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Toward a Combined DFT/QTAIM Description of Agostic Bonds: The Critical Case of a Nb(III) Complex

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A detailed analysis concerning the effect of the exchange-correlation functional on a prototypical agostic niobium complex has been carried out, with particular attention to a fundamental property of the functional, namely, the recovering of the uniform electron gas limit. The obtained results allow for revisiting the role of this limit for a proper description of the β-H agostic interaction. Starting from these results, a new criterion for the bond analysis based on the electron density behavior is proposed. Indeed, the density homogeneity between the metal and the involved hydrogen has been evaluated at the bond critical point, as defined in the framework of Bader's atoms in molecules theory, by calculating the average variation rates of the (reduced) density gradients. Such descriptors not only provide useful insights on the nature of such an interaction but also could be used as a starting point for a deep (and new) analysis of the chemical bond.

1. Introduction

It is very common in the fields of organometallic chemistry and catalysis to isolate or to postulate the existence of compounds in which a hydrogen linked to a carbon atom interacts with a metallic center. Such a molecular structure can only be obtained if a consequent geometric distortion, including C−H lengthening and acute metal−carbon−hydrogen or metal−carbon−carbon angles, is possible (see for instance refs 1 and 2). Using such structural criteria, Brookhart and Green[3] coined the term "agostic bond". This interaction plays a fundamental role in intermediates in polymerization processes, as in the famous Cossee mechanism, and, notably, in the product eliminations.[4] Since the recognition of its importance, the agostic bond[5] has stimulated numerous debates and consequent studies (see, for instance, ref 6). However, despite the advocated role, its nature and description are still controversial, from both theoretical and experimental points of view.[7]

Some efforts have been done in order to define computational protocols able to correctly describe such an interaction within the framework of the density functional theory (DFT).[8] In particular, McGrady and co-workers have recently investigated the description and the origin of agostic interactions in the $\text{Tp}^{\text{Me2}}\text{NbCl(MeCCMe)}i\text{Pr}$ niobium complex (Figure 1).[9−11] They have analyzed the role of the correlation functional for a proper description of the β-H agostic bond, suggesting that functionals whose correlation part does not obey to the exact uniform electron gas (UEG) limit are intrinsically unable to locate an agostic structure. Such a relationship between a theoretical requirement and structural characteristics had also been stressed for other systems, such as metallic solid[12] or the Ag_3 cluster.[13]

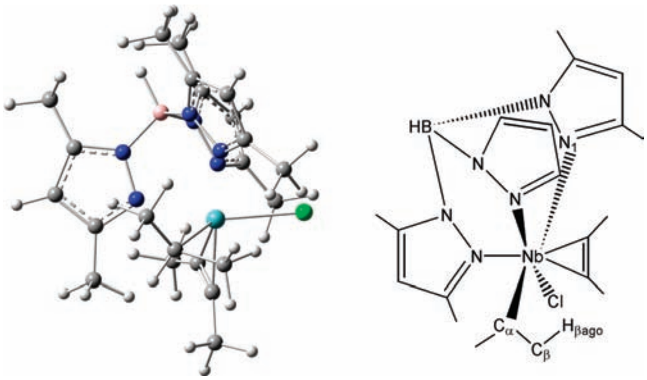

Figure 1. View of the SLYP optimized agostic niobium complex (green, Cl; gray, C; white, H; blue, N; pink, B).

At the same time, some efforts have been done in order to analyze the chemical bond in terms of basic DFT variables, such as the reduced density gradient, s (see below for the definition).[14,15] It has been suggested, for instance, that a well-designed behavior of the exchange functional for values of s between 0.5 and 2.5 improves the description of the bond properties (i.e., chemisorptions or atomization energies).[15,16]

Starting from these considerations, it could be interesting to deeply investigate the possibility of a direct link between the DFT physical background and an important chemical interaction such as the agostic bond. In particular, in this paper, the capability of selected exchange-correlation functionals to predict the presence of an agostic interaction (in the above-mentioned niobium complex) has been investigated in relation to their UEG limit properties. Then molecular descriptors derived from electron density properties and computed at the bond critical point as defined by the quantum theory of atoms in molecules (QTAIM) have been used to gain some insights on the investigated interaction.

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TABLE 1: Structural Optimized Parameters of the Niobium Complex (angles in degree, distances in angstroms) Depending on the Exchange-Correlation Functional Used for Full Optimizations

		exact UEG?[b]	$NbC_\alpha C_\beta$	$Nb-C_\beta$	$Nb-H_\beta$	$C_\beta-H_\beta$[c]	$C_\beta-H_\beta'$[d]	Nb−Cl
	expt[a]		87.0	2.608	2.175	1.11(5)		2.493
LDA	SVWN[a]	$\mathrm{Yes^{XC}}$	83.4	2.524	2.063	1.150	1.101	2.466
	SRC	$\mathrm{Yes^{X}No^{C}}$	83.4	2.526	2.064	1.152	1.102	2.468
	SLYP	$\mathrm{Yes^{X}No^{C}}$	82.8	2.496	2.034	1.161	1.106	2.445
	PBE[a]	$\mathrm{Yes^{XC}}$	86.8	2.640	2.213	1.131	1.098	2.502
GGA	TCA	$\mathrm{Yes^{X}No^{C}}$	88.8	2.694	2.293	1.121	1.096	2.499
	*Rev*TCA	$\mathrm{Yes^{X}No^{C}}$	109.3	3.176	3.227	1.095	1.100	2.437
	BLYP[a]	$\mathrm{Yes^{X}No^{C}}$	109.1	3.178	3.246	1.095	1.101	2.453
hybrids	M05-2X	$\mathrm{Yes^{X}No^{C}}$	90.1	2.677	2.315	1.110	1.086	2.511
	LC-PBE	$\mathrm{Yes^{X}No^{C}}$	85.5	2.532	2.107	1.127	1.088	2.477
MetaGGA	BRPBE	$\mathrm{No^{X}Yes^{C}}$	88.9	2.711	2.318	1.121	1.096	2.524
dispersion	B97D	$\mathrm{Yes^{X}No^{C}}$	106.7	3.091	3.340	1.092	1.100	2.431

[a] From ref 9. [b] $\mathrm{Yes^{X}}$ (or $\mathrm{No^{X}}$) means that the considered functional obeys (or not) the exact UEG limit for the exchange energy; $\mathrm{Yes^{C}}$ (or $\mathrm{No^{C}}$) is related to the exact UEG limit for the correlation counterpart. [c] $C_\beta-H_\beta$ bond with the shortest $Nb-H_\beta$ distance. [d] Mean value of the other $C_\beta-H_\beta$ bond lengths.

2. Computational Details

All calculations were carried out with the development version of the Gaussian package,[17] within the spin-restricted formalism. Several exchange-correlation functionals were considered: the local SVWN and SRC[18] approaches (S denotes the Slater exchange functional[19]), the gradient corrected SLYP,[20] PBE,[21] TCA,[22] *Rev*TCA,[23] and the hyper-GGA M05-2X.[24] To these, three other functionals were added: the so-called B97D[25,26] that incorporates dispersion corrections, the range-separated hybrid LC-PBE[27] (the Coulomb attenuating parameter μ being equal to 0.47), and the BRPBE functional that combines the PBE correlation functional with the Becke−Roussel[28] exchange.

Furthermore a family of functionals, based on the Becke exchange, has been defined, according to the equation

$$B^b\mathrm{Corr} = E_x^{\ S} + b\Delta E_x^{\ \mathrm{B88}} + E_\mathrm{c}^{\ \mathrm{Corr}} \qquad (1)$$

In this formula, the correlation contribution, $E_\mathrm{c}^{\ \mathrm{Corr}}$ is evaluated using either the LYP or the P86[29] functional and b is a parameter that weights the Becke exchange gradient correction.[30] Changing the b value, B^bCorr continuously evolves from a pure local scheme ($b = 0$) to the standard BLYP or BP86 functionals ($b = 1$).

Let us recall that SVWN, PBE, LC-PBE, M05-2X, and B^bP86 verify the exact UEG limit for correlation,[31] whereas SRC, TCA, *Rev*TCA, all based on the local Ragot−Cortona correlation functional,[32] do not. Similarly, SLYP, B^bLYP, and B97D do not fulfill this condition (see Table 1). Among the exchange functionals used in this paper, only the one designed by Becke and Roussel, based on the exchange hole of the hydrogen atom, does not recover the exact UEG limit for the exchange part.

Consistently with refs 9 and 10, the chlorine atom and the isopropyl moiety were described using the valence triple-ζ polarized basis set by Ahlrichs and co-workers (TZVP),[33] whereas the valence double-ζ polarized (SVP) one was used for the alkyne ligand and the $\mathrm{Tp^{Me2}}$ backbone. Finally, the unpolarized SV basis set was used for the methyl substituents on this last group.[34] Niobium was described with the Stuttgart-Dresden (SDD) valence basis sets in conjunction with the associated quasi-relativistic small core (28 electrons) effective core-potential (ECP).[35] The nature of the minima was verified by analytically computing the nuclear Hessian matrix.

The topologic analysis was performed using the program MORPHY98.[36,37] Unless specified, atomic units are used throughout this paper.

3. Results and Discussion

As with many other concepts in chemistry, the nature of the so-called agostic bond[5] is far from being unequivocally assessed despite very promising efforts.[38] In the following we will use a (generally admitted) criterion based on structural modifications that we have recently validated on a set of bis(imino)pyridyl complexes:[39] a typical CH ($C_\beta-H_\beta$) bond with the H atom involved in a β agosticity is longer than 1.110 Å and the corresponding $MC_\alpha C_\beta$ angle is smaller than 100°. For instance the experimental structure of $[\mathrm{EtTiCl_3(dmpe)}]$[1] is characterized by a $C_\beta-H_\beta$ bond equal to 1.13 Å and $TiC_\alpha C_\beta$ equal to 84.4°, whereas $C_\beta-H_\beta$ and $NiC_\alpha C_\beta$ are equal to 1.16 Å and 77°, respectively, in the calculated structure of Ni(II) β-diketiminates complexes.[2]

3.1. Geometries, Functionals, and UEG. Table 1 gathers the main structural parameters obtained by fully optimizing the Ni-complex structure. As previously reported,[9] the SVWN and PBE functionals succeed in finding a minimum energy structure characterized by a β agostic interaction, as evidenced by the consequent lengthening of one of the $C_\beta-H_\beta$ bonds and by the acute $NbC_\alpha C_\beta$ angle. It is worth mentioning that the obtained agostic $C_\beta-H_\beta$ bond lengths are generally longer than the experimental one, except when the M05-2X functional is considered: in this case theoretical and experimental values are close. In contrast, B97D (like B97) fails in locating such an agostic minimum. Similarly, BLYP is not successful, but if the Becke exchange is replaced by the Slater local approach, giving the SLYP functional, the agostic minimum is recovered. In a similar manner, the SRC functional, including the local RC correlation, correctly locates the agostic structure. These last two examples clearly suggest that the fulfilment of the (exact) correlation UEG limit is not a necessary condition for a proper description of the agostic interaction in the considered niobium complex. Furthermore, the fact that BLYP and SLYP give opposite results shows that the exchange counterpart also plays a fundamental role.

In order to better investigate this point, the variations of the structural parameters as function of the b coefficient in the B^bLYP model (as defined by eq 1) have been considered. This coefficient determines the behavior of the exchange functional for small values of the reduced density gradient. More precisely, the coefficient of the s Taylor second-order expansion is equal to βb where β is an empirical parameter.[30] The obtained results, summarized in Figure 2, show that for b smaller than 0.80 the minimum energy structure exhibits an agostic interaction, characterized by a $NbC_\alpha C_\beta$ angle smaller than 90°. In contrast,

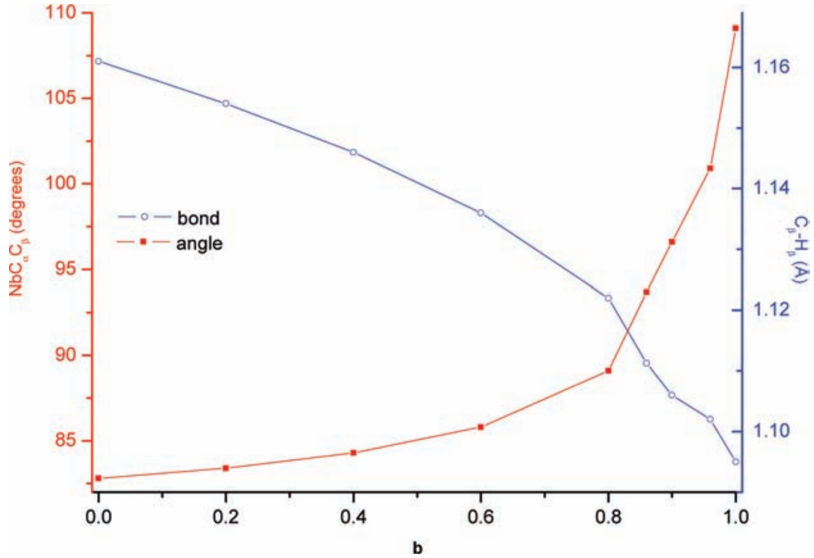

Figure 2. Variations of the NbC$_\alpha$C$_\beta$ angle (squares) and C$_\beta$−H$_\beta$ bond distance (circles) with the *b* coefficient of the B^{b}LYP exchange-correlation functional.

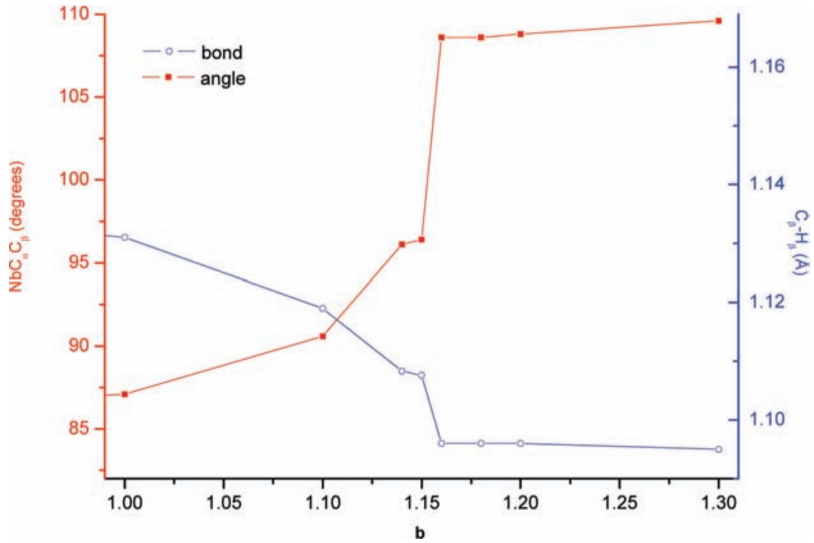

Figure 3. Variations of the NbC$_\alpha$C$_\beta$ angle (squares) and C$_\beta$−H$_\beta$ bond distance (circles) with the *b* coefficient of the B^{b}P86 exchange-correlation functional.

large variations of the NbC$_\alpha$C$_\beta$ angle have been obtained starting from $b = 0.80$ but without any net discontinuity in the curves. These results suggest that the ability of a functional to correctly describe this niobium complex could be related to the small-gradient behavior of the exchange functional. This last point would be in contradiction with the fact that TCA allows the agostic geometry to be found whereas *Rev*TCA cannot. These two last functionals actually have the same small-gradient expansion of the exchange functional, since they only differ for the value of the κ coefficient which drives the high reduced gradient asymptotic behavior.[23] Therefore, from these two remarks, it can be argued that the entire interval of the reduced density gradient values play a role in the identification of an agostic structure.

In summary, even if exchange plays a determinant role, it seems not possible to find a simple criterion to (a priori) establish the ability of a given functional to predict the presence of an agostic interaction. Furthermore, our results also suggest that a functional whose correlation part does not obey to the exact UEG limit can yet provide reasonable geometries. Such conclusions however do not exclude the possibility that an exchange-correlation functional, whose correlation part recovers the exact UEG limit for the correlation, could not locate the β-agostic interaction.

To gain some insights on this point the B^{b}P86 functional has been considered since, in contrast with the B^{b}LYP model, its correlation part (P86) does recover the UEG limit. Figure 3 collects the variations of selected optimized geometrical parameters as a function of the *b* coefficient. All the points obtained for *b* smaller than 1.15 correspond to agostic energy minima, whereas greater *b* values lead to unagostic structures. The two curves show an important discontinuity for *b* values around 1.15. It can be noticed that agostic stationary points can also be found for *b* values greater than 1.16, but they correspond to the transition state (TS) associated to the rotation of the C$_\beta$H$_3$ methyl group. For instance, for *b* equal to 1.16 (1.18) this TS has the C$_\beta$−H$_\beta$ bond equal to 1.105 Å (1.104 Å) and the NbC$_\alpha$C$_\beta$ angle value is 98.6° (99.2°), while for *b* equal to 1.15 an agostic minimum is obtained, with C$_\beta$−H$_\beta$ = 1.108 Å and NbC$_\alpha$C$_\beta$ = 96.4°. These structural values are close to each other, but the corresponding curvatures of the potential energy surface (PES) are clearly different (minimum vs TS). Unfortunately, the relationship between the density and the PES is so intricate that it is not possible to uncouple these effects and to propose a simple explanation based on the mathematical form of the functional.

Concerning the unagostic minima, it is possible to locate stable structures with B^{b}P86 and b equal to 1.16 and 1.18, characterized by twisted NbC$_\alpha$C$_\beta$H$_\beta$ dihedral (−49.6° and −63.8°, respectively) which avoid the alignment of the atoms potentially involved in the agostic interaction (Nb, C$_\beta$ and H$_\beta$). It is worth mentioning that, surprisingly, in these unagostic geometries the most elongated C$_\beta$−H bond is that farthest (H$_{\text{far}}$) from the metallic atom (that is to say pointing oppositely to the Nb coordination sphere, C$_\beta$−H$_{\text{far}}$ = 1.107 Å). Such a particularity can also be noticed in the *Rev*TCA, BLYP, and B97D structures.

Accordingly, by only slightly increasing the amount of the gradient correction for the exchange contribution (b from 1.15 to 1.16), it is possible to obtain a reasonable functional which has the exact UEG limit for correlation but is unsuccessful in finding the agostic minimum. It could also be noticed that such b values do not lead to an exotic functional. Indeed, the mean absolute error for the atomization energies of the reduced 55 molecules G2 set[40] is divided by 2 when going from the original BP86 functional ($b = 1.0$) to the one with $b = 1.16$ (5.2 vs 10.5 kcal·mol^{-1}, respectively). Such a result is consistent with the features already observed in modified BP86 functionals, like mBP86.[41]

Finally, in order to have a more complete picture, the importance of the exact UEG limit for exchange is examined, by looking at the BRPBE results. It is found that this functional is able to locate an agostic minimum (with C$_\beta$−H$_\beta$ = 1.121 Å), thus proving that the recovering of the exact UEG limit for exchange cannot be a criterion to predict the existence or not of agosticity.

In conclusion, our results suggest that the influences of exchange and of correlation cannot be dissociated due to fortuitous error compensations between these two terms. Accordingly, it seems difficult, if not illusory, to find a rationalization of the obtained results based on the general features of the considered exchange and correlation functionals.

3.2. Evaluation of the Electron Density Homogeneity at the Agostic Bond Critical Point. The role of the UEG limit for the description of such agostic bonds has been related to the fact that the density should be highly homogeneous in the region lying between Nb and H atoms,[9,10] presumably also characterized by low values for the density gradient. Therefore, it could be of paramount importance to directly relate, in a quantitative sense, density and/or density gradient behavior to such interaction. However, most of the functionals do not directly deal with these variables, but rather with reduced density gradients (generically hereafter referred as $\boldsymbol{P}$). The most used ones, s and t, are defined as

$$\boldsymbol{P}(\vec{r}) = A_{\boldsymbol{P}}\frac{\|\vec{\nabla}\rho(\vec{r})\|}{\rho(\vec{r})^{\alpha}}\begin{cases} A_s = \dfrac{1}{2(3\pi^2)^{1/3}}, & \alpha = \dfrac{4}{3} \text{ for } s(\vec{r}) \\ A_t = \dfrac{1}{4}\left(\dfrac{\pi}{3}\right)^{1/6}, & \alpha = \dfrac{7}{6} \text{ for } t(\vec{r}) \end{cases} \tag{2}$$

For instance, the TCA and HCTH functionals are built on s, whereas PBE uses both s and t. It is worth mentioning that the UEG limit obtained from these functionals (whether it is equal to the exact one or not) does not correspond to very small values of the density gradient but to very small values of s or t, these two conditions not being strictly equivalent. For instance, in the exponential tail in molecules (far away from the nuclei), the gradient values are small, while s and t tend to infinity. As a consequence, in this region of space, the mentioned functionals do not reduce to their UEG limit, even if the density is almost homogeneous. To illustrate this point, we can take the example of PBE: in the exponential tail, the exchange component reaches its saturation limit (driven by the Lieb-Oxford bound[42]) equal to $1.804 \times e_x^{\text{local}}$.[21] This discrepancy is even more pronounced with the Becke exchange since the enhancement factor tends to infinity in order to recover the exact asymptotic behavior of the exchange-energy density.[30]

Let us now consider the Nb−H agostic bond region. The most homogeneous part, from the density point of view, is expected to be at the point where the gradient density and, therefore, s and t are strictly equal to 0. Such a point ($\vec{r}_c$) is the bond critical point (BCP) between the Nd and H atoms, as defined by the quantum theory of atoms in molecules (QTAIM) terminology.[43,44] The consequent natural question is to what extent is the density homogeneous from the s and t points of view around BCP? In order to answer this question, the variation rates of these quantities, in other terms, their first derivatives at the BCP, have been considered. High derivative values correspond, therefore, to low homogeneities (in the sense of s and t), so that the UEG could be a poor reference model for such an interaction.

More precisely, let $\vec{e}_i$ and λ_i denote the eigenvectors and eigenvalues of the density Hessian $\underline{\underline{H}}$, respectively. Let $\varepsilon\vec{u}$ be an infinitesimal vector, with $\vec{u}$ a unitary one characterized by the usual azimuthal θ and zenith φ angles (defined according to the convention adopted by Zwillinger[45]). In the vicinity of the BCP

$$\begin{cases} \rho(\vec{r}_c + \varepsilon\vec{u}) \approx \rho(\vec{r}_c) + \dfrac{\varepsilon^2}{2}\vec{u}\cdot\underline{\underline{H}}\vec{u} \\ \vec{\nabla}\rho(\vec{r}_c + \varepsilon\vec{u}) \approx \varepsilon\underline{\underline{H}}\vec{u} \end{cases} \tag{3}$$

so that, at the ε zeroth order

$$\boldsymbol{P}'(\vec{u}) = \lim_{\varepsilon\to 0}\left(\frac{A\dfrac{\|\vec{\nabla}\rho(\vec{r}_c + \varepsilon\vec{u})\|}{\rho(\vec{r}_c + \varepsilon\vec{u})^{\alpha}} - A\dfrac{\|\vec{\nabla}\rho(\vec{r}_c)\|}{\rho(\vec{r}_c)^{\alpha}}}{\varepsilon}\right) \approx \frac{A}{\rho(\vec{r}_c)^{\alpha}}\|\underline{\underline{H}}\vec{u}\| = \frac{A}{\rho(\vec{r}_c)^{\alpha}}\sqrt{\sum_i(\lambda_i\vec{u}\cdot\vec{e}_i)^2} \tag{4}$$

.

The average value for $\boldsymbol{P}'$ will be obtained by summing over all possible angular orientations for $\vec{u}$ (spherical average)

$$\begin{aligned}\langle\boldsymbol{P}'\rangle &= \frac{1}{4\pi}\int_{\theta=0}^{2\pi}\int_{\varphi=0}^{\pi}\boldsymbol{P}'(\theta,\varphi)\sin\varphi\,\mathrm{d}\theta\,\mathrm{d}\varphi \\ &= \frac{A_{\boldsymbol{P}}}{4\pi\rho(\vec{r}_c)^{\alpha}}\int_{\theta=0}^{2\pi}\int_{\varphi=0}^{\pi}\times \\ &\quad\sqrt{\lambda_1^2\sin^2\varphi\cos^2\theta + \lambda_2^2\sin^2\varphi\sin^2\theta + \lambda_3^2\cos^2\varphi}\,\sin\varphi\,\mathrm{d}\theta\,\mathrm{d}\varphi\end{aligned} \tag{5}$$

It can be noticed that it is a similar procedure that links the charge depletion or creation at the BCPs and the Laplacian value at these points. Moreover, if $A = 1$ and $\alpha = 0$ in eq 5, the spherical average of the gradient variation rate $\langle ||\nabla\vec{\rho}||' \rangle$ is obtained.

The obtained values (using the PBE functional) are gathered in Figure 4. For the sake of comparison, several BCPs, involving atoms other than Nb and H_β, have also been considered. It immediately appears that, contrary to the intuition, the reduced gradients at the BCP for $Nb-H_{\beta ago}$ are those increasing the most rapidly. It must also be noticed that there is no other BCP between the metal and a hydrogen atom other than that involved in the agostic bond. More generally, as suggested by the high values also obtained for $Nb-N_1$, it may be a direct effect of the metallic atom. Conversely, s and t slowly vary for the $C_\alpha-C_\beta$ and the $C_\beta-H_{\beta(')}$ bonds. Besides, for this last bond, the values obtained for the agostic and the unagostic hydrogens are very close, so that agosticity seems to have little impact on the density homogeneity measured in terms of s and t for C−H bonds, while the corresponding bond lengths are quite different. Thus these descriptors exhibit a quite interesting bond transferability. Finally, an inversion between $\langle s' \rangle$ and $\langle t' \rangle$ is observed. From eqs 2 and 5, one can obtain that $\langle t' \rangle$ becomes greater than $\langle s' \rangle$ when $\rho(\vec{r}_c) > 64/3\pi^5 \approx 0.070$. Such a criterion could be possibly used to classify various bonds. Indeed, for instance, in the PBE functional, s controls the variation (to the second order) of the exchange contribution (owing to the exact Svendsen−von Barth expansion[46]) while t drives the variation of the correlation counterpart (due to the Ma−Brueckner expansion of the correlation energy[47]). These remarks have recently led us to design new QTAIM local descriptors that are capable of building a bridge between DFT and QTAIM.[48]

On the other hand, the variation rates for $||\nabla\vec{\rho}||$ do not follow the same trend. As intuitively expected, the gradient evolves less rapidly near the BCP between Nb and H_β than for all the other reported bonds. It is also interesting to remark that, contrary to what would be observed for density variations, the ratio between two values of $\langle ||\nabla\vec{\rho}||' \rangle$ at two given BCPs is not equal to the ratio of the corresponding Laplacian values. This fact can be qualitatively justified: the Laplacian is the algebraic sum of the three eigenvalues, so that compensation between the positive and the two negative roots occur even if the eigenvalues are high in absolute value. On the contrary, eq 5 involves the eigenvalues squares. For instance

$$\frac{\langle ||\vec{\nabla}\rho|| \rangle'(RCP_{C_\alpha-C_\beta})}{\langle ||\vec{\nabla}\rho|| \rangle'(RCP_{Nb-H_\beta})} \approx 4.7$$

whereas

$$\frac{\nabla^2\rho(RCP_{C_\alpha-C_\beta})}{\nabla^2\rho(RCP_{Nb-H_\beta})} \approx 3.9$$

From a more qualitative point of view, all of the previously reported trends can be easily rationalized. Indeed, even if the Laplacian does not exactly measure the gradient variations, it provides a rough approximation for it. Now, it has been shown that the Laplacian, as well as the density, is smaller (in absolute value) at the BCP for agostic bonds than for covalent bonds.[38,39] If the density difference between these two kinds of bonds is greater than the Laplacian difference, the reduced gradient variations will be higher for agostic bonds than for covalent ones. Such an observation can partly explain why the middle and high reduced gradient ranges play an important role, and it can help to understand the reasons of the differences observed between TCA and *Rev*TCA.

4. Conclusions

In this paper the role played by a fundamental physical property of the exchange-correlation functional, namely, the exact UEG limit, in determining the presence of agostic interaction in a niobium complex has been investigated. The obtained results suggest that a direct relationship between the recovering of the UEG limit and a correct description of the β-agosticity cannot be established. Indeed, it has been also shown that the exchange counterpart has a fundamental role for a correct description of the agostic bond, so that the behavior of the whole (exchange-correlation) functional must be considered. In order to have deeper insights on this point, the average variation rates of the reduced electron density gradients at the bond critical point have been considered. The numerical values of such indices are high, so that it could be argued that the

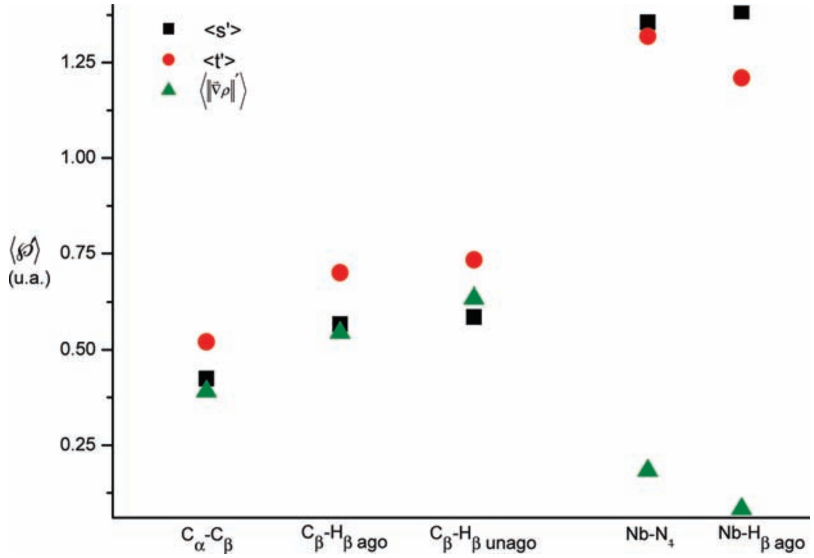

Figure 4. Evolution of average reduced density gradients $\langle s' \rangle$ and $\langle t' \rangle$ and of the average density gradient, $\langle ||\nabla\vec{\rho}||' \rangle$ as function of the considered bond critical points.

UEG limit is surprisingly less important for agostic than for the covalent bonds. Finally, it has been suggested that such average values can provide useful insights on the nature of chemical bonds, notably due to their transferability.

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