
Principal Interacting Spin Orbital: Understanding the fragment interactions in open-shell systems

Fu Kit Sheong,^[a,b] Jing-Xuan Zhang,^[a] and Zhenyang Lin^{*[a]}

[a] Dr. F. K. Sheong, J.-X. Zhang, Prof. Z. Lin
Department of Chemistry
The Hong Kong University of Science and Technology
Clear Water Bay
Kowloon, Hong Kong (P.R. China)
E-mail: chzlin@ust.hk

[b] Dr. F. K. Sheong
Institute for Advanced Study
The Hong Kong University of Science and Technology
Clear Water Bay
Kowloon, Hong Kong (P.R. China)

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Abstract: Due to the recent rise in the interests and research effort on first-row transition metal catalysis and other radical-related reactions, open-shell system is playing a much more important role in modern chemistry. However, the development of bonding analysis tools for open-shell system is still lagging behind. In this work, we will present the principal interacting spin orbital (PISO) analysis, which is an analysis framework developed based on our previous principal interacting orbital (PIO) analysis. We will demonstrate the power of our framework to analyze different kinds of open-shell systems, ranging from simple organic radicals to much more complicated coordination complexes, from which we can see how different kinds of odd electron bonds could be identified. We will also illustrate its ability to be used in the analysis of chemical reaction, through which we can observe subtle patterns that could be helpful for tuning or rational design of related reactions.

Introduction

Chemistry is centered on the understanding of electronic structures of molecular systems. Conventional wisdom has led us to a simplified picture of “electron pairs”. That is, instead of considering each individual electron separately, the alpha and beta electrons are considered to be paired up in most of the chemical systems. Despite the usefulness and success of such “closed shell” simplification, they cannot be applied to the numerous open-shell systems that play important role in chemistry.

For example, research on transition metal catalysis has shifted to first-row transition metal in recent years.^[1–3] These species can often adopt high-spin states, making the consideration of unpaired electron inevitable. High-spin states give rise to special chemical properties differing from their 2nd or 3rd row counterparts, but the presence of unpaired electrons also serves as a hurdle we need to overcome when we continue to develop non-precious metal catalysis. To make things more complicated, the role of unpaired electron on the interactions of different chemical fragments is often hard to analyze, but they do play a

key part in catalytic reactions. Even though we can often identify “spin polarization” in many transition metal systems,^[4] how/whether these polarizations affect the interaction between fragments are still not well studied, and handy tools for analyzing such chemical interactions involving unpaired electron are quite limited. The fact that electrons of different spin can behave differently in a chemical system causes quite a hassle because different patterns may emerge.

Same case also applies to other fields in chemistry. For example radicals have long been known to play an important role in organic chemistry, and more ways to utilize the radical feature to perform reactions have been developed in the recent years.^[5,6] However, the understanding of how radicals interact with other chemical fragments is way behind their popularity in application, and how the interaction of different chemical moieties that can stabilize the intermediates is far from well-understood. The wide availability and applicability of transition metal catalysts and radicals, each with their own unique chemical or physical properties, marked the importance of understanding the role of unpaired electrons and their interaction with the neighboring chemical environment.

In this work, we will present our new approach, which we called “Principal Interacting Spin Orbital” (PISO) analysis, to analyze the chemical interactions in open-shell systems. This new approach complements our previously reported “Principal Interacting Orbital” (PIO) analysis for closed-shell systems,^[7] and allows us to analyze the alpha and beta orbitals separately. We found that separating the alpha and beta electrons opens up our in-depth understanding of many open-shell chemical systems, which we have examined in detail in this work.

Theory

Principal Interacting Orbital analysis

Principal Interacting Orbital analysis is a technique we recently developed to analyze the interaction between two chemical

fragments. It is based on the decomposition of the first order reduced density matrix (1RDM, spinless 1RDM to be exact). In non-interacting systems, including both Hartree-Fock or Density Functional Theory reference system, 1RDM can be easily represented on the “orbital” basis (Hartree-Fock orbital or Kohn-Sham orbital)

$$\mathbf{D} = 2 \sum_{i=1}^{occ} \mathbf{c}_i \mathbf{c}_i^\dagger$$

where \mathbf{c}_i is the column vector of expansion coefficients when the i^{th} occupied canonical MO is expressed on the specified orthogonal basis (in PIO analysis, the basis was chosen to be Natural Atomic Orbital (NAO)^[8]).

In 1RDM (no matter whether it is from HF/DFT calculations or not), the diagonal elements could be interpreted as the “population” located on the corresponding basis function, while the off-diagonal elements are “density correlations”. A technique commonly used in bonding analysis is the “Wiberg bond index”,^[9] which is the square sum of all the diagonal elements corresponding to two atoms of interest. Such bonding analysis is commonly adopted to estimate the “bond order” between atoms.

$$\text{WBI}_{AB} = \sum_{\substack{i \in A \\ j \in B}} |D_{ij}|^2$$

where A and B represent the sets of orbital (usually NAOs) located on atoms A and B respectively.

On the other hand, PIO takes a slightly different approach, instead of simply computing the square sum, we perform two rounds of principal component analysis (PCA) (or equivalently, one round of singular value decomposition) on the off-diagonal block. Thus, the “total interaction between two fragments” is decomposed into a set of eigenvalues (resulted from PCA) as well as principal components. In PIO analysis, the “principal components” are called “principal interacting orbitals” and the eigenvalues of the correlation matrix (which is also equal to the square of singular values of the sub-block) are called “PIO-based bond index”. The Principal Interacting Orbitals can indicate how the two fragments under consideration interact with each other.

Moreover, we have also proven that if a “complete fragmentation” is adopted, (i.e. all the bases are in either of the fragments), the PIOs will also be diagonalized into their corresponding principal block in the density matrices (see Ref ^[7] for more mathematical details).

Principal Interacting Spin Orbital analysis

For open-shell system, the alpha and beta 1RDMs will no longer be the same, thus merging them into the “spinless” 1RDM will lose important details. Thus, when we extend the PIO analysis to open-shell system, we would handle the alpha-1RDM and the beta-1RDM separately.

$$\mathbf{D} = \mathbf{D}_\alpha + \mathbf{D}_\beta$$

If an HF/DFT calculation is adopted, the density matrix could be represented as

$$\mathbf{D} = \sum_{i=1}^{\alpha-occ} \mathbf{c}_{i\alpha} \mathbf{c}_{i\alpha}^\dagger + \sum_{j=1}^{\beta-occ} \mathbf{c}_{j\beta} \mathbf{c}_{j\beta}^\dagger$$

where $\mathbf{c}_{i\alpha}$ is the column vector of expansion coefficients when the i^{th} occupied canonical α -MO is expressed on the specified orthogonal basis (in PISO, the basis is again chosen to be the Natural Atomic Orbital (NAO)).

Because \mathbf{D}_α and \mathbf{D}_β are no longer the same, PCA procedure similar to that in PIO analysis has to be performed on the two matrices separately, and the resulting eigenvectors are collectively called Principal Interacting Spin Orbitals (PISOs). All the properties of PIO remain, except that 1RDM would have different normalization. This normalization issue would cause a difference in PBI if the same calculation procedure is adopted. Thus we would define a “normalized PBI” (which will still be called “PBI” unless otherwise stated in the context of PISO). Basically,

$$\text{PBI}_i(\text{PISO}) = 2 \times \sigma_i^2$$

That is, the i -th PBI is defined to be two times the square of i -th singular value for the corresponding off-diagonal block of \mathbf{D}_α or \mathbf{D}_β . Under this definition, the “maximum PBI” of either alpha or beta PISO would then be 0.5, that is, each of them contribute 0.5 to the actual “bond order”, and summing up all the alpha and beta PBIs in a closed shell system will give rise to the same result as summing up all the PBIs in a PIO analysis. This means that, if we wish to compare a closed-shell system and an open-shell system, we can divide the population and PBI of the PIO analysis results by 2 to directly compare against the PISO result.

Results and Discussion

In this section, we will try to examine different kinds of open-shell systems to demonstrate how PISO analysis is able to cope with different kinds of chemical interaction pattern. We will begin by presenting a number of simple organic radicals that illustrate this feature, and then proceed to more sophisticated cases in which more complicated bonding patterns exist.

Fluoroethane radical cation

We will begin by examining some simple organic radicals. The first example we would like to examine is the fluoroethane radical cation. Despite its simple structure, the orbital in which the unpaired electron locates might not be so obvious. Previous study^[10] by Bouchoux and coworkers shows that many $\text{CH}_3\text{CH}_2\text{X}^+$ radicals have two possible electronic states, one with a' symmetry and the other with a'' symmetry. In the case of $\text{CH}_3\text{CH}_2\text{F}^+$, it has been reported that the a' state is dominant and the C-C bond in the ground state of $\text{CH}_3\text{CH}_2\text{F}^+$ is believed to closely resemble a “two center one electron bond”.

When we apply our PISO analysis to the C-C bond, we found that the alpha and beta interactions show very different patterns (Figure 1). The first alpha PISO pair illustrates a clear sigma bond between the two carbon atoms, corresponding to the “one electron bond”. On the other hand, the next two PISO pairs that have subsequently largest contributions to total interactions are

two beta PISO pairs (but still much smaller than the alpha PISO pair) which show a hyperconjugation pattern. Basically, because the first alpha PISO pair (basically a hybridized orbital on each carbon atom) is filled while the corresponding beta space is unfilled, the beta electrons are “polarized” and delocalized into the other side, forming two sets of hyperconjugation (Figure 1).

This observation is closely related to the results of PIO analysis on ethane,^[7] from which we can identify a clear sigma bond

together with a number of hyper-conjugation patterns. However, different from the closed shell systems handled by PIO analysis, this radical system can give many other patterns. For example, in the case of fluoroethane radical cation, we can identify one set of primary interaction (resembling C-C sigma bond) in the alpha space, but only secondary interactions (hyperconjugation) could be seen in the beta space.

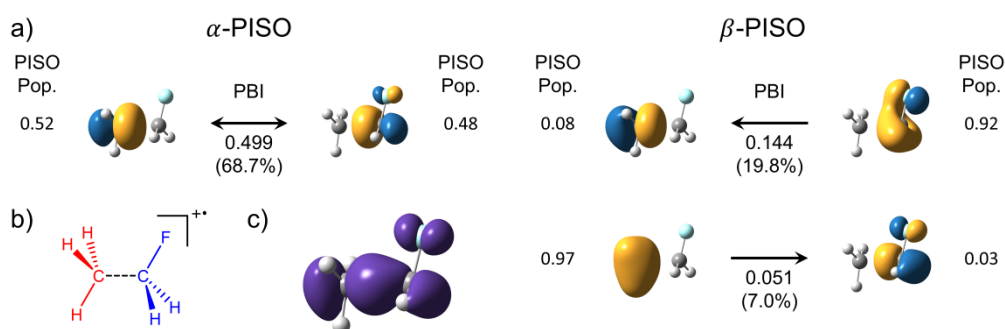


Figure 1. PISO analysis of fluoroethane radical cation. (a) Dominant PISOs for the interaction across the C-C bond. One can see that close to 70% of interaction is contributed by an α -PISO pair, and the secondary interactions come from two β -PISO pairs resembling a “hyperconjugation”. (b) Fragmentation scheme for the presented PISO analysis. (c) Spin density plot for fluoroethane radical cation. An isovalue of $0.07 a_0^{-3/2}$ was adopted for the PISOs and $0.0049 a_0^{-3/2}$ was adopted for the spin density.

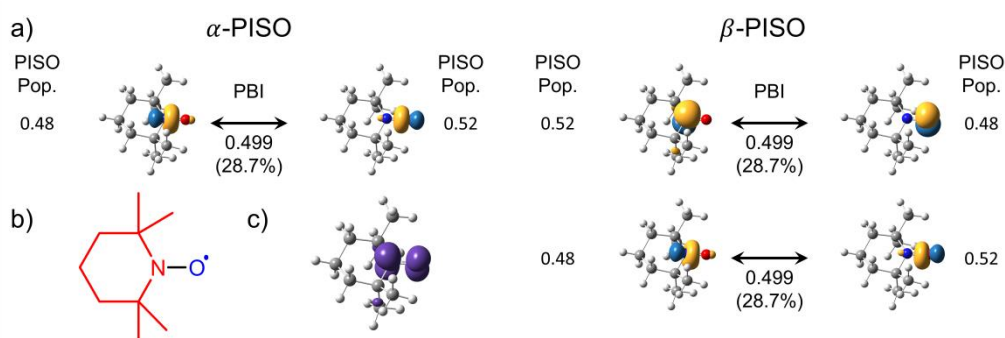


Figure 2. PISO analysis of TEMPO. (a) Dominant PISOs for the interaction across the N-O bond. One can see that a very similar σ -bonding pattern is seen in the first α -PISO pair and the second β -PISO pair. However, the first β -PISO pair resembles a π -type interaction that is not seen as a dominant α -PISO. (b) Fragmentation scheme for the presented PISO analysis. (c) Spin density plot for TEMPO. An isovalue of $0.07 a_0^{-3/2}$ was adopted for the PISOs and $0.0049 a_0^{-3/2}$ was adopted for the spin density.

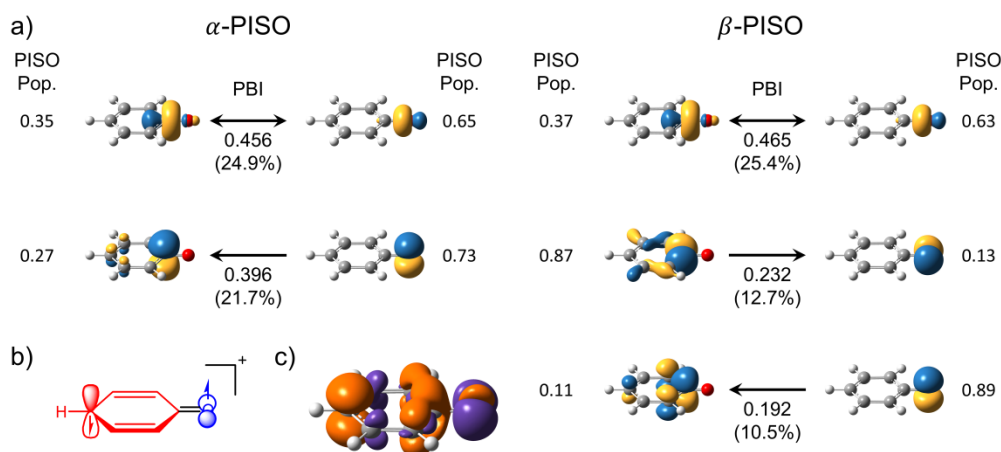


Figure 3. PISO analysis of phenyloxenium ion. (a) Dominant PISOs for the interaction across the C-O bond. One can see that a very similar σ -bonding pattern is seen in the first α -PISO pair and the first β -PISO pair, but the remaining three dominant PISOs do not have clear resemblance. (b) Fragmentation scheme for the presented PISO analysis. (c) Spin density plot for phenyloxenium ion. An isovalue of $0.07 a_0^{-3/2}$ was adopted for the PISOs and $0.0049 a_0^{-3/2}$ was adopted for the spin density.

TEMPO

We will then proceed to another simple radical, commonly used as radical scavenger: TEMPO. In its Lewis structure (Figure 2), TEMPO is usually labeled with the radical located on the oxygen. We may perform a PISO analysis by considering a fragmentation across the N-O bond. In an attempt to figure out the effect of the unpaired electron on the N-O bond. Interestingly, although we also have an odd-electron bond here, the pattern from PISO analysis is quite different from the aforementioned $C_2H_5F^+$ case.

When we examine the PISO analysis results (Figure 2), we can find only one alpha PBI close to 0.5, whereas there are two beta PBIs close to 0.5, even though there are more alpha electrons than beta electrons. The dominant alpha PISO pair basically resembles the sigma bond between the N and O, with each PISO corresponding a hybrid orbital pointing towards the opposite atom. On the other hand, there are two dominant PISOs for the beta interactions. The first beta PISO pair resembles a pi-type interaction between the nitrogen p orbital and the oxygen p orbital, a pattern that is not found in the dominant alpha interactions. The second beta PISO resembles the s-p hybridized orbital of the N and O, very similar to those of the first alpha PISO pair.

Note that, even though this case is similar to that of $C_2H_5F^+$ at first glance, in the sense that there is an unpaired electron lying around a bond, the outcome of the analysis is actually very different. In $C_2H_5F^+$, we can see a prominent alpha sigma bond without a beta counterpart (only hyperconjugation pattern is seen), whereas in TEMPO, we can see a prominent beta pi bond without an alpha counterpart. These two cases differ because the bonds have different nature. The C-C bond in the former case is a “two center one electron bond”, whereas the N-O bond in TEMPO resembles a “three-electron bond” proposed by Pauling as early as 1931^[11]. More analysis comparing the two cases will be elaborated in later sections.

Phenyloxenium ion

The phenyloxenium ion (Figure 3) is reported to have a chemically important low-lying open-shell singlet state.^[12] In the Lewis structure, we can see one unpaired electron (say with alpha spin) on the O atom and the other unpaired electron with opposite spin (say with beta spin) on the *para* carbon.

Through PISO analysis based on the chosen broken-symmetry state (with net alpha density on oxygen in-plane p orbital), we see a more complicated interaction pattern here. First, we can see that the first alpha-PISO pair is quite similar to the first beta-PISO pair, resembling the sigma bond between carbon and oxygen (Figure 3).

We found a prominent beta interaction resembling an in-plane pi-type donation from the phenyl ring to the oxygen, and a similar pattern was not seen in the alpha-PISO pair. Moreover, even though there is an oxygen-to-ring donation seen as the second alpha-PISO pair and the third beta-PISO pair, when we take a look at the PISO on the ring side, we can spot some differences in the accepting spin-orbital. All these differences could be attributed to the open-shell singlet nature of the species, in which an unpaired alpha electron is localized on one fragment and the unpaired beta electron is localized on the other. Such drastic difference in spin density (Figure 3c) would often give rise to very complicated patterns, and such subtle differences in the spin polarization of bonds would be hard to spot using other analysis techniques.

Brief discussion of the interaction patterns

In the previous examples, we have come across some patterns in fragment interaction that could only be present in open-shell systems. The first two cases are basically “odd-electron bonds”, meaning that the number of electrons involving in the bonding is

an odd number (1 or 3).^[11] When we come across an odd-electron bond, we would see an unpaired PISO.

At the same time, even though there are locally more alpha electrons, the two cases give different results. Basically, for a “one-electron bond”, we can see an alpha PISO pair without a corresponding dominant beta PISO pair, while for a “three-electron bond”, we can see a beta PISO pair without a corresponding dominant alpha PISO pair. The difference between the two could be understood through the orbital interaction diagram shown in Figure 4. From the schematic orbital diagram, we can see that when there is net alpha electron population between the fragments, a net alpha PISO implies a “one electron bond”, while a net beta PISO implies a “three electron bond”. The beta PISO arises because the “extra” alpha electron is populating the anti-bonding orbital, cancelling out only the alpha bonding interaction but not beta one, thus only a

beta PISO is seen in a “three electron bond” with net alpha population.

For these simple cases, these arguments could also be supported by examination of their spin densities. The spin density in $C_2H_5F^+$ is localized between the two carbons, resembling the C-C σ bonding orbital. On the other hand, the spin density in TEMPO is localized on N and O with a node in the middle, suggesting its resemblance to pi antibonding orbital as opposed to localizing on the oxygen atom as suggested by the Lewis structure (Figure 2b and 2c). The in-plane pi interaction in the phenyloxenium cases also has a similar pattern that there is a beta PISO without an alpha counterpart (Figure 3a).

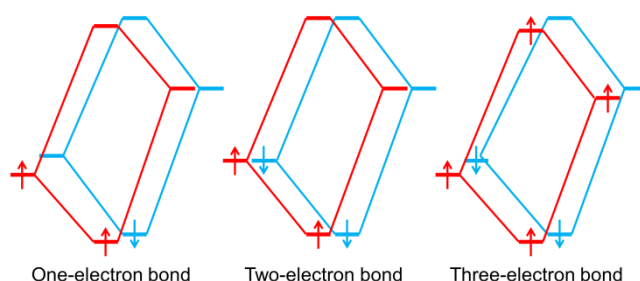


Figure 4. Three types of fragment interaction patterns. The two-electron bond could be clearly analysed using PIO analysis, but the one-electron bond and three-electron bond requires PISO analysis.

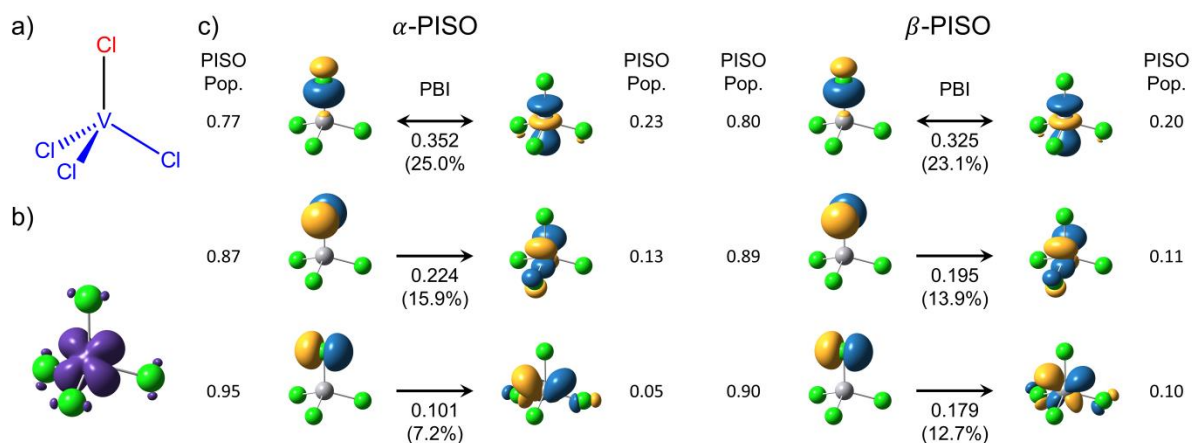


Figure 5. PISO analysis of VCl_4 . (a) Fragmentation scheme for the presented PISO analysis. (b) Spin density plot for the molecule. (c) Dominant PISOs for the interaction across one V-Cl bond. One can see that a very similar σ -bonding pattern is seen in the first α -PISO pair and the first β -PISO pair. The second α -PISO pair is also quite similar to the second β -PISO pair, showing a π -donation from Cl to the metal center. The third α -PISO and the third β -PISO on the Cl side are also the similar p orbital on Cl, however, one can also see the difference in the accepting orbitals on the vanadium center. An isovalue of $0.07 a_0^{-3/2}$ was adopted for the PISOs and $0.0049 a_0^{-3/2}$ was adopted for the spin density.

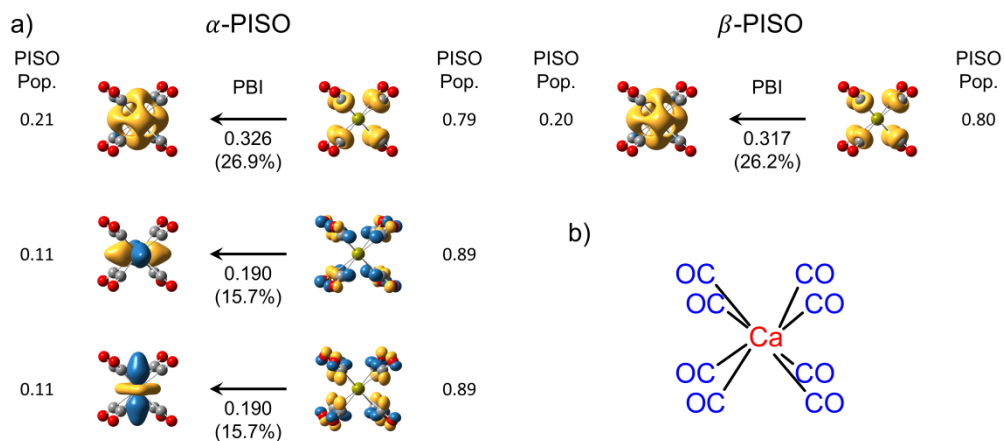


Figure 6. PISO analysis of $\text{Ca}(\text{CO})_8$. (a) Dominant PISOs for the interaction between the metal center and the eight ligands. One can see that a very similar σ -bonding pattern is seen in the first α -PISO pair and the first β -PISO pair. However, the second and third α -PISO pairs are not seen as dominant β -PISO pairs, and they play a significant role in the interaction between the metal and the ligands. (b) Fragmentation scheme for the presented PISO analysis. An isovalue of $0.05 a_0^{-3/2}$ was adopted for the PISOs.

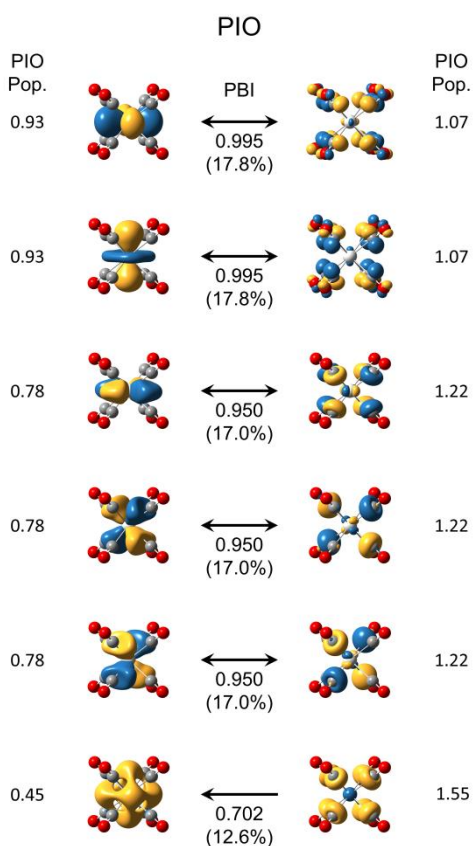


Figure 7. PIO analysis of $[\text{Sc}(\text{CO})_8]^+$. It can be seen that six dominant PIOs on the Sc side are basically five d orbitals and one s orbital. An isovalue of $0.05 a_0^{-3/2}$ was adopted for the PIOs.

Advanced Example 1: VCl_4

One might wonder whether every open-shell system has an odd-electron bond or alpha-beta mutual delocalization clearly seen from PISO analysis, this is in fact not the case. In certain chemical systems, the unpaired electron could be quite localized, and the way they affect the chemical bonding is not to make it into an odd-electron bond, but impact the bonding in a slightly different way. We will demonstrate this case with a very simple example, VCl_4 .

VCl_4 is a simple molecule with one unpaired electron on the vanadium center. From our chemical intuition, the unpaired electron is localized on the vanadium (a fact that can be easily verified from the examination of spin density^[4]) and would have minimal effect on V-Cl bond. If we examine a V-Cl bond by PISO analysis, considering one Cl as fragment A and the remaining VCl_3 as fragment B, we can see three significant interactions for both alpha and beta electrons

Specifically, we found one sigma-type and two pi-type interactions as the top 3 PISO pairs (Figure 5). The sigma one being the strongest, consistent with our view that there exists a sigma bond between V and Cl. The two pi-type interactions are mainly the Cl to V donation, and we note that while one of the pi interactions has very similar PIO between the alpha and beta interaction, the other pi interaction differs more significantly, which could be explained by the net alpha density occupying the d orbital disfavoring the alpha donation from Cl in the same direction, so the accepting orbital has more p-orbital feature than the beta counterpart. A similar pattern could also be seen in the aforementioned phenyloxenium ion, in which the oxygen out-of-plane p orbital is involved in both the second alpha-PISO and third beta-PISO pairs, but the accepting orbital on phenyl ring side is clearly different. This could again be explained by the unpaired beta density on the phenyl ring.

An important feature in this case is that, the dominant PBIs of the alpha and beta 1RDMs are largely comparable, even though there is net alpha density. We also see that most of alpha and the corresponding beta PIOs also look identical. These support the usual belief that we might still consider the metal-ligand bond as a usual two-electron bond, even though there might be net alpha density on the metal center. On the other hand, we can also see the effect of the unpaired electron, in the sense that it occupies one of the orbital and causes the alpha and beta interactions to be polarized differently, and such difference would be difficult, if not impossible, to be caught by other analysis methods.

Advanced Example 2: $\text{Ca}(\text{CO})_8$ vs $[\text{Sc}(\text{CO})_8]$

Another interesting example is the analysis of $\text{Ca}(\text{CO})_8$,^[13] $\text{Ca}(\text{CO})_8$ is one example of a series of complexes with an alkaline earth metal center coordinated by 8 carbonyl ligands reported in 2018. It has an astonishing cubic coordination geometry, with a claimed "18-electron count".^[14] Very recently, Van der Maelen has reported an topological analysis on this series of

complexes.^[15] Since the ground state of $\text{Ca}(\text{CO})_8$ is actually a triplet state, meaning that at least 2 unpaired electrons are present, the tool we adopt to analyze the interaction between the Ca center and the CO "ligands" must be able to properly handle open-shell systems. PISO is exactly the right tool for this.

Also in 2018, another series of 8-coordinated complexes $[\text{M}(\text{CO})_8]$ were reported.^[16] This series of complexes involve group 3 transition metal and each consists of 20 valence electrons in the coordination sphere. However, it was noted that this series of complexes are closed-shell systems. Because of the marked similarity between the two series of complexes, we will analyze both systems and compare their similarities and differences.

In the presented PISO analysis for $\text{Ca}(\text{CO})_8$, we can see that there are 6 dominant alpha interactions in total between the Ca center and the eight CO ligands outside (Figure 6). They are basically the interactions of the metal valence s orbital as well as five d orbitals. For the beta interactions, we have identified 4 dominant PISO pairs, corresponding to one s-type and 3 d-type interactions.

The two extra alpha-type interactions manifest the two extra alpha electrons present in the triplet complex, and we can see that these alpha interactions play a significant role in the interaction between the central metal and the CO ligands (they simply serve as alpha bonds). Though unlike the case above, these two "alpha bonds" are not two-center-one-electron bond, but instead are two interactions that are delocalized and involving all the atoms (mostly the Ca center and the 8 carbon atoms). Moreover, we can see that the fragment populations and the PBIs are quite similar for the S-type interactions (and also three less dominant D-type interactions shown in SI Fig S1), indicating that, similar to the case of sigma bond in VCl_4 discussed above, they are not quite affected by the presence of unpaired electrons.

We may also compare these results against the PIO analysis of $[\text{Sc}(\text{CO})_8]$ (Figure 7), a closed-shell 20-electron complex also with eight CO ligands.

In this complex, we can see that there are six dominant PIOs, one s-type and five d-type, similar to the alpha interactions present in $\text{Ca}(\text{CO})_8$. However, we found that the d-type interactions become very prominent, with all PBIs ≥ 0.95 . This is understandable as Sc is a transition metal, which we know d-orbitals play an important role in the interaction with ligands, unlike the case in $\text{Ca}(\text{CO})_8$. When we take a closer look at the s-type interaction of both $\text{Ca}(\text{CO})_8$ and $[\text{Sc}(\text{CO})_8]$, we can see that both the PBI and the population are actually quite comparable (except that in the Ca case the alpha and beta interactions are calculated separately, so the populations and interactions are halved), unlike the noticeable change in the role of d orbitals.

Advanced Example 3: $\text{EDT-TTF-Im}^{+\cdot}-\text{F}_4\text{TCNQ}^-$

Our final example for analysis of structure and bonding concerns a case in which the bonding was previously reported to be

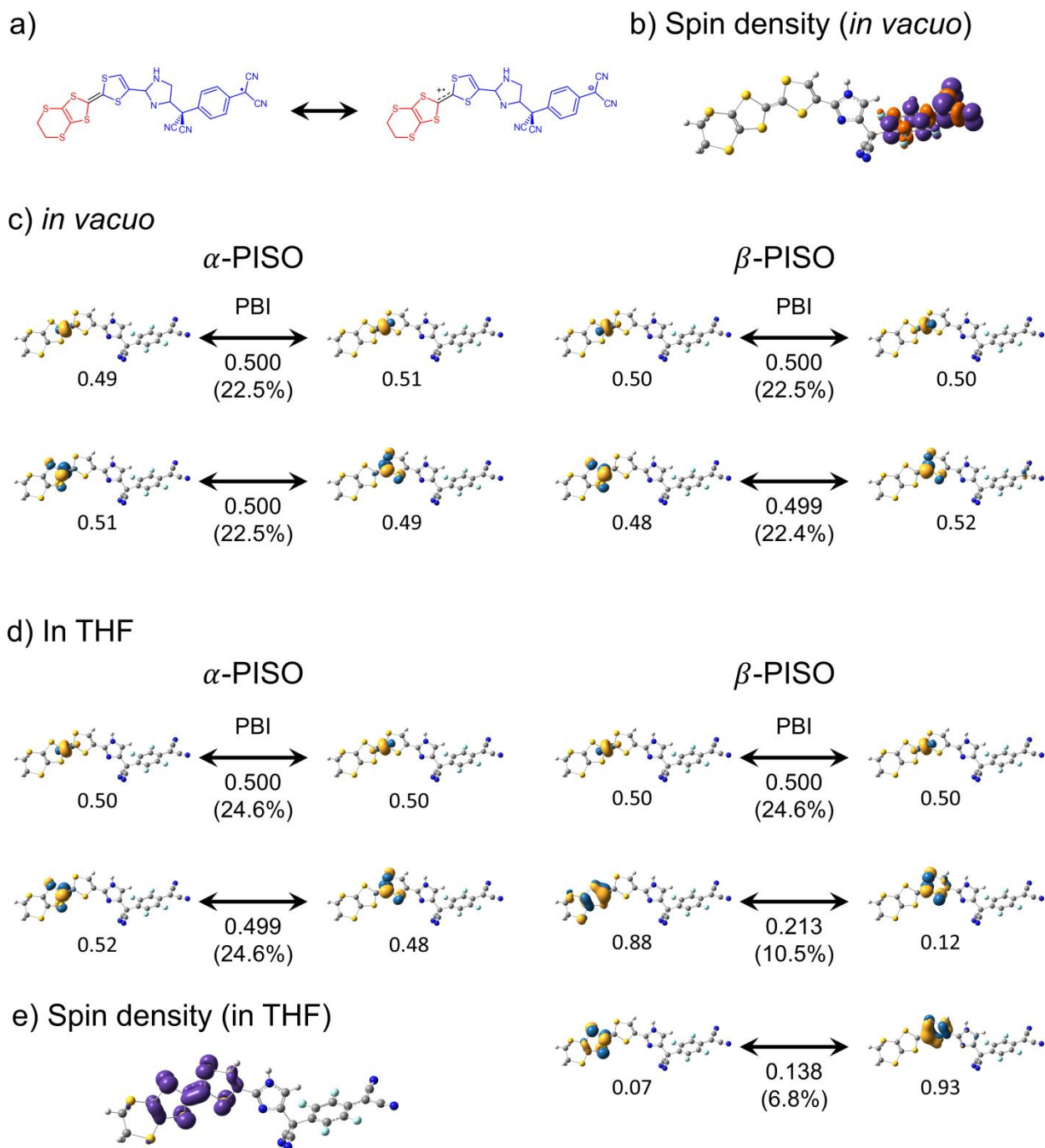


Figure 8. PISO analysis of (EDT-TTF-Im-F₄TCNQ)^{•+}. (a) Two kinds of possible electronic structures. The red and blue parts denote the fragmentation scheme adopted in the presented PISO analysis. (b) Spin density for the ground state of the system in vacuum. (c) PISO analysis of the system in vacuum. (d) PISO analysis of the system in THF. (e) Spin density for the ground state of the system in THF. An isovalue of 0.05 a₀^{-3/2} was adopted for the PISOs and 0.0025 a₀^{-3/2} was adopted for the spin density.

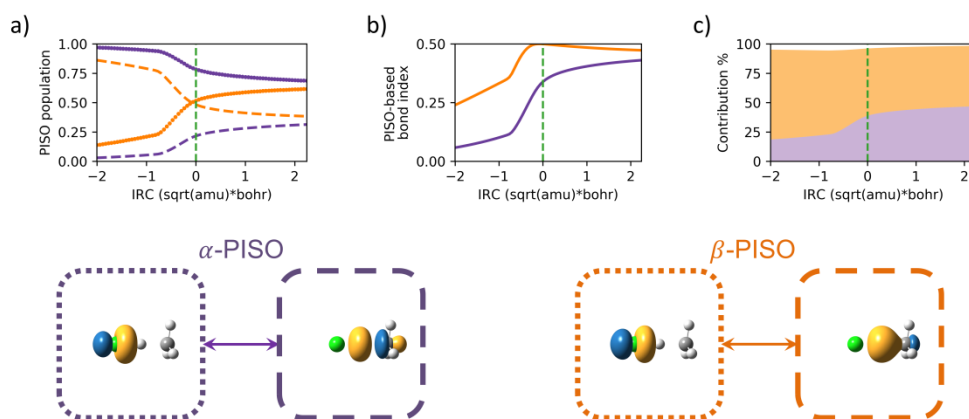


Figure 9. PISO analysis over the course of reaction between chlorine radical and methane. (a) PISO population of the two fragments. The dotted line denotes the population of the Cl fragment, and the long-dash line denotes the population of the CH₄ fragment. The purple ones denote the alpha-populations and the orange ones denote the beta-populations. (b) Evolution of the two dominant PISOs (purple as alpha, orange as beta) over the course of reaction. (c) Contribution of the two PISO pairs shown, note that the total interaction of these two pairs account for almost all inter-fragment interactions. An isovalue of $0.07 \text{ a}_0^{-3/2}$ was adopted for the PISOs, the PISO pairs shown are computed based on the transition state structure (denoted as green dashed line in the IRC plots).

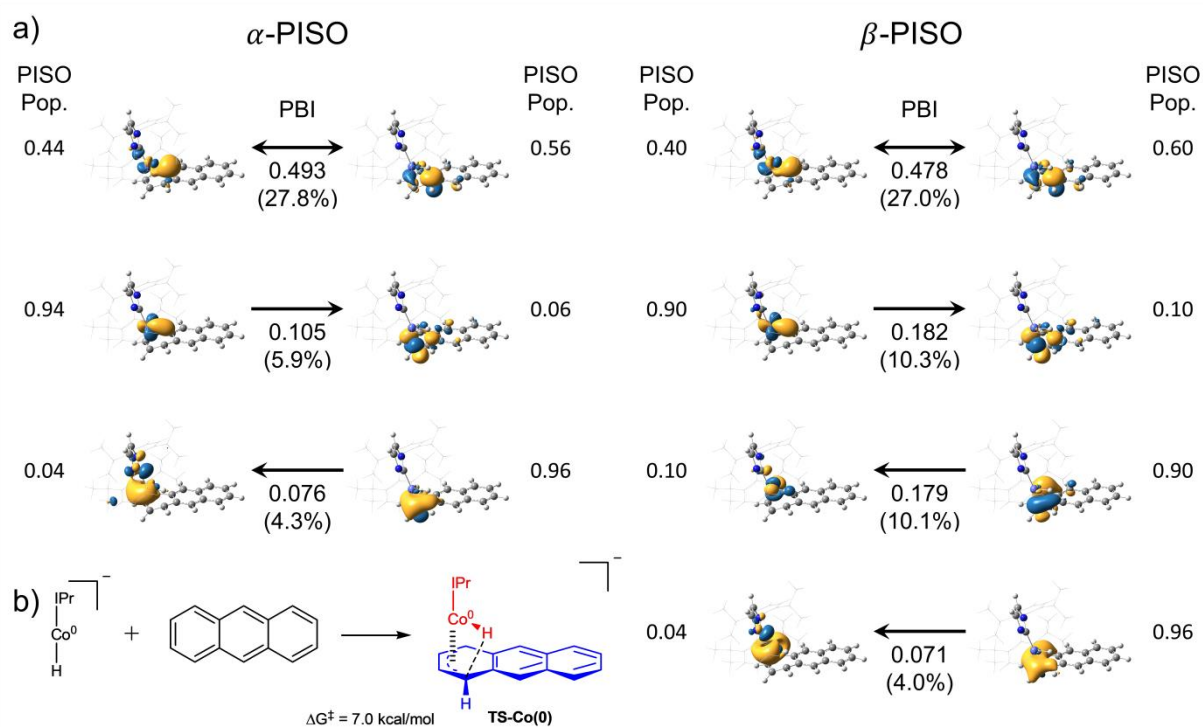


Figure 10. PISO analysis of the transition state for anthracene insertion to Co(0)-H bond. An isovalue of $0.05 \text{ a}_0^{-3/2}$ was adopted for the PISOs. The activation barrier comes from Ref^[17].

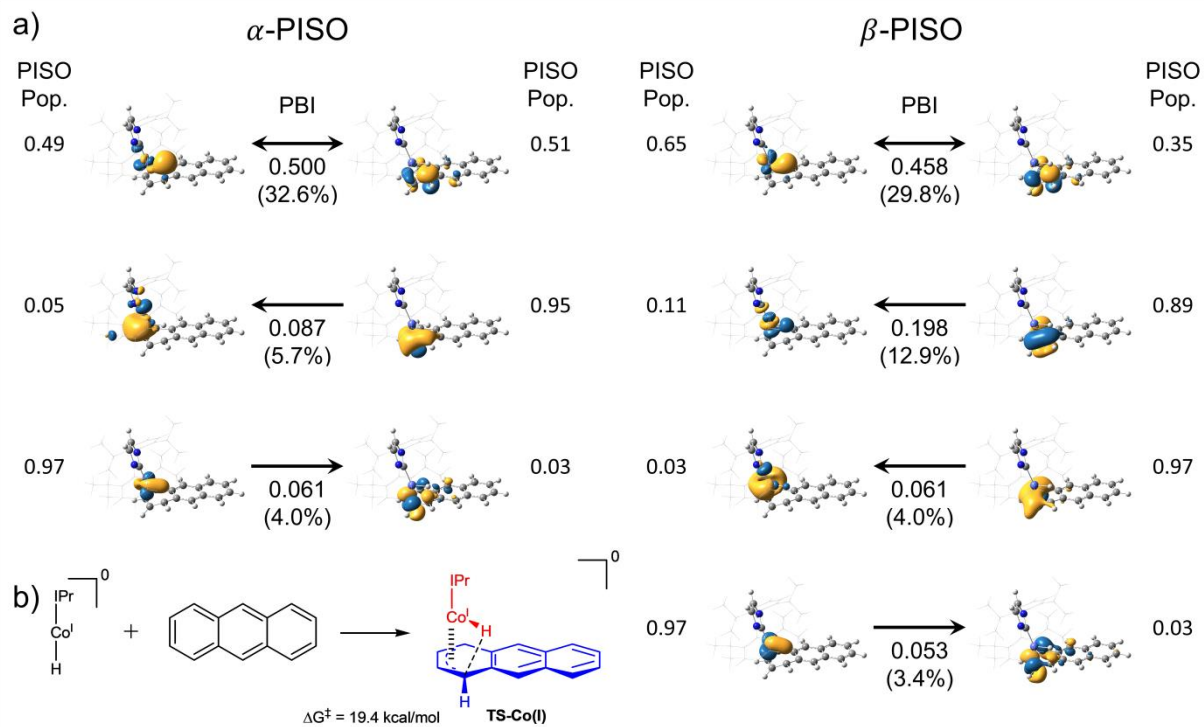


Figure 11. PISO analysis of the transition state for anthracene insertion to Co(I)-H bond. An isovalue of $0.05 \text{ a}_0^{-3/2}$ was adopted for the PIOs. The activation barrier comes from Ref ^[17].

different under different conditions, EDT-TTF-Im⁺-F₄TCNQ⁻.^[18] This and many other tetrathiafulvalene(TTF)-based compounds have special electronic properties and is commonly employed in study of organic electronics.^[19,20] This compound is even more interesting because it was reported to have a “Chameleon ground state”, in the sense that the ground state electronic structure would undergo significant change when different solvents are adopted. In this section, we would like to employ PISO to examine the “bond” between the two five-member rings of TTF, by considering one side as fragment A and the other side (together with the F₄TCNQ substituent) as fragment B.

We will begin by the examining the *in vacuo* calculation, of which the spin density is considered to be mostly localized on the F₄TCNQ substituent. PISO analysis (Figure 8) reveals the dominant alpha and beta interactions across the two fragments are roughly the same, with the two dominant PBIs each equal to 0.500 for both alpha and beta interactions. This is consistent with the aforementioned VCl₄ case, meaning that the unpaired electrons have minimal effect on the interaction between the two fragments under consideration. This supports the Lewis structure with two double bonds across the two carbons.

On the other hand, the calculation with THF solvent tells a different story. We can see that there are obvious spin densities on the C-C bond across the two rings of the TTF unit, consistent with previous reports. From the PISO analysis (Figure 8), we can still see two dominant alpha-PISO pairs. However, the second dominant beta-PISO is greatly diminished. Specifically, the dominant PISO localized on the two rings of the TTF unit is quite different. Instead of a “bonding” between the two rings, two secondary PISO pairs are found, resembling a hyperconjugation (or “mutual delocalization”) pattern. Thus, by comparing the alpha and beta PISOs, we can see that there is one more “bond” in alpha than in beta for the case in THF. One way to understand such “alpha bond” is that, other than the sigma bond, there is also a two-center-one-electron pi bond between the two carbons (or between two C₃S₂ rings). This also illustrates how PISO analysis is able to capture the subtle differences in electronic structure due to the change in solvation environment.

Application in reactions 1: Cl + CH₄

Understanding chemical reactions is also an indispensable part of chemical property analysis. Our last two examples present the possible applicability of PISO to reaction analysis. The first one is a simple organic radical propagation reaction and the second one is a step in transition metal catalysis. Basically, the PISO could help us trace the course of reaction, and allow us to study the change of orbital population/contribution along the reaction coordinate.

We took a simple textbook-level model system, the reaction between chlorine radical and methane, as an example. This serves as the chain propagation step in the free radical substitution between methane and chlorine radical, and has been studied extensively.^[21] Here, instead of considering the exact dynamics of the system, we will only focus on the motion along the intrinsic reaction coordinate (IRC).^[22,23] Interestingly, although the chlorine radical has an extra alpha electron, the interaction between the two fragments is always dominated by

the beta interaction (Figure 9). We can also see that, in the beginning of the reactions, the alpha electron stays around the Cl center and the beta electron stays around the CH₄, while at the end, both electrons are close to the Cl (although the Cl alpha electron is already partially donated to the CH₄ side). It is also interesting to note the difference between the top alpha-PISO and the top beta-PISO, as two different orbitals of CH₄ (one as C-H bonding and the other as C-H antibonding) are used to interact with chlorine radicals in the two spins.

Application in reactions 2: Co-catalysed hydrogenation of PAHs

We all know that a large number of catalytic reactions involve the use of first-row transition metal centers, and these transition metal centers can have different spin states. Different spin states could have very different reactivities, because of the possible polarization effects of the unpaired electrons. In this work, we have attempted to demonstrate the use of PISO in analyzing the transition states for the selected reactions. Here, we would examine an example of Co-catalyzed hydrogenation of polycyclic aromatic hydrocarbons (PAHs).^[17] We would take a look at the transition states for the insertion of PAH to the Co-H bond, in which changing the d electron count of the Co is known to have a prominent effect on the activation barrier.

First, we will take a look at the Co(0) case (Figure 10). The top PISO pair for either the alpha or beta interaction is mainly the interaction between the hydride and the anthracene ring, accompanied by some contributions of metal d orbitals. The second PISO pair, also quite similar for alpha and beta interactions, basically involves the interaction between the metal d orbital and the anthracene ring. The third alpha-PISO pair is the donation of ring to the metal s orbital, and a similar pattern is also found in the fourth beta-PISO pair, with a comparable PBI. The third beta-PISO pair involves another interaction between metal d orbital and the ring. Note that, unlike the second beta-PISO pair, this donation is from anthracene ring to the metal center instead of the other way around. This could be understood based on the fact that Co(0) has 9 d electrons, meaning that one of the alpha or beta d orbitals is unfilled. This third beta-PISO pair means that the unfilled d orbital plays a prominent role in accepting the coordination from anthracene ring.

When we examine the Co(I) case (Figure 11), we can see the alpha-PISO pattern is quite similar, except the order of second and third PISOs is swapped (but the actual PBIs do not differ too much even though the order is changed). A more prominent difference lies in the beta interactions, in which we can see that the PBI of the second beta-PISO pair of the Co(0) case is greatly diminished in the Co(I) system, such that now it only serves as the fourth beta PISO pair. These results also give us a hint on the possible reason why the insertion was found to be slightly more favorable for Co(0) than Co(I).

Conclusion

In this paper, we have developed the Principal Interacting Spin Orbital (PISO) analysis for open-shell systems. We have illustrated how it could be applied to analyze the electronic

structures of open-shell systems, as well as demonstrated its potential in analyzing catalytic processes involving open-shell systems, especially transition metal catalysis. The PISO analysis not only inherits the advantages of the PIO analysis we developed earlier, especially its ability to present a clear picture for chemical interactions, but also reveals a number of bonding patterns that are unique to open shell systems. We see rich opportunities for PISO to extend our understanding of open shell systems.

Computational Details

All DFT calculations are performed with the Gaussian 09 program.^[24] Other than those systems specified below, all presented PISO analysis are based on the optimized structure computed using PBE0 functional^[25] and def2-TZVP basis set^[26] with the associated effective core potential if present. To generate the open-shell singlet state for phenyloxonium ion, the electronic state was restricted to be 1A_2 during the optimization. The two analyses of EDT-TTF-Im⁺-F₄TCNQ⁻ are based on the same geometry optimized with M05/6-31+G*,^[27,28] except that the THF solvent correction is introduced through the default polarization continuum model (PCM). The analysis of PAH insertion into Co-H bond are based on B3LYP/def2-TZVP single-point calculation^[26,29,30] using the geometry provided in the original reference, together with THF solvent correction using the SMD model. The PISO analyses are performed based on the Natural Atomic Orbitals (NAOs) obtained from NBO6.0 software.^[31]

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