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Application of Condensed Fukui Functions to Cobalt Macrocycle Complexes

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A theoretical analysis at the ROB3LYP/3-21G* level of theory of the condensed Fukui function (f_k) applied to a set of eight cobalt macrocycles derived of the porphyrine is performed. Two approximations for f_k are used, finite difference (fd) and frozen core (fc), and the f_k^- and f_k^+ indices are evaluated for determining the most probable reaction site for the attack of an electrophile and of a nucleophile, respectively. We found a good agreement between fd and fc calculated for f_k^-, in the sense that both predict that the cobalt atom is the preferred reaction site receiving an electrophile. In the case of a nucleophilic attack, the comparison between the fd and fc approximations shows that both predict the cobalt atom as the most probable reaction site receiving a nucleophile. We conclude that realistic (fd) as approximate (fc) estimates of the condensed Fukui function used here in general can work very well in diagnosing reactivity trends in cobalt porphyrine and derivatives.

1. Introduction

The study of local properties is very important when we are interested to obtain a reactivity oriented description of molecular systems. Local reactivity descriptors defined in the formalism of the density functional theory (DFT) can be considered themselves as local responses to global perturbations on the electronic system, and therefore, they have been related with the chemical selectivity in many chemical reactions. The electronic density distribution ($\rho(r)$) is a property that contains all of the information about the molecular system properties and therefore takes a fundamental role in the discussion of chemical reactivity. Parr and Yang[1] defined the Fukui function (FF) of a molecule as the change in the electronic density $\rho(r)$ as a response to a change in the total number of electrons. Since the change in $\rho(r)$ is stated locally in the molecule, the FF may be used to determine quantitatively the nature of the reactive sites of the molecule, and from this information, it would be possible to rationalize their behavior when the molecule reacts with other species.

A number of methods and algorithms have been developed to evaluate condensed FF, that is, FF condensed to atomic regions. Parr and Yang[1] proposed a finite difference (fd) approach in which nucleophilic, electrophilic, and radical FFs are obtained from molecular orbital calculations for the neutral and the two ionic species. Yang and Mortier[2] proposed to express FF in terms of the variation of the Mulliken gross charges of an atom in a molecule. Cioslowski et al.[3] developed a fd approach based on the spin polarized method to obtain FF in the framework of the atoms in molecules method of Bader. A variational method[4] and an SCF approximation[5] were proposed to determine FF. Different methods of fd were formulated[6−8] to calculate FF in the framework of the Kohn−Sham[9] density functional theory. With the use of a frozen core (fc) approximation, condensed FFs were also derived.[7,10,11] Some algorithms have been proposed using the derivatives of the molecular orbitals with respect to the global number of electrons.[7,12−15]

In the last years, we have focused our attention on the study of the reactivity of cobalt phthalocyanines and some cobalt porphyrins.[16−29] These molecules present the disadvantage that as they are large systems some convergence problems occur and the theoretical calculations sometimes are more difficult. At theoretical level, the point more interesting is that usually these macrocycles present a well-defined reactivity due to the presence of a metallic atom. This fact helps when reactivity indices are applied because the results are very clear. In this article, we analyze the nature of the condensed FF, that is, the reaction site considering the meaning of a maximum or minimum value for FF, applied to a set of cobalt macrocycles, which differ in the ligand kind and in the number of aza nitrogen atoms belonging to the ligand. The condensed FF obtained from a finite difference approximation is determined using the partitioning schemes for the electronic population given by natural atomic orbital (NAO) population analysis. We also use the frozen core approximation using the Kohn−Sham molecular orbitals to obtain the condensed FF.

2. Theoretical Aspects

The Fukui function ($f(\vec{r})$) or frontier function is a local reactivity descriptor and provides the reactivity site most probable in a molecule where the reaction would occur. It was first introduced by Parr and Yang and defined as[1]

$$f(\vec{r}) \equiv \left(\frac{\delta\mu}{\delta\nu(\vec{r})}\right)_N = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_\nu \qquad (1)$$

Equation 1 shows that the functional derivative of the chemical potential (μ) with respect to a change in the external potential ($\nu(\vec{r})$) is identical to the change in the electron density driven by a change in the number of electrons (N). Then $f(\vec{r})$ as defined in eq 1 measures the sensitivity of a system's chemical potential to an external perturbation at a particular point. Since for an atom or molecule the derivative in eq 1 is discontinuous and

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difficult to evaluate, Parr and Yang proposed to associate it to different reactivity indices.[1] In the case of a nucleophilic attack on a system where an electron receiving process occurs,

$$f^{+}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{+}_{\nu(\vec{r})} = \rho_{N+1}(\vec{r}) - \rho_{N}(\vec{r}) \qquad (2)$$

for an electrophilic attack where an electron withdrawing process is present,

$$f^{-}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{-}_{\nu(\vec{r})} = \rho_{N}(\vec{r}) - \rho_{N-1}(\vec{r}) \qquad (3)$$

and in the case of a radical attack, which constitutes an average of the above relations,

$$f^{0}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{0}_{\nu(\vec{r})} = \frac{1}{2}[f^{+}(\vec{r}) + f^{-}(\vec{r})] \qquad (4)$$

where $\rho_N(\vec{r})$, $\rho_{N+1}(\vec{r})$, and $\rho_{N-1}(\vec{r})$ are the electronic densities of the system with N (ground state), $N + 1$ (anion state), and $N - 1$ (cation state) electrons, respectively.

In a finite difference approximation, $f(\vec{r})$ may be condensed to individual atoms in the molecule. In this context, the condensed Fukui functions (f_{k}) in analogy with eqs 2−4 are given by[2]

$$f_{\mathrm{k}}^{+} = \rho_{\mathrm{k}}(N+1) - \rho_{\mathrm{k}}(N) \qquad (5)$$

$$f_{\mathrm{k}}^{-} = \rho_{\mathrm{k}}(N) - \rho_{\mathrm{k}}(N-1) \qquad (6)$$

$$f_{\mathrm{k}}^{0} = \frac{1}{2}(\rho_{\mathrm{k}}(N+1) - \rho_{\mathrm{k}}(N-1)) \qquad (7)$$

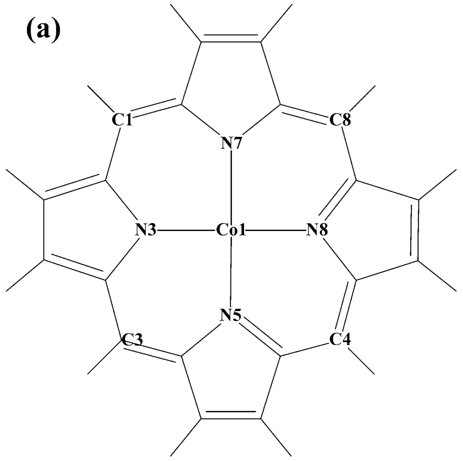
Note that ρ_{k} represents the atomic electronic population of an atom k, and therefore, the resulting value of f_{k} will be dependent on the partition scheme used, that is, on the approximation chosen in the definition of the atomic region, Mulliken partitioning, natural orbital population analysis, electrostatic potential based charges (CHELPG), Bader analysis, atomic polar tensor method, or others.[30]

The Fukui functions are also expressed in terms of the frontier orbital density through the frozen core approximation.[1,31] In such an approximation, it is accepted that the differences in the electronic densities appearing in eqs 5−6 correspond to the density of the populated or depleted frontier orbitals associated with the electron attachment or ionization processes, respectively. Thus, in analogy with eqs 5 and 6, the Fukui functions in the fc approximation are obtained by[1,30−32]

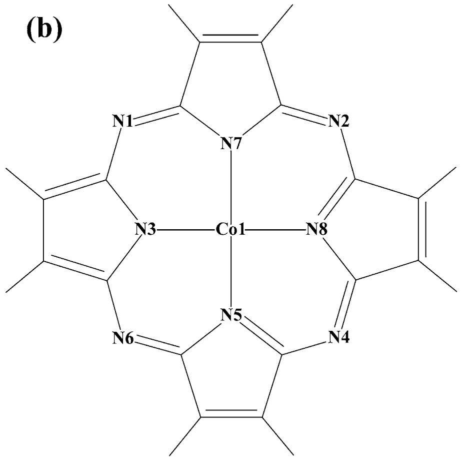
$$\begin{aligned} f_{\mathrm{k}}^{+} &= |\psi_{\mathrm{LUMO}}^{\alpha,\mathrm{k}}|^2 + |\psi_{\mathrm{LUMO}}^{\beta,\mathrm{k}}|^2 \\ &= \rho_{\mathrm{LUMO}}^{\alpha,\mathrm{k}} + \rho_{\mathrm{LUMO}}^{\beta,\mathrm{k}} \\ &= {c_{\alpha,\mathrm{k},\mathrm{LUMO}}}^2 + {c_{\beta,\mathrm{k},\mathrm{LUMO}}}^2 \end{aligned} \qquad (8)$$

$$\begin{aligned} f_{\mathrm{k}}^{-} &= |\psi_{\mathrm{HOMO}}^{\alpha,\mathrm{k}}|^2 + |\psi_{\mathrm{HOMO}}^{\beta,\mathrm{k}}|^2 \\ &= \rho_{\mathrm{HOMO}}^{\alpha,\mathrm{k}} + \rho_{\mathrm{HOMO}}^{\beta,\mathrm{k}} \\ &= {c_{\alpha,\mathrm{k},\mathrm{HOMO}}}^2 + {c_{\beta,\mathrm{k},\mathrm{HOMO}}}^2 \end{aligned} \qquad (9)$$

α and β refer to the electron spin. Note that in our case we have a SOMO instead of HOMO, but eq 9 is equally applied. Equations 8 and 9 are an advantage over eqs 5 and 6 because they are easier to calculate since we only need the wave functions for the frontier molecular orbitals of the ground state. Any approximation used for the condensed FF, whether fd or fc, gives information of the softer site in the molecule for a maximal FF value and harder site in the molecule for a minimal FF value.[33]



CoP

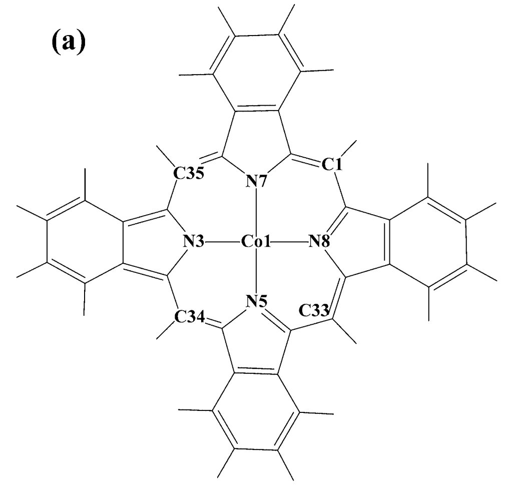


CoTAP

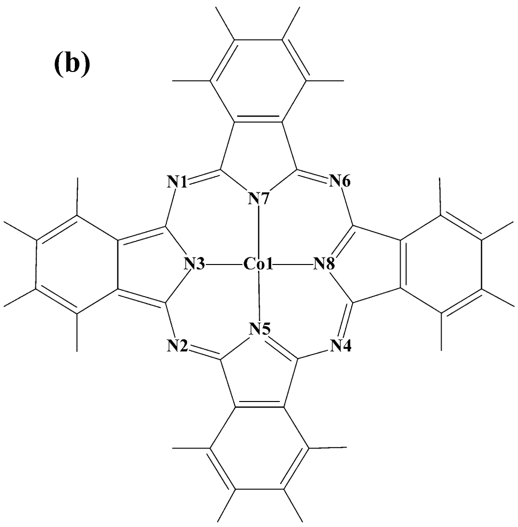
Figure 1. Structural view including the numeration of the analyzed atoms of (a) CoP and (b) CoTAP.

3. Computational Aspects

All calculations have been carried out in gas phase using the TITAN package.[34] To get a good guess wave function for the ground state, initially the geometries of the chemical systems, cobalt porphyrin (CoP), cobalt tetraazaporphyrin (CoTAP), cobalt tetrabenzoporphyrin (CoTBP), cobalt phthalocyanine (CoPc), cobalt tetrachloroporphyrin ($CoPCl_4$), cobalt tetrachlorotetraazaporphyrin ($CoTAPCl_4$), cobalt tetranitroporphyrin ($CoP(NO_2)_4$), and cobalt tetranitrotetraazaporphyrin ($CoTAP(NO_2)_4$), were optimized at the PM3(tm) (tm = transition metal) semiempirical level. A structural view of the molecules including the numeration of the atoms analyzed in this work is presented in Figure 1 for CoP and CoTAP, Figure 2 for CoTBP and CoPc, Figure 3 for $CoPCl_4$ and $CoTAPCl_4$, and Figure 4 for $CoP(NO_2)_4$ and $CoTAP(NO_2)_4$. A vibrational analysis was done for each optimized molecule, and in all cases it was verified that all of the vibrational frequencies were positive indicating that all of the structures were an energy minimum. Then, starting from these optimized structures, a full geometry optimization was performed at the density functional level with the hybrid exchange-correlation functional named B3LYP (Becke for the



CoTBP



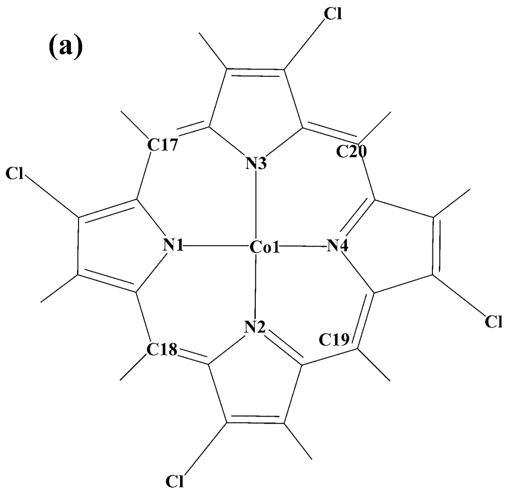
CoPc

Figure 2. Structural view including the numeration of the analyzed atoms of (a) CoTBP and (b) CoPc.

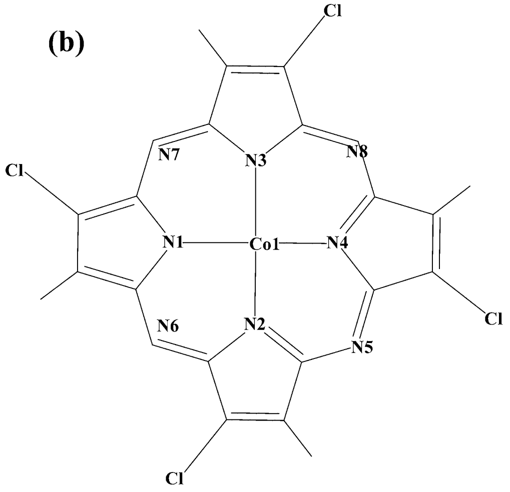
exchange and Lee, Yang, and Parr for the electronic correlation)[35−37] and a 3-21G* basis set.[38−44] Single-point calculations at ROB3LYP (restricted open B3LYP)/3-21G(d) level of theory of the anions and the cations using the ground-state optimized structure were also obtained. The multiplicity used for all of the structures is a doublet given by the presence of the cobalt atom with a +2 oxidation state, that is, a d^7 configuration, which presents an unpaired electron in their HOMO molecular orbital (SOMO).

4. Results and Discussion

Tables 1−4 present the results obtained for the condensed FFs, f_k^- and f_k^+, applied to the eight molecules studied in this paper using the finite difference approximation and frozen core approximation as shown in section 2. Table 1 contains the condensed FF results for CoP and its analogue containing the aza nitrogen atoms CoTAP, Table 2 presents those results for the pair CoTBP and CoPc, Table 3 shows the results obtained for the pair CoPCl$_4$ and CoTAPCl$_4$, and Table 4 displays the calculated results for the pair CoP(NO$_2$)$_4$ and CoTAP(NO$_2$)$_4$. In the case of fd, we use the natural atomic orbital (NAO) partioning scheme for the calculation of the electronic population. To analyze the reaction sites for each molecule and due to the large amount of atoms, we only reported in Tables 1−4 the FF values of the atoms appearing to be the most important defining the reactivity of the system. We refer to the cobalt atom and the nitrogen atoms, either the aza nitrogen atoms connecting two pyrrol rings or the nitrogen atoms directly bonded to the cobalt atom. In the case of the non-aza porphyrin molecules, that is CoP, CoTBP, CoPCl$_4$, and CoP(NO$_2$)$_4$, we consider the carbon atoms placed in the same position as the aza nitrogen atoms. For the condensed Fukui function obtained with the frozen core approximation, we use ρ_{SOMO} to get at f_{fc}^- and f_{fc}^+ because the molecules studied in this paper are open shell with one electron at the SOMO molecular orbital. Thus, the population and the depletion by one electron in these molecules occurs on the same molecular orbital, SOMO.



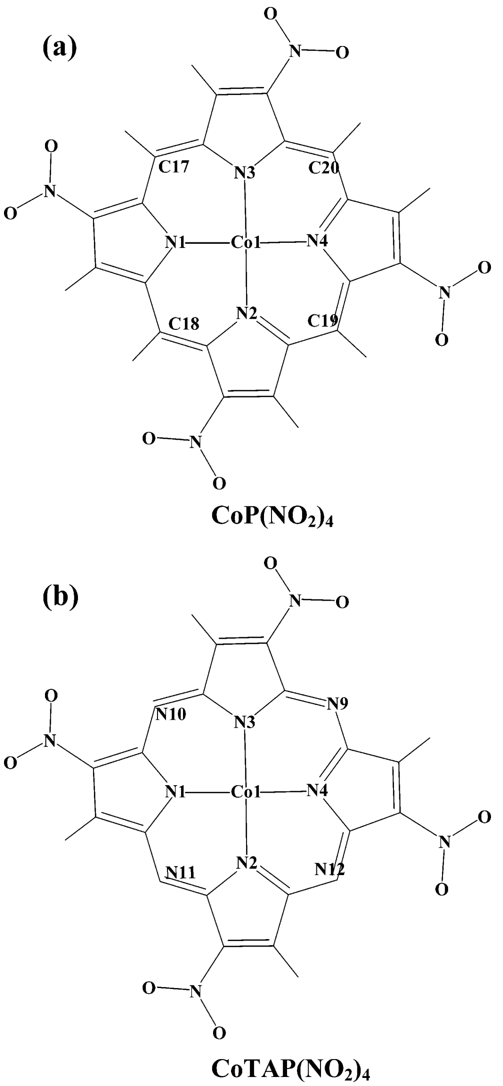
CoPCl$_4$



CoTAPCl$_4$

Figure 3. Structural view including the numeration of the analyzed atoms of (a) CoPCl$_4$ and (b) CoTAPCl$_4$.

4.1. f_k^- Fukui Function. The results obtained for f_k^- are analyzed in the context of an electrophilic attack, and then the larger value for f_k^- corresponds to the most probable reaction site available for receiving an electrophile. We found, as may be seen in Tables 1−4, for the four non-aza systems (CoP, CoTBP, CoPCl$_4$, and CoP(NO$_2$)$_4$) that the preferred site for the attack of an electrophile is clearly predicted on the cobalt atom by fd and by fc. That is, the highest positive value of f^- for the cobalt atom in these systems is obtained. When the aza nitrogen atoms are included in these molecules (CoTAP, CoPc, CoTAPCl$_4$, and CoTAP(NO$_2$)$_4$) we found a slight difference



$CoP(NO_2)_4$

$CoTAP(NO_2)_4$

Figure 4. Structural view including the numeration of the analyzed atoms of (a) $CoP(NO_2)_4$ and (b) $CoTAP(NO_2)_4$.

between that predicted by fd and by fc for some of them. The fc approach predicts for these four molecules the cobalt atom as the reaction site with the highest positive value. By the definition used in this paper for the fc approach, the f^- values obtained by fc always will be positive numbers because they have been calculated by c_k^2. The f^- results by fc suggest that the aza nitrogen atoms do not modify the reaction site for an electrophile attack from that obtained for the non-aza systems. An analysis of the orbital composition of the SOMO molecular orbital shows that in all cases, with the exception of CoTBP and $CoTAP(NO_2)_4$, the higher participation is domained by the cobalt atom through the d_{z^2} atomic orbital. In the case of CoTBP and $CoTAP(NO_2)_4$, the SOMO molecular orbital is given by the d_{yz} atomic orbital of the cobalt atom. Figure 5 shows as an illustration the SOMO corresponding to CoTBP. The fd approximation predicts negative values for all of the atoms studied in CoTAP and CoPc but also predicts the lowest value of f^- for the cobalt atom. A negative value is obtained because the ρ_{Co} value for the cation state is higher than the ρ_{Co} value for the ground state (eq 6). In the context of the Li and Evans rationalization,[33] a minimum f^-_{fd} resulting value for cobalt would be an indicator that the aza nitrogen atoms maximize the hardness of the cobalt atom. These results suggest that the aza nitrogen atoms modify the reactivity of the cobalt atom from a soft site in CoP and in CoTBP to a hard site in CoTAP and in CoPc. In the case of $CoTAPCl_4$ and $CoTAP(NO_2)_4$, the cobalt atom has a positive maximum value of f^-_{fd} indicating that the aza nitrogen atoms do not produce an important effect, that is,

TABLE 1: Condensed Fukui Function Obtained Using the Finite Difference (fd) Approximation and the Frozen Core (fc) Approximation at ROB3LYP/3-21G* Level of Calculation for CoP and CoTAP and at ROB3LYP/LACVP(d) Level of Theory for CoTAP

CoP

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc}= f^-_{fc}= \rho_{SOMO}$
Co1	0.2322	0.1163	2.3468
C1	0.0259	0.0101	0.0133
C8	0.0259	0.0098	0.0133
N3	−0.0184	0.0079	0.0317
C4	0.0259	0.0147	0.0133
N5	−0.0184	0.0057	0.0317
C3	0.0259	0.0145	0.0133
N7	−0.0183	0.0031	0.0317
N8	−0.0184	0.0078	0.0317

CoTAP

atom	f^+_{fd}	f^-_{fd}	f^-_{fd} [a]	$f^+_{fc} = f^-_{fc}= \rho_{SOMO}$	$f^-_{fc} = \rho_{SOMO}$[a]
Co1	0.2177	−0.1583	0.0917	2.4091	1.6745
N1	0.0327	−0.0218	0.0206	0.0037	0.0002
N2	0.0326	−0.0192	0.0284	0.0038	0.0002
N3	−0.0221	−0.0035	0.0178	0.0280	0.0026
N4	0.0327	−0.0225	0.0390	0.0037	0.0002
N5	−0.0221	−0.0037	0.0100	0.0280	0.0026
N6	0.0326	−0.0248	0.0390	0.0038	0.0002
N7	−0.0221	−0.0016	−0.0423	0.0280	0.0026
N8	−0.0221	−0.0018	−0.0318	0.0280	0.0026

[a] ROB3LYP/LACVP(d).

TABLE 2: Condensed Fukui Function Obtained Using the Finite Difference (fd) Approximation and the Frozen Core (fc) Approximation at ROB3LYP/3-21G* Level of Calculation for CoTBP and CoPc and at ROB3LYP/LACVP(d) Level of Theory for CoPc

CoTBP

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$
Co1	0.1118	0.1527	1.3754
C35	0.0068	0.0100	0.0056
C34	0.0067	−0.0164	0.0053
N3	−0.0212	−0.0174	0.0068
C33	0.0064	−0.0167	0.0047
N5	−0.0010	−0.0235	0.0006
C1	0.0067	0.0096	0.0038
N7	−0.0009	−0.0100	0.0006
N8	−0.0210	−0.0173	0.0066

CoPc

atom	f^+_{fd}	f^-_{fd}	f^-_{fd} [a]	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$	$f^-_{fc}= \rho_{SOMO}$[a]
Co1	0.2151	−0.1994	0.1112	2.3767	1.6504
N1	0.0122	−0.0170	0.0176	0.0042	0.0002
N2	0.0120	−0.0171	0.0171	0.0042	0.0002
N3	−0.0260	0.0035	0.0382	0.0286	0.0143
N4	0.0123	−0.0168	0.0185	0.0042	0.0002
N5	−0.0261	0.0036	0.0135	0.0286	0.0000
N6	0.0122	−0.0162	0.0190	0.0042	0.0002
N7	−0.0261	0.0038	0.0126	0.0285	0.0000
N8	−0.0261	0.0040	0.0372	0.0284	0.0143

[a] ROB3LYP/LACVP(d).

TABLE 3: Condensed Fukui Function Obtained Using the Finite Difference (fd) Approximation and the Frozen Core (fc) Approximation at ROB3LYP/3-21G*Level of Calculation for $CoPCl_4$ and $CoTAPCl_4$

$CoPCl_4$

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$
Co1	0.2240	0.1056	2.3489
N1	−0.0185	0.0071	0.0314
N2	−0.0186	0.0032	0.0314
N3	−0.0186	0.0034	0.0314
N4	−0.0186	0.0077	0.0314
C17	0.0253	0.0110	0.0143
C18	0.0251	0.0102	0.0143
C19	0.0252	0.0110	0.0143
C20	0.0251	0.0104	0.0143

$CoTAPCl_4$

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$
Co1	0.2169	0.0616	2.4095
N1	−0.0232	0.0068	0.0277
N2	−0.0232	0.0035	0.0277
N3	−0.0233	0.0036	0.0277
N4	−0.0232	0.0064	0.0277
N7	0.0281	0.0125	0.0039
N6	0.0281	0.0112	0.0039
N5	0.0281	0.0119	0.0039
N8	0.0281	0.0111	0.0039

TABLE 4: Condensed Fukui Function Obtained Using the Finite Difference (fd) Approximation and the Frozen Core (fc) Approximation at ROB3LYP/3-21G*Level of Calculation for $CoP(NO_2)_4$ and $CoTAP(NO_2)_4$

$CoP(NO_2)_4$

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$
Co1	0.1831	0.0991	2.3507
N1	−0.0153	0.0099	0.0285
N2	−0.0153	0.0032	0.0283
N3	−0.0153	0.0040	0.0284
N4	−0.0154	−0.0067	0.0282
C17	0.0249	0.0099	0.0154
C18	0.0248	0.0113	0.0153
C19	0.0248	0.0116	0.0154
C20	0.0248	0.0150	0.0155

$CoTAP(NO_2)_4$

atom	f^+_{fd}	f^-_{fd}	$f^+_{fc} = f^-_{fc} = \rho_{SOMO}$
Co1	0.0808	0.1888	1.3514
N1	0.0021	−0.0145	0.0000
N2	−0.0246	0.0023	0.0056
N3	−0.0247	0.0027	0.0056
N4	0.0019	−0.0140	0.0000
N10	0.0224	0.0218	0.0001
N11	0.0213	0.0196	0.0001
N12	0.0223	0.0225	0.0001
N9	0.0212	0.0201	0.0002

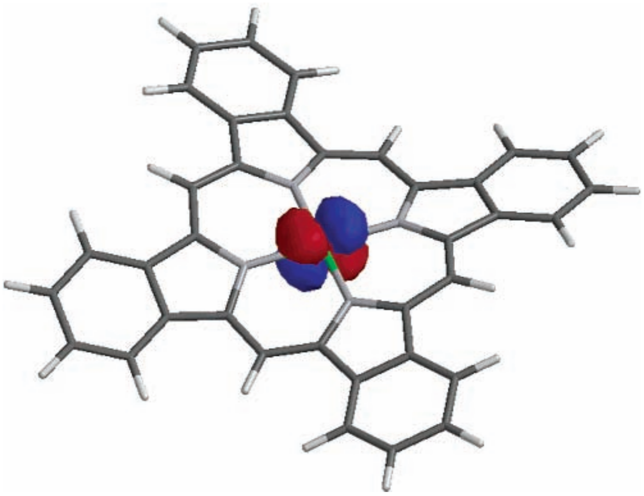


Figure 5. Graphical results of the SOMO molecular orbital obtained with full geometry optimization to the ROB3LYP/3-21G* level of theory for CoTBP.

in the sense that they do not change drastically the softness or hardness of the cobalt atom, which follows being a soft reaction site with respect to the non-aza molecules. To investigate, the reason there is nonagreement between f^-_{fd} and f^-_{fc} for the CoTAP and CoPc molecules and an extremum negative value is obtained, we performed a full geometry optimization in these molecules to the ROB3LYP/LACVP(d) level of theory. Then, we use the latter geometries to do single-point calculations at the ground state and the anion and cation states. The f^-_k condensed FFs evaluated by fd and fc were obtained for CoTAP and CoPc from the newer calculations, and the results are included in Tables 1 and 2. LACVP(d) is a pseudopotential basis set provided by the TITAN package[34] that includes an effective core potential to calculate the heavy elements, in our case the cobalt atom, and a 6-31G(d) basis set to calculate the light elements, in our case the carbon, nitrogen, and hydrogen atoms.[45−47] We chose a LACVP(d) basis set because it is a larger basis set than 3-21G(d) and in consequence the results should be better. In the CoTAP case, we found that the maximum value for f^-_{fd} is located on the cobalt atom with an important difference with respect to the remaining atoms. The same trend is obtained for CoTAP by f^-_{fc} where the higher value is concentrated on the cobalt atom. In the CoPc case, we obtained the higher value of condensed FF by both approximations, f^-_{fd} and f^-_{fc}, on the cobalt atom. Thus, we verified that in large molecules such as the derivative cobalt porphyrins the basis set can affect the resulting value of a condensed Fukui function including leading to wrong conclusions. This is the reason that we used both fd and fc approximations to verify our results. Similar conclusiones were obtained by Gilardoni et al.[48] in the sense that the values of condensed Fukui functions are sensitive to the basis sets. These authors calculated 7650 f_k values applied to several molecules by varying the basis set, the radial and angular grids, and the exchange−correlation functionals. Values of f_k, derived from a Mulliken population analysis, for maleimide molecules using a subset of six basis sets showed that the absolute values for each atom are very dependent on the basis set. However, the results obtained indicated that always the carbon atom located at the α position (C_b) presents a higher value of f^+_k than the carbonyl carbon atom (C_a).

4.2. f^+_k Fukui Function. The resulting values for f^+_k are analyzed in the context of a nucleophilic attack; thus the maximum value for f^+_k is associated with the most probable reaction site receiving a nucleophile. As was mentioned at the beginning of section 4, all of the molecules studied here are open shell with one electron located in the SOMO molecular orbital. Then, to do an analysis of a nucleophilic attack in the context of a fc approximation, we have considered ρ_{SOMO} to get f^+_{fc}. These molecules can gain one electron from the same molecular orbital. From Tables 1−4, we found that f^+_{fc} predicts the cobalt atom as the reactive site for receiving a nucleophile.

On the other hand, the fd approximation predicts in all cases the cobalt atom as the site with a positive maximum value for f^+, and therefore this atom will correspond to the preferred reaction site for a nucleophile. Thus, a good agreement between that predicted by fd and that predicted by fc is found. Finally, on the basis of the results obtained for f_{fd}^+ and f_{fc}^+, we concluded that the cobalt atom corresponds to the preferred reaction site for a nucleophilic attack on these molecules.

5. Conclusions

An analysis about the nature of the condensed Fukui function with respect to a nucleophilic (f^+) and electrophilic attack (f^-) on a set of cobalt macrocycles is performed. Two approximations were used to calculate f^+ and f^-, the finite difference approximation and the frozen core approximation. We found a good agreement between the obtained results of f_{fc}^- and f_{fd}^- for all of the molecules, both predicting that the reactive site with a higher probability to receive an electrophile corresponds to the cobalt atom. For this condensed Fukui function, we observed for two molecules of the eight studied a dependence of the results on the size of the basis set. For a nucleophilic attack, we found that f_{fd}^+ is well compared with f_{fc}^+ predicting that the cobalt atom is the more reactive site receiving a nucleophile. Thus, we found in this kind of cobalt complexes that the cobalt atom is a good electron-donor atom (electrophilic attack) and also a good electron-withdrawing atom (nucleophilic attack). This information is relevant when a study of an oxidation−reduction reaction is carried out.

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References and Notes

(1) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
(2) Yang, W.; Mortier, W. *J. Am. Chem. Soc.* **1986**, *108*, 5708.
(3) Cioslowski, J.; Martinov, M.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 10948.
(4) Chattaraj, P. K.; Cedillo, A.; Parr, R. G. *J. Chem. Phys.* **1995**, *103*, 7645.
(5) Liu, S. B.; Parr, R. G. *J. Chem. Phys.* **1997**, *106*, 5578.
(6) Senet, P. *J. Chem. Phys.* **1997**, *107*, 2516.
(7) Michalak, A.; De Proft, F.; Geerlings, P.; Nalewajski, R. F. *J. Phys. Chem. A* **1999**, *103*, 762.
(8) Mineva, T.; Parvanov, V.; Petrov, I.; Neshev, N.; Russo, N. *J. Phys. Chem. A* **2001**, *105*, 1959.
(9) Kohn, W.; Sham, L. *J. Phys. Rev.* **1965**, *A140*, 1130.
(10) Pérez, P.; Contreras, R. *Chem. Phys. Lett.* **1998**, *293*, 239.
(11) Contreras, R. R.; Fuentealba, P.; Galván, M.; Pérez, P. *Chem. Phys. Lett.* **1999**, *304*, 405.
(12) Nalewajski, R. F. *Int. J. Quantum Chem.* **1998**, *69*, 591.
(13) Komorowski, L.; Lipinski, *J. Chem. Phys.* **1991**, *157*, 45.
(14) Senet, P. *J. Chem. Phys.* **1996**, *105*, 6471.
(15) Balawender, R.; Komorowski, L. *J. Chem. Phys.* **1998**, *109*, 5203.
(16) Zagal, J. H.; Gulppi, M.; Isaacs, M.; Cárdenas-Jirón, G. I.; Aguirre, M. J. *Electrochim. Acta* **1998**, *44*, 1349.
(17) Zagal, J. H.; Gulppi, M.; Caro, C.; Cárdenas-Jirón, G. I. *Electrochem. Commun.* **1999**, *1*, 389.
(18) Aguirre, M. J.; Cárdenas-Jirón, G. I.; Toro-Labbé, A.; Zagal, J. *J. Mol. Struct. (THEOCHEM)* **1999**, *493*, 219.
(19) Zagal, J. H.; Gulppi, M. A.; Cárdenas-Jirón, G. I. *Polyhedron* **2000**, *19*, 2255.
(20) Zagal, J. H.; Cárdenas-Jirón, G. I. *J. Electroanal. Chem.* **2000**, *489*, 96.
(21) Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Electroanal. Chem.* **2001**, *497*, 55.
(22) Cárdenas-Jirón, G. I.; Gulppi, M. A.; Caro, C. A.; del Río, R.; Páez, M.; Zagal, J. H. *Electrochim. Acta* **2001**, *46*, 3227.
(23) Cárdenas-Jirón, G. I.; Caro, C. A.; Venegas-Yazigi, D.; Zagal, J. H. *J. Mol. Struct. (THEOCHEM)* **2002**, *580*, 193.
(24) Cárdenas-Jirón, G. I. *J. Phys. Chem. A* **2002**, *106*, 3202.
(25) Cárdenas-Jirón, G. I.; Venegas-Yazigi, D. A. *J. Phys. Chem. A* **2002**, *106*, 11938.
(26) Cárdenas-Jirón, G. I. *Int. J. Quantum Chemistry* **2003**, *91*, 389.
(27) Venegas-Yazigi, D.; Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Coord. Chem.*, in press.
(28) Ríos-Escudero, A.; Estiú, G. L.; Costamagna, J.; Cárdenas-Jirón, G. I. *J. Coord. Chem.*, in press.
(29) Caro, C. A.; Bedoui, F.; Páez, M. A.; Cárdenas-Jirón, G. I.; Zagal, J. H. *J. Electrochem. Soc.*, in press.
(30) Chermette, H. *J. Comput. Chem.* **1999**, *20*, 129.
(31) Yang, W.; Parr, R. G.; Pucci, R. *J. Chem. Phys.* **1984**, *81*, 2862.
(32) Pearson, R. G. In *Chemical Hardness*; Wiley-VCH: New York, 1997.
(33) Li, Y.; Evans, J. N. S. *J. Am. Chem. Soc.* **1995**, *117*, 7756.
(34) *TITAN 1.0.7*, Wavefunction, Inc. and Schrodinger Inc.: Irvine, CA.
(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
(36) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.
(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(38) Review of ab initio methods: Hehre, W. J.; Radom, L.; Schleyer, P.v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(39) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(40) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.
(41) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.
(42) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1986**, *7*, 359.
(43) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1987**, *8*, 861.
(44) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1987**, *8*, 880.
(45) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
(46) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284.
(47) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(48) Gilardoni, F.; Weber, J.; Chermette, H.; Ward, T. R. *J. Phys. Chem. A* **1998**, *102*, 3607.