On the Interpretation of the Source Function

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The chemical information present in the source function (SF) is analyzed in several case studies by decomposition into the relative contributions from the core and valence densities. Both experimental and quantum derived densities are examined, and for the latter case, the decomposition of the SF into contributions from the individual Kohn−Sham molecular orbitals is also investigated. For pairs of atoms A and B, the orbital decomposition of the SF at the A−B bond critical point $SF(A-B)_{bcp}$ is compared with that for the delocalization index $\delta(\Omega_A,\Omega_B)$. For second and third period atoms, the valence density generally provides the determining contribution to the total SF, but for heavier elements such as transition metals, the core density plays an increasingly important role. Moreover, when the reference point is close to the nodal plane of an orbital, this orbital makes a low to negligible contribution to the SF, which has clear implications for the interpretation of π-interactions. This leads us to recommend caution in associating some chemical concepts with features of the SF, especially for heavier elements.

1. Introduction

The Quantum Theory of Atoms in Molecules (QTAIM)[1,2] provides a well-established framework for extracting information of chemical significance from the total charge density, one that is applicable to experimental densities[3] as well as theoretically derived densities. In addition to furnishing an unambiguous definition of the chemical structure in terms of the network of bond paths (i.e., the molecular graph), QTAIM also provides a quantitative methodology for the characterization of chemical bond types. As originally proposed by Bader and Essén,[4] the magnitudes of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at the bond critical points (bcp's) are very useful single-point indicators of the chemical bond type, particularly for compounds of the elements of the second and third periodic row. However, this partitioning of chemical bond types into shared-shell and closed-shell interactions solely on the basis of the sign of $\nabla^2\rho(\mathbf{r}_b)$ has proved too simplistic, in particular for heavier elements such as the transition metals. Other QTAIM indicators of bond critical point properties, such as the total energy density[5] H_b or the ratio of $|V_b|/G_b$[6] or other basin defined properties such as the delocalization index[7] or the integrated density over the zero flux surface shared by the two atoms,[5] $\oint_{A\cap B}\rho(\mathbf{r})$ have all been proposed as additional tools. The use of these QTAIM indicators to describe chemical bonding in transition metal compounds has been elaborated in considerable detail in two recent reviews.[8,9] It should be stressed that the relationship between classical chemical concepts such as *covalency* and most QTAIM indicators is purely an inductive one, relying on heuristic connections, rather than one that flows unambiguously from theory. A notable exception is the electron delocalization index $\delta(\Omega_A,\Omega_B)$ introduced by Bader and Stephens,[7] that in fact provides a quantitative measure of the electron pairs actually shared between two atomic basins. Recent work by Francisco et al.[10] generalizes the quantum mechanical interpretation of $\delta(\Omega_A,\Omega_B)$. Unfortunately however, the calculation of delocalization indices requires the first- and second-order density matrices. These are not available from experiment, unless using the wave function constrained method[11] or, in principle, from density matrix refinements.[12]

Gatti and co-workers[13] have recently proposed using the source function (SF) as an indicator of the nature of the chemical bonding, thereby enabling such information directly from the experimental electron density. The SF was first described in 1998 by Bader and Gatti,[14] who showed that the electron density at any reference point (rp) $\mathbf{r}$ can be viewed as consisting of contributions from a source operating at all other points $\mathbf{r}'$. The local source[13b] (*LS*) at reference position $\mathbf{r}$ from point $\mathbf{r}'$ is given by

$$LS = -\frac{\nabla^2\rho(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|} \qquad (1)$$

The term $(4\pi|\mathbf{r}-\mathbf{r}'|)^{-1}$ is a Green's function or influence function[15] that represents the effectiveness of the cause $\nabla^2\rho(\mathbf{r})$ giving rise to the effect $\rho(\mathbf{r})$. By integration over the regions of space bounded by the zero-flux surfaces, the atomic source $S(\mathbf{r},\Omega)$ of the density at $\mathbf{r}$ is obtained. The total density $\rho(\mathbf{r})$ at the reference point $\mathbf{r}$ is then simply the sum of all such atomic sources

$$\rho(\mathbf{r}) = \sum_{\Omega}\int_{\Omega} LS(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}' \equiv \sum_{\Omega} S(\mathbf{r},\Omega) \qquad (2)$$

It is important to stress that the atomic source is *not* an atomic population in the sense of familiar molecular orbital decomposition schemes such as Mulliken's. More precisely, we believe it is important to focus on the physical interpretation, namely that the Laplacian distribution *determines* the electron density at any point in space, rather than the formal mathematical interpretation of expression 2 that a basin *contributes* to the density.

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Expression 2 is formally identical to the well-known Poisson relationship between the electric potential $\varphi(\mathbf{r})$ (effect) and the charge density $\rho(\mathbf{r})$ that causes it, and the analogy with $\varphi(\mathbf{r})$ and $\nabla^2\varphi(\mathbf{r})$ (the charge distribution) is illuminating in this context. There is no *contribution* of charge density at a point **r** to the electric potential at another point **r′**, rather the charge distribution *determines* the electric potential. Likewise, the atomic basin integrated source function $S(\mathbf{r},\Omega)$ provides a *measure of the influence* of atomic basin Ω on the density at any reference point **r**. The SF thus provides a model-independent method for determining nonlocal influences on $\rho(\mathbf{r})$, and since it depends only on the derivative $\nabla^2\rho(\mathbf{r})$, it may be obtained from experimental densities without further approximation. It is normal practice to use the bond critical points in $\rho(\mathbf{r})$ as the rp, as these provide the least biased positions for information on chemical bonding.

To demonstrate that the SF is not merely a mathematical identity for a tautological reconstruction of $\rho(\mathbf{r})$ but can also provide chemical insight, Gatti and co-workers[13a] examined the SF for the second period diatomics HX (X = Li−F). They showed that $S(\mathbf{r},\Omega_X)$ decreases significantly (in relative terms) with increasing electronegativity of X, as would be expected if the SF carried chemical information. In this study, they also examined the SF in Li_n clusters and the H_2O H-bonded dimer and laid the groundwork for the chemical interpretation of the SF. Since then, the SF has been utilized in an increasing number of charge density studies investigating such disparate types of chemical interactions as strong hydrogen bonds,[16,17] metal−metal bonds,[18−20] transition metal σ-silane bonds,[21] dimeric Cu(II) coordination complexes,[22] transition metal−π-hydrocarbyl interactions,[23,24] and aziridine/oxirane ring bonds.[25] In most of these studies, the SF has been obtained from theoretical densities, but recently there have been reports[19−21,24,25] using experimental densities. The use of the SF in chemical characterization has been recently reviewed.[13c]

In view of the growing number of theoretical and experimental studies using electron density to understand and explain chemistry,[26] it is becoming increasingly important to assess the relationships between classical chemical concepts and QTAIM indicators and attempt to place them on a firmer basis. As mentioned above, these connections are sometimes purely heuristic, because the broad definitions associated with many chemical concepts do not link directly with the first principles mathematical approach of QTAIM. In this context, it is important to stress that the SF itself is not defined in terms of chemical concepts and, like the Laplacian $\nabla^2\rho(\mathbf{r})$, its interpretation might be complicated. While the Laplacian defines a rigorous mathematical concept (local concentration or depletion of a three-dimensional function), its connection to chemistry is not so obvious. For instance, while a strong homopolar covalent bond produces a local concentration of electron density at the bcp, the absence of such a concentration does not necessarily indicate missing covalent character. The so-called "local virial theorem" (expression 3), which relates the Laplacian to the local potential $V(\mathbf{r})$ and kinetic $G(\mathbf{r})$ energy densities, might provide a link between the Laplacian and chemical understanding.

$$\frac{1}{4}\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}) \qquad (3)$$

In an examination of the local source, Gatti et al.[13b] have used this theorem to underline the relationship between the source function and chemical interpretation. According to their arguments, a dominant potential energy density (weighted by the influence function) will make a given atom act as a source for the density at the reference point, while a dominant kinetic energy will make that atom a sink. However, it is now quite well established that properties evaluated only at the bond critical point may not be sufficiently representative of an interatomic interaction. In accordance with this, Gatti et al.[13b] have also analyzed *LS* profiles along the bond paths and have proposed[13c] the calculation of an "ambiguity free" population analysis, obtained by integrating over an atomic basin the SF of another atom. Unfortunately, this latter calculation is computationally extremely expensive, and is also affected by numerical instabilities in the evaluation of the double integral. For this reason, application of this interesting approach is at the moment limited and is not discussed here. Instead, we will concentrate on the analysis of $S(\mathbf{r},\Omega)$ at the bond critical points, which is the approach most commonly adopted so far.

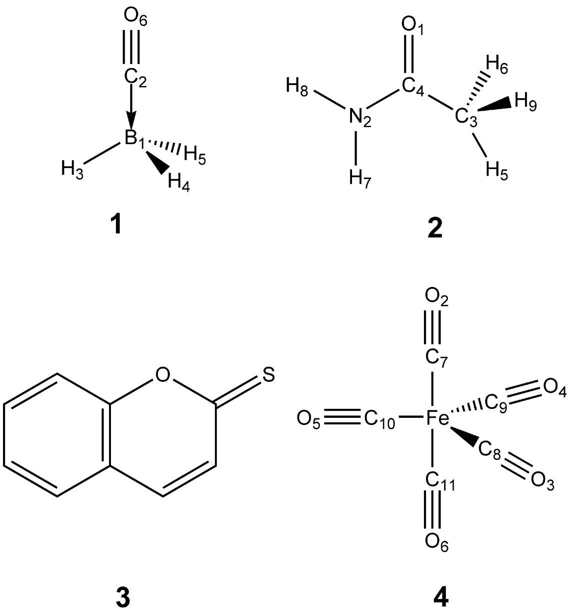
The purpose of the analysis presented in this paper is to ascertain whether the SF in fact carries information comparable with other well-established decomposition schemes that relate, more or less straightforwardly, to commonly accepted chemical concepts. For this reason, we critically analyze whether the SF is useful or not in representing specific chemical concepts, in particular the electron delocalization. As there is no formal relationship between the SF and the delocalization index, we instead test it inductively by comparing the "machinery" of the two indicators using the molecular orbital (MO) wave function approach. For example, it is beyond dispute that most of the electron sharing in a covalent chemical bond comes from the atomic valence shells. For this reason, we examine how the SF and the delocalization indices decompose in terms of the valence and core MO's and, for the theoretical SF, also in terms of individual MO's. The interpretation of the SF, in circumstances where the relative roles of the core and valence densities are unknown has not been explored so far. From expression 1 above, it is also clear that the almost invariant core density of an element will provide an almost constant contribution to the SF in all chemical environments, which will depend primarily on the distance of the rp to each atom (and to a lesser extent on the shape of the atomic basin). Of course, the shapes and dimensions of atomic basins are themselves sensitive to the chemical environment and evaluation of local properties (including the typical SF analyses) at a bcp is one way to account for this "chemical information" in a QTAIM analysis.

2. Computational Methods

We first present a detailed analysis of the theoretical source function and delocalization indices in borane carbonyl BH_3CO (**1**) and then compare the SF derived from both theoretical and experimental electron densities in three representative compounds for which high resolution experimental X-ray data are available, namely acetamide (**2**),[27] thiocoumarin (**3**),[28] and iron pentacarbonyl (**4**).[29] DFT/B3LYP wave functions for **1**−**4** were obtained using the GAUSSIAN03 program,[30] with 6-311++G** bases for all atoms except the Fe atom, for which the Wachters+f basis[31] was used. Single point calculations at the experimental geometries for **2**−**4** were used in this study, while the optimized C_{3v} geometry was used for **1**. Delocalization indices were computed from the atomic overlap matrices provided by the highly efficient basin integration routines of the AIMall code.[32] The atom numbering (where relevant) is shown in Scheme 1.

The program DenProp[33] computes integrated atomic and molecular properties from wave functions constructed using Gaussian or Slater basis functions. We have modified this

SCHEME 1



program to compute the source function and to decompose the SF into the contributions from individual MO's (and hence into core and valence contributions). The decision as to which subset of MO's constitutes the core is straightforwardly based on the core/valence division used in the multipole analysis (see below) and also on chemical sense. In some cases, e.g., for transition metals, the division is less clear (see below) and this caveat should be borne in mind by the reader. In general, a large gap separates the kinetic energies of the core orbitals from the remaining occupied orbitals. In any case, the same orbital partitioning is applied to the delocalization indices and the SF reconstruction, as we are interested in exploring similarities or differences between these two indicators.

Complex static X-ray structure factors to a resolution of $(\sin \theta)/\lambda \leq 1.1$ Å^{-1} were obtained from the molecular wave function of **1** by numerical integration of the charge density for reciprocal lattice points corresponding to a pseudocubic unit cell with $a = 30$ Å by using the program WFN2HKL.[34]

For the experimental studies, the XD2006 program suite[35] was used, which utilizes the Hansen−Coppens multipole formalism.[36] The aspherical atomic electron density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + P_v\kappa^3\rho_v(\kappa\mathbf{r}) + \rho_d(\kappa'\mathbf{r}) \tag{4}$$

where ρ_c and ρ_v are respectively the core and spherical valence densities and

$$\rho_d(\kappa'\mathbf{r}) = \sum_{l=0} \kappa'^3 R_l(\kappa'\mathbf{r}) \sum_{m=0}^{l} P_{lm\pm} y_{lm\pm}(\mathbf{r}/r) \tag{5}$$

is the term accounting for the deformation valence densities. The $y_{lm\pm}$ are density-normalized, real spherical harmonics and P_v and $P_{lm\pm}$ are the refinable populations. Within this formalism, the atomic scatterings corresponding to the atomic core density $\rho_c(\mathbf{r})$ and to the atomic valence density $\rho_v(\mathbf{r}) + \rho_d(\mathbf{r})$ are clearly separated. The set of atomic orbitals used to construct the core scattering are user-definable in XD, and for this study the 1s orbital was treated as core for the second period elements, the 1s, 2s, 2p for third period elements, while for Fe all atomic orbitals other than the 4s and 3d were treated as core. In XD, the atomic core density $\rho_c(\mathbf{r})$ does not involve any refinable parameters and so is identical for each scattering type specified. The topological analysis was performed using the TOPINT routine in the XD properties module XDPROP, which was modified to decompose the SF from atomic basins into respective contributions from the core and valence densities.

The multipole populations obtained by least-squares refinement with XDLSM were used by TOPINT to compute the SF at all bond critical points. The calculations reported here were based on refinements against experimental structure factors for **2** and **3** and synthetic structure factors for **4**. A projection of the quantum density of **1** into a multipole model was obtained by refinement against the static structure factors obtained as above. The final accuracy of the SF reconstruction of the density $\rho(\mathbf{r})$ is determined by the accuracy of the numerical integration, which in turn may be gauged by the magnitude of the integrated atomic Lagrangian. This function should vanish in the ideal case, and values less than 10^{-4} e Å^{-5} are usually considered acceptable for second period elements. The Lagrangian error function L_{err}

$$L_{\text{err}} = \sqrt{\sum_{\Omega} L_{\Omega}^{\,2}/N} \tag{6}$$

has also been suggested by Flensburg and Madsen[37] as a measure of the integration error, with typical values of 3×10^{-3} e Å^{-5}. In all our studies, L_{err} was at or below this value. Other measures of the integration accuracy are the overall summed charge $\Sigma(\Omega_A)$ and the accuracy in the SF reconstruction of the density ρ_{SF} at the reference point, as previously discussed by Gatti and Lasi.[18a] The mean values of $\Sigma(\Omega_A)$ (e) and the percentage error in ρ_{SF} for compounds **1**−**4** respectively were 0.005, 0.28%; 0.02, 0.9%; 0.003, 0.25%; 0.02, 0.84%.

3. Results and Discussion

To examine the chemical information present in the source function, we compare the SF(A−B)$_{\text{bcp}}$ (i.e., the SF at the reference point comprising the A−B bond critical point) with another QTAIM indicator which has a well-established relationship to the concept of electron sharing, i.e., the delocalization index $\delta(\Omega_A,\Omega_B)$.[7] As is made clear above and also stated explicitly by Gatti and Lasi,[18a] there is no direct physical relationship between $\delta(\Omega_A,\Omega_B)$ and the SF(A−B)$_{\text{bcp}}$. Nevertheless, these latter authors[18a] have emphasized their heuristic connections in a study on metal−metal bonding. The QTAIM indicators are obtained by partitioning the density and its derivatives in real space, but we also choose to analyze them in Hilbert space, by examining contributions from the constituent MO's of the wave function. The possibility of analyzing the SF in terms of atomic basis functions has been already discussed (see ref 18b, pp 136−137) and a similar orbital decomposition of the ELI-D has been recently reported by Wagner et al.[38] for examining the chemical information of this function.

Borane carbonyl BH_3CO (**1**) was chosen as a simple model[9] for carbonyl coordination to a strong Lewis acid and, by extension, to transition metals. With only 11 occupied MO's, it is quite feasible to present here a detailed analysis of the contributions from the individual MO's to the source function and the delocalization indices. The Kohn−Sham canonical valence orbitals for **1** are shown in Figure 1; the three core orbitals (MO's 1−3) that are not shown are the essentially

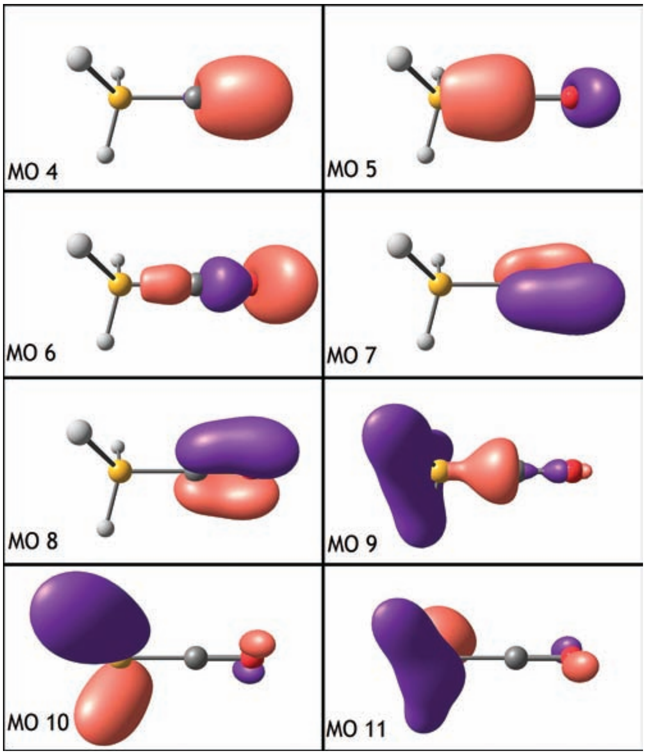


Figure 1. Isosurface (0.07 au) representations of the Kohn−Sham canonical valence orbitals of **1**.

TABLE 1: Delocalization Indices and Percentage Orbital Contributions for 1

MO no.	$\delta(\Omega_B,\Omega_C)$	$\delta(\Omega_C,\Omega_O)$	$\delta(\Omega_B,\Omega_H)$	$\delta(\Omega_B,\Omega_O)$
	0.478	1.650	0.546	0.040
1	0.00	0.00	0.00	0.00
2	0.00	0.34	0.00	0.00
3	0.70	0.00	0.29	0.00
4	0.26	18.11	0.01	−2.16
5	45.19	5.08	8.00	−17.33
6	10.95	12.05	5.61	40.96
7	3.26	34.39	1.56	−15.05
8	3.26	34.39	0.12	−15.05
9	14.24	1.67	30.27	23.64
10	11.07	−3.02	2.99	42.49
11	11.07	−3.02	51.16	42.29

unhybridized 1s orbitals on the O, C, and B atoms respectively. The unique delocalization indices are given in Table 1, and the SF for the three unique bcp's is shown in Figure 2. Further details are given in Table 2, which lists the overall percentage contributions from each MO to the QTAIM descriptor. The chemical bonds in **1**, especially B−C and C−O, are quite polarized, so that the bcp's are displaced toward the most electropositive atom. This accounts for the significant core density contributions from individual atomic basins for all three independent bcp's.

First considering the B−H σ-bond, we observe that the two descriptors $\delta(\Omega_B, \Omega_H)$ and $SF(B{-}H)_{bcp}$ have strikingly similar overall MO contributions. This suggests a good heuristic relationship between them, but unfortunately it is not generally the case, as can be seen for the two bonds that lie on the symmetry axis and have π-components. Thus for $\delta(\Omega_C,\Omega_O)$, the major contribution comes from the E pair of orbitals, MO's 7/8, but these orbitals make effectively no contribution to the $SF(C{-}O)_{bcp}$. This latter observation is a trivial result, since the source at a reference point from an MO integrated over all space is nothing more than the orbital density at that point (both values are provided in Table 2 as an indicator of the accuracy of the SF reconstruction). Since the reference point (the C−O bcp) lies on (or very close to) the nodal plane of these orbitals, a zero overall SF contribution results. This observation can be generalized by saying that the SF taken at the C−O bcp cannot provide any information about the extent of C−O π-bonding. Complex **1** is not expected to have any significant π-back-donation; nevertheless it is important to stress that the $SF(C{-}O)_{bcp}$ would not reveal this. While this is an obvious conclusion, as far as we are aware, it has never been explicitly mentioned in print. It acts as a limitation on the interpretation of the SF, and as we show below for complex **4**, it also applies to metal−carbonyl bonding. While this problem might affect also traditional QTAIM analysis based on the electron density at bcp only, it is notable that π-bonding is usually revealed by the bond ellipticity, which is computed from the second derivative of the density (hence accounting for the density out of the nodal plane).

Although the global orbital contributions to the SF are of some interest, it is more important from a QTAIM perspective to consider the orbital contributions for each atomic basin, which are given in Tables 3−5 respectively. First considering the $SF(C{-}O)_{bcp}$, it is clear that only a few MO's are of any significance. The principal contributions from the C atomic basin come from MO 2 (the C 1s orbital) and MO 6 (the CO σ-donor orbital), while for the O basin they arise from MO 2 (a sink), MO 4 (the C−O σ-bonding orbital), and MO 6. At variance from the delocalization indices then, a substantial contribution to the SF comes from core electrons. This reinforces the idea that $\delta(\Omega_A,\Omega_B)$ is more closely reproducing the chemical concepts of electron sharing. Moreover, the dominance of MO 4 toward the O basin suggests that the overall SF contribution from this basin will not be very sensitive to the nature of the Lewis acid attached to the CO group. The overall SF contribution from the C basin may be more chemically sensitive, since a relatively high proportion comes from MO 6. This latter orbital, the CO σ-donor orbital, is expected to become more delocalized if there is strong σ-donation from the CO ligand. Most importantly, the π-bonding MO's 7/8 and 10/11 make negligible contributions from the atomic basins, for the reasons discussed above, so that essentially no information about the extent of π-bonding or π-back-donation is contained in the SF at this reference point.

As shown in Table 4, the situation for the $SF(B{-}C)_{bcp}$ is less clear-cut. Many more MO's make non-negligible contributions, and most importantly, they may act as either sources or sinks. For instance, the overall contribution of 37.6% for the C atomic basin comprises a source of 91.98% from 4 MO's and a sink of 54.4% from 6 MO's. These opposing contributions complicate any understanding of their chemical significance. Moreover, although the π-bonding MO's 7/8 still make little contribution, as was found for the $SF(C{-}O)_{bcp}$, the same is not true for MO's 10/11. This suggests that the $SF(B{-}C)_{bcp}$, or in general for metal−carbonyl bonding the $SF(M\text{-}C)_{bcp}$, may provide (depending on the symmetry of the fragment ML_n) a more sensitive measure of any effects of π-bonding or π-back-donation than the $SF(C{-}O)_{bcp}$. The relatively large contribution of 11.3% from the O atom basin (similar contributions are observed in metal carbonyl complexes[18−20,23,24]) may be ascribed to the dominating importance of the σ-orbital MO 4, which has a high density on the O atom. The $SF(B{-}H)_{bcp}$ (Table 5) again shows the importance of the core contribution for the B atomic basin, and

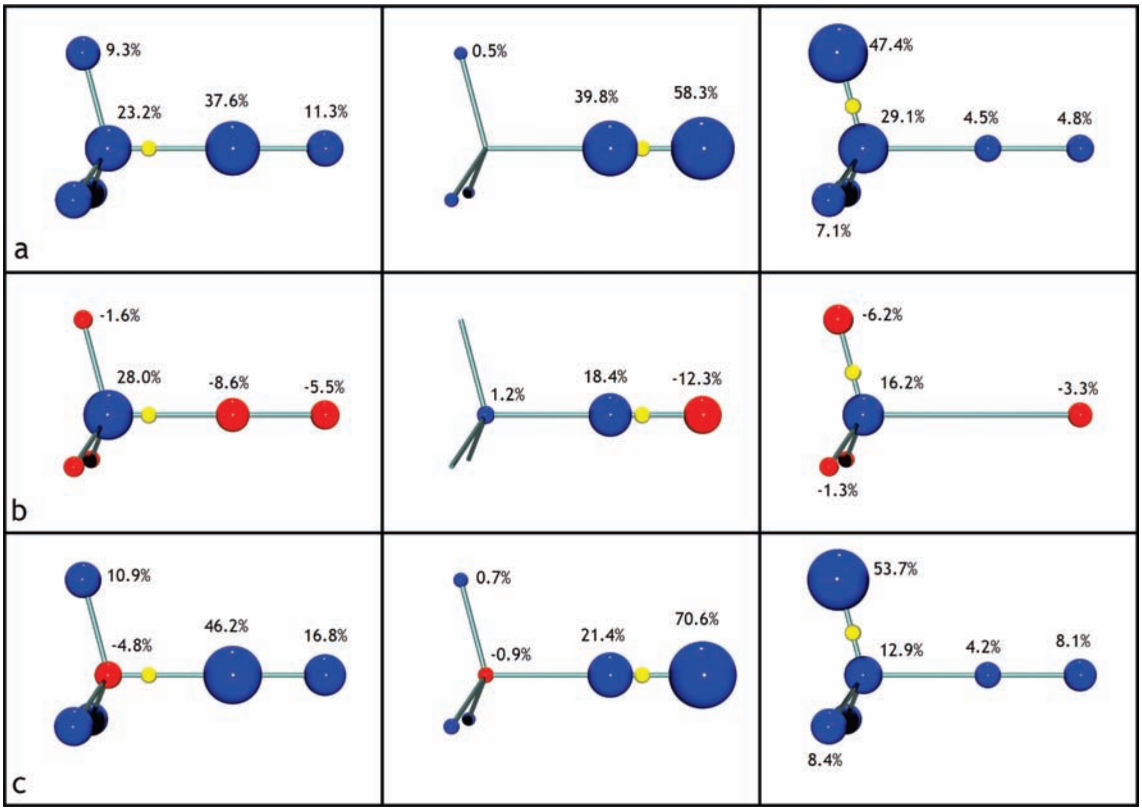


Figure 2. Atomic basin contributions to the SF for H_3BCO (**1**). The volume of the spheres is proportional to the percentage contributions from the atomic basins; positive contributions (sources) are shown in blue, and negative contributions (sinks) in red. The positions of the reference points are shown as yellow spheres, and absolute source contributions less than 0.5% are not shown. The contributions for each atomic basin from the total, the core, and the valence densities are shown in rows a, b, and c respectively.

TABLE 2: Percentage Orbital Contributions to the Density at the SF Reference Points for 1

MO no.	SF(B−C)$_{bcp}$	SF(C−O)$_{bcp}$	SF(B−H)$_{bcp}$
	0.1486 (0.1487)[a]	0.4989 (0.4989)	0.1671 (0.1671)
1	0.00 (0.00)[b]	0.00 (0.00)	0.00 (0.00)
2	0.00 (0.00)	6.78 (6.87)	0.00 (0.00)
3	9.08 (9.19)	0.00 (0.00)	4.35 (4.38)
4	0.06 (0.06)	53.11 (53.04)	0.00 (0.00)
5	52.03 (51.97)	0.79 (0.78)	5.96 (5.96)
6	16.50 (16.48)	34.74 (34.68)	4.40 (4.40)
7	0.00 (0.00)	−0.02 (0.00)	1.59 (1.58)
8	0.01 (0.00)	−0.02 (0.00)	0.01 (0.00)
9	22.32 (22.30)	4.64 (4.63)	21.95 (21.95)
10	−0.01 (0.00)	0.00 (0.00)	0.00 (0.00)
11	−0.02 (0.00)	0.00 (0.00)	61.78 (61.73)

[a] The SF reconstructed density ρ_{SF} (au) at the bcp is given first, with the exact density in parentheses. [b] The overall percentage contribution from each MO by summation of the SF over all basins is given first, with the exact contributions from the orbital densities in parentheses.

TABLE 3: Molecular Orbital Decomposition of $S(\mathbf{r}_b,\Omega)$ for the C−O Bond in 1 ($\mathbf{r}_b$ = Bond Critical Point)

MO	B1	C2	H3	H4	H5	O6
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	19.03	0.00	0.00	0.00	−12.25
3	1.23	−0.64	−0.20	−0.20	−0.20	0.00
4	−0.01	1.96	0.00	0.00	0.00	51.16
5	−0.28	3.64	−0.31	−0.31	−0.31	−1.65
6	0.10	12.97	−0.05	−0.05	−0.05	21.82
7	−0.02	0.81	−0.03	−0.03	−0.03	−0.71
8	−0.02	0.81	−0.04	−0.03	−0.03	−0.71
9	−0.70	4.28	0.05	0.05	0.05	0.91
10	0.01	−1.51	−0.60	1.11	1.11	−0.11
11	0.00	−1.51	1.68	−0.03	−0.03	−0.11
total	**0.3**	**39.8**	**0.5**	**0.5**	**0.5**	**58.4**

TABLE 4: Molecular Orbital Decomposition of $S(\mathbf{r}_b,\Omega)$ for the B−C Bond in 1

MO	B1	C2	H3	H4	H5	O6
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	5.48	0.00	0.00	0.00	−5.49
3	27.98	−14.12	−1.59	−1.59	−1.59	0.00
4	−0.05	−14.77	−0.01	−0.01	−0.01	14.91
5	3.91	55.68	−1.32	−1.32	−1.32	−3.60
6	2.59	9.84	0.05	0.05	0.05	3.91
7	−0.47	−0.87	0.00	−0.15	−0.15	1.66
8	−0.47	−0.87	−0.21	−0.05	−0.05	1.66
9	−2.49	20.98	1.69	1.69	1.69	−1.25
10	−3.88	−11.89	−3.75	9.87	9.87	−0.23
11	−3.89	−11.88	14.41	0.79	0.79	−0.23
total	**23.2**	**37.6**	**9.3**	**9.3**	**9.3**	**11.3**

for both atoms MO 11 is the major contributor as it contains significant B−H σ-bonding.

While the analysis of the SF in terms of individual MO contributions is illuminating, the reader should be aware that the decomposition of an observable in terms of molecular orbitals is arbitrary and subject to the particular choice of MO settings (which might have considerable implications in the case of subtle chemical bonds). Another, potentially more useful, approach is to examine the decomposition into core and valence contributions, particularly as this is feasible for both experimental (multipole modeled) and theoretical densities. By combining the contributions from MO's 1−3 and MO's 4−11, we can assess the relative importance of the core and valence densities respectively to the SF in **1**, which are shown in Figure 2. It is important to stress that the *global* contributions from the core orbitals to the SF is quite small and never exceeds 10%, because individual basins may be sources or sinks and hence make opposing contributions. The SF(B−C)$_{bcp}$ is quite

TABLE 5: Molecular Orbital Decomposition of $S(\mathrm{r_b},\Omega)$ for the B−H3 Bond in 1

MO	B1	C2	H3	H4	H5	O6
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	3.33	0.00	0.00	0.00	−3.33
3	16.20	−3.02	−6.24	−1.30	−1.30	0.00
4	−0.03	−8.22	−0.01	−0.01	−0.01	8.29
5	−5.17	15.54	0.01	−1.00	−1.00	−2.42
6	−0.21	0.85	1.72	0.02	0.02	2.00
7	0.44	0.12	0.56	−0.12	−0.12	0.72
8	−0.27	0.02	−0.35	−0.04	−0.04	0.69
9	2.42	4.55	12.24	1.78	1.78	−0.82
10	−3.58	−4.26	−7.70	7.85	7.85	−0.15
11	19.28	−4.43	47.21	−0.06	−0.06	−0.16
total	**29.1**	**4.5**	**47.4**	**7.2**	**7.2**	**4.8**

delocalized over all atomic basins and the B atom core provides the overwhelming contribution (28.0%) to the total SF from the B atom (23.2%). In fact, the valence density here acts as a sink (−4.8%) rather than a source. Conversely, the relatively large contribution from the O atomic basin of 11.3% is dominated by the valence density (16.8%), with the core acting as a sink (−5.5%). The highly localized $\mathrm{SF(C{-}O)_{bcp}}$ is quite typical also for metal carbonyl complexes[18−20,23,24] and can be easily rationalized by the dominating contributions from σ-MO's 4 and 6, which have almost their entire densities contained within the C and O atomic basins. Again the core densities provide important contributions from individual basins toward the total SF.

An important consideration when a theoretical core/valence decomposition of the SF is compared with an experimentally derived one is the adequacy of the multipole model. To this end, the SF in **1** was also derived from multipole modeling of the wave function density projected into static structure factors, using the XD2006 program suite.[35] The results, shown in Figure S1 (Supporting Information) indicate a reasonable qualitative agreement in terms of the total SF and its decomposition into core and valence contributions. Nevertheless, despite the use of a very flexible multipole model, and despite the excellent least-squares agreement [$R = 0.27\%$, $\Delta\rho = \pm 0.03$ e Å^{-3}], the quantitative agreement is evidently not exact. This discrepancy may be partially attributed to the well-known deficiencies of the multipole model,[39] which in turn lead to differences in the positions of the bcp's and hence a bias in the SF contributions when the reference point is a bcp, as shown recently by Lo Presti and Gatti.[40] The B−C bcp is shifted 0.024 au toward the C atom in the multipole modeled density, the B−H bcp shifted ∼0.04 au toward the H atom, while the C−O bcp is shifted only 0.007 au toward the C atom. Consistent with this view, the best agreement is found for the $\mathrm{SF(C{-}O)_{bcp}}$. The profiles of the atomic basin contributions to SF(B−C) for reference points along the B−C bond vector are shown in Figure 3. In the vicinity of the B−C bcp, the percentage basin contributions from the B and C atoms are very sensitive to the position of the rp. In contrast, those for the H atoms and particularly the O atom are rather stable over a wide range of rp positions. Clearly, the SF and its core and valence contributions may be significantly affected by (albeit rather small) shifts in the positions of the rp's. While, in this case, the reason for these small shifts lies in the deficiencies of the multipole model, it nevertheless demonstrates that the position of the reference point is an important factor to be taken into consideration in the quantitative chemical interpretation of the SF.

Finally, we note we can also compute the $\mathrm{SF_{pro}}$, i.e., the SF for the pro-molecule density consisting of the superposition of spherical atomic densities at the atomic positions. This is shown in Figure S2 (Supporting Information) and reveals a considerable qualitative similarity with the SF of the "true" density. While the pro-molecule density itself is a nonphysical quantity, the $\mathrm{SF_{pro}}$ emphasizes the strong connection that the SF has with the molecular geometry. The quantitative differences arise in part from chemical bonding effects, though the quite different atomic basins (see Table S1, Supporting Information) in the pro-molecule density undoubtedly have a considerable influence as well.

Many of the considerations discussed above also apply to the other systems we have examined. The SF contributions for acetamide (**2**), with the breakdown into the core and valence contributions, are given in the Supporting Information in Figures S3−S8 and Tables S2−S8. The agreement between the theoretical and experimental SF is excellent, and it is immediately obvious that, in contrast to **1**, the SF in **2** is definitely dominated by the valence density. The *overall* contribution from the core density is very small for all reference points and is generally much less than 1%. The $\mathrm{SF(A{-}B)_{bcp}}$ is generally quite localized into the two atoms sharing the interatomic surface, particularly so for the X−H bonds, where the contributions from the two atoms typically exceed 80%. The core contributions to the SF are only significant for the carbonyl atoms C4 and O1 and it is notable that the core electrons of these atoms always act as a source and sink, respectively, regardless of the placement of the reference point. Likewise, the N2 core density always acts as a sink, though its absolute contribution is smaller and only above 0.5% for reference points 2 and 9 (Figures S4 and S7, Supporting Information). On the other hand, the contributions from C3 and the H atoms are always negligible. The orbitals of π-symmetry (MO's 11, 14, and 15, Figure S14, Supporting Information) make very little contribution to the $\mathrm{SF(C{-}O)_{bcp}}$, though they are more important for $\delta(\Omega_\mathrm{O},\Omega_\mathrm{C})$, as similarly noted above for **1**. The SF in **2** was also computed at the midpoint of the H5−H7 vector, at a point where the density is very low and models that observed in typical weak chemical interactions such as H−H bonding.[41] At this reference point 9 (Figures S2−S8, Supporting Information), the SF is very delocalized and difficult to rationalize in terms of a naive chemical interpretation. Both experiment and theory agree that the largest positive contributions come from the O atom and those H atoms furthest from the rp.

The thiocoumarin **3**[28] was chosen as an example of a compound containing a third period element. The agreement between the theoretical and experimental SF, and the breakdown into core and valence contributions, is generally excellent. The degree of localization of $\mathrm{SF(A{-}B)_{bcp}}$ into the atomic basins sharing the interatomic surface is greater than 80% for all C−O and C−C bonds and ∼90% for all C−H bonds. Even with the heavier element S present, the global contributions from the core density are negligible, except for the polarized C−S and C−O bonds. The basin contributions for the $\mathrm{SF(C{-}S)_{bcp}}$ are shown in Figure 4. For the theoretical density, the core contribution from the S atom is quite significant, whereas for the experimental density, it is very marginal. We suggest the main reason for this difference lies in the substantial shift of the bcp, ∼0.33 au toward the S atom in the theoretical topology, compared with the experimental one. This results in a 4% larger contribution from the S atomic basin and a 3.5% smaller contribution from the C atomic basin to the SF in the theoretical topology. A similar, though less striking, effect is seen for the polarized C−O bonds shown in Figure S9 (Supporting Information). These results further emphasize the crucial importance of the position of the rp in determining the SF. Moreover, while

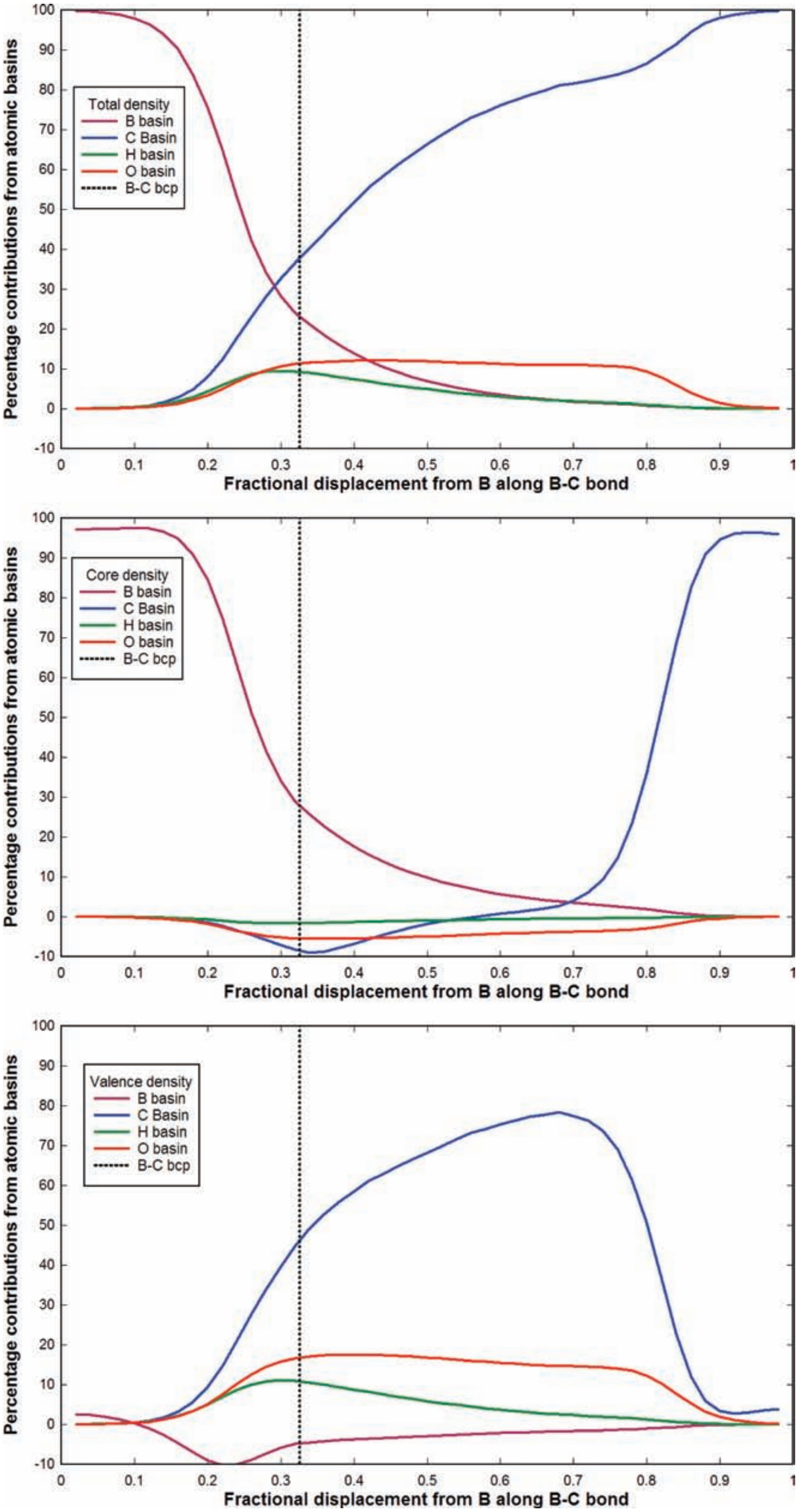


Figure 3. Percentage contributions from the atomic basins to the theoretical SF(B−C) in H_3BCO (**1**), with reference points along the B−C bond vector.

the five highest lying MO's, which are of π-symmetry, contribute 46.5% toward the delocalization index $\delta(\Omega_S,\Omega_C)$ associated with the S═C bond, these same orbitals only contribute 3.8% toward the $SF(S-C)_{bcp}$. This again suggests that orbitals with nodal planes barely contribute toward the SF when the rp lies on the nodal plane, and furthermore explains why the π-electron delocalization in the benzene ring is not manifest in the SF when the reference point is taken at the C−C bcp's.

As a final example, we examine $Fe(CO)_5$ (**4**),[29] a compound containing a first row transition metal. Here the situation regarding the involvement of core density is more complex (see

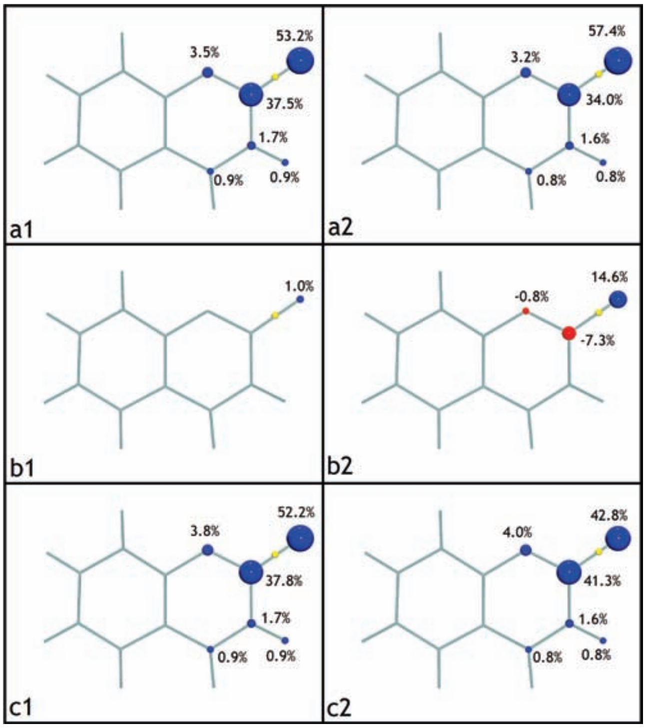


Figure 4. Experimental (column 1) and theoretical (column 2) atomic basin contributions to the SF(C−S)$_{\mathrm{bcp}}$ for thiocoumarin (**3**). The contributions for each atomic basin from the total, the core, and the valence densities are shown in rows a, b, and c respectively.

Computational Methods for core definition for Fe). Details are given in Tables S9−S14 and the SF and valence orbital representations in Figures S10−S13 and S15 in the Supporting Information. None of the delocalization indices $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{C}})$, $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{O}})$, and $\delta(\Omega_{\mathrm{C}},\Omega_{\mathrm{O}})$ contain any significant contributions from the core orbitals (MO's 1−19). However, as observed for H_3BCO, a vital component of the electron sharing involves orbitals of π-symmetry. For instance, for $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{O}})_{\mathrm{axial}}$ the overwhelmingly important orbital contributors are MO's 45/46, which are out-of-phase combinations of the Fe d_{xz}/d_{yz} with p_x/p_y on the O atoms. They provide some 90% of $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{O}})_{\mathrm{axial}}$ and clearly relate to Fe−CO π-backbonding, as was originally suggested by Macchi and Sironi.[8] Likewise for $\delta(\Omega_{\mathrm{C}},\Omega_{\mathrm{O}})_{\mathrm{axial}}$, some 50% of the electron sharing arises from the four symmetry-adapted C−O π-bonding MO's 31−34. The indices $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{C}})$ on the other hand have a more even spread of orbital contributions and any interpretation of course depends on the symmetry adapted molecular orbitals involved in the Fe−C bonds.

In contrast, for the SF(Fe−C)$_{\mathrm{bcp}}$, the core density of the Fe atom plays a significant role, while the π-symmetry orbitals play only a minor role. The considerable positive core contributions outweigh the negative (sink) contributions from the valence density and leave an overall positive source contribution. In fact, by comparing the SF for a "small" [Ne] core on Fe with the standard "large" [Ar] core shown in Figure 5, one can see that the overall Fe basin contribution for the total density comes almost entirely from the relatively diffuse 3s and 3p density. This leads to the possibility that, in compounds of this type, the SF contribution from the metal may not show much dependence on the chemical bonding. The role of $(n-1)$s and $(n-1)$p orbitals in the electron sharing of transition metal complexes is generally quite negligible, according to many partitioning schemes.

The O atomic basin contribution of ∼14% is typical of that seen in other metal carbonyls[18−20,23,24] and arises mainly from the low-lying C−O σ-bonding orbitals MO's 20−24 (Figure S15, Supporting Information). This contribution is again expected to be rather insensitive to chemical bonding and, unlike the delocalization index $\delta(\Omega_{\mathrm{Fe}},\Omega_{\mathrm{O}})$, it does not contain any information on the Fe−O delocalization of π density. In contrast, the C atomic basin contribution is more widely sourced among the MO's, including orbitals of π-symmetry and it is probable that this contribution will be the most sensitive to π-bonding effects.

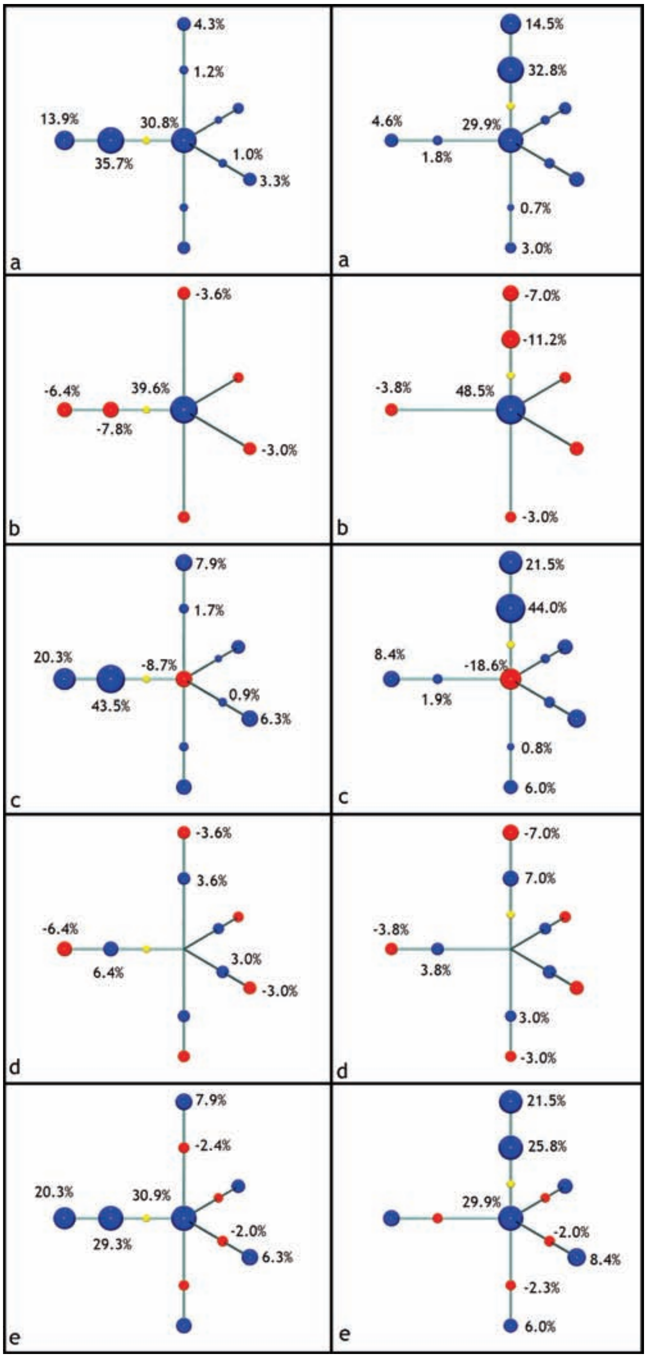


Figure 5. Atomic basin contributions to the theoretical SF(Fe−C)$_{\mathrm{bcp}}$ in $Fe(CO)_5$. The percentage contributions from each atomic basin due to the total, core, and valence densities are shown in rows a−c respectively for a "large" Fe core ≡ [Ar]. Rows d and e show the core and valence densities respectively for a "small" Fe core ≡ [Ne].

The SF(C−O)$_{\mathrm{bcp}}$ shows features similar to those already observed in H_3BCO and in other metal carbonyls,[18−20,23,24] with the C and O basins contributing 40 and 58%, respectively. The

O atomic basin's contribution arises almost entirely from the low-lying C−O σ-bonding orbitals MO's 20−24 and is hence unlikely to be sensitive to the chemical environment. The C−O orbitals of π-symmetry make only very small individual, and negligible global, contributions so that for metal carbonyls, the $SF(C-O)_{bcp}$ is insensitive to π-bonding effects. This restriction may be partially raised in systems of low symmetry, due to orbital mixing. Around 50% of the contribution from the C atomic basin comes from the 1s core orbital on C, with the rest being widely spread. Some sensitivity to chemical bonding effects may be therefore expected for this contribution, but certainly quite different from that of the delocalization indices.

4. Conclusion

This study has shown that, while the SF might contain some information about the chemical bonding, it is often distinct from that of electron delocalization between two or more atomic basins. This means that its interpretation cannot be so straightforward and we suggest that scientists making use of the SF for an electron density analysis should consider the following issues:

1. If a single reference point is considered (for example, the bcp), then the SF may not be sufficiently informative about the chemical bond. In addition, it can be quite sensitive to the choice of the reference point. Both these issues represent common limitations to all QTAIM indicators evaluated at a single point **r**, although derivatives of the density at **r** may provide information that is not strictly local (for example Laplacian, ellipticities etc.). This is missing in the SF reconstruction of the density at a single point **r**, despite using all points **r′** in space to determine this property through the influence function. Core electrons may become extremely important at the bcp if the interatomic surface is significantly shifted toward one atom in a bonded pair, as generally occurs in polar bonds. The same is not observed for delocalization indices, because the double integration of the pair density in two atomic basins cancels those terms strongly localized in one basin only.

2. For the transition metal compound we have examined, the contributions to the SF from the $(n-1)$s and $(n-1)$p are more important than those from the ns and $(n-1)$d. If this is true generally, it should be borne in mind when analyzing the chemical influence in the SF contributions from transition metal basins. Again, the SF and delocalization indices contain different information.

3. While the SF is able, in certain circumstances, to represent the localized or delocalized nature of a given chemical interaction, it is not safe to conclude that it *always* contains information primarily from the electron sharing density.

While we find no reason to criticize the QTAIM analyses that have made use of the SF in the current literature, we advise great caution in the (over)interpretation of its chemical significance, particularly if the SF is computed only at one reference point. Double integration of the local source in two atomic basins might give a less biased picture, by showing the influence of one atom on another and vice versa (notably these two terms are not identical by definition). However, the current state of the research in this direction is not sufficiently advanced and further studies are necessary.

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Supporting Information Available: Tables of the orbital and core/valence breakdown of the SF in compounds **1−4**, SF, and orbital representations (Figures S1−S17 and Tables S1−S14). This material is available free of charge via the Internet at http://pubs.acs.org.

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