

Theoretical model for the polarization molecular and Hückel treatment of PhosphoCyclopentadiene in an external electric field: Hirschfeld study

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Abstract In this study we relate the Hückel method and molecular polarization of PhosphoCyclopentadiene (P-cyclopentadiene) with respect to the Cyclopentadienyl, and its consequent separation of charges of particular set of conjugated diene systems. The Hückel method and Molecular Polarization of P-cyclopentadiene is expressed as a function of the induced polarizability of Cyclopentadienyl in an external electric field, presenting a technique to express the molecular polarizabilities and Hückel method of diene systems as a function of another in an external electric field, using local quantum similarity index (LQSI) based on the Hirschfeld partitioning in the framework of conceptual density functional theory, this index was introduced in the molecular polarization of cyclopentadienyl in an external electric field and in the secular determinant of the Hückel method applied to the Cyclopentadienyl in order to express the molecular polarization and Hückel method as a function of P-cyclopentadiene using six local similarity index: Overlap, Overlap-Interaction, Coulomb, Coulomb-Interaction, Overlap-Euclidian distance and Coulomb-Euclidian distance. The topo-geometrical superposition approach (TGSA) was used as method of alignment, which allows us to obtain high results in the proposed LQSIs, this method to be a straightforward procedure to cope with the problem of relative orientation of the molecules when evaluating, developing a new technique that will allow us to study structural systems that differ in

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one atom in its structure, and proposing methodologies for future studies on a much broader range of systems in which the Hückel method and molecular polarization of two species that differ only in one atom in its structure can be approximated in this way.

Keywords Hückel method · TGSA · Quantum similarity · Molecular polarizability.

1 Introduction

Ab initio calculations in computational chemistry are performed routinely and successfully applied nowadays to the study of a vast range of problems of chemical interest [1–3]. In recent years, efficient techniques have been developed for the *ab initio* calculation for the calculation of molecular properties. The great development that has had computational chemistry is due to development in software and hardware which allowed a significant advance in the calculation of a lot molecular properties. Despite of the success of *ab initio* calculations some elemental methods such as Hückel still are used. Actually the use of the Hückel approximation is justified because through it is possible to illustrate some quantum fundamental concepts at the price of little calculation [4–9].

In line with the increasing importance of applying of quantum techniques to study the properties and reactions of molecules, the indexes based in quantum similarity has received very attention; a example of this methodologies is the molecular quantum similarity index (MQSI) based on the electronic density proposed by Carbó [10–17], now almost three decades ago, MQSI can be considered as the prototype of such index and nowadays continues to play an important role.

In this study was related the (MQS) with the molecular polarizability and Hückel method, in order to find some application of this theoretical model using the Phospho-Cyclopentadiene (P-cyclopentadiene, point group C_{2v}) and Cyclopentadienyl (point group D_{5h}) molecules as model of this application. We proposed a local similarity index based using the Hirschfeld partitioning technique [18], enabling us to evaluate (dis)similarity at the atomic level.

A second reason for the interest in these systems is the development of a methodology for analysing molecular similarity with the molecular polarization and Hückel method applied to P-cyclopentadiene that differ only by the presence of a different atom in its structure with respect to Cyclopentadienyl. The discussion on the relation between the dissimilarity, Polarization molecular and the Hückel method of P-cyclopentadiene and Cyclopentadienyl, should be considered as only being introductory and will be elaborated in the near future on the basis of a study on a much wider series of systems in which approximates the Polarization molecular of two species that differ only in one atom in its structure.

In this paper, was taken the carbon–carbon bond in the Cyclopentadienyl as a molecular fragment so it can be approximated to a diatomic molecule, in this since we can focused the attention in the C–C bond and C–P bond in the case of P-cyclopentadiene, taking into account this idea is proposed design a theoretical model that allows relate

the induced polarizability under an electric field in two molecules through six molecular similarity descriptors, the descriptor of overlap and overlap-interaction that quantify the structural similarity, the descriptor of Coulomb and coulomb-interaction that quantify the electrostatic similarity between the two charge densities of the molecules, the other descriptors are respectively the Overlap and Coulomb Euclidean distances, respectively. This will allow to relate the different molecular polarities, taking in account that the application of dielectric material extending daily [19–26].

The use of Hückel approximation is interesting since many quantum fundamental concepts can be illustrated at the price of little calculation within of this method. In this way is possible to performed calculations of electronic structure of molecules in terms of elementary Hückel theory and molecular polarizability obtaining outcomes according to experimental facts [27–33]. From this perspective was possible in this work exploit the Hückel method using some of its characteristic in order to create new tools that permit us to correlate a particular group of chemical molecules to get non-degenerate characteristic values of a particular dienes systems (P-cyclopentadiene), with this purpose, we use the field of molecular quantum similarity (MQS), which allows make some interesting molecular correlations.

The structure of this paper will be as follows: The theory and computational details is described in Sect. 2. The results and discussion are developed in Sect. 3 and finally, in Sect. 4 are discussed the most important conclusions.

2 Theory and computational details

2.1 Molecular polarization of molecules in an external electric field

In order to obtain the molecular description of polarization in the P-cyclopentadiene in this model is proposed the application of the molecular polarization of two identical atoms which can by the (C1–C2) bond in the Cyclopentadienyl, proposed by Khvalchenko et al. [34] taking in account the correlation structural and electronic in the compounds studied.

The model of polarization of two identical atoms under the action of an electric field, consider the molecular polarization of two identical atoms (carbon–carbon) in an electric field; designate the Cyclopentadienyl as molecule A. Suppose that the electrons can do transitions of the form $2s \rightarrow 3p$. All possible initial states of the system under study are described by wave functions.

$$\Psi_m^L = \sum_{\mu} s_{L,\mu,m-\mu}^{(l,\bar{l})} \Psi_{\mu} \bar{\Psi}_{m-\mu} \quad (1)$$

where $s_{L,\mu,m-\mu}^{(l,\bar{l})}$, are the Wigner coefficients [35] and the over barred symbols refer to the states of the second atom. Using the relation (1) can be determined the 16 initial states of the system of atoms, see Appendix 1.

2.2 Linearly polarized field

Under the action of an electric field $\mathbf{E} = (\mathbf{E}_1\mathbf{i} + \mathbf{E}_2\mathbf{j} + \mathbf{E}_3\mathbf{k})\cos(\omega\mathbf{t})$. The quantum states of this system can be given by the equation:

$$i\hbar \frac{\partial}{\partial t} = (\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_0 + \hat{\mathbf{V}}) \Psi \quad (2)$$

where

$$\Psi = \sum_{k=1}^{16} a_k \Psi_k \exp(-i\omega_k t) \quad (3)$$

$$\omega_k = \begin{cases} 2\omega_1, & k = 1 \\ \omega_1 + \omega_2, & k = \overline{2}, \overline{7} \\ 2\omega_2, & k = \overline{8}, \overline{16} \end{cases} \quad (4)$$

where $\hbar\omega_1$ and $\hbar\omega_2$ are the energies of the 2s and 3p, \hat{H}_0 and \hat{H}_0 represent the Hamiltonians of the atoms, and $\hat{V} = -(D, E)$, $D = d + \bar{d}$, $d + \bar{d}$ are the operators of the dipole moments of the atoms. Equation 3 yields the system of differential equations (\dot{a}).

$$i\hbar \dot{a} = Va \quad (5)$$

To solve this Eq. 5, is used the method of successive approximations given in Eq. 4 [34].

$$a = I - \int_0^t V(\tau) d\tau \quad (6)$$

where (\mathbf{a}) denotes a square matrix of order 16 where each column defines the wave function $|\Psi_k\rangle$ of the atoms-plus-field system in the corresponding initial state see Appendix 1. For calculate the polarization of this system is used the Eq. 7, for the molecule A.

$$\mathbf{P}_{\mathbf{kA}} = Sp \hat{\rho}_k \mathbf{D} \quad (7)$$

Here $\hat{\rho}_k = |\Psi_k\rangle \langle \Psi_k|$, and the operator \mathbf{D} is constructed using the basis of functions (Eq. 1). This allows obtain the following expressions for the corresponding initial states given in Appendix 1, and which can be seen in Appendix 2.

Taking in account the Eq. 7, proposed the multiplication of this equation by the similarity descriptors, this new local descriptor can be named “*Induced Molecular Polarizability Descriptor (IMPD)*” and postulate as quantifier of (dis)similarity between the molecular polarization and the quantum similarity.

2.3 Similarity index

The MQS field was introduced by Carbó [12–17]. He defined the Euclidean distance, d_{AB} , between the electronic densities $\rho_A(r)$ and $\rho_B(r)$ of two molecules A and B as:

$$d_{AB} = \int |\rho_A(r) - \rho_B(r)|^2 dr = \int \rho_A^2(r) dr + \int \rho_B^2(r) dr - 2 \int \rho_A(r) \rho_B(r) dr \quad (8)$$

Now this index can be represented geometrically using the concept of cosine of angle subtended between the density functions, considering as vectors. It is written as:

$$R_{AB} = \frac{\int \rho_A(r) \rho_B(r) dr}{[(\int \rho_A^2(r) dr) (\int \rho_B^2(r) dr)]^{1/2}} = \frac{Z_{AB}}{\sqrt{Z_{AA} Z_{BB}}} \quad (9)$$

This equation involving the overlap integral Z_{AB} , often called molecular quantum similarity measure (MQSM), between the electronic densities of molecules A and B. Z_{AA} and Z_{BB} are called the molecular quantum self-similarity measures of molecules A and B [36,37].

2.3.1 Local quantum similarity index (LQSI) for the structures

For the conversion of the global Carbó index into a local index was possible using the Hirschfeld partitioning [18]. The calculation of LQSI with density functional theory (DFT) is a very used method [38,39], taking into account that the point Group of Cyclopentadienyl D_{5h} with P-cyclopentadiene C_{2v} structurally differ only by the presence of a different atom.

According to the idea of Hirschfeld, obtaining atoms-in-molecules densities by defining the “stock-amount” or weight of an atom **P** in the electronic density at **r** as

$$w_P(r) = \frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \quad (10)$$

Here, $\rho_P^0(r)$ is the electronic density of the isolated phosphor atom in the molecule, and $\sum_X \rho_{X,P}^0(r)$ is the promolecular density of the molecule, obtained as the sum of the isolated atom densities in the same molecular geometry as the actual molecule. The Hirschfeld atomic electronic density of the atom a in the molecule, denoted, can be calculated as

$$\rho_P(r) = w_P(r) \rho_P(r) \quad (11)$$

Analogously, for the Cyclopentadienyl

$$w_C(r) = \frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \quad (12)$$

The numerator of the Carbó index then becomes

$$Z^{local,P} = \int w_P \rho(r) dr = \int \left(\frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \right) \rho_P(r) dr \quad (13)$$

and, for the Cyclopentadienyl

$$Z^{local,C} = \int w_C \rho(r) dr = \int \left(\frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \right) \rho_C(r) dr \quad (14)$$

where as the self-similarities $Z_{PP} = (Z^{local,P})^2$ and $Z_{CC} = (Z^{local,C})^2$ can be written analogously in terms of atomic contributions, using the Eqs. (16 and 17) in the expression of the Carbó index (Eq. 12), the global index is converted into a local analogue:

$$\begin{aligned} R_{PC}^{local} &= \frac{Z^{local,P} Z^{local,C}}{\sqrt{(Z^{local,P})^2 (Z^{local,C})^2}} \\ &= \frac{\int \left(\frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \right) \left(\frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \right) \rho_P(r) \rho_C(r) dr}{\left[\int \left(\frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \right)^2 \rho_P(r) \rho_P(r) dr \right]^{1/2} \left[\int \left(\frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \right)^2 \rho_C(r) \rho_C(r) dr \right]^{1/2}} \end{aligned} \quad (15)$$

The principal problem with the calculation of Carbó and Hodgkin–Richards index is their dependence with the relative orientation of the molecules. The problem has been addressed through the use several methodologies with criterions such as aligning of the molecules according to common physicochemical features (for example, matching different three-dimensional molecular fields such as steric, electrostatic, or hydrophobic fields) [40] or alignment of the molecules based on topological and geometrical features only, as has been implemented in the methodology called Topo-Geometrical Superposition Algorithm (TGSA) [38] this algorithm is based on comparisons of atom types and interatomic length.

Other methods are based in the maximizing of the similarity measure [41]. In this framework, a new algorithm, the quantum similarity superposition algorithm (QSSA), was recently designed by Bultinck et al. [42–48], expressing the relative position of two molecules in terms of mutual translation in three Cartesian directions and three Euler angles. The quantum similarity overlap, considering the electronic densities of the molecules within the promolecular atomic shell approximation (PASA) [49] and considering the atomic electronic densities within the atomic shell approximation (ASA) [50,51], is then used to optimize the mutual positions and similarity of the molecules, using a Lamarckian genetic algorithm. In this paper, we decided to superimpose the common fragment shown in Fig. 1, using the (TGSA), taking into account the rigidity of the rings, as relevant structural criteria [52].

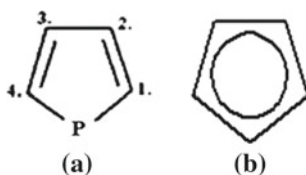


Fig. 1 **a** Structure of the P-cyclopentadiene, (point group C_{2v}), **b** Cyclopentadienyl (point group D_{5h}) this atoms used for superposition are labeled and the Topo-Geometrical Superposition Approach (TGSA) by Girones, Robert and Carbó [38] is based on the recognition of the largest common substructure in the aligned molecules. Common substructure searching is an active field of research; for a lucid review of the different aspects in substructure searching, the reader is referred to the work by Chen et al. [52]

All charge densities used in this work were calculated using the **Gaussian 03** [53] program at the B3LYP/6-31G* level [54–56] which can be expected to be adequate for the purpose of our study.

3 Results and discussion

In order to describe the similarity electronic from the viewpoint of the resonant systems in this study is expressed the Hückel method to P-cyclopentadiene molecule (Fig. 1), as a function of Cyclopentadienyl, instead of taking into account the interactions of phosphor with the neighboring carbon atoms, we are proposing the introduction of local similarity index of the Phosphor atom in P-cyclopentadiene with respect to the carbon of Cyclopentadienyl in the construction of the secular determinant, the P-cyclopentadiene belong to the point group C_{2v} , with a set of five p π orbitals (see Fig. 2).

Using the expression (16), n time the i th reducible representation occurs in a irreducible representation ($\Gamma_{\pi} = E = 5$, $C_2 = -1$, $\sigma_v(xz) = -5$, $\sigma_v(yz) = 1$) where we know only the characters of each representation by the Eq. 16, (see Appendix 3).

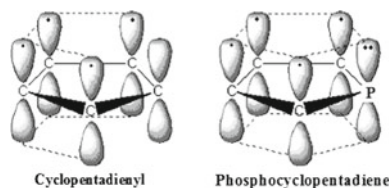
$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R) \quad (16)$$

where h represents the order of the group. We find the secular determinant of the linear combinations of atomic orbitals adapted to the symmetry (SALCs).

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & \dots & 0 \\ H_{21} & H_{22} - E & \dots & \dots & 0 \\ \vdots & \vdots & H_{33} - E & H_{34} & H_{35} \\ \vdots & \vdots & H_{43} & H_{44} - E & H_{45} \\ 0 & 0 & H_{53} & H_{54} & H_{55} - E \end{vmatrix} = 0 \quad (17)$$

Applying Hückel approximations. We have

Fig. 2 Comparison of the resonant system of Cyclopentadienyl with respect to the P-cyclopentadiene



$$\begin{aligned}
 H_{11} &= \int \psi_1 H \psi_1 d\tau = \alpha, & H_{12} &= \int \psi_1 H \psi_2 d\tau = \beta, & H_{22} &= \int \psi_2 H \psi_2 d\tau = \alpha - \beta, \\
 H_{33} &= \int \psi_3 H \psi_3 d\tau = I^S \alpha, & H_{34} &= \int \psi_3 H \psi_4 d\tau = \sqrt{2}\beta, & H_{35} &= \int \psi_3 H \psi_5 d\tau = 0, \\
 H_{44} &= \int \psi_4 H \psi_4 d\tau = \alpha, & H_{45} &= \int \psi_4 H \psi_5 d\tau = \beta, & H_{55} &= \int \psi_5 H \psi_5 d\tau = \alpha + \beta.
 \end{aligned}$$

where (I^S) in H_{33} represents the proposed local quantum similarity of the P-cyclopentadiene phosphor atom with respect to the carbon atom of the Cyclopentadienyl, therefore the two components secular determinant is $\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$, whose solutions represent the energies associated with the dimension $A_2(E_1 = \alpha - 1.618\beta, E_2 = \alpha + 0.618\beta)$, similarly for the other determinant, taking into account that the difference between the P-cyclopentadiene and the Cyclopentadienyl is the presence of phosphor, we intend to introduce the local similarity index Overlap, Coulomb with their Euclidean distances, specifically in the integral H_{33} in the secular determinant, resulting

$$\begin{vmatrix} I^S \alpha - E & \sqrt{2}\beta & 0 \\ \sqrt{2}\beta & \alpha - E & \beta \\ 0 & \beta & \alpha + \beta - E \end{vmatrix} = 0 \quad (18)$$

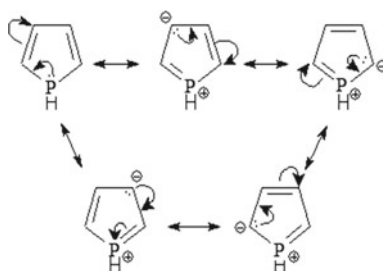
This determinants, will allow us to express the application of the method Hückel in the P-cyclopentadiene (point group C_{2v}) in function of the application of the method applied in the Cyclopentadienyl of symmetry D_{5h} .

The first descriptor will use the local similarity index of overlap, which will allow us to quantify the structural similarity between the phosphor atom and carbon atom of the Cyclopentadienyl, with their Euclidean distance, when decrease the Euclidean distance indicates that the structures are structurally very similar, due a that the structures differ only by a single atom, we associate these lengths with the local structural similarity of overlap between the two atoms, in Table 1 show the values of the six indexes of MQS.

In Table 1 we can see a local similarity index Overlap of **0.964** and of Coulomb **0.996**, this allows say that the effects associated with the structure as bond distance, atomic size and hybridization sp^2 of the atom phosphor with respect to the some hybridization of atom carbon in the Cyclopentadienyl of symmetry D_{5h} , are more appreciable that the electronic effects as the location of the resonant system Fig. 2, and presence of an additional electron in the P-cyclopentadiene with respect to the

Table 1 Local similarity index (Eq. 15) (analytical and numerical methods) and Euclidean distance (Eq. 8), using global densities for the P-cyclopentadiene versus Cyclopentadienyl

Structure	$Z_{CP}(O)^c$	$Z_{CP}(C)^d$	$LSI(O)^e$	$LSI(C)^f$	$D_{CP}(O)^g$	$D_{CP}(C)^h$
P-cyclopentadiene ^a versus Cyclopentadienyl ^b	2.860	188.767	0.964	0.996	0.461	1.426

^a Point group C_{2v} ^b Point group D_{5h} ^c Interaction of overlap^d Interaction of Coulomb^e Local similarity index of overlap^f Local similarity index of Coulomb^g Euclidean distance of overlap^h Euclidean distance of Coulomb**Fig. 3** Resonance structures of P-cyclopentadiene

Cyclopentadienyl, such results can be checked with their Euclidean distances that for the local similarity index overlap is **0.461** and for the local similarity index Coulomb is **1.426**.

The Fig. 3 shows the chemical behaviour of P-cyclopentadiene in the electronic distribution indicated by the respective resonance structures (Fig. 2), such behaviour is associated with a low acid character due a that the phosphorus and carbon atoms are protonated and the resonant system is very stable, showing opposition to donate a hydrogen atom, in agreement with the chemical formalism of Bronsted–Lowry theory.

In the Fig. 4, we can see in contrast the electronic properties for Cyclopentadienyl, these having more anionic characteristic in their behavior, according with the rule of $(4n + 2)$ electrons) in the P-cyclopentadiene. Sp^2 carbon of Cyclopentadienyl (quantified by the local MQS index with respect to Overlap of the P-cyclopentadiene), is very acidic because the conjugate base of the Cyclopentadienyl anion is aromatic and therefore very stable.

In Table 1 we can see that the Euclidean distance of overlap are larger than those of Coulomb, this is because the bond length (C–P) in the P-cyclopentadiene are higher that the of the (C–C) in the Cyclopentadienyl (see Fig. 5), and this is evidenced by the lower local similarity index of Overlap with respect to the Coulomb index.

The high values in the local similarity indexes observed in Table 1, show that the method **TGSA** alignment is a method suitable for our purpose, taking into account that the **TGSA** method considers the molecules as rigid bodies; also it is able to recognize a common substructure, providing a coherent alignment with chemical intuitive sense.

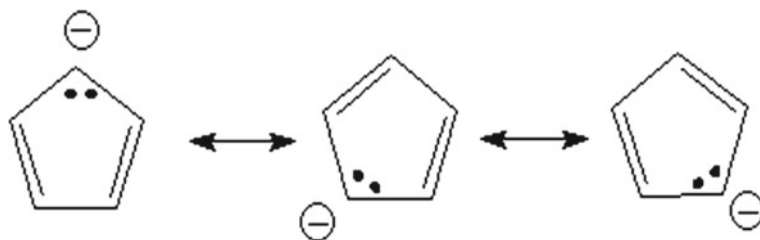
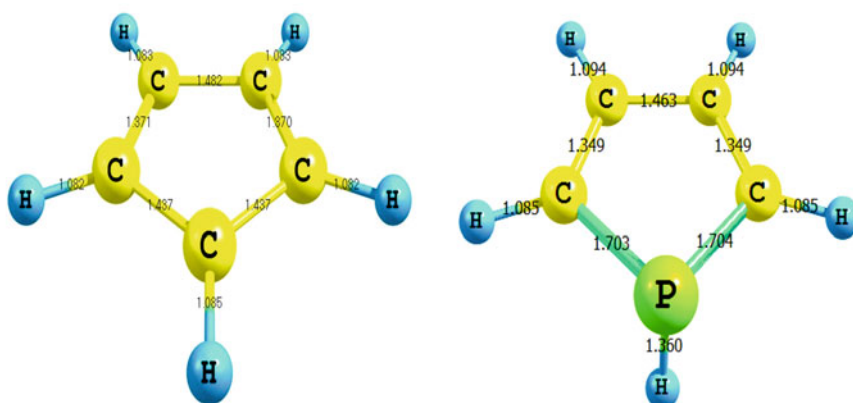


Fig. 4 The Cyclopentadienyl anion resonance forms are all aromatic, with respect to the electronic behaviour of P-cyclopentadiene



(a) Bond distance of Cyclopentadienyl. **(b)** Bond distance of P-cyclopentadiene.

Fig. 5 Comparison of the bond length (\AA Armstrong units) of **a** Cyclopentadienyl and **b** P-cyclopentadiene

In the Fig. 6, we can see different in the length among the carbon–carbon bond in Cyclopentadienyl and the phosphor-carbon bond of the P-cyclopentadiene, which give rise to different molecular polarizations, also this Fig. 5 shows that the lengths between bonds on the actual structure of Cyclopentadienyl compared with those of P-cyclopentadiene are peers, so our initial hypothesis does not consider the polarization of the atoms neighboring the site of interest is well justified (see Table 1).

In Fig. 6 are depicted the tendency of the dipole moment and total atomic charges; we see that the trend for the P-cyclopentadiene is oriented toward the phosphor atom, due to the electronegative character (with a total atomic charge of 0.436), which results in the loss of symmetry of the molecular orbital, and the probability of finding the electron is greater in the vicinity of the more electronegative atom, unlike in the Cyclopentadienyl of orientation toward the center of the ring, this is due to the resonant characteristic of the ring (see Fig. 2) where the asymmetric carbon has a total atomic charge of -0.099 , these characteristics for the electric charge in the rings is measured by the Coulomb index (see Table 1).

In Table 2 we can observe that the energies of the orbitals of P-cyclopentadiene as a function of the energies of Cyclopentadienyl has nondegenerate values, taking into

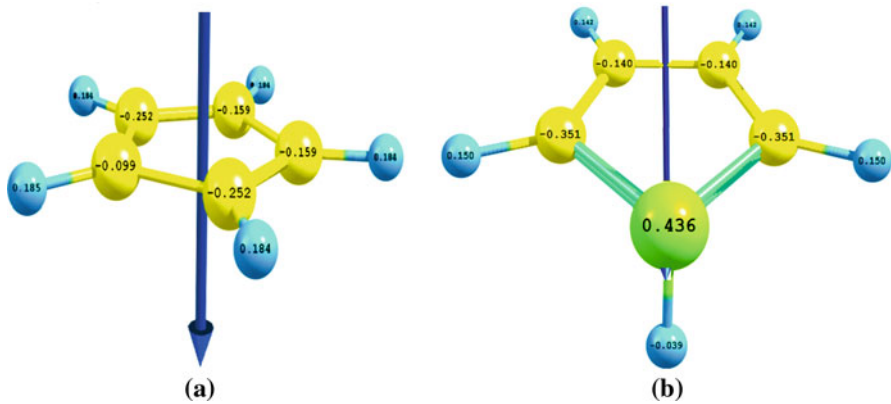


Fig. 6 Dipole moment and total atomic charges: **a** Cyclopentadienyl and **b** P-cyclopentadiene

Table 2 Orbital energies values of P-cyclopentadiene as a function of the orbital energies of Cyclopentadienyl, for each similarity descriptor (Table 1)

Energy values			
Index	E_3	E_4	E_5
$LSI(O)^a$	$0.964\alpha + 1.928\beta$	$0.964\alpha + 0.190\beta$	$0.964\alpha + 3.666\beta$
$LSI(C)^b$	$0.996\alpha + 1.992\beta$	$0.996\alpha + 0.189\beta$	$0.996\alpha + 3.789\beta$
$DCP(O)^c$	$0.461\alpha + 0.922\beta$	$0.461\alpha + 0.090\beta$	$0.461\alpha + 1.753\beta$
$DCP(C)^d$	$1.426\alpha + 2.852\beta$	$1.426\alpha + 0.271\beta$	$1.426\alpha + 5.423\beta$
$i-(O)^e$	$2.860\alpha + 5.720\beta$	$2.8860\alpha + 0.564\beta$	$2.8860\alpha + 0.564\beta$
$i-(C)^f$	$188.767\alpha + 377.534\beta$	$188.767\alpha + 35.865\beta$	$188.767\alpha + 717.843\beta$

- ^a Local similarity index of overlap
- ^b Local similarity index of Coulomb
- ^c Euclidean distance of overlap
- ^d Euclidean distance of Coulomb
- ^e Overlap-interaction
- ^f Coulomb-interaction

account their local indexes of similarity are approximately the unit (Table 1), naturally the Carbó index is limited to the range (0, 1), where $C_{AB} = 1$ means perfect similarity, according to the Schwartz integral inequality [57]:

$$\left[\int \rho_A(r) \rho_B(r) dr \right]^2 \leq \int \rho_A^2(r) dr \int \rho_B^2(r) dr \quad (19)$$

When ρ_A equals ρ_B are the electronic density.

In the Table 2, we see that the energetic characteristics of the rings from their atomic interactions are different due to the presence of phosphorus atom finding different ways to obtain nondegenerate energies using similarity descriptors in the Hückel method of the P-cyclopentadiene, these results demonstrate that the quantum similarity is an alternative, which allowed us to break the energy degeneration, providing alternatives

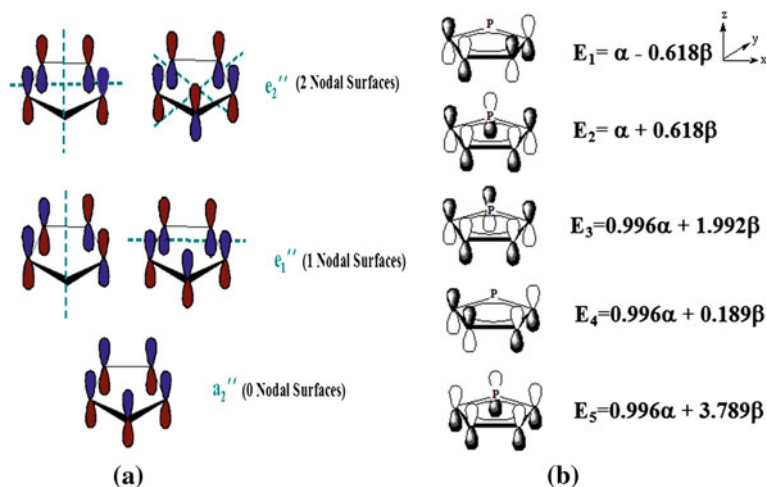


Fig. 7 **a** Orbital degeneration of Hückel method in the Cyclopentadienyl, **b** breaking the orbital degeneracy in the Hückel method of P-cyclopentadiene, proposed in this study. In the Fig. 7b is used the orbital energy of Coulomb index of Table 2

Table 3 Molecular polarizability descriptors for the P-cyclopentadiene (P_B) in function of molecular polarizability of Cyclopentadienyl (P_A), proposed in this study

Induced molecular polarizability index for P_B :

$$2.860P_{nA}^{a,b} \quad 188.767P_{nA}^{a,c} \quad 0.964P_{nA}^d \quad 0.996P_{nA}^e \quad 0.461P_{nA}^f \quad 1.426P_{nA}^d$$

^a Analytical method

^b Interaction of overlap

^c Interaction of Coulomb

^d Local similarity index of overlap

^e Local similarity index of Coulomb

^f Euclidean distance of overlap

^d Euclidean distance of Coulomb

P_A : Eq. 7. With respect to the polarizability states (see Appendices 1 and 2)

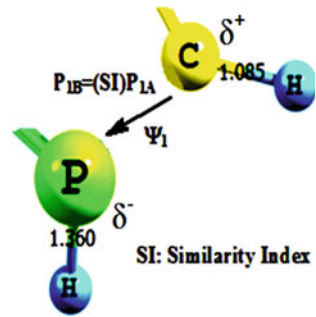
Note n is the quantum state (see Appendices 1 and 2)

to solve the problem of obtaining nondegenerate values in systems where the approximations of the Hückel method provide degenerate values, presenting a new technique to students of quantum chemistry for obtain nondegenerate characteristic values of a particular conjugated systems, in addition these results allowed us to solve the Hückel method for P-cyclopentadiene without taking into account the interactions of neighboring atoms to phosphor, using local similarity index of overlap and coulomb which allowed us consider the P-cyclopentadiene (C_{2v}) according to the Cyclopentadienyl of D_{5h} symmetry, in the Fig. 7 is performed the comparison in the orbital degeneration between Cyclopentadienyl and P-cyclopentadiene.

In Table 3 shows the values of the molecular polarizations using the Eq. 7, which allows quantify the molecular polarization in the (C–P) bond of P-Ciclopentadienyl.

The importance of these new techniques lies in the finding of similar characteristics that allow us to correlate members [58]. This model suggests a new perspective on

Fig. 8 IMPD for the P-Cyclopentadienyl in an external electric field proposed in this study. Note P_{1A} : is the Eq. 7 and R_{PC}^{local} : is the Eq. 15



induced polar chemical bonding, that arises naturally as a result of elastic deformation of the cloud of electrons around of the atomic nuclei of molecules A and B, and express the induced polarization in the molecule A as a function of the molecule B, this new property is quantified by the proposed descriptor Eq. 20.

In the Fig. 8, is shows the molecular polarization for the first quantum state (see Appendices 1 and 2) related by the molecular descriptor proposed (Table 3), expressing the molecular polarization of P-cyclopentadiene (P_B) in function of molecular polarizability of Cyclopentadienyl (P_A), for the ground-state Ψ_1 . where:

$$\begin{aligned}
 P_{1B} &= (P_{1A}) [SI] = (Sp\hat{\rho}_k\mathbf{D}) \left[R_{PC}^{local} \right] \\
 &= (Sp\hat{\rho}_k\mathbf{D}) \left[\frac{\int \left(\frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \right) \left(\frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \right) \rho_S(r)\rho_C(r) dr}{\left[\int \left(\frac{\rho_P^0(r)}{\sum_X \rho_{X,P}^0(r)} \right)^2 \rho_P(r)\rho_P(r) dr \right]^{1/2} \left[\int \left(\frac{\rho_C^0(r)}{\sum_Y \rho_{Y,C}^0(r)} \right)^2 \rho_C(r)\rho_C(r) dr \right]^{1/2}} \right] \quad (20)
 \end{aligned}$$

This model includes interactions of the induced dipoles by the atoms, considering that this model is not of point masses and inelastic collisions, therefore this interactions allow asymmetric charge distribution resulting a induced polarization, taking in account the induced dipole moment concept [59], in addition this descriptor (Eq. 20) can relate different dipole moments depending of the polarizability states (see Appendix 2), (see Fig. 6).

These methodological proposals allow us to find new molecular descriptors of energy and local polarizability in an external electric field, relating local atoms in the structures studied and can be complementary to the reported by Krishtal et al. [27,28], so we can define these new local descriptors as potential descriptors taking into account that is with respect to another molecule that are calculated and this is the main reason to express a system in terms of another according to Morales-Bayuelo et al. [19,29,60].

4 Conclusion

In this paper is proposed a theoretical model to relate the induced molecular polarizability of P-cyclopentadiene as a function of the induced polarizability of Cyclopentadienylin an external electric field (see Eq. 20), for relationship the molecular polarization together with the quantum similarity descriptors (see Table 1), also is proposed a new technique that allows us to express the energies values of P-cyclopentadiene as a function of the energies of Cyclopentadienyl by the introduction of local similarity index of overlap and coulomb with their Euclidean distances in the secular determinant of the Hückel method, this technique allows us to develop this method in the P-cyclopentadiene without considering the interactions with neighboring atoms (see Fig. 7).

Additionally this technique gives us a tool that will allow us to express a particular system as a function of an analogy that differs by one atom and associated aromatic, not aromatic and antiaromatic systems. From all the results in this paper emerges that the use of the global Carbó index into a local index using the Hirschfeld partitioning, reveals a structure that dependent of the induction of asymmetry on two structures that differ only in atom, which can be important for centers situated at large distance from two structures that differ only in an atom and is a adequate methodology to evaluate (MQS) of the structures, in the context of the density functional theory (DFT). Allowing obtain the polarization of P-cyclopentadiene as a function of Cyclopentadienyl (see Fig. 8), using the alignment method TGSA (see Fig. 1), obtaining high results in local similarity indexes (see Table 1), this method to be a straightforward procedure to cope with the problem of relative orientation of the molecules when evaluating (MQS).

The descriptors proposed in this study also help to describe new phenomena associated with local molecular orbital energies and molecular polarization in systems that are characterized by rigid structures and differing by a single atom, in addition this proposed methodologies are very complementary and allow relate local physicochemical properties which can be very useful, taking into account that in recent times has been a growing interest determine local descriptors that allows obtain information of systems that involving dipoles under external conditions [20–25, 61, 62].

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Appendix 1

$$\begin{aligned}\Psi_1 &= \Psi_{200}\bar{\Psi}_{200}, & \Psi_2 &= \Psi_{200}\bar{\Psi}_{31-1}, & \Psi_3 &= \Psi_{200}\bar{\Psi}_{310}, \\ \Psi_4 &= \Psi_{200}\bar{\Psi}_{311}, & \Psi_5 &= \Psi_{31-1}\bar{\Psi}_{200}, \\ \Psi_6 &= \Psi_{310}\bar{\Psi}_{200}, & \Psi_7 &= \Psi_{311}\bar{\Psi}_{200}, & \Psi_8 &= \Psi_{31-1}\bar{\Psi}_{31-1}, \\ \Psi_9 &= \frac{1}{\sqrt{2}}(\Psi_{31-1}\bar{\Psi}_{31-0} + \Psi_{310}\bar{\Psi}_{31-1}),\end{aligned}$$

$$\begin{aligned} \Psi_{10} &= \frac{1}{\sqrt{6}} (\Psi_{31-1} \bar{\Psi}_{311} + 2\Psi_{310} \bar{\Psi}_{310} + \Psi_{311} \bar{\Psi}_{31-1}), \\ \Psi_{11} &= \frac{1}{\sqrt{2}} (\Psi_{310} \bar{\Psi}_{311} + \Psi_{311} \bar{\Psi}_{310}), \\ \Psi_{12} &= \Psi_{311} \bar{\Psi}_{311}, \quad \Psi_{13} = \frac{1}{\sqrt{2}} (\Psi_{310} \bar{\Psi}_{31-1} - \Psi_{31-1} \bar{\Psi}_{310}), \\ \Psi_{14} &= \frac{1}{\sqrt{2}} (\Psi_{311} \bar{\Psi}_{31-1} - \Psi_{31-1} \bar{\Psi}_{311}), \\ \Psi_{15} &= \frac{1}{\sqrt{2}} (\Psi_{311} \bar{\Psi}_{310} - \Psi_{310} \bar{\Psi}_{311}), \\ \Psi_{16} &= \frac{1}{\sqrt{3}} (\Psi_{31-1} \bar{\Psi}_{311} - \Psi_{310} \bar{\Psi}_{310} + \Psi_{311} \bar{\Psi}_{31-1}) \end{aligned}$$

Appendix 2

$$\begin{aligned} \mathbf{P}_{1A} &= 4X(E_1\mathbf{i} + E_2\mathbf{j} + E_3\mathbf{k}), \quad \mathbf{P}_{2A} = (XE_1 + YE_2)\mathbf{i} + (YE_1 + XE_2)\mathbf{j} + 2XE_3\mathbf{k}, \\ \mathbf{P}_{3A} &= 2X(E_1\mathbf{i} + E_2\mathbf{j}), \quad \mathbf{P}_{4A} = (XE_1 + YE_2)\mathbf{i} + (-YE_1 + XE_2)\mathbf{j} + 2XE_3\mathbf{k}, \\ \{\mathbf{P}_{5A} = \mathbf{P}_{2A}, \mathbf{P}_{6A} = \mathbf{P}_{3A}, \\ \mathbf{P}_{7A} = \mathbf{P}_{4A}\} &= \text{Degenerates states, } \mathbf{P}_{8A} = -2[(XE_1 - YE_2)\mathbf{i} + (-YE_1 + XE_2)\mathbf{j}], \\ \mathbf{P}_{9A} &= (-XE_1 - YE_2)\mathbf{i} + (YE_1 - XE_2)\mathbf{j} - 2XE_3\mathbf{k}, \\ \mathbf{P}_{10A} &= -2X(E_1\mathbf{i} + E_2\mathbf{j} + 4E_3\mathbf{k})/3, \\ \mathbf{P}_{11A} &= (-XE_1 + YE_2)\mathbf{i} + (-YE_1 - XE_2)\mathbf{j} - 2XE_3\mathbf{k}, \\ \mathbf{P}_{12A} &= -2[(XE_1 - YE_2)\mathbf{i} + (YE_1 + XE_2)\mathbf{j}], \\ \mathbf{P}_{13A} &= (-XE_1 + YE_2)\mathbf{i} + (YE_1 - XE_2)\mathbf{j} - 2XE_3\mathbf{k}, \quad \mathbf{P}_{14A} = -2X(E_1\mathbf{i} + E_2\mathbf{j}), \\ \mathbf{P}_{15A} &= (-XE_1 + YE_2)\mathbf{i} + (-YE_1 - XE_2)\mathbf{j} - 2XE_3\mathbf{k}, \\ \mathbf{P}_{16A} &= -4X(E_1\mathbf{i} + E_2\mathbf{j} + E_3\mathbf{k})/3 \end{aligned}$$

with

$$\begin{aligned} X &= \frac{d^2\omega_0 [\cos \omega_0 t - \cos \omega t]}{3\hbar [\omega^2 - \omega_0^2]}, \quad Y = \frac{d^2\omega_0 [\omega_0 \sin \omega_0 t - \omega \sin \omega t]}{3\hbar [\omega^2 - \omega_0^2]}, \\ d &= -e \int_0^\infty R_{20} R_{31} r^3 dr \end{aligned}$$

R_{20}, R_{31} are the radial functions, e represent the charge of a positron, and $\omega_0 = \omega_2 - \omega_1, \omega^2 \neq \omega_0^2$.

Appendix 3

Of the Eq. 16 the irreducible representation is $\Gamma_\pi = 2A_2 + 3B_2$, using the notation $N_1 = \phi_1$, $C_2 = \phi_2$, $C_3 = \phi_3$, $C_4 = \phi_4$, $C_5 = \phi_5$ and using the relationship projection operator

$$\hat{P}^j = \frac{l_j}{h} \sum_R \chi(R)^j \hat{R}$$

where l_j represents the dimension of the group, we have:

$$\Psi_1^{A_2} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_5)$$

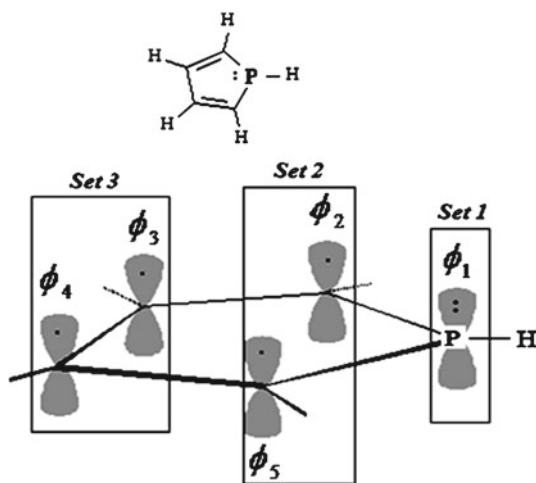
$$\Psi_2^{A_2} = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4)$$

$$\Psi_3^{B_2} = \phi_1$$

$$\Psi_4^{B_2} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_5)$$

$$\Psi_5^{B_2} = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4)$$

where the set molecular of $p\pi$ orbitals in the P-cyclopentadiene is represented by:



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