Density functional theory and Bader’s atoms-in-molecules theory: towards a vivid dialogue†

Vincent Tognetti* and Laurent Joubert

Density functional theory and Bader’s atoms-in-molecules theory share the same primary ingredient: the electron density, which is the fundamental physical observable in quantum chemistry. In this paper, we elaborate on the decomposition of the Kohn–Sham molecular energy in terms of Bader’s partition, discussing how Pendás’ Interacting Quantum Atoms framework could be adapted to a DFT context. Besides, another bridge between these two theories is built through a general formalism able to generate new local descriptors from any second-order density gradient expansion. These approaches are then applied to two classes of intramolecular bonds: between two electronegative atoms and intramolecular hydrogen bonds, illustrating how fruitful a dialog between both theories can be.

1. Introduction

Chemical transformations are almost always qualitatively described by identifying and focusing on interactions between a few selected atoms or functional groups, which provide a kind of coarse grain account of reactivity. Although such an approximation constitutes a convenient and useful framework, it may seem to be in contradiction to the quantum nature of electrons that are delocalized in the whole space. Rigorous schemes have thus been proposed to restore a localized picture of chemical interactions, aiming at theoretically translating the empirical concepts of bonds and atomic interactions. One can for instance refer, among others, to the valuable Natural Bonding Orbitals (NBO) and Electron Localization Function (ELF) analyses.

A different way was proposed fifty years ago by Richard Bader with the development of his Quantum Theory of Atoms-in-molecules (QTAIM). At variance with other approaches, it does not imply the definition of auxiliary functions, but directly focuses on the primary physical quantum observable, the electron density. As a consequence of the density gradient zero-flux condition (zfc), the real space is divided into non-overlapping domains, called "quantum atoms" or atomic basins. Two main ways for dividing the total molecular energy can then be considered.

The first one, which derives from the extension of quantum physics to open systems and which is based on the atomic virial theorem, is that pioneered by Bader and is one of QTAIM fundamental cornerstones. The second, more recent, shows that, using such a real space partition, the total energy of any chemical system can be exactly expressed as a sum of monobasin and dibasin contributions. This is the so-called “Interacting Quantum Atoms” (IQA) scheme, notably pioneered by Pendás and coworkers.

A priori a typical Bader’s topological analysis can be performed, provided the only electron density is known: it can thus be carried out either from experimental (X-ray diffraction) measurements or from computational calculations, whether they are based on wavefunction (wf) approaches or on Density Functional Theory (DFT).

As this paper is intended for the PCCP Themed Collection on Density Functional Theory and its Applications, associated with the DFT2013 conference, we decided to focus on the links that can be forged between DFT and QTAIM, which are both based on the same ingredient and which share, from our viewpoint, the same deep physical roots.

Interestingly, while Bader himself emphasized that “many of the observable properties of a molecule are determined in whole or in part by the simple three dimensional electron-density distribution” as early as in 1963, that is to say, before the advent of modern DFT and of QTAIM, he exclusively made use of Hartree–Fock (HF) and post-HF calculations to apply his own theory, initially because before the end of the ’80s, practical DFT implementations were not easily available.

Does this imply that despite their apparent similarities, these two theories cannot actually converse? In this paper we intend to give some hints that a fruitful dialogue is bound to exist, provided some precautions are taken. With these caveats in mind, we will illustrate its potential efficient use for the detailed characterization of “weak” intramolecular bonds. To this last aim, two types of analysis can be generally carried out: the study of the general topology (existence or absence of bond

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paths. . . and of the most salient critical point properties, and the inspection of integrated properties (population, delocalization indices . . . ). They usually provide complementary information, but linking them may not be straightforward. We intend here to suggest that DFT can efficiently play this role of interpretative “linker”.

Thus this paper will be structured as follows: we will first discuss QTAIM molecular energy partitioning in the framework of Kohn–Sham (KS) DFT, then examine whether and to what extent interatomic energies can be converted in terms of local properties, and finally how these local properties may enable us to discriminate between different intramolecular bond types.

2. Partitioning molecular energies

2.1. Kohn–Sham DFT energetic decomposition based on QTAIM partition

We begin with the exact total molecular energy, assuming Born–Oppenheimer approximation, obtained from the polyatomic wavefunction $\psi$:

$$E^\psi = V_{NN} + V_{Ne}[\psi] + \int \frac{\rho^0(\mathbf{r}_1, \mathbf{r}_2)}{||\mathbf{r}_1 - \mathbf{r}_2||} d^3r_1 d^3r_2 + T[\psi],$$  \hspace{1cm} (1)

where $V_{NN}$ denotes the nuclear repulsion energy, $V_{Ne}$ the attraction energy of the electrons by the nuclei, $T$ the electronic kinetic energy, and $\rho^0$ the diagonal element of the spinless second-order density matrix, which embodies the electron–electron repulsion.\(^{19,20}\) Unfortunately its evaluation is cumbersome for complicated correlated wfs. As an approximation, it can be expanded in terms of natural orbitals (see the very stimulating recent study\(^{21}\) by Pendas and coworkers for this approach in a QTAIM-IQA context).

Alternatively, in the KS flavor of DFT, the molecular energy exactly reads:

$$E^{KS} = V_{NN} + \int \rho(\mathbf{r}) v(\mathbf{r}) d^3r + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{||\mathbf{r}_1 - \mathbf{r}_2||} d^3r_1 d^3r_2 + E^{\text{classical electrostatic}}[\rho] + \frac{1}{2} \int \frac{2 \rho^0(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{||\mathbf{r}_1 - \mathbf{r}_2||} d^3r_1 d^3r_2 + T_c[\rho] + T_s[\{\psi^{KS}\}].$$ \hspace{1cm} (2)

The sum of the first three contributions represents the total classical electrostatic energy. $T$ is now divided into the correlation counterpart, $T_c$, and the kinetic energy of the fictitious KS system (whose exact wf is the Slater determinant built on the $\psi^{KS}$ orbitals). The fourth and fifth terms define the so-called exchange–correlation (xc) energy. In virtue of the Hohenberg–Kohn theorems, it can be cast into an electron density functional $E^{KS}[\rho]$.

Let us now apply Bader’s space partition:

$$R^3 = \prod_A Q_A.$$ \hspace{1cm} (3)

It is straightforward to show that the electrostatic energy reads (where $E^{\text{AB}_{\text{Ne}}}$ for instance, stands for the energy due to the attraction of electrons in basin $A$ by the nucleus in basin $B$):

$$E^{\text{classical electrostatic}}[\rho] = \sum_A E^{\text{AB}_{\text{Ne}}}_A + \sum_{A < B} E^{\text{AB}_e}_A + \sum_{A < B} E^{\text{AB}_o}_A + \sum_{A < B} E^{\text{AB}_{\text{excl}}}.$$ \hspace{1cm} (4)

As $\psi^{KS}_i$ are monoelectronic functions, one has similarly:

$$T_s[\rho] = \sum_A T^A_s.$$ \hspace{1cm} (5)

Up to now, no approximations have been made. Unfortunately, the exact xc functional is not analytically known. Firstly, we consider pure local (in the mathematical sense) functionals, encompassing the first three rungs of Perdew’s ladder\(^{22}\) (LDA, GGA, and metaGGA):

$$E_{xc}[\rho] = \int c_{xc}(\mathbf{r}) d^3r. \hspace{1cm} (6)$$

The total energy can then be partitioned according to:

$$E^{KS}[\rho] = \sum_A E^{A}_{\text{Ne}} + \sum_A T^A_s + \sum_A E^{A}_{\text{excl}} + \sum_{A < B} E^{AB}_{\text{cl}} + \sum_{A < B} E^{AB}_{\text{excl}}.$$ \hspace{1cm} (7)

In this case, self atomic energies ($E^{\text{AB}_{\text{loc}}}$) include quantum effects, while atoms interact between them only in a pure classical way (even if the density involved in $E^{\text{AB}_{\text{excl}}}$ indirectly includes quantum effects). Eqn (7), to the best of our knowledge, has not been used so far in practice.

A popular alternative (implemented in the AIMAll software\(^{23}\)) uses the pair density associated with the KS fictitious system wf instead of that derived from the (unknown) real system wf. As $\psi^{KS}$ is a single determinant, the second order density matrix can be expressed in terms of the first order density matrix, $\rho_1$, only:\(^{24}\)

$$\rho^{KS}_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \frac{1}{3} \rho_1(\mathbf{r}_1; \mathbf{r}_1') \rho_1(\mathbf{r}_2; \mathbf{r}_2') - \rho_1(\mathbf{r}_1; \mathbf{r}_2') \rho_1(\mathbf{r}_1'; \mathbf{r}_2),$$ \hspace{1cm} (8)

so that $p^{\text{KS}}_2(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^{KS}_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \rho_1(\mathbf{r}_1; \mathbf{r}_2)$, and finally:

$$E^{\text{exchange–correlation}}[\{\psi^{KS}\}] = -\frac{1}{2} \int \frac{\rho^0(\mathbf{r}_1, \mathbf{r}_2)^2}{||\mathbf{r}_1 - \mathbf{r}_2||} d^3r_1 d^3r_2 + T_s[\{\psi^{KS}\}] - E^{\text{exchange–correlation}}[\rho].$$ \hspace{1cm} (9)

Actually, the double integral corresponds to the exchange energy (as defined in wf theories), $E_{\text{ex}}$, calculated from the KS orbitals. Note that, as in general HF and KS orbitals differ, KS $E_x$ will be different from the HF one. More problematically, in case the exact xc correlation functional could be used, one will then exactly get $\rho(\{\psi^{KS}\}) = \rho_{\text{real}}$, but in general $\rho_1(\{\psi^{KS}\}) \neq \rho_{1,\text{real}}$.\(^{25}\)
Coming back to eqn (9), atomic $T_c$ can be evaluated.\textsuperscript{25} However, the implementation is complex (requiring the xc potential), but fortunately this contribution was shown to be generally negligible. Hence (note that at variance with eqn (7), the sum now differs from the SCF energy):

$$E^{KS} = \sum_A E_{Ne}^{KS} + \sum_A T^A \left[ \{ \psi_j^{KS} \} \right]$$

$$+ \sum_{A < B} E_{AB}^{disp} + \sum_{A < B} E_{AB}^{KS} \psi_i^{KS} \psi_j^{KS} .$$  

(10)

It is obvious that a correlation contribution in $E_{int}$ is missed. In ref. 26, we compare such values with those obtained at the full valence complete active space (CAS) level by Pendás and coworkers.\textsuperscript{11} Obviously, one must be cautious when making such comparisons. Indeed, only the electrostatic interaction energies $E_{cl}$, which only involve the electron density, must exactly be identical in principle. We can however expect KS DFT and wavefunction $E_{int}$ to be close enough to one another, so that chemical conclusions and insights are compatible. We found indeed a satisfying agreement: eqn (10), despite its underlying approximations, could be safely used at least for semi-quantitative purposes.

Finally, it can be noted that this formalism can in principle be applied to any real space partition into non-overlapping domains, whether they correspond or not to the QTAIM partition, even if this last approach is, from our viewpoint, natural and appealing when dealing with the electron density.

2.2. Possible extensions

An improvement could be obtained by adding energetic contributions similar to the ones entering the fully non-local van der Waals density functionals, where a kernel $\phi(\vec{r}_1,\vec{r}_2)$ (only depending on the density, its derivatives, and distances) captures the essential of dispersion energy.\textsuperscript{27,28} One would then have:

$$E^{AB}_{int} = E_{cl}^{AB} (\rho) + E_x^{KS} \{ \psi_i \} + \sum_{\vec{r}_1,\vec{r}_2} \phi(\vec{r}_1,\vec{r}_2) \rho(\vec{r}_1) \rho(\vec{r}_2) d^3 r_1 d^3 r_2 .$$  

(11)

Such an approach may also enable a direct comparison with Grimme’s type dispersion corrections\textsuperscript{29} that make use of atomic (classical) pair potential according to $E_{disp} = \sum_{A < B} C_6^{AB} / R_{AB}^6$. Interestingly, the so-called D3 method\textsuperscript{30} uses environment-dependent $C_6$ coefficients. It could be compared and may be improved using data generated by eqn (11).

Similar non-local kernels are also at work in the design of $T_s$ kinetic energy functionals.\textsuperscript{31} This will result in a partition into monoatomic and diatomic contributions. Such a decomposition could seem unphysical since the kinetic operator is an one-electron operator. However, the molecular virial theorem states that (at equilibrium geometries) $T = T_s + T_e$ equals the opposite half of the potential energy, whose decomposition into mono and dibasin terms is physically relevant.

2.3. Comparison with virial-based QTAIM energetic partitioning

Actually, Bader proved that the zfc enables to derive the so-called “atomic (or regional) virial theorem” that enables to properly define atomic energies.\textsuperscript{32,33} Thanks to it, an atom in a molecule is a fully determined entity, with boundaries and energy that directly follow from the extension of quantum physics to open-systems through the appropriate subsystem variational principle. As a consequence, the molecular energy is simply the sum of atomic virial energies: no interaction term appears. Even if this formalism is fully exact and has been successfully and powerfully used for the last few decades (see ref. 34 and 35 for recent examples), its translation into the usual chemical language (which relies on interactions between reactive sites) is not intuitive. Furthermore, in practice, it employs $\rho_i$, which KS DFT cannot in principle exactly provide. Of course, this is only a limitation due to KS DFT and not to QTAIM.

In order to bypass it, some approximations to these atomic energies were developed, notably by Abramov.\textsuperscript{36} This last one is a pure, but quite rough, DFT estimation, based on Thomas–Fermi–von Weizsäcker (TFvW) energy density at each real space point. This method is fast and is particularly useful for crystallographers to treat data directly stemming from X-ray diffraction experiments (that do not provide $\rho_i$, but only $\rho$). However, the sum of atomic energies (due to the crudeness of the TFvW functional) could considerably differ from the exact molecular one.

3. A local point of view of interatomic interactions

3.1. Critical point local properties

The evaluation of eqn (10) is unfortunately time-consuming and is prohibitive for extended systems. It would be highly beneficial if the properties of some points between two nuclei could afford valuable information about the interaction between these atoms. At equilibrium geometries, points of choice are the bond critical points (BCPs), which form the corresponding bond paths (BPs).

The most often used CP descriptors are the electron density ($\rho$), Laplacian $\nabla^2 \rho$, (trace of the density Hessian matrix $H$), Lagrangian ($G_c$) and Hamiltonian ($K_c$) kinetic energy, virial $V_c$, and energy $H_c$ density values. Once more, these last quantities were initially defined in a wf context (based on density matrices), so that they are not directly transposable in the KS framework.

In order to make DFT and QTAIM converse, we propose instead the following formalism. Consider the following general second-order gradient expansion where $g$ denotes the pure “local” (in the DFT sense) contribution depending only on the density, which is corrected by a general gradient term that usually takes the following form:

$$f(\vec{r}) = g(\rho(\vec{r})) + \gamma \frac{\left\| \nabla \rho(\vec{r}) \right\|^2}{\rho(\vec{r})} .$$  

(12)
Consider now a small sphere $\Sigma$ around a given critical point with an infinitesimal radius $\varepsilon$. A Taylor expansion at any $\Sigma$ point located by the azimuthal $\theta$ and zenith $\phi$ angles (with Zwillinger’s convention) and by the $\vec{u}$ unitary vector gives:\(^{17}\)

\[
\begin{aligned}
\rho(\vec{r}_c + \varepsilon \vec{u}) &\approx \rho(\vec{r}_c) + \frac{\varepsilon^2}{2} \vec{u} \cdot \nabla^2 \rho(\vec{r}_c) \vec{u} \\
\nabla \rho(\vec{r}_c + \varepsilon \vec{u}) &\approx \varepsilon \nabla \rho(\vec{r}_c) \vec{u}
\end{aligned}
\]

Let us introduce the variation:

\[
\delta f(\varepsilon, \vec{u}) := f(\vec{r}_c + \varepsilon \vec{u}) - f(\vec{r}_c)
\]

\[
= g(\rho(\vec{r}_c + \varepsilon \vec{u})) + \frac{\varepsilon^2}{2} \left| \nabla \rho(\vec{r}_c) \vec{u} \right|^2 - g(\rho(\vec{r}_c)).
\]

Only retaining the first non-vanishing order in $\varepsilon$,

\[
\left| \frac{\nabla \rho(\vec{r}_c + \varepsilon \vec{u})}{\rho(\vec{r}_c + \varepsilon \vec{u})} \right|^2 \approx \left| \frac{\nabla H(\vec{r}_c) \vec{u}}{\rho(\vec{r}_c)} \right|^2
\]

\[
= \varepsilon^2 \lambda_1 \lambda_2 \sin^2 \phi \cos^2 \theta + \lambda_2 \sin^2 \phi \sin^2 \theta + \lambda_3 \cos^2 \phi
\]

while (with an obvious derivative notation):

\[
\delta g(\varepsilon, \vec{u}) := g'(\rho(\vec{r}_c + \varepsilon \vec{u})) - g(\rho(\vec{r}_c))
\]

\[
\approx g'(\rho(\vec{r}_c)) \times [\rho(\vec{r}_c + \varepsilon \vec{u}) - \rho(\vec{r}_c)] = \frac{\varepsilon^2}{2} g'(\rho(\vec{r}_c)) \vec{u} \cdot \nabla H(\vec{r}_c) \vec{u},
\]

which is equivalent to:

\[
\delta g(\varepsilon, \vec{u}) \approx \frac{\varepsilon^2}{2} g'(\rho(\vec{r}_c)) \left[ \lambda_1 \sin^2 \phi \cos^2 \theta + \lambda_2 \sin^2 \phi \sin^2 \theta + \lambda_3 \cos^2 \phi \right]
\]

\[
= \frac{\varepsilon^2}{2} g'(\rho(\vec{r}_c)) f(\lambda_1, \lambda_2, \lambda_3, \theta, \phi)
\]

A spherical average makes the angular distance dependences disappear:

\[
(\delta f)^{(2)} := \lim_{\varepsilon \to 0} \frac{1}{4\pi \varepsilon^2} \int_{0}^{2\pi} \int_{0}^{\pi} \delta f(\varepsilon, \vec{u}) \sin \phi \, d\phi \, d\theta.
\]

Using eqn (14–17):

\[
(\delta f)^{(2)} = \frac{g'(\rho(\vec{r}_c))}{8\pi} \int_{0}^{2\pi} \int_{0}^{\pi} f(\lambda_1, \lambda_2, \lambda_3, \theta, \phi) \sin \phi \, d\phi \, d\theta
\]

\[
+ \frac{\varepsilon^2}{4\pi \rho(\vec{r}_c)} \int_{0}^{2\pi} \int_{0}^{\pi} \delta g(\varepsilon, \vec{u}) \sin \phi \, d\phi \, d\theta
\]

affording the final general result (where $\nabla \rho(\vec{r}_c) = \lambda_1 \hat{\lambda}_1 + \lambda_2 \hat{\lambda}_2 + \lambda_3 \hat{\lambda}_3$):

\[
(\delta f)^{(2)} = \frac{1}{6} \frac{\varepsilon^2}{\rho(\vec{r}_c)} \nabla^2 \rho(\vec{r}_c) + \frac{\gamma}{3} \frac{\rho(\vec{r}_c)}{\rho(\vec{r}_c)}.
\]

The right-hand in eqn (20) can be described as follows: the variation of the local contribution $g$ around the CP is multiplied by the Laplacian, while the contribution from the gradient inhomogeneity around the CP (controlled by $\gamma$) is multiplied by the similarity invariant $\rho \rho \rho$. We refer the reader to ref. 38 for a discussion about the information it conveys.

Still aiming at making QTAI and KS DFT converge, we now deal with xc energy densities (Eisrelson’s use of related quantities\(^ {39,40}\) from a different perspective, definitively deserves to be mentioned). The reduced density gradients (RDGs) $u$, $s$, and $t$, which are main ingredients of all xc functionals, are defined by:

\[
\nu(\vec{r}) = A_c \frac{\nabla \rho(\vec{r})}{\rho(\vec{r})} \quad \text{with} \quad \begin{cases}
A_u = 1, z_u = 0 \\
A_s = \frac{1}{2(3\pi^2)^{1/3}}, z_s = \frac{4}{3} \\
A_t = \frac{1}{4(3\pi^2)^{1/6}}, z_t = \frac{7}{6}
\end{cases}
\]

In case the density varies slowly, the xc energy densities can be approximated by the second order Svendsen–von Barth\(^ {41}\) and Ma–Brueckner\(^ {42}\) expansions (in their spin-unpolarized forms):

\[
\begin{aligned}
\epsilon_{xc}^{SvB} &= e_c^{Slater}(\vec{r}) \left[ 1 + \frac{1}{15} \rho(\vec{r}) + O(\nabla^4 \rho(\vec{r})) \right] \\
\epsilon_{xc}^{MB} &= e_c^{UEG}(\vec{r}) + \beta_c \rho(\vec{r}) \rho(\vec{r})^2 + O(\nabla^4 \rho(\vec{r}))
\end{aligned}
\]

where $e_c^{Slater} = -3 (\frac{3}{\pi})^{1/3} \rho(\vec{r})^{3/3}$ is the famous Dirac–Slater local exchange functional and $e_c^{UEG}$ denotes the uniform electron gas (UEG) correlation functional. For this, no exact closed form is known, but very accurate parameterizations exist based on Monte-Carlo simulations. As we are mainly interested in low density regions, we calculated the simplified (2,2) Padé approximant of the PW92 functional\(^ {13}\) at $\rho = 0.06$:

\[
\epsilon_{xc}^{UEG}(\vec{r}) = \frac{a_0 + a_1 \rho(\vec{r}) + a_2 \rho(\vec{r})^2}{b_0 + b_1 \rho(\vec{r}) + b_2 \rho(\vec{r})^2}
\]

with $a_0 = 0.00002$, $a_1 = -0.02112$, $a_2 = -0.48363$, $b_0 = 0.53682$, $b_1 = 7.87476$, and $b_2 = -2.58486$.

We stress that eqn (22) has no validity when the density rapidly varies. We thus recommend their use only in the vicinity of critical points. It can be easily shown that they are only particular cases of eqn (12), which describes the general second order gradient expansion. Eqn (20) then directly gives:

\[
\begin{aligned}
\langle \delta \epsilon_c \rangle^{(2)} &= -\frac{1}{2(9\pi^2)^{1/3}} \rho(\vec{r}) \frac{1}{\rho(\vec{r})} \nabla^2 \rho(\vec{r}) - \frac{\mu}{16(3\pi^2)^{1/3}} \frac{\rho(\vec{r})}{\rho(\vec{r})} \\
\langle \delta \epsilon_c \rangle^{(2)} &= a_1 b_0 - a_0 b_1 + 2(a_2 b_0 - a_0 b_2) \rho(\vec{r}) + (a_2 b_1 - a_1 b_2) \rho(\vec{r})^2 \\
&\times \left[ 6 \left( b_0 + b_1 \rho(\vec{r}) + b_2 \rho(\vec{r})^2 \right) + \frac{\pi^{1/3} \rho(\vec{r})^2}{\rho(\vec{r})^{1/3}} \right]
\end{aligned}
\]
For the kinetic energy, one can consider the TFvW expression: \[ e^T_{\text{TFvW}}(\overline{r}) = \frac{3}{10} (3\pi^2)^{2/3} \rho(\overline{r})^{5/3} \left( \frac{1}{8} \left\| \nabla \rho(\overline{r}) \right\|^2 + O(\nabla^4 \rho(\overline{r})) \right) \].

(25)

Once more, this form is a particular case of eqn (12), so that: \[ \langle \delta e_{\text{ex-c.e.}} \rangle^{(2)} = \frac{\pi^{4/3}}{3\sqrt{3}} \rho^{2/3} \nabla^2 \rho(\overline{r}) + \frac{1}{24} \rho(\overline{r}) \].

(26)

All \( \langle \delta e_{\text{ex-c.e.}} \rangle^{(2)} \) measure the variation rates of the (exchange, correlation, and kinetic) energy density around a given CP.

Similarly, one can evaluate the RDG variation rates around the CP.\(^{15}\) The variation is in first order in \( e_i \) and the integral must be numerically computed:

\[ \langle \psi_i \rangle^{(1)} = \frac{1}{4\pi \rho} \int_{0=0}^{2\pi} \int_{\phi=0}^{\pi} [\psi(\overline{r}_c + \overline{w}) - \psi(\overline{r}_c)] \sin \phi \, d\phi \, d\theta = \frac{A_{\overline{w}}}{4\pi \rho(\overline{r}_c)^{2\pi}} \int_{0=0}^{2\pi} \int_{\phi=0}^{\pi} \sqrt{\frac{3}{2}} \sin^2 \phi \cos^2 \theta + \lambda^2 \sin^2 \phi \sin^2 \theta + \lambda^2 \cos^2 \phi \sin \phi \, d\phi \, d\theta. \]

(27)

Interestingly, such descriptors are less sensitive\(^{46}\) than Laplacian\(^{37}\) to the computational protocol, also disclosing additional information.

### 3.2. Critical point and global energies

The aim of these new DFT based QTAIM descriptors is to characterize the interactions between the atoms linked by a BP, and to find correlations between them (easily rapidly calculated) and IQA interaction energies that require time-consuming protocols.

It may seem reasonable to aver that such correlations exist, since many were reported for intermolecular interactions (hydrogen, halogen bonds...).\(^{48,49}\) However, such a statement should be toned down. For instance, we considered in ref. 46 the source function.\(^{51,52}\)

### 5. Results and discussion

#### 5.1. Intramolecular interactions between electronegative atoms: integrated properties

This section is dedicated to the study of intramolecular bonds between oxygen–oxygen (19 cases), oxygen–halogen (X = F, Cl, and Br, 78 molecules in total), and oxygen–sulfur (19 cases) atoms, defining a dataset composed of 116 compounds (see Scheme 1).

The corresponding compounds are denoted \( \text{Of} \) and \( \text{Si} \) (\( i = 1, 8–18 \), \( X_5–14 \) and \( X_6–14 \) (\( X = F, Cl, \text{and} Br \)), \( \text{Oph}_1–7 \) and \( \text{Sph}_1–7, \text{Pph}_1–f \)), \( \text{O}_1, \text{O}_8, \text{O}_13, \text{X}_5, \) and \( \text{Xm}_5 \) were initially proposed by Jablonski\(^{34}\) (but not studied from an IQA perspective) in his important study on nonbonding BCPs, and were investigated from an IQA perspective by us in two recent papers,\(^{26,55}\) along with the new \( \text{O}_9–11, \text{S}_1, \text{S}_8–11, \text{S}_13, \text{O}_14–18, \text{S}_14–18, \text{S}_8–13, \text{X}_6–14, \) and \( \text{Xm}_6–8 \). Here, we added \( \text{O}_12, \text{S}_2, \text{Fm}_9–14, \text{Clm}_9–14, \) and \( \text{Brm}_9–14 \), which were not yet considered. In order to enlarge the chemical span of interest, we now include aromatic molecules featuring a benzene cycle. \( \text{Oph}_1–4 \) were studied by Paul and Guichhait,\(^{56}\) while \( \text{Clph}_1 \) and \( \text{Clph}_b \) were examined by Silla et al.\(^{57}\) (in both cases not from an IQA perspective). Here, we add the \( \text{Oph}_5–7, \text{Sph}_1–7, \text{Cph}_1–f, \text{Fph}_1–f, \) and \( \text{Brph}_1–f \) derivatives. This dataset now incorporates aliphatic and aromatic compounds, and the most important functional groups or substituents in chemistry (alkyl chains, alcohol, carboxylic acids, amides, and halogens), covering a large scope of effects (inductive or mesomeric, attractor or donor...).

We now briefly discuss the results for the new compounds of the \( \text{Of}, \text{Si,} \) and \( \text{Xm}_5 \) families. There is a BCP between the two oxygen atoms in \( \text{O}12 \), whose presence cannot be rationalized in terms of distance as shown by the following sequence: 2.82 Å (\( \text{O}12, \text{BCP} \)), 2.86 Å (\( \text{O}10, \text{no} \) BCP), and 2.90 Å (\( \text{O}1, \text{BCP} \)). As for all compounds of the \( \text{Of} \) group, the interaction energy between the two oxygen atoms in \( \text{O}12 \) is strongly positive (123.7 kcal mol\(^{-1} \)), and mainly of electrostatic nature (\( E_{\text{AB}}^{\text{int}} = 129.9 \) kcal mol\(^{-1} \)). It is interesting to compare these values with, for instance, \( \text{O}9 \) for which \( E_{\text{AB}}^{\text{int}} = 127.8 \) kcal mol\(^{-1} \); this last interaction is more destabilizing while the oxygen atoms are paradoxically farther (2.90 Å) than in \( \text{O}12 \).

Interestingly, the distance (2.84 Å) between O and S in the new \( \text{Si} \) compound is very similar as in \( \text{O}12 \), but the bond is of completely different nature: it is stabilizing (\( E_{\text{AB}}^{\text{int}} = -52.6 \) kcal mol\(^{-1} \)), and exchange is no longer negligible since it amounts to almost 25% of \( E_{\text{AB}}^{\text{int}} \). As for the \( \text{Xm}_5 \) group, the results for the 18 novel molecules are fully in line with the results gathered in ref. 26: no BCP was located, and all O···X interactions are destabilizing: strongly with fluorine (average \( E_{\text{AB}}^{\text{int}} \) equals 68 kcal mol\(^{-1} \) for the whole \( \text{F}3–14 \) set), and considerably less for chlorine (average 21 kcal mol\(^{-1} \)), with an increasing weight of exchange.
We now treat in greater detail the aromatic compounds Oph1–7 and Sph1–7. Interestingly, the interaction energies are very similar to those of aliphatic systems (about 120 kcal mol\(^{-1}\) for Oph1–7, and \(-50\) kcal mol\(^{-1}\) for Sph1–7). There are however four exceptions: Oph4, Sph4, Oph7 and Sph7. Actually, due to the presence of a bulky D substituent adjacent to the carboxylic group, the OC\(_1\)C\(_2\)Y moiety is no longer planar, as evidenced by the corresponding dihedral angles (about 90°). The O–C\(_1\)C\(_2\)Y distances are consequently much higher (3.3 Å for instance in Oph4 and 3.2 Å in Sph4), and the interaction energies are lower in absolute value (\(E_{\text{int}} = 119.8\) in Oph7 and \(-24.7\) kcal mol\(^{-1}\) in Sph7). These four compounds are also the only ones in these groups where a BCP is not present between O and Y atoms.

As already stated, distances and interaction energies are not appropriate to account for the existence or absence of a BCP. In ref. 26, we instead proposed to compare exchange energies between primary and secondary interactions. In Scheme 1, primary interactions (those for which we want to know if a BCP exists) are depicted in red, while secondary interactions (defined as interactions between one atom involved in the primary interaction with an atom directly linked with the other atom of the primary interaction) are colored in green.\(^{58}\)

The competition between these exchange channels (as they were named by Pendás and coworkers,\(^{59}\) see also ref. 60) can be summarized by a competition index:

\[
\beta_{\text{comp}} = \frac{|E_{\text{primary}}|}{\text{Max}|E_{\text{secondary}}|}
\]  

(28)

For Oph1–7 and Sph1–7, all \(\beta_{\text{comp}}\) values are higher than 4, except for the molecules without primary BCP for which \(\beta_{\text{comp}}\) equals 0.4 (Oph4), 0.2 (Oph7), 1.3 (Sph4), and 0.9 (Sph7), all being lower than the threshold value (1.6) determined in ref. 26, confirming the dichotomy previously advanced.
We now deal with the Xph1a–f derivatives. In the case of fluorine, the interaction is still considerably destabilizing (more than 70 kcal mol\(^{-1}\)), while \(E_{\text{max}}^2\) takes low values (average = 4.6 kcal mol\(^{-1}\)), and, in contrast, \(E_{\text{min}}^2\) reveals to be negative (average value: \(-15.9\) kcal mol\(^{-1}\)). This is reminiscent of aliphatic compounds belonging to the Br5–14 group, with a similar average value (\(-16.9\) kcal mol\(^{-1}\)).

It is worth mentioning that for all 116 compounds the electrostatic part of the interaction for the primary interaction has always the same sign as the total primary interaction energy. However, in the case of Br5–14, the electrostatic contribution is remarkably negligible (for instance it equals \(-0.7\) kcal mol\(^{-1}\) for Brph1c), and is mainly ascribable to multielectronic effects (see for instance ref. 61 for a study of the convergence of electrostatic interaction energies in terms of multipole ranks). In fact, the QTAIM charges of bromine and oxygen atoms are both positive (0.05 \(e\) and 1.09 \(e\), respectively), erroneously suggesting a destabilizing electrostatic interaction (more precisely, \(q(\text{Br})q(\text{O})/d_{\text{Br-O}} = 6.0\) kcal mol\(^{-1}\)). It turns out that for bromine aromatic compounds, the stabilizing O···Br interaction is predominantly due to exchange.

We now summarize the conditions for the absence or presence of a BCP in these 116 compounds: in 55% of the cases (46 over 84) a BCP was observed for aliphatic compounds, while this proportion rises up to 87% (28 over 32) for the considered aromatic derivatives. As shown in Chart 1, an almost perfect dichotomy is confirmed:

\[
\beta_{\text{comp}} > 1.59 \iff \text{primary BCP}
\]

\[
\beta_{\text{comp}} < 1.35 \iff \text{no primary BCP}.
\]

Qualitatively, eqn (29) tells that if there is a secondary competing exchange channel, no BCP is found; conversely, the BCP existence is related to the fact that the primary exchange channel is dominating.

We reported in ref. 26 a linear correlation (\(R^2 = 0.95\)) between \(\beta_{\text{comp}}\) and \(E_{\text{primary}}\). The increase of the number of molecules decreases the correlation coefficient (\(R^2 = 0.90\) when only considering aliphatic compounds. Unfortunately, the correlation fully disappears when aromatic compounds are included. It is nevertheless interesting to note that in the presence of a BCP, the \(\beta_{\text{comp}}\) values are significantly higher in aromatic products than in aliphatic ones, meaning that the secondary exchange channels tend to be deactivated.

Indeed, the secondary exchange energy average value for the Oi (resp. Si) group equals \(-3.6\) (\(-4.8\)) kcal mol\(^{-1}\), while the corresponding value for the Oph (Sph) is \(-1.5\) (\(-2.4\)) kcal mol\(^{-1}\). It is worth noting that the primary exchange energy remains quite constant when going from aliphatic to aromatic compounds since the mean values are equal to \(-6.3\) (Oi), \(-5.9\) (Oph), \(-14.1\) (Si), and \(-12.3\) kcal mol\(^{-1}\) (Sph). These conclusions still hold in one-to-one comparisons for molecules bearing the same substituents: for instance, in the case of R=\(\text{R''-A-B-D-H}\), the primary and secondary exchange energies are, respectively, equal to \(-14.9\) and \(-5.8\) kcal mol\(^{-1}\) (Si) and \(-15.4\) and \(-2.9\) kcal mol\(^{-1}\) (Sph). Such a deactivation (the ring “pumping” the secondary exchange channel) probably deserves further consideration.

5.2. Intramolecular hydrogen bonds: integrated properties

We now turn our attention to another kind of ubiquitous intermolecular interactions, namely hydrogen “bonds”: 34 systems represented in Scheme 2. The Ohi1–8 and Shl1–8 families are the hydrogen-bonded systems equivalent to the Oi and Si groups, built on an enone scaffold. OphH1–5 and SphH1–5 are aromatic and parallel to the OphH and SphH compounds. OphHc was investigated in ref. 54 (but not from an IQA perspective). In addition to these O···H−O and O···H−S bonds, NHh gives an example of N···H−N intramolecular bonds. The last three systems were recently studied by Lane et al.62 They involve O···H−O interactions in 1,\(n\)-alkanediols (ethane, propane, and butane chains are considered here).

We first begin with Oh molecules. The average for the primary O···H interaction energy is \(-140\) kcal mol\(^{-1}\), with, as expected, a dominating electrostatic counterpart (\(-124\) kcal mol\(^{-1}\) in average), exchange representing about 10% of the stabilizing interaction.

Two secondary interactions are considered: O···O and C1′···H. The first one is strongly destabilizing (the average interaction energy is equal to \(+150\) kcal mol\(^{-1}\)), being once more of electrostatic nature (+160 kcal mol\(^{-1}\)). It is thus of the same magnitude as the primary interaction (average value for \(|E_{\text{int}}^{\text{O}}|/|E_{\text{int}}^{\text{H}}|\) is equal to 1.07). The C1′···H interaction is also destabilizing and not at all negligible (105 kcal mol\(^{-1}\) in average). It is characterized by very low exchange (lower in absolute value to 0.4 kcal mol\(^{-1}\)), so that the secondary competing exchange channel is the O···O one. All \(\beta_{\text{comp}}\) values are higher than 1.32, so that the H bond exchange channel is the privileged one. This is consistent with the presence of a H bond BCP for all cases.

It is interesting to note that the sum of these three interactions is always higher than +90 kcal mol\(^{-1}\). This could suggest
that such a H bond is unstable. This is of course not the case. Indeed, the total molecular energy also depends on longer range (electrostatic) interactions. It also depends on the atomic ("self") energies.11 However, such a detailed analysis is outside the scope of this paper.

Let us now examine the Sh compounds. The O⋯H–S interaction energy is significantly lower in absolute value than for the related O⋯H–O ones, although it remains negative (average value is equal to $-36$ kcal mol$^{-1}$). The fundamental difference is that the O⋯S secondary interaction is now stabilizing: $-35.2$ kcal mol$^{-1}$. This agrees with what was found for the O⋯S interaction within the Sj and Sphj groups, for which the values were slightly higher in absolute value. There are as many cases for which $|E^\text{Sh}_\text{int} | > |E^\text{Sh}_\text{int} |$ (for instance in Sh1: 40.2 > 34.1 kcal mol$^{-1}$) and where $|E^\text{Sh}_\text{int} | < |E^\text{Sh}_\text{int} |$ (for example, Sh4: 27.7 < 38.9 kcal mol$^{-1}$). Conversely, the C1⋯H interaction remains destabilizing (average interaction energy is equal to $18$ kcal mol$^{-1}$).

For the primary O⋯H–S interaction, the exchange contribution is consequent (representing in average 40% of the interaction energy). This ratio decreases when considering the secondary O⋯S interaction, exchange only representing 18%. This can be qualitatively accounted for by noting that exchange generally tends to decrease faster with the distance than electrostatics. All $\beta_{\text{comp}}$ values are higher than 2.0, which explains why all these molecules feature a BCP for the primary interaction.

The very same conclusions hold when considering the OphH and SphH families. In brief, for the first aromatic group, O⋯H–O interaction energy is in average equal to $-140$ kcal mol$^{-1}$, the secondary O⋯O and C1⋯H to 150 and 113 kcal mol$^{-1}$ respectively. For the O⋯H–S aromatic molecules, the interaction energy averages are equal to $-39$ (O⋯H), $-29$ (O⋯S), and $+19$ kcal mol$^{-1}$ (C1⋯H), while exchange represents in average 41% (O⋯H) and 22% (O⋯S) of the interaction energy. More importantly, all $\beta_{\text{comp}}$ values are higher than 1.54, and all show a BCP for the primary interaction. They can thus be rigorously called “hydrogen bonds”.

As for the N⋯H–N interaction in NNh, the N2⋯H primary and N1⋯N2 secondary interactions are quite similar in energy and in nature as the O⋯H–O ones, the major difference being the secondary C1⋯H interaction that is almost half less stabilizing in NNh. There is a H bond BCP, consistent with the high (1.9) $\beta_{\text{comp}}$ value.

Alkanediols are the last systems we will investigate in this paper. The interaction energies for the O1⋯H–O2 interaction in the three compounds (ED, PD, and BD) are, respectively, equal to: $-82.2$, $-100.9$, and $-114.3$ kcal mol$^{-1}$. The secondary O1⋯O2 interaction energies increase with the alkyl chain length, but the variations are small compared to those obtained for the primary interaction: 127.2 (ED), 128.7 (PD), and 132.7 (BD) kcal mol$^{-1}$. Finally, the destabilizing C1⋯H interaction is almost not sensitive to the number of carbon atoms: 37.8 (ED), 37.6 (PD), and 38.4 (BD) kcal mol$^{-1}$, the exchange contribution.
always being negligible (lower than 0.3 kcal mol$^{-1}$ in absolute value).

As reported in ref. 61, there is no O$_2$···H BCP for ED, while a H bond critical point appears in PD and BD. One can thus wonder whether this can be rationalized in terms of competition between exchange channels. To this aim, we presented in Fig. 1 the topologies and the relevant exchange contributions to the interaction energies.

In ED, the primary exchange interaction energy is equal to $-2.4$ kcal mol$^{-1}$. It is lower in absolute value than the one obtained for the secondary interaction between the two oxygen atoms ($-4.3$ kcal mol$^{-1}$). This last one thus wins the competition between channels ($\rho_{\text{comp}} = 0.56$), forbidding the presence of the hydrogen BCP. One can now wonder if a BCP may appear between O atoms. To answer this question, one should inspect the secondary interactions: O$_1$···C$_2$ and O$_2$···C$_3$. The corresponding exchange energies are both equal to $-8.5$ kcal mol$^{-1}$. Thus, O$_2$···C$_3$ (for instance) wins over the O$_1$···O$_2$ channel from an exchange point of view, precluding the presence of an O–O BCP. Finally, no BCP is located for the O$_2$···C$_1$ primary interaction since the secondary covalent O$_2$···C$_2$ exchange energy is much higher in absolute value ($-170$ kcal mol$^{-1}$). The full molecular topology is thus recovered step by step. Note that such reasoning can be performed as well for intermolecular interactions.$^{83}$

The situation is opposite in PD and BD: the primary O$_1$···H exchange interaction energies (respectively, equal to $-7.2$ and $-11.9$ kcal mol$^{-1}$) are higher in absolute value than the O$_1$···O$_2$ ones (respectively, $-5.5$ and $-6.8$ kcal mol$^{-1}$). There are then no efficient competing exchange channels, so that a hydrogen BCP arises. The absence of a BCP does not eventually constitute a failure of QTAIM: it is conversely the physical signature of an existing competing exchange channel, which can be revealed by the IQA approach.

### 5.3. BCP local properties

In this section, we intend to show how the local descriptors presented in Section 3.1 could be revealed to be useful to characterize intermolecular interactions. First, the variation rates for the (reduced) density gradients are considered. For the 74 molecules featuring a O···X,Y BCP, the average values are, respectively, equal to: 0.038 ($\langle u' \rangle^{(0)}$), 1.87 ($\langle s' \rangle^{(0)}$), and 1.42 ($\langle t' \rangle^{(1)}$). For the 33 H bonds, these values are: 0.126 ($\langle u' \rangle^{(1)}$), 1.68 ($\langle s' \rangle^{(1)}$), and 1.50 ($\langle t' \rangle^{(1)}$).

From u point of view, the density near the O···X,Y BCP is very homogeneous with respect to H bonds. In contrast, on average, H bonds are slightly more homogeneous from s point of view. This proves that the various inhomogeneity measures are not equivalent. This is however not unexpected since this is already the case at other real space points. Indeed, in the density exponential tail far from the nuclei, s and t diverge while u tends toward zero. This has also consequences in terms of xc functionals. Indeed, most of GGAs are built (due to the exact gradient expansions, eqn (22)) so that $\langle x_c \rangle u(r) \rightarrow e^{LDA}(r)$, a condition that is not equivalent to $\langle x_c \rangle u(r) \rightarrow -1/r$. This last one thus wins the competition between channels ($\rho_{\text{comp}} = 0.56$), forbidding the presence of a hydrogen BCP. Finally, no BCP is located for the O$_2$···C$_3$ primary interaction since the secondary covalent O$_2$···C$_2$ exchange energy is much higher in absolute value ($-170$ kcal mol$^{-1}$). The full molecular topology is thus recovered step by step. Note that such reasoning can be performed as well for intermolecular interactions.$^{83}$

An interesting combination of the two previous descriptors is the so-called $P_{xc}$ quantity$^{38}$ defined as the ratio of the BCP exchange and correlation energy densities. It equals 4.4 for O···X,Y bonds and 5.3 for H bonds, so that exchange is slightly more predominant than correlation in the last group. It is worth noting that this ratio is lower than that of the total molecule, the total $E_x/E_c$ ratio being about 10. In other words, correlation has an increased contribution at the BCP.

The xc variation rates can now be analyzed. As BCP Laplacian values are positive, eqn (24) implies that $\langle \delta x \rangle^{(0)}$ is always negative: exchange thus increases in absolute value when moving away from the BCP. Conversely, for correlation, two opposite effects confront: the variation of the LDA contribution (the first contribution in the right-hand term in the second eqn (24)) is negative, while that due to the gradient inhomogeneity (second term) is positive.

Our results show that this last effect always dominates, so that $\langle \delta c \rangle^{(2)}$ is positive for all compounds, with the following average value: 1.9 $\times 10^{-3}$ a.u. (O···X,Y) and 5.4 $\times 10^{-3}$ a.u. (H bonds). For exchange, one has $-3.3 \times 10^{-3}$ a.u. (O···X,Y) and $-9.9 \times 10^{-3}$ a.u. (H bonds). The $Q_{xc}$ ratio$^{38}$ (\langle \delta x \rangle^{(2)}/\langle \delta c \rangle^{(2)})$ is in average equal to $-1.8$ for both families. The correlation variation rate is thus very comparable to that for exchange, but opposite. In ref. 36, we used the ($P_{xc}Q_{xc}$) representation to discriminate between hydrogen and agostic bonds. Interestingly, it also succeeds in differentiating hydrogen and O···X,Y bonds, as evidenced in Chart 2.

### 5.4. A semilocal approach to exchange interaction energies

As shown is Sections 5.1 and 5.2, exchange interaction energies are the relevant quantities to account for the absence or
presence of BCPs. Unfortunately, their numerical evaluation is not straightforward. Following our recent letter,\textsuperscript{55} we now show how it is possible to accurately reproduce these values only using BCP and ring critical point (RCP) properties. Firstly, it is appealing to note that the BCP density cannot be universally used for this purpose. Indeed, as shown in Chart 3, no model based on this descriptor can simultaneously describe H bonds in \textit{Oh}1–8 and \textit{Sh}1–8 compounds. This is because $\rho_{\text{BCP}}$ is a local property, while exchange is a non-local effect. A non-locality element can be introduced by adding information about RCP. Indeed, in virtue of the Poincaré–Hopf theorem, the existence of intramolecular BCPs is correlated with the apparition of a RCP. If the distance between them, $\delta_{\text{CP}}$, is small, the BCP is unstable, being possibly annihilated with the RCP. In such cases, we also expect exchange interaction energy to be small in absolute value (see Sections 5.1 and 5.2). $\delta_{\text{CP}}$ distance may thus be an ingredient to insert in a simple model. To this aim, we consider a sphere (but now not infinitesimal) centered at the BCP–RCP midpoint and with diameter equal to $\delta_{\text{CP}}$. In the first approximation, the exchange energy inside this sphere (that is made of the self exchange energy inside each basin and the exchange interaction energy between the two basins inside this sphere) can be evaluated using Slater’s exchange:

$$E_{\text{sphere}}^{x} = -\frac{3}{4 \pi} \frac{3}{4} \int_{\text{sphere}} \rho_{\text{BCP}}^{4/3} d^{3}r \approx -\frac{3}{4 \pi} \frac{3}{4} \left( \langle \rho \rangle^{3/4} \right)$$

where $\langle \rho \rangle$ denotes the average value of $\rho$ inside the sphere. $\langle \rho \rangle$ can be approximated using weighted BCP and RCP density values. As explained in ref. 55, $l_{s} = 1/(s^{(1)})$ has the dimension of a distance, measuring the size of the region where $s$ remains small, and thus where Slater’s exchange is relevant. It is then reasonable to write:

$$\langle \rho \rangle \approx \frac{l_{s} \rho_{\text{BCP}} + l_{s} \rho_{\text{RCP}}}{l_{s} + l_{s}}$$

Using eqn (30) and (31), Chart 4 is obtained. A nice linear correlation is obtained ($R^{2} = 0.98$) that enables us to describe all aliphatic hydrogen bond compounds (\textit{Oh}1–8 and \textit{Sh}1–8) with only one common model. Similarly, three other accurate models are obtained for the 14 aromatic hydrogen bond compounds (\textit{Oph}1–5 and \textit{Sph}1–5) with $R^{2} = 0.96$, for the 46 aliphatic compounds.
O - X, Y derivatives (X5–14 and Y1–18) with $R^2 = 0.95$, and for the 28 aromatic O - X, Y molecules (Yph1-6 and Xphta-f) with $R^2 = 0.95$, suggesting the reliability of such a correspondence between DFT and QTAIM.

6. Conclusions

In this paper for this special issue on density functional theory and its applications, we presented evidence that Bader’s atoms-in-molecules and density functional theories could engage in a fruitful dialogue. As natural and intuitive as it seems, since both approaches are based on the same primary ingredient, the existence of such bridges was however rarely investigated in the past. At first, we discussed in detail several possible ways for decomposing DFT molecular energies into mono- and diatomic contributions in the spirit of Pendas’ interacting quantum atoms scheme. Then, we derived a general formula to design new descriptors from any second-order density gradient expansion. These tools were subsequently applied to study 150 molecules featuring intramolecular interactions of two types (between two electronnegative atoms and hydrogen bonds) and were shown to provide valuable insights into the nature of the interaction, into the topology it induces (the absence of a bond path being the physical signature of a competing exchange channel), and into how different types of interactions could be discriminated. These results constitute, from our viewpoint, incentive elements to foster the use of combined DFT/QTAIM strategies in quantum chemistry.

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References

20 See the special issue in Computational and Theoretical Chemistry, 2013, 1003, 1–134.
37 The x, y, z axes are directed by P’s eigenvectors associated to the $\lambda_1 < \lambda_2 < \lambda_3$ eigenvalues.
47 It can be noticed that if one puts \( g(\rho) = \rho \) and \( \gamma = 0 \) in eqn (12), \( (\delta f)^2 \), measures the averaged variation rate of the density around the BCP. Eqn (20) then immediately shows that it is proportional to laplacian, a very well known result.
58 Note that, for sake of simplicity, we here intentionally excluded the O···H secondary interactions, which were considered in the previous paper, since we definitely proved that they are not relevant to discuss exchange channels competitions.