Treatment of non-nuclear attractors within the theory of atoms in molecules II: Energy decompositions

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Abstract

This work describes the partitioning of the electronic energy in systems in which the atoms in molecules theory predicts the existence of non-nuclear attractors. The procedure is based on our previous proposals within studies of topological population analysis [D.R. Alcoba, L. Lain, A. Torre, R.C. Bochicchio, Chem. Phys. Lett. 407 (2005) 379]. Numerical determinations in the acetylene and dilithium molecules are reported and compared with those arising from other approaches.

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1. Introduction

The decomposition of the molecular electronic energy into mono- and diatomic contributions presents a great interest since it allows one to identify bondings and to describe bonding strengths among the different atoms which compose the chemical systems (molecules, radicals, clusters, crystals, etc.). Consequently, in the last years, a considerable effort has been dedicated to this kind of studies trying to set up a rigorous and reliable methodology to deal with this subject [1–8]. Some reported procedures [3,6,8] are based on the Bader partitioning of the three-dimensional physical space into atomic domains described in the atoms in molecules (AIM) theory [9]. In that theory, each atom or nucleus (nuclear attractor) is associated with a determined spatial domain delimited by a surface. However, as is well-known, the AIM theory also predicts, in determined situations [10–12], the existence of pseudoatoms or non-nuclear attractors which are local maxima of electron density out of nuclear positions. The occurrence of non-nuclear attractors hampers the interpretation of the decomposition of the molecular energy, mainly by the monoatomic and diatomic terms involving non-nuclear attractors, which have not a clear chemical meaning.

On the other hand, the techniques of topological population analysis allow one to perform distributions of the $N$ electrons of the system into the Bader domains providing suitable descriptions of atomic populations, bond indices and other related quantities [13–16]. In this kind of analyses, the existence of non-nuclear attractors in determined systems presents identical problems to those found in the energy decomposition treatments. It turns out to be difficult to interpret the resulting bondings between a domain associated to an ordinary atom and the one corresponding to a non-nuclear attractor. Moreover, the appearance of non-nuclear attractors breaks the one-to-one correspondence between atoms and Bader domains [10,12] which is generally admitted in the topological treatments. Recently, in Ref. [17], we have reported several procedures to overcome the non-nuclear attractor problem redistributing certain overlap matrix elements by means of effective overlap matrices. Our treatments have led to satisfactory results describing suitable atomic localization and delocalization indices in good agreement with the genuine chemical knowledge. The aim of this Letter is to extend our procedures successfully used in these studies of population analysis to the decomposition of the energy. It must be pointed
out that the formulation of the molecular energy partitioning involves operators depending on the relative positions of particles (nuclei and electrons) which is not the case for the population analysis [17]. This fact implies a stronger dependence of the energy analysis upon the spatial re-assignment of the non-nuclear electron cloud which deserves to be studied.

The work is organized as follows. In Section 2, we describe the algorithms required to partition the energy and the changes proposed here to deal with the non-nuclear attractors (the mathematical details are shown in the Appendix which complements this section). Section 3 reports the results obtained in the acetylene and dilithium molecules which have been chosen as test examples of systems where non-nuclear attractors appear. The numerical determinations obtained in these molecules allow us to compare our results with those arising from other treatments providing the corresponding discussion. Finally, in Section 4 we summarize the concluding remarks.

2. Decomposition of energy

We will express the non-relativistic electronic energy, \( E \), corresponding to a determined state of an \( N \)-electron system as

\[
E = \sum_{i,j,k} T_{ij}^{kl} \delta_{i,j} + \sum_{i,j,k} A^{V_{ij}} D_{ij}^{kl} \delta_{i,j} + \sum_{i,j,k,l,m,n} B_{ijkl}^{mn} \delta_{m,n} + \sum_{A,B} Z_A Z_B \frac{R_{AB}}{\Omega_A \Omega_B}
\]

(1)

in which \( T_{ij}^{kl} \) are the matrix elements of the kinetic energy operator \( -1/2 \nabla^2 \) related with an orthogonal basis set \( \{i,j,k,l, \ldots\} \); \( A, B, \ldots \) stand for the nuclei of the system; \( Z_A, Z_B, \ldots \) are their nuclear charges and \( R_{AB} \) the distance between the nuclei \( A \) and \( B \). \( A^{V_{ij}} \) denote the matrix elements of the \( (\frac{1}{2} \nabla^2) \) operator and \( B_{ijkl}^{mn} = (i(1|k(2)|l(1))|j(1)l(2)) \) the standard two-electron integrals. \( 1D_{ij}^{kl} \) and \( 2D_{ij}^{kl} \) are the matrix elements of the spin-free first- and second-order reduced density matrix, respectively.

Although the use of Kronecker deltas in expression (1) is unnecessary, they have explicitly been written in order to accomplish the partitioning

\[
\delta_{ij} = \langle ii \rangle = \sum_{\Omega_i} S_{ij}^{\Omega_i}(\Omega_i)
\]

(2)

where \( \Omega_i \) is the Bader’s atomic region corresponding to the atom \( A \) and \( S_{ij}^{\Omega_i}(\Omega_i) = \langle ii \rangle_{\Omega_i} \) are the elements of the overlap matrices calculated over the regions \( \Omega_{\Omega_i} \) [9]. As is well-known, the AIM theory of Bader allows one to partition the whole physical space \( \Omega \) into disjunct domains bounded by surfaces with zero flux in the gradient vector field of the electron density, holding \( \Omega = \cup_{A} \Omega_{A} \) and \( \Omega_{A} \cap \Omega_{B} = \emptyset \) \((A \neq B)\) [9].

The substitution of formula Eq. (2) into Eq. (1) leads to partition the electronic energy \( E \) into mono- and diatomic contributions [6]

\[
E = \sum_{\Omega_A} E_{\Omega_A} + \sum_{\Omega_A < \Omega_B} E_{\Omega_A,\Omega_B}
\]

(3)

in which

\[
E_{\Omega_A} = \sum_{i,j,k} T_{ij}^{kl} D_{ij}^{kl}(\Omega_A) + \sum_{i,j,k} A^{V_{ij}} D_{ij}^{kl}(\Omega_A)
\]

\[
+ \sum_{i,j,k,l,m,n} B_{ijkl}^{mn} D_{ijkl}^{mn}(\Omega_A) S_{ij}^{\Omega_A}(\Omega_A)
\]

(4)

and

\[
E_{\Omega_A,\Omega_B} = \sum_{i,j,k} A^{V_{ij}} D_{ij}^{kl}(\Omega_B) + \sum_{i,j,k} B_{ijkl}^{mn} D_{ijkl}^{mn}(\Omega_A) D_{ij}^{kl}(\Omega_B)
\]

\[
+ 2 \sum_{i,j,k,l,m,n} B_{ijkl}^{mn} D_{ijkl}^{mn}(\Omega_A) S_{ij}^{\Omega_B}(\Omega_B) + \frac{Z_A Z_B}{R_{AB}}
\]

(5)

As can be seen, the mono- and diatomic energy contributions are expressed by a weighted average in which the overlap integrals over the regions \( \Omega_{\Omega_A} \) act as weight factors over the one- and two-electron terms [18]. However, the presence of non-nuclear attractors, \( X \), produces the appearance of terms such as \( E_{\Omega_A} \) and \( E_{\Omega_A,\Omega_B} \), depending on the \( S_{ij}^{\Omega_A}(\Omega_A) \) matrix elements, which have not a clear chemical meaning. To avoid this problem we propose the use of effective overlap matrices \( (S_{ij}^{\Omega_A}(\Omega_A)) \) resulting from redistributing the \( S_{ij}^{\Omega_A}(\Omega_A) \) matrix elements such as has been reported in our previous studies of population analysis [17]. Within this treatment the formulas (4) and (5) are rewritten as

\[
E_{\Omega_A} = \sum_{i,j,k} T_{ij}^{kl} D_{ij}^{kl}(S_{ij}^{\Omega_A}(\Omega_A)) + \sum_{i,j,k} A^{V_{ij}} D_{ij}^{kl}(S_{ij}^{\Omega_A}(\Omega_A))
\]

\[
+ \sum_{i,j,k,l,m,n} B_{ijkl}^{mn} D_{ijkl}^{mn}(S_{ij}^{\Omega_A}(\Omega_A)) S_{ij}^{\Omega_A}(\Omega_A) \quad (\Omega_A \neq \Omega_X)
\]

(6)

\[
E_{\Omega_A,\Omega_B} = \sum_{i,j,k} A^{V_{ij}} D_{ij}^{kl}(S_{ij}^{\Omega_B}(\Omega_B)) + \sum_{i,j,k} B_{ijkl}^{mn} D_{ijkl}^{mn}(S_{ij}^{\Omega_A}(\Omega_A)) D_{ij}^{kl}(\Omega_B)
\]

\[
+ 2 \sum_{i,j,k,l,m,n} B_{ijkl}^{mn} D_{ijkl}^{mn}(S_{ij}^{\Omega_A}(\Omega_A)) S_{ij}^{\Omega_B}(\Omega_B) + \frac{Z_A Z_B}{R_{AB}} \quad (\Omega_A, \Omega_B \neq \Omega_X)
\]

(7)

Three different proposed procedures to formulate the \( (S_{ij}^{\Omega_A}(\Omega_A)) \) overlap matrices are shown in the Appendix. In the following section we report the results arising from these three procedures in the acetylene and Li2 molecules in which the occurrence of non-nuclear attractors has widely been described [10–12]. We also report, in that section, results obtained with other treatments for these molecules in order to assess our procedures.

3. Results

Although the algorithms reported in previous sections can be used at any level of theory (correlated and uncorrelated wave functions) we have limited ourselves to the Hartree-Fock (HF) level to avoid the calculation of the second-order reduced density matrix which is always cum-
bersome. The acetylene and Li₂ molecules have been chosen as test examples to check the proposed algorithms. Each of these systems shows different features in the appearance of non-nuclear attractors within AIM approaches. The results for the acetylene molecule in the ground state have been calculated with the basis set 6-31G(d,p), optimizing the geometry for that basis set within closed-shell HF wave function. In the case of the Li₂ molecule a stretched geometry has been studied using an identical procedure. The one-electron integrals $T'_i$ and $V'_{ij}$ as well as the two-electron integrals $R^{kl}_{ij}$ and the HF molecular orbitals have been computed using a modified version of GAMESS program [19]. The overlap integrals over the Bader domains, $S^i(X)$, have been obtained from a modified version of the GAUSSIAN 03 program [20]. The integrals $\langle i | w_j | j \rangle_{\Omega_i}$ (see Appendix) have been calculated numerically with a modified Proaim code [21] using the weight functions reported in Ref. [22]. These weight functions depend on the empirical Slater–Bragg atomic radii of the atoms composing the system and an iteration order which defines the cutoff profiles of the functions. We have performed three iterations and increased the radius of hydrogen to the value 0.35 Å following Ref. [5].

Table 1 reports the results of the partitioning of the electronic energy for the acetylene molecule obtained from several approaches. Within AIM schemes, this molecule exhibits a non-nuclear attractor at the equilibrium geometry for the 6-31G(d,p) and many other basis sets, although the use of smaller basis sets skips its appearance. In the second column of that Table 1 we have included values arising from Ref. [6] which refer to a direct application of our AIM treatment according to Eqs. (4) and (5) above reported. As can be observed, the appearance of a non-nuclear attractor, $X$, in the midpoint of the internuclear distance of the C–C bond leads to numerical values having no clear chemical meaning. However, the three proposed methods to formulate the effective overlap matrices (see Appendix) get rid of the non-nuclear attractor, leading to more reasonable results (provided by Eqs. (6) and (7)), which are reported in columns 3, 4 and 5 of Table 1. For the sake of comparison we have also included, in the sixth and seventh columns, results picked up from Ref. [5] that correspond to a fuzzy atom treatment in the versions ‘simple’ and ‘improved’, respectively. Likewise, in eighth column, we have written the corresponding results reported by Mayer in Ref. [4] obtained with a Mulliken-type treatment. A survey of all the results reported in Table 1 shows that our procedures to formulate effective overlap matrices lead to decompositions of the energy in terms which are similar (and competitive) to those obtained with other methods. Furthermore, our treatments make possible to benefit the physical grounds of the AIM theory even when these non-nuclear attractors occur. We must highlight that the results arising from Eq. (11) are quite close to the experimental values found for the energies of the bonds C–C and C–H, which are reported in the last column of Table 1 [23]. Consequently, it deserves to be regarded as the best of three proposed procedures.

In Table 2 we have gathered the results corresponding to a stretched configuration of the Li₂ molecule as an example of system having more than one non-nuclear attractor. At a Li–Li distance 3.81 Å this molecule presents two non-nuclear attractors (Li–X–X–Li at distances Li–X and X–X Li 1.67 Å) [17]. The occurrence of more than one non-nuclear attractor requires to generalize the calculation of the effective overlap matrix elements taking into account all non-nuclear attractors, e.g. Eq. (11) is transformed into $\sum_{k\neq l} (S^i)^k(X) = S^i(X) + \sum_{k\neq l} \sum_{j} (S^j)^k(X)(S^j)^l(X)$ and similarly for the counterpart versions of Eqs. (8) and (13). Columns 2, 3, 4 and 5 of Table 2 report for the Li₂ molecule counterpart results to those described for the C₂H₂ in the same columns in Table 1. The results in columns 6 and 7, corresponding to the method reported in Ref. [5], have been obtained with a modified version of the code

<p>| Table 1 |
| Calculated mono- and diatomic energy (a.u.) components for the acetylene molecule in the 6-31G(d,p) basis set at HF level |</p>
<table>
<thead>
<tr>
<th>Energy</th>
<th>$E^a$</th>
<th>$E^b$</th>
<th>$E^c$</th>
<th>$E^d$</th>
<th>$E^e$</th>
<th>$E^f$</th>
<th>$E^g$</th>
<th>$E^{exp. h}$</th>
</tr>
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<tr>
<td>C</td>
<td>−37.3601</td>
<td>−37.4811</td>
<td>−37.6208</td>
<td>−37.5569</td>
<td>−37.3109</td>
<td>−37.6429</td>
<td>−37.5545</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>−0.4681</td>
<td>−0.4782</td>
<td>−0.4658</td>
<td>−0.4680</td>
<td>−0.4175</td>
<td>−0.4759</td>
<td>−0.4407</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>1.9010</td>
<td>1.9010</td>
<td>1.9010</td>
<td>1.9010</td>
<td>1.9010</td>
<td>1.9010</td>
<td>1.9010</td>
<td></td>
</tr>
<tr>
<td>C–C</td>
<td>0.7505</td>
<td>−0.6276</td>
<td>−0.3325</td>
<td>−0.4692</td>
<td>−0.8078</td>
<td>−0.2588</td>
<td>−0.4853</td>
<td>−0.3665</td>
</tr>
<tr>
<td>C–H</td>
<td>−0.1061</td>
<td>−0.1420</td>
<td>−0.1559</td>
<td>−0.1500</td>
<td>−0.2707</td>
<td>−0.1549</td>
<td>−0.1567</td>
<td>−0.1992</td>
</tr>
<tr>
<td>H–H</td>
<td>0.0355</td>
<td>0.0016</td>
<td>−0.0040</td>
<td>−0.0045</td>
<td>−0.0045</td>
<td>−0.0045</td>
<td>−0.0045</td>
<td>−0.0056</td>
</tr>
<tr>
<td>C–X</td>
<td>−1.7562</td>
<td>−0.0839</td>
<td>−0.0051</td>
<td>0.0037</td>
<td>0.0040</td>
<td>0.0040</td>
<td>0.0040</td>
<td></td>
</tr>
<tr>
<td>X–H</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td>−0.8391</td>
<td></td>
</tr>
</tbody>
</table>

<p>| | | | | | | | | |
|          |           |           |           |           |           |           |           |           |</p>
<table>
<thead>
<tr>
<th>Energy</th>
<th>$E^a$</th>
<th>$E^b$</th>
<th>$E^c$</th>
<th>$E^d$</th>
<th>$E^e$</th>
<th>$E^f$</th>
<th>$E^g$</th>
<th>$E^{exp. h}$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
<td>−76.8218</td>
</tr>
</tbody>
</table>

a Standard AIM treatment. Calculated in Ref. [6].
b Calculated using Eqs. (8) and (9).
c Calculated using Eq. (11).
d Calculated using Eq. (14).
e Reported in Ref. [5] (‘simple’).
f Reported in Ref. [5] (‘improved’).
g Reported in Ref. [4].
h Experimental energy.
Table 2
Calculated mono- and diatomic energy (a.u.) components for the Li₂ molecule in the 6-31G(d,p) basis set at HF level

<table>
<thead>
<tr>
<th>Energy</th>
<th>(E^a)</th>
<th>(E^b)</th>
<th>(E^c)</th>
<th>(E^d)</th>
<th>(E^e)</th>
<th>(E^f)</th>
<th>(E^g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.0740</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li–Li</td>
<td>0.0350</td>
<td>–0.1001</td>
<td>–0.0777</td>
<td>–0.0874</td>
<td>–0.0843</td>
<td>–0.0732</td>
<td>–0.0892</td>
</tr>
<tr>
<td>Li–X</td>
<td>–0.1245</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li–X</td>
<td>–0.0590</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X–X</td>
<td>–0.0257</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Distance Li–Li 3.81 Å (stretched).

\(^a\) Standard AIM treatment. Calculated following Ref. [6].
\(^b\) Calculated using Eqs. (8) and (9).
\(^c\) Calculated using Eq. (11).
\(^d\) Calculated using Eq. (14).
\(^e\) Calculated following Ref. [5] (‘simple’).
\(^f\) Calculated following Ref. [5] (‘improved’).
\(^g\) Calculated following Ref. [4].

provided by Ref. [24]. The values in column 8 have been calculated by our own computational implementation according to the method reported in Ref. [4]. As can be observed, our numerical determinations for this system with two non-nuclear attractors are again similar to those obtained by other methods in which the appearance of non-nuclear attractors do not occur. Moreover, the value \(E^c = –0.0777\) arising from Eq. (11) for the energy of the bond Li–Li is quite close to the value \(E^d = –0.0732\) obtained with the ‘improved’ version of Ref. [5]. This confirms the above comment about the calculation of the effective overlap matrices by means of Eq. (11) as leading to the most satisfactory results. The treatments arising from Eqs. (8) and (9) (Mulliken-type) and from Eq. (11), which uses the \(S^\text{eff}l_A\) matrix elements (see Appendix), are in a sense related to non-orthogonal and orthogonal population analysis procedures [25].

4. Concluding remarks

In this Letter we have extended our previous reported procedures to redistribute the electron density assigned to non-nuclear attractors which appear in AIM theory to the partitioning of the molecular energy. This approach has allowed us to decompose the electronic energy into chemically meaningful mono- and diatomic contributions, in systems having this kind of features. Our proposals are based on the construction of effective overlap matrices, which can be formulated according to several criteria. A comparison of our results in the acetylene molecule (having one non-nuclear attractor) and in the stretched Li₂ molecule (having two non-nuclear attractors), with those arising from other methods of energy partitioning (of Mulliken-type and fuzzy atom schemes) where the appearance of non-nuclear attractors does not occur, reveals the usefulness of our numerical determinations. It must be pointed out that our second proposal to set up the effective overlap matrices, based on the Löwdin orthogonalization procedure (see Eq. (11)), leads to the closest values to the experimental bond energies or to those arisen from the improved treatments in other partitioning schemes.

Acknowledgements

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Appendix

We will use the greek symbols \(\mu, \nu, \ldots\) to denote the usual atomic functions. In a first procedure we will construct effective overlap matrices by distributing \(S^\text{eff}_\nu\) matrix elements as

\[
(S^\text{eff}l_\nu)(\Omega_A) = S^{\nu\nu}_\nu(\Omega_A) + S^{\nu\nu}_\nu(\Omega_X) \quad (\mu \in A)
\]

\[
(S^\text{eff}l_\nu)(\Omega_A) = S^{\nu\nu}_\nu(\Omega_X) \quad (\mu \notin A)
\]

where \(\mu \in A\) means that the atomic function \(\mu\) is centered on the atom \(A\); once this step has been implemented the matrix elements \((S^\text{eff}l_\nu)(\Omega_A)\) are transformed back to obtain the matrix elements \((S^\text{eff}l_\nu)(\Omega_A)\) in the molecular orbital set which are used in Eqs. (6) and (7) that is

\[
(S^\text{eff}l_\nu)(\Omega_A) = \sum_{\mu} \sum_{\nu} c^{\mu}_{\nu} c^{\nu}_{\nu} (S^\text{eff}l_\nu)(\Omega_A)
\]

where \(c^{\mu}_{\nu}\) and \(c^{\nu}_{\nu}\) are the corresponding coefficients which express the atomic orbitals as functions of the molecular ones. This is a Mulliken-type procedure [26] since the atomic functions \(\mu \in A\) belong to a determined nucleus \(A\). It turns out to be very simple in a computational point of view but the resulting overlap matrices are not symmetric.

In a second method, the distribution of the \(S^\text{eff}_\nu\) matrix elements is performed as:
\[(S_{\text{eff}})_{ij}^{\nu}(\Omega_X) = S_{ij}^{\nu}(\Omega_X) + \sum_{k \in A} (S_{ik}^{\nu})(\Omega_X)(S_{kj}^{\nu}(\Omega_X) - \langle i | w_{A}(\mathbf{r}) | j \rangle_{\Omega_X}) \quad (A \neq X) \quad (11)\]

in which the matrix elements \((S_{ij}^{\nu})(\Omega_X)\) are obtained following the same procedure than that used in the well-known Löwdin orthogonalization method \cite{27} and again a subsequent transformation to the molecular basis set is carried out according to Eq. (10). The resulting overlap matrices are symmetric as can easily be checked.

The third proposal to decompose the \(S_{ij}^{\nu}(\Omega_X)\) matrix elements belongs to a fuzzy atom approach \cite{28,29,30} in which the partitioning of these elements is performed in the physical space instead of in the Hilbert space as the two previous treatments do. A non-negative continuous weight function \(w_{A}(\mathbf{r})\) is assigned to each atom \(A\) measuring the degree in which a determined point of space \(\mathbf{r}\) belongs to atom \(A\) fulfilling

\[\sum_{A} w_{A}(\mathbf{r}) = 1, \quad (A \neq X) \quad (12)\]

which allows one to write

\[S_{ij}^{\nu}(\Omega_X) = \sum_{A} \langle i | w_{A}(\mathbf{r}) | j \rangle_{\Omega_X}, \quad (A \neq X) \quad (13)\]

and the \((S_{ij}^{\nu})(\Omega_X)\) matrix elements are formulated as

\[(S_{ij}^{\nu})(\Omega_X) = S_{ij}^{\nu}(\Omega_X) + \langle i | w_{A}(\mathbf{r}) | j \rangle_{\Omega_X}, \quad (A \neq X) \quad (14)\]

The resulting overlap matrices elements \((S_{ij}^{\nu})(\Omega_X)\) are also symmetric and no intermediate transformation to atomic basis set is required.

References