Parameterization Study of LRC Functional Applied to Optical Properties of Carotenoids

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Introduction

Solar energy is considered the most promising renewable energy source to attend the increasing global demand in green energy applications[1,2]. Nowadays, dye-sensitized solar cells (DSSCs), pioneering developed by Grätzel[3-5], are recognized as excellent candidates to replace the current silicon-based photocell technology. Advantages such as relatively high light-harvesting efficiency, low cost, simple synthesis process, and large-scale production make the DSSCs attractive for both academic and industrial applications. The working principle of a DSSC involves the optical absorption and charge separation processes by the association of a sensitizer as a light-absorbing material with a wide band-gap semiconductor[6]. In this sense, the carotenoids (polyene-like molecules), which are natural pigments in plants and animals, can be employed as sensitizers by presenting interesting characteristics for photonics applications as, for example, ultrafast optical response[7,8]. In order to improve the efficiency of DSSCs, the optoelectronic properties of dye molecules, such as the energy gap, should be carefully investigated. It is known that the energy gap of molecular systems calculated by solving the Kohn-Sham equation, with conventional Density

Functional Theory functional (DFT), is usually small compared to the gap values obtained experimentally. These errors indicate a clear failure of the approximated functional often used in DFT, and can often lead to misinterpretations regarding the optical properties of these systems. This work proposes a new methodology for functional parameterization that includes longrange corrections, dedicated to the molecules of the main carotenoids present in the Buriti oil (see Figure 1). Such functional contains 100% of the exact Hartree-Fock exchange, a non-local operator extremely important for a realistic description of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbita (LUMO) energies and other properties of the excited state. The group of carotenoids investigated has high potential for application in organic photovoltaic devices and has been extensively explored both theoretically and experimentally.

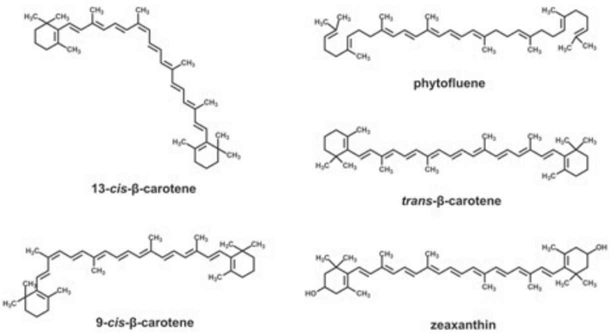

Figure 1. The carotenoid molecules investigated in this work. As a common trait, we can see that all molecules possess isoprene groups - that could act as an electron acceptor in an organic electronic device - and a backbone bridge - a possible donor.

Methods

In this work, we investigate the optoelectronic properties of a group of carotenoids derivatives contained in the Buriti oil (Mauritia flexuosa L.), which presents interesting optical properties for applications in optoelectronic devices based on organic materials. In order to do so, the DFT and Time Dependent DFT (TDDFT) approaches are used considering the functionals B3LYP, LCBLYP and ϖB97. The B3LYP functional is traditionally used in DFT calculations. However, it is well known that this functional causes the delocalization of the wave function. This is a huge challenge in the modeling of organic semiconductor materials, as localized quasiparticles are responsible for the charge transport mechanism in these systems. On the other hand, the LC-BLYP and ϖB97 functionals already include a parameter for long-range corrections.

The central idea in the conception of these functionals is the separation of the Coulomb operator into two terms that take into account the short-range (SR) and long range (LR) interactions, considering the standard error function (erf):

$$\frac{1}{r} = erf\frac{(\omega r)}{r} + erfc\frac{(\omega r)}{r}$$

Thus the Hartree-Fock contribution of long-range, which is essential to maintain the correct description of the system, can be obtained completely. Moreover, the optimization of the correction parameter (ϖ) for long-range interactions can provide better results for excited state properties when compared to the usual approach.

Optical excitations in molecular dyes can be computed within the TDDFT formalism. Nevertheless, the use of conventional semi-local and standard hybrid DFT functionals (such as the popular B3LYP functional) can lead to poor descriptions of charge-transfer like excitations due to limitations associated with multi-electron selfinteraction errors. To overcome these limitations, we have used the functional LRC where the tuning of the range-separation parameter is based on gap fitting[9,10]

$$J_{IP}(\omega) = \left|\varepsilon_H^{\omega}(N) + E_{gs}^{\omega}(N-1) - E_{gs}^{\omega}(N)\right|$$

$$J_{EA}(\omega) = \left|\varepsilon_H^{\omega}(N+1) + E_{gs}^{\omega}(N) - E_{gs}^{\omega}(N+1)\right|$$

$$J_{gap}(\omega) = J_{IP}(\omega) + J_{EA}(\omega) \quad ,$$

where ε_H^{ω} (N) is the HOMO energy for the Nelectron system and E_{gs}^{ω}(N) is the corresponding ground state energy. The ω optimization through these equations can lead to an improvement of the description of the properties calculated using LRC functionals. For each system, with its optimized geometry, and for each functional, the ω value that minimized J_{gap} is chosen as the optimum value. All excited states are evaluated at TDDFT level using functional LC-BLYP and ϖB97 (with both default and tuned ω values) as well as with B3LYP and basis set 6-31G(d,p). Optical absorption spectra were simulated through convolution of the vertical transitions (characterized by a given wavelength and oscillator strength) with Gaussian functions with a full width at half-maximum (FWHM) of 30nm. All calculations were performed with Gaussian 09 (Rev.D.01) software.

Results and Discussion

In this study, we performed a theoretical investigation concerning the properties of the five main carotenoids present in Buriti oil, namely 13- cis-β-carotene, 9-cis-β-carotene, phytofluene, trans-β-carotene and zeaxathin. The main goal of our work consists in evaluating whether this specific tuning for each system provides better qualitative results than the usual approach. The optimization procedure of the five structures was initially done with the B3LYP functional and the basis set 6-31G (d,p). The carbon atoms are moved until they are in a situation of equilibrium in which the total energy is minimized.

The optimization of the geometry was performed by establishing some important considerations, such as the molecules are in gas phase and in the ground state. The new positions of the atoms are then the primary source of information that we have used as parameters for subsequent calculations. A complete investigation of the optimized geometrical parameters, including the angles was also performed.

After perform a pre-optimization with the usual B3LYP functional and the 6-31G (d,p) basis set, we begin the search for the optimal longrange parameter ω. The ω minimization procedure was performed systematically and iteratively. Our aim was to clarify the requirement for a parameter that is totally dependent on the system. The adjustment procedure is classified as ab-initio, since the results are obtained through the own calculations, without any reference to other computations or experimental results. The ω parameter is chosen initially as imposed by the Koopman's theorem, i. e., the first ionization energy should be equal to $-\varepsilon$HOMO . Thus, we conducted a survey of the curves of the ionization potential and electron affinity making single point calculations of molecules in its neutral state and the corresponding cation and anion. Figure 2 present the curves for the functional LC-BLYP considering the molecule 13-cis-β-carotene. As a result, the optimized values for ω, considering each system with functional LC-BLYP and ωB97, are presented in the following table. We realized that the optimal values of the parameter ω for both functional are very close, with the exception of phytofluene. The value found for this molecule deviates significantly from the others. The evolution of the ω parameter suggests that the characteristic length (1/ω) depends directly on the chemical nature, structure and system size.

The main goal of the present work, however, is to investigate the absorption spectra of the carotenoids. Since it is known that the number of conjugated bonds as well as the end groups influence on the absorption spectra of carotenoids. We expect a large deviation of the phytofluene peak from that of the other molecules.

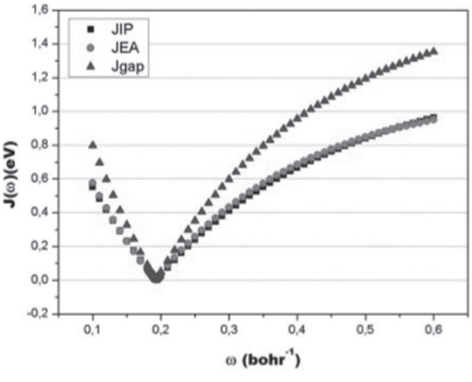

Figure 2. Curves J_{IP} , J_{EA} , and J gap obtained by the optimization process.

Table 1. Optimized ϖ values for both functionals for the five carotenoids.

Molecule	tuned LC-BLYP	tuned ωB97
13-cis-β-carotene	0.152	0.150
9-cis-β-carotene	0.152	0.150
phytofluene	0.193	0.187
trans-β-carotene	0.151	0.149
zeaxanthin	0.149	0.147

Figure 3 presents a comparison of the absorption spectra for the five molecules at the B3LYP/6- 31G(d,p) level of theory (up) together with the results obtained with the tuned LCBLYP/6-31G(d,p) (down). For sake of succinctness, we omitted the tuned ωB97 spectra, as the results were similar to those shown in figure 3 for the LC-BLYP functional. One important feature of this work is to improve the description of the absorption spectra, with respect to the experimental result, when compared to what was obtained using the B3LYP. We can observe the red shift of the tuned spectra when compared to the regular B3LYP. Indeed, the general trend is to obtain the main peaks nearer to the experimentally expected, i.e., associated to smaller wave-length.

While for the functional optimized LC-BLYP, the wavelength difference obtained for trans-β- carotene compared to the experimental was 68 nm, not optimized for this functional difference reaches 99 nm, which is very significant. The amount of wavelength closest to the experimental value was calculated for phytofluene with the functional optimized LC-BLYP where we obtained a difference of only 8 nm, against 57 nm obtained via LC-BLYP with the default value of β to this functional. In all the cases the accordance between the values obtained through our methodology was better than 87% against 72% of the standard technique. At this point we should emphasize that the success of the results presented so far is not due to the mere use of some ω parameter. Rather, it is the very specific tuning of this parameter for each molecule, which allows this methodology to achieve such improvement as far as experimental accordance is considered. This can be confirmed by the use of the standard values of the ω parameter for the used orbitals. Therefore, it is clear that the long-range ω correction parameter tuning technique is a crucial procedure to obtain the excited state properties more accurately. The methodology, in fact, was superior in the description of the properties of the studied systems.

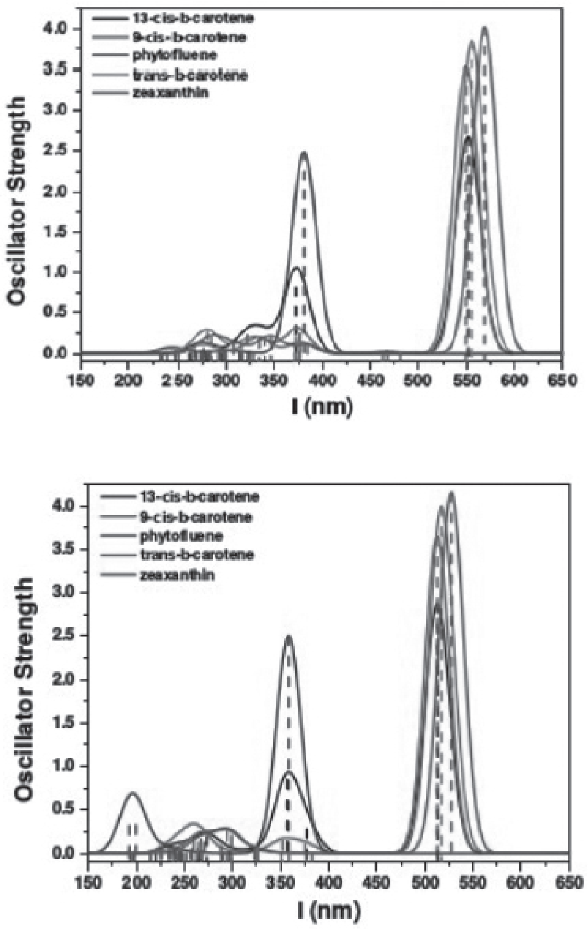

Figure 3. Absorption spectra for the five molecules computed at B3LYP (up) and LCBLYP (down).

Conclusions

In summary, we have demonstrated the importance of using a systematic way of refinement for determining the optimal ϖ parameter. The procedure is necessary because as there is no single ϖ value that is ideally universal, optimization gives us a natural way to find a parameter that is dependent on the system, maintaining a correct balance between the exchange and the correlation.

The method to provide a more localized description and, consequently, better donoracceptor character of low band gap copolymers optical reference, shows that the optical and electronic properties of systems covered here are in good agreement with the which is experimentally expected. It was observed that ϖ parameter to be sensitive to the system under consideration. The ϖ a optimized values generally decrease with increasing chain length, whatever the nature of the functional. As the electronic delocalization increases with system size, it is necessary that the exact exchange has lower weight; thus we have an ϖ optimally adjusted should exceed a fixed amount. Here, it was found that the values of ϖ parameter have total dependence on the degree of system combination.

Finally, we can state that here explored approach offers a much more accurate alternative to evaluate electronic and optical properties of such a system, since the use of conventional hybrid functional underestimate the orbital energies and the calculations with functional including long range, using the default values for each functional ϖ lead to an overestimation of the orbital energies.

Acknowledgments

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References

1. 1B. C. Thompson, J. M. J. Frechet, Angew. Chemie Inter. 47, 58, (**2008**).
2. 2S. Gunes, H. Neugebauer, N. S. Sariciftci. Chem. Rev. 107,1324, (**2007**).
3. 3M. Gratzel. J. Photochem. Photobio. C. 4, 255, (**2003**).
4. 4M. Gratzel. Inorg. Chem. 44, 6841, (**2005**).
5. 5A. Hagfeldt, M. Gratzel. Acc. Chem. Res. 33, 269, (**2000**).
6. 6A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson. Chem. Rev. 110, 6595, (**2010**).
7. 7A. J. Heeger, D. Moses, M. Sinclair. Shynt. Metals 15, 95, (**1986**).
8. 8D. Polli, G. Cerullo, G. Lanzani, S. de Silvestri, K. Yanagi, H. Hashimoto, R. J. Cogdell. Phys. Rev. Lett. 93, 163002, (**2004**).
9. 9 L. Kronik, T. Stein, S. Rafaely-Abramson, R. Baer, J. Chem. Theory Comput, 8(5), 1515, (**2012**).

10. N. Kuritz, T. Stein, R. Baer, L. Kronik, J.Chem.
11. Theory Comput, 7(8), 2408, (**2011**).

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