion of the electromagnetic spectrum, [4, 18] as well as chemical and thermal stability [3, 8, 11]. Because it also favors favorable electronic coupling between molecules in the solid state, [7] and a high level of conjugation, phthalocyanine derivatives report excellent semiconducting properties [9, 18] and are, therefore, the aim of intense research at both industry and academy [3].

Apart from these properties, the phthalocyanine molecule also presents an interesting geometrical structure. As can be seen in see Fig. 1, it is planar and symmetric, and the central portion of the molecule has a radius that can arrange over 70 atoms [4, 6, 8, 10]. Its peripheral portion, on the other hand, can easily be doped with various branched chains [4, 11]. The former fact allows for a number of possibilities of functionalization, whereas the later eases the dissolution of PC derivatives in several solvents. These facts make the phthalocyanine derivatives (PCs) one of the most versatile class of organic semiconductors known to date.

Because of all these attributes, PCs have been applied on various electronic devices [19] and applications of the modern

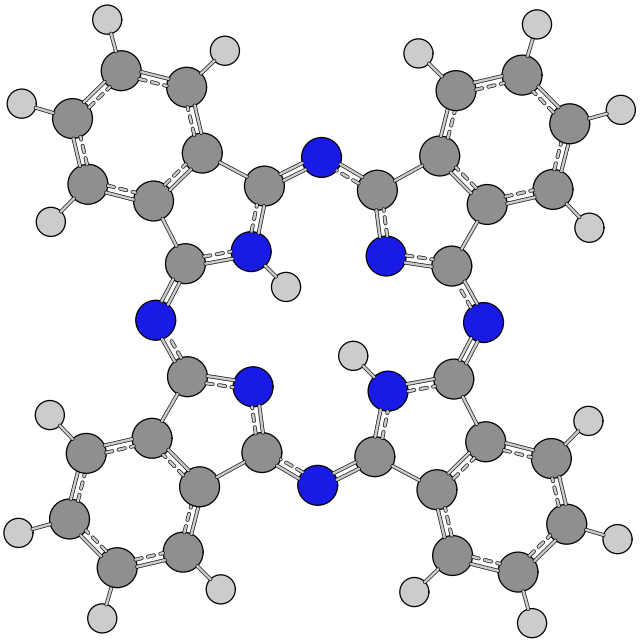


Fig. 1 Representation of phthalocyanine geometry complex used in this work

world, such as organic field effect transistors (OFETs), [4, 8, 10] sensors, [4, 8, 10, 20], photodynamic therapy (PDT), [4, 8, 11] organic light-emitting diodes (OLED), [4, 8, 11] organic photovoltaics (OPVs), [6, 8, 10, 11] optical discs, [4, 6, 8] and liquid crystals [4, 23].

Naturally, the course of improving the efficiency of the existing devices, as well as of conceiving new applicabilities, passes through a correct computational modeling of the molecule itself and also experimental investigations in order to assess the properties of the proposed systems. In this sense, several studies related to PCs have been performed in the previous years, both from theoretical and experimental point of view [4–6, 8–12, 16–20].

Among these studies, a number of density functional theory DFT) calculations on these systems have been carried out in the hope of understanding its electronic properties.

However, the literature is still eager to obtain results from calculations that would investigate the influence of tuned functionals on the absorption spectra of these complexes. Although many studies have been performed within this methodology, [13–15] no information can be found on whether the application of optimized functionals for this specific molecular system can be of use.

Therefore, careful consideration in the light of this procedure would be of great value to the scientific community. The hope is that such an approach can arguably improve the theoretical prediction for important properties from the electronic structure viewpoint. Some of the earliest DFT works have obtained electronic structure and optical phenomena descriptions in decent agreement with experiments [21, 22].

As the tuned scheme of DFT functionals has proven to yield excellent agreement for other class of systems, one can argue that it is worth to try to investigate if the same applies to the absorption spectra of PCs.

In this sense, the present work is devoted to the description of electronic and optical properties of the phthalocyanine molecule, making use of one optimally tuned BLYP functional.

The functional optimization allows better control of both short- and long-range parts of Coulomb operator. Because of this, a possible improvement on the system's characterization when compared with the original functional might be achieved. Head-Gordon et al. [24] have already shown that time-dependent DFT (TDDFT) application on Zincbacteriochlorin–Bacteriochlorin and Bacteriochlorophyll–Spheroidene complexes fails due to the self-interaction error in the orbital energies from the ground-state DFT calculation. Such deficiency can be partially mitigated within the long-range corrected scheme because by virtue of this method one can employ different percentages of Hartree–Fock (which, by definition, is 100 % self interaction free) exchange for the long range [25, 26]. In this case, making use of such optimization scheme is actually essential and leads to a fundamental improvement of the description. The same is true for fundamental characteristics such as charge transfer, Rydberg states, and absorption spectra.

Therefore, verifying whether optical gaps can be better described by making use of optimized functionals [27] is an important issue on assessing their suitability. The present paper carries out a systematic study concerning the short- and long-range corrections applied to the PC molecule and brings a comparison with other functionals. We show that, indeed, the use of tuned functionals is well suited to obtain optical properties of the PC molecule.

In order to do so, we organized the remaining of this paper in three sections: "Computational details" presents the main features of the computational method applied in our calculations; we report our results and carry out their discussion in "Results"; Conclusions summarize our findings.

Computational details

As a first step, we optimized the geometrical structure of the phthalocyanine molecule by making use of the B3LYP functional and 6-31+G(d,p) Cartesian basis set. This choice is explained by the fact that for isolated organic molecules, this combination of functional and basis set has been widely employed in the literature [28] and resulted in an excellent agreement when compared to the experimental geometry obtained by means of X-ray crystallography procedure [29].

Moreover, it has been observed that other functionals tend to overestimate molecular orbital energies [30].

The main idea of the present work is to conduct a direct comparison between optical properties of the PC molecule obtained using different functionals. As these properties result from excited-state calculations performed in different schemes (different functionals), it is only logical to consider a single geometry procedure, otherwise one would not be sure on whether to attribute possible discrepancies to the functional itself or to differences in the geometry.

After obtaining the optimized geometry, we apply time-dependent DFT (TDDFT) calculations to consider the first 50 excited states of the system. In the present paper, we report results of TDDFT calculations within the scope of five different functionals: B3LYP, BLYP, CAM-B3LYP, ωB97XD and OT-LC-BLYP. The last functional represents a modification of the BLYP to include long-range correction. The reasoning behind this method is to separate the electron-electron interaction in the Coulomb operator into two parts: long-range (LR) and short-range (SR) terms. On LR, the exchange term applies the exact Hartree–Fock term, a fact that is particularly useful to partially mitigate problems with the self interaction error. This separation is performed as:

$$\frac{1}{r_{12}} = \frac{erfc(\omega r_{12})}{r_{12}} + \frac{erf(\omega r_{12})}{r_{12}}, \quad (1)$$

where *erf* denotes the error function and ω is considered the adjustable parameter in order to change the short and long range. The first term of the equation is the Coulomb SR and the second one is the LR term. r_{12} is the inter-electronic distance between electrons at coordinates r_1 and r_2. We carried out a tuning procedure of the ω parameter, by spanning its value and computing the associated value of $J = \sqrt{(J_{IP})^2 + (J_{EA})^2}$, as described in [33]. We took the value of ω that minimized the V-shaped curves $J(\omega)$ as the optimum value of the parameter. In this work, the reasonable value of 0.166 m^{-2} was obtained.

Finally, it should be stressed that for all the considered functionals, two basis set are employed: 6-31G(d,p) and 6-31G+(d,p). This was done in order to provide a fair comparison between our results and others from the literature since they have used both schemes. The use of diffuse basis functions is important in situations where it is likely for the electron to be very far away from its core. Therefore, it is certainly justified for the heavy atoms treated in the present work. When it comes to the hydrogen atoms, however, the literature shows [34] that applying diffuse functions on hydrogen is somewhat redundant, except in situations where hydrogen bonding or hydrogen transfer are considered. As these are not the interest of the present work, we chose to apply diffusiveness only where necessary, in order to achieve a better compromise between accuracy and computation feasibility. All our calculations were carried out using the Gaussian'09 package [35].

Results

As we have employed the same optimization technique previously reported in the literature, it becomes unnecessary to discuss structural properties of the system, which is shown in Fig. 1. Therefore, we begin our discussion with a description of the absorption spectra for the system considering all functionals listed before and the 6-31G(d,p) basis set.

Previous experimental results show that two main peaks can be evidenced on the PCs spectrum: one band (*Q band*) lies in around 620 nm [4] and the other one (*Soret band*) around 335 nm [18]. Comparing these values with the theoretical results presented in Fig. 2, one can conclude that B3LYP/6-31G(d,p) and OT-LC-BLYP/6-31G(d,p) are the levels of theory that better correspond to these experimental results. However, we can see that the spectra as a whole are blue-shifted from the experimentally expected data.

An attempt to settle this discrepancy is the addition of diffuse functions to the basis sets. These functions are usually of some importance when excited states are considered in the framework of DFT, because the very nature of the technique tends to delocalize orbitals.

Therefore, Fig. 3 is devoted to present the same spectra using the 6-31G+(d,p) basis set instead. Two interesting features can be noted in this case. The first one is that, again, B3LYP/6-31G(d,p) and OT-LC-BLYP/6-31G(d,p) levels of theory resulted in the best agreement to experimental results. This time, however, we observed a considerable red shift for all the spectra when compared to the previous case. This makes all the considered spectra lie closer to

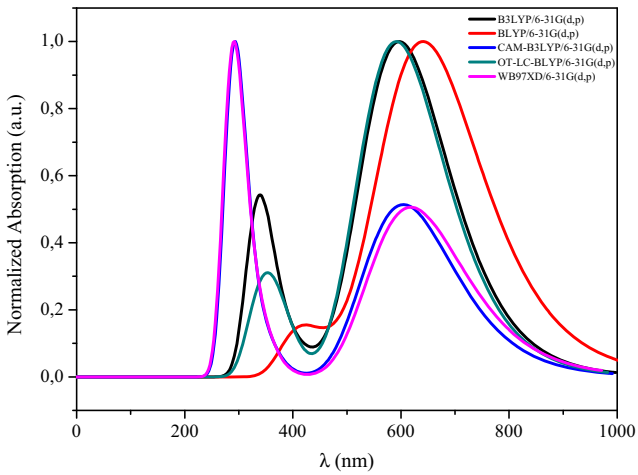


Fig. 2 PC molecule-normalized absorption spectra for different functionals and the 6-31G(d,p) basis set

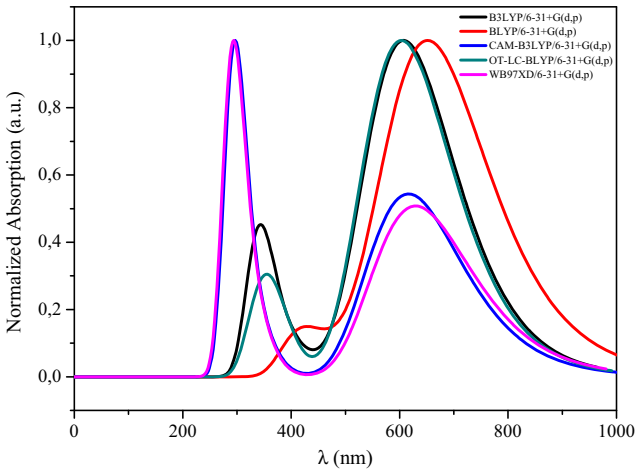


Fig. 3 PC molecule absorption spectra for different functionals and 6-31+G(d,p) basis set

the experimental spectrum than those of Fig. 2, which were computed with 6-31G(d,p). The clear conclusion is that the consideration of diffuse primitives in the basis set is important to accurately describe the absorption spectra of the PC molecule.

We have thus rescued the result that B3LYP/6-31+G(d,p) is known to suitably describe the PC molecule, including from the optical properties point of view. However, we went beyond and showed that the tuning of the long range corrected BLYP not only improves the results of BLYP itself but rather makes this scheme to be competitive—and, actually, slightly superior—with the B3LYP/6-31+G(d,p) scheme. The B3LYP/6-31+G(d,p) level resulted in a first peak at 337 nm and the second one is at 606 nm. This results in absolute deviations of, respectively, 2 nm and 14 nm, when compared to experimental results.

Our tuned OT-LC-BLYP/6-31+G(d,p) level, in its turn, presented peaks at 330 nm and at 625 nm, which corresponds to absolute deviations of 5 nm for both peaks. Moreover, we can see that the spectra are qualitatively similar throughout the UV-Vis region. These facts reassure that OT-LC-BLYP/6-31+G(d,p) is an excellent combination to study the phthalocyanine molecule. If one takes into account that long-range corrected schemes are fundamental in other applications in which PCs are important—charge transfer is a distinctive example—the logical conclusion is that the tuned OT-LC-BLYP/6-31+G(d,p) should be the first choice for this type of system.

Naturally, other factors beyond absorption spectra are extremely important in the description of PCs. Therefore, in order to analyze the characteristics of the system of interest, we performed calculations concerning other optical and electrical properties. We included such results coming from all the analyzed functionals and both basis sets in Tables 1 and 2. Table 1 shows results of frontier orbitals and optical gap together with the experimental data of the later property for means of comparison [32]. The importance of this table lies in the well-known fact that the fundamental gap underestimates the gap energy of the system [31] and, therefore, the optical gap actually reports more realistic values.

Interestingly, the functional that most closely matches the experimental optical gap result is BLYP, both in the situation with and without diffusion basis functions. One can see, however, that the tuned OT-LC-BLYP/6-31+G(d,p) functional also provides an excellent agreement with experimental evidences for this property. Because of this fact, by combining the results of Table 1 and Figs. 2 and 3, we conclude that OT-LC-BLYP/6-31+G(d,p) is the most interesting choice among the investigated ones when it comes to describe the optical properties of the PC molecule in general.

Table 1 HOMO/LUMO Energies and subsequently fundamental gap described as $E_{LUMO} - E_{HOMO}$ and theoretical optical gap description and a comparison with experimental data [32]

6-31G(d,p)	E_{HOMO} (eV)	E_{LUMO} (eV)	Fundamental GAP (eV)	Optical GAP (eV)	Experimental optical gap
B3LYP	4.98	2.84	2.14	2.07	
BLYP	4.44	3.06	1.38	1.92	
CAM-B3LYP	5.70	2.01	3.69	2.02	1.88
OT-LC-BLYP	5.93	1.63	4.30	1.99	
WB97XD	6.20	1.55	4.65	1.97	
6-31+G(d,p)	E_{HOMO} (eV)	E_{LUMO} (eV)	GAP (eV)	Optical GAP (eV)	Experimental optical gap
B3LYP	5.27	3.15	2.12	2.03	
BLYP	4.78	4.78	1.36	1.89	
CAM-B3LYP	5.98	2.32	3.66	1.99	1.88
OT-LC-BLYP	6.29	2.03	4.26	1.95	
WB97XD	6.42	1.55	4.65	1.94	

Table 2 PC most intense transition and its properties for different functionals and basis set

6-31G(d,p)	Energy (eV)	λ_{max} (nm)	Oscillator force (a.u.)	Contribution	State
B3LYP	2.09	594	0.44	H → L (69 %)	2
BLYP	1.94	638	0.33	H → L (68 %)	2
CAM-B3LYP	4.25	292	1.26	H-3 → L (61 %)	11
OT-LC-BLYP	2.12	586	0.43	H → L (68 %)	2
WB97XD	4.30	288	1.21	H-3 → L (58 %)	10
6-31+G(d,p)	Energy (eV)	λ_{max}	Oscillator Force (a.u.)	Contribution	State
B3LYP	2.05	605	0.45	H → L (69 %)	2
BLYP	1.91	649	0.35	H → L (68 %)	2
CAM-B3LYP	4.20	295	1.28	H-3 → L (61 %)	10
OT-LC-BLYP	2.07	598	0.45	H → L (69 %)	2
WB97XD	4.26	291	1.22	H-3 → L (59 %)	10

Finally, we can summarize our results by making a direct comparison between the transitions observed in Fig. 2 and the results presented in Table 2. This comparison is included in Table 2, in which we present the energies of the main transitions, its percentage contribution, the corresponding wavelength, the oscillator strength, and the corresponding excited state number. Comparing all energies and the correspondent wavelengths, we confirm the arguments aforementioned presented. In other words, for OT-LC-BLYP/6-31+G(d,p), the peak of transitions are in good agreement with experimental data [4, 18]. Table 1 shows how the optical gap can be described in good agreement with experimental results [32] when OT-LC-BLYP is considered.

In addition, it is clear from Fig. 2 and Table 2 that OT-LC-BLYP/6-31+G(d,p) level presents a considerable red-shift when compared with B3LYP/6-31+G(d,p) and this shift, indeed, makes the peak closer from the experimental results.

Conclusions

We have conducted a systematic procedure comparing five functionals and two basis sets applied to electronic structure and optical properties of the phthalocyanine molecule. Our main goal was to show that optimally tuned functionals can improve optical properties of a specified system when compared with experimental results.

Specifically, we concluded that the main transitions of the phthalocyanine molecule not only could be better described with our own optimized version of the OT-LC-BLYP/6-31+G(d,p) functional, but could also be improved when compared with the widely used B3LYP/6-31+G(d,p). Our tuning procedures showed superior results on the positioning of the experimental peaks as well as on the evaluation of optical gaps. As the long-range corrected scheme is indispensable for uses such as in charge transfer states study, we conclude that the natural choice for investigating properties of the phthalocyanine molecule is the one proposed by our results. With the contribution of the present work, we hope to have provided some guidance on future initiatives that aim to include detailed on the competition of different classes of functionals for a specific system.

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