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Energy decomposition in the topological theory of atoms in molecules and in the linear combination of atomic orbitals formalism: a note

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Abstract. It is shown that the molecular energy calculated at the self-consistent-field level can be strictly expressed as a sum of one- and two-atom energy components in the framework of Bader's topological theory of atoms in molecules (AIM). The expressions of our recent "chemical energy component analysis" can be obtained from the AIM ones as some linear combination of atomic orbitals mappings of the integrations over the atomic basins.

Key words: Atoms in molecules – Linear combination of atomic orbitals – Chemical energy component analysis – Intramolecular interactions – Energy decomposition

1 Introduction

At the workshop [1], when one of us presented his lecture about our recent "chemical energy component analysis" [2, 3], Richard Bader asked whether that scheme can also be used in his topological theory of atoms in molecules (AIM theory). In the closing discussion of the workshop it was reported that "yes, the approach is applicable to the AIM theory – moreover, in the AIM case the decomposition is exact". The conjuncture has also been made that the expressions of the "chemical energy component analysis" (CECA) presented at the workshop can be obtained as linear combination of atomic orbitals (LCAO) mappings of the AIM energy components.

The aim of this note is to present the (very simple) proof of the energy decomposition in the AIM framework and to discuss how the CECA expressions can be obtained as some LCAO mappings (or approximations) of the AIM ones.

2 Energy decomposition in the AIM theory

For the sake of simplicity we speak about AIM basins, but our considerations apply to any theory (e.g., electron localization function) in which the physical space is decomposed into disjunct basins (or domains) which can be put into a one-to-one correspondence with the nuclei of the molecular system. We may call these domains "AIM atoms". We consider explicitly the closed-shell restricted Hartree–Fock case, but the considerations also apply with trivial modifications to the unrestricted Hartree–Fock case[1].

If there are n doubly occupied molecular orbitals (MOs), φ_i, the total self-consistent-field (SCF) energy is

$$E = 2\sum_{i}^{n}\langle\varphi_i|\hat{h}|\varphi_i\rangle + \sum_{i,j=1}^{n}\left(2[\varphi_i\varphi_j|\varphi_i\varphi_j] - [\varphi_i\varphi_j|\varphi_j\varphi_i]\right) + \sum_{A<B}\frac{Z_A Z_B}{R_{AB}} \tag{1}$$

Here $\hat{h}$ is the one-electron Hamiltonian and we use the [12|12] convention for the two-electron integrals:

$$[\varphi_i\varphi_j|\varphi_k\varphi_l] = \int\int \varphi_i^*(\vec{\mathbf{r}}_1)\varphi_j^*(\vec{\mathbf{r}}_2)\frac{1}{r_{12}}\varphi_k(\vec{\mathbf{r}}_1)\varphi_l(\vec{\mathbf{r}}_2)\mathrm{d}v_1\mathrm{d}v_2 \ . \tag{2}$$

We can decompose the integral

$$\langle\varphi_i|\hat{h}|\varphi_i\rangle = \int \varphi_i^*(\vec{\mathbf{r}})\hat{h}\varphi_i(\vec{\mathbf{r}})\mathrm{d}v \tag{3}$$

into a sum of integrals over the individual atomic domains, Ω_A:

$$\langle\varphi_i|\hat{h}|\varphi_i\rangle = \sum_A \int_{\Omega_A} \varphi_i^*(\vec{\mathbf{r}})\hat{h}\varphi_i(\vec{\mathbf{r}})\mathrm{d}v = \sum_A \langle\varphi_i|\hat{h}|\varphi_i\rangle_A \tag{4}$$

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[1] The approach can be generalized to correlated wave functions, too

Here and further on subscript A indicates that the integration is restricted to the Ath atomic basin. Quite similarly, the two-electron integrals can be presented as double sums over the "AIM atoms":

$$
\begin{aligned}
&[\varphi_i\varphi_j|\varphi_k\varphi_l] \\
&\quad = \int\int \varphi_i^*(\vec{\mathbf{r}}_1)\varphi_j^*(\vec{\mathbf{r}}_2)\frac{1}{r_{12}}\varphi_k(\vec{\mathbf{r}}_1)\varphi_l(\vec{\mathbf{r}}_2)\mathrm{d}v_1\mathrm{d}v_2 \\
&\quad = \sum_{A,B}\int\limits_{\Omega_A}\int\limits_{\Omega_B} \varphi_i^*(\vec{\mathbf{r}}_1)\varphi_j^*(\vec{\mathbf{r}}_2)\frac{1}{r_{12}}\varphi_k(\vec{\mathbf{r}}_1)\varphi_l(\vec{\mathbf{r}}_2)\mathrm{d}v_1\mathrm{d}v_2 \\
&\quad = \sum_{A,B}[\varphi_i\varphi_j|\varphi_k\varphi_l]_{A,B} \ .
\end{aligned} \tag{5}
$$

In the last expression the first subscript indicates the domain of integration for electron 1, the second that for electron 2. On substituting Eqs. (4) and (5) into Eq. (1), we obtain

$$
\begin{aligned}
E = &\sum_A 2\sum_i^n \langle\varphi_i|\hat{h}|\varphi_i\rangle_A \\
&+\sum_{A,B}\sum_{i,j=1}^n(2[\varphi_i\varphi_j|\varphi_i\varphi_j]_{A,B} - [\varphi_i\varphi_j|\varphi_j\varphi_i]_{A,B}) \\
&+\sum_{A<B}\frac{Z_AZ_B}{R_{AB}} \ .
\end{aligned} \tag{6}
$$

Now, we observe that the one-electron Hamiltonian, $\hat{h}$, can be presented as

$$
\hat{h} = -\frac{1}{2}\Delta - \sum_C \frac{Z_C}{R_C} \equiv \hat{h}^A - \sum_{\substack{C\\C\neq A}}\frac{Z_C}{R_C} \ , \tag{7}
$$

where $\hat{h}^A = -\frac{1}{2}\Delta - \frac{Z_A}{R_A}$ is the intraatomic one-electron Hamiltonian corresponding to atom A. By using this, the integral $\langle\varphi_i|\hat{h}|\varphi_i\rangle_A$ can be written as a sum of one-center and two-center components:

$$
\langle\varphi_i|\hat{h}|\varphi_i\rangle_A \ = \ \langle\varphi_i|\hat{h}^A|\varphi_i\rangle_A - \sum_{\substack{C\\C\neq A}}\langle\varphi_i|\frac{Z_C}{R_C}|\varphi_i\rangle_A \ . \tag{8}
$$

Analogously, the two-electron integrals on the right-hand-side of Eq. (6) are either of one- or of two-center character, depending on whether $A = B$ or not.

According to these considerations, in the framework of the AIM theory the SCF energy can be strictly decomposed into one-center and two-center components:

$$
E \equiv \sum_A E_A + \sum_{A<B}E_{AB} \ , \tag{9}
$$

where (utilizing in E_{AB} the symmetry of the two-electron integrals for the interchange of the electrons)

$$
\begin{aligned}
E_A = &\, 2\sum_{i=1}^n\langle\varphi_i|\hat{h}^A|\varphi_i\rangle_A \\
&+\sum_{i,j=1}^n(2[\varphi_i\varphi_j|\varphi_i\varphi_j]_{A,A} - [\varphi_i\varphi_j|\varphi_j\varphi_i]_{A,A})
\end{aligned} \tag{10}
$$

$$
\begin{aligned}
E_{AB} = &-2\sum_{i=1}^n(\langle\varphi_i|\frac{Z_B}{R_B}|\varphi_i\rangle_A + \langle\varphi_i|\frac{Z_A}{R_A}|\varphi_i\rangle_B) \\
&+2\sum_{i,j=1}^n(2[\varphi_i\varphi_j|\varphi_i\varphi_j]_{A,B} - [\varphi_i\varphi_j|\varphi_j\varphi_i]_{A,B}) \\
&+\frac{Z_AZ_B}{R_{AB}} \ .
\end{aligned} \tag{11}
$$

We consider this simple result to be of considerable conceptual chemical significance.

3 LCAO mapping of the AIM integrals

The "AIM atom" is essentially a nucleus and the corresponding atomic basin defined in the physical space, while in the Mulliken-type analyses one identifies the atom with the nucleus and the subspace of the one-electron Hilbert space spanned by the basis orbitals centered on that nucleus.

As noted in Ref. [4], there is a mapping between the AIM theory and Mulliken-type analyses permitting one to find a one-to-one correspondence for quantities such as atomic populations, bond orders and valences defined in these two frameworks. This was formulated [4] in terms of atomic basis orbitals, χ_μ, as

$$
\langle\chi_\mu|\chi_\nu\rangle_A \implies \gamma_\nu^A S_{\mu\nu} \ , \tag{12}
$$

where $S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle$ is the conventional overlap matrix element and the function γ_ν^A introduces a summation restriction: γ_ν^A is 1 if orbital χ_ν is centered on atom A (this we shall denote as $\nu \in A$) and 0 otherwise (if $\nu \notin A$). The same mapping has been used, for example, in Ref. [4], to obtain some LCAO approximations of the AIM integrals.

The important property of this mapping is that it puts into correspondence the AIM atomic population with Mulliken's gross atomic population. This is in agreement with the fact that both these populations sum over the total number of electrons in the molecule[2].

The molecular orbitals are defined by their expansions

$$
\varphi_i = \sum_\mu c_\mu^i\chi_\nu \tag{13}
$$

and, using Eq. (12), one has for an integral over the MOs the mapping

$$
\begin{aligned}
\langle\varphi_i|\varphi_j\rangle_A \ &= \ \sum_{\mu,\nu}c_\mu^{i*}c_\nu^j\langle\chi_\mu|\chi_\nu\rangle_A \\
&\implies \sum_{\mu,\nu}c_\mu^{i*}c_\nu^j\gamma_\nu^A S_{\mu\nu} \ \equiv \ \langle\varphi_i|\varphi_j^A\rangle \ ,
\end{aligned} \tag{14}
$$

---

[2] If we were to introduce restrictions for both indices μ and ν in Eq. (12), we would get Mulliken's net atomic populations, which does not satisfy this requirement

where we have introduced the "piece" φ_j^A of the molecular orbital φ_j corresponding to the individual atom A:

$$\varphi_j^A = \sum_{\mu \in A} c_\mu^j \chi_\mu \ . \tag{15}$$

Now, we shall consider the problem how one can generalize the mapping (Eq. 14) for cases when we are interested in integrals other than overlaps. In order to get such a generalization, we observe that Eq. (14) implicitly contains a projection operator:

$$\left\langle \varphi_i | \varphi_j \right\rangle_A \Longrightarrow \langle \varphi_i | \varphi_j^A \rangle \equiv \langle \varphi_i | \hat{P}^A \varphi_j^A \rangle \equiv \langle \hat{P}^A \varphi_i | \varphi_j^A \rangle \ , \tag{16}$$

where

$$\hat{P}^A = \sum_{\rho,\tau \in A} |\chi_\rho^A\rangle S^{-1}_{(A)\rho\tau} \langle \chi_\tau^A| \tag{17}$$

is the projector on the subspace of basis orbitals centered on atom A. The inverse of the atomic overlap matrix, $\mathbf{S}_A$, appears in this expression because the basis orbitals on A are, in general, not orthogonal. Here and further on we use the shorthand $S^{-1}_{(X)\mu\nu} = (\mathbf{S}_X^{-1})_{\mu\nu}$ for the elements of the inverse overlap matrix corresponding to the atomic or diatomic fragment, X.

In analogy with the last term in Eq. (16) we get the generalization of the mapping appropriate for our purpose:

$$\left\langle \varphi_i | \hat{L}^A | \varphi_j \right\rangle_A \Longrightarrow \ \langle \hat{P}^A \varphi_i | \hat{L}^A | \varphi_j^A \rangle \ , \tag{18}$$

where $\hat{L}^A$ is any one-electron linear operator of atomic character related to the same atom on which φ_j^A is centered. It shows that the molecular orbital φ_i contributes to the value of the intraatomic quantity $\hat{L}^A$ to the extent of its projection $\hat{P}^A \varphi_i$ on the subspace of the atom in question.

Using the turn-over rule once more, we get the expression actually used in the following derivations:

$$\left\langle \varphi_i | \hat{L}^A | \varphi_j \right\rangle_A \Longrightarrow \ \langle \varphi_i | \hat{P}^A \hat{L}^A \varphi_j^A \rangle \ . \tag{19}$$

This form indicates that one considers only that part of the "intraatomic" function $\hat{L}^A \varphi_j^A$ which can be expanded in the atomic basis. As the basis on atom A increases and approaches completeness, the projector $\hat{P}^A$, in principle, tends to the unit operator. (The practical basis sets are far from this limit, however.) The presence of the projector in Eqs. (18) and (19) provides that the atomic components contain only intraatomic matrix elements of operator $\hat{L}$ – and different quantities formed from the overlap matrix.

If the operator $\hat{L}^B$ is related to another atom than φ_j^A – like the nuclear attraction terms in Eq. (11) – then one has to use projector $\hat{P}^{AB}$ on the orbitals of the diatomic fragment AB, i.e., on the union of the basis sets centered on atoms A and B. Its definition is quite analogous to Eq. (17). Then we obtain

$$\left\langle \varphi_i | \hat{L}^B | \varphi_j \right\rangle_A \Longrightarrow \ \langle \varphi_i | \hat{P}^{AB} \hat{L}^B \varphi_j^A \rangle \tag{20}$$

For the two-electron integrals one has to consider projectors for both electrons; the corresponding mapping is

$$[\varphi_i \varphi_j | \varphi_k \varphi_l]_{A,B} \\ \Longrightarrow \langle \varphi_i(1) \varphi_j(2) | \hat{P}^{AB}(1) \hat{P}^{AB}(2) \frac{1}{r_{12}} \varphi_k^A(1) \varphi_l^B(2) \rangle \ , \tag{21}$$

where we have taken into account that the integral considered is, in general, of diatomic nature. (If $A = B$, one has to use $\hat{P}^A$ instead of $\hat{P}^{AB}$, of course.)

It is to be stressed, that these mappings may be considered as some approximations to the AIM integrals, but do not represent equalities.

4 LCAO energy components – the simple expression

Substituting the mappings (Eqs. 19–21) into Eqs. (10) and (11) of the one- and two-center energy components, one obtains an approximate energy decomposition formula for the LCAO case:

$$E \approx \sum_A E_A + \sum_{A<B} E_{AB} \ , \tag{22}$$

where

$$\begin{aligned} E_A = {} & 2 \sum_{i=1}^{n} \langle \varphi_i | \hat{P}^A \hat{h}^A \varphi_i^A \rangle \\ & + \sum_{i,j=1}^{n} \Bigg(2 \langle \varphi_i(1) \varphi_j(2) | \hat{P}^A(1) \hat{P}^A(2) \frac{1}{r_{12}} \varphi_i^A(1) \varphi_j^A(2) \rangle \\ & - \langle \varphi_i(1) \varphi_j(2) | \hat{P}^A(1) \hat{P}^A(2) \frac{1}{r_{12}} \varphi_j^A(1) \varphi_i^A(2) \rangle \Bigg) \ , \end{aligned} \tag{23}$$

$$\begin{aligned} E_{AB} = {} & -2 \sum_{i=n}^{n} \left(\langle \varphi_i | \hat{P}^{AB} \frac{Z_B}{R_B} \varphi_i^A \rangle + \langle \varphi_i | \hat{P}^{AB} \frac{Z_A}{R_A} \varphi_i^B \rangle \right) \\ & + 2 \sum_{i,j=1}^{n} \Bigg(2 \langle \varphi_i(1) \varphi_j(2) | \hat{P}^{AB}(1) \hat{P}^{AB}(2) \frac{1}{r_{12}} \varphi_i^A(1) \varphi_j^B(2) \rangle \\ & - \langle \varphi_i(1) \varphi_j(2) | \hat{P}^{AB}(1) \hat{P}^{AB}(2) \frac{1}{r_{12}} \varphi_j^A(1) \varphi_i^B(2) \rangle \Bigg) \\ & + \frac{Z_A Z_B}{R_{AB}} \ . \end{aligned} \tag{24}$$

By substituting the expression of the projectors and performing straightforward manipulations we can present this result as

$$\begin{aligned} E_A = {} & \sum_{\mu,\nu \in A} h_{\mu\nu}^A B_{\nu\mu}^A \\ & + \frac{1}{2} \sum_{\mu,\nu,\vartheta,\rho \in A} [\chi_\mu \chi_\nu | \chi_\vartheta \chi_\rho] \left(B_{\vartheta\mu}^A B_{\rho\nu}^A - \frac{1}{2} B_{\vartheta\nu}^A B_{\rho\mu}^A \right) \ , \end{aligned} \tag{25}$$

$$\begin{aligned} E_{AB} = {} & - \sum_{\tau \in AB} \left(\sum_{\mu \in A} B_{\mu\tau}^{AB} \langle \chi_\tau | \frac{Z_B}{r_B} | \chi_\mu \rangle + \sum_{\mu \in B} B_{\mu\tau}^{AB} \langle \chi_\tau | \frac{Z_A}{r_A} | \chi_\mu \rangle \right) \\ & + \sum_{\vartheta \in A} \sum_{\rho \in B} \sum_{\mu,\nu \in AB} [\chi_\mu \chi_\nu | \chi_\vartheta \chi_\rho] \left(B_{\vartheta\mu}^{AB} B_{\rho\nu}^{AB} - \frac{1}{2} B_{\vartheta\nu}^{AB} B_{\rho\mu}^{AB} \right) \\ & + \frac{Z_A Z_B}{R_{AB}} \ , \end{aligned} \tag{26}$$

where

$$h^A_{\mu\nu} = \langle \chi_\mu | \hat{h}^A | \chi_\nu \rangle \ , \tag{27}$$

and we have introduced matrix $\mathbf{B}^X$ $(X = A \text{ or } AB)$

$$B^X_{\mu\nu} = \sum_\gamma D_{\mu\gamma} A^X_{\gamma\nu} \tag{28}$$

representing a generalization of the usual "density matrix", **D**,

$$D_{\mu\nu} = 2 \sum_i^{occ.} c^i_\mu c^{i*}_\nu \ . \tag{29}$$

Matrix $\mathbf{B}^X$ contains matrix $\mathbf{A}^\mathbf{X}$ closely related to the projector $\hat{P}^X$:

$$A^X_{\lambda\mu} = \sum_{\sigma\in X} S_{\lambda\sigma} S^{-1}_{(X)\sigma\mu} \quad (\mu \in X, \ X = A \text{ or } AB) \ , \tag{30}$$

This result essentially coincides with the energy decomposition formula of Ref. [6], the analysis of the two–center exchange components of which led to the introduction of the useful bond order index [7, 8]. However, the few exploratory calculations performed indicate that this formula – although it qualitatively accounts for the main bonding features of a molecule – does not give a particularly good approximation of the total energy, at least for moderate basis sets.

5 Extended diatomic energy components

The mapping formula (Eq. 19) contains a projector on the atomic subspace, i.e., the component $(1 - \hat{P}^A)\hat{L}^A \varphi^A_j$, which lies in the orthogonal subspace, is completely neglected, even if it enters a two-center integral. As we are interested in approximating the total energy as a sum of one- and two-center components, it is a legitimate modification of the approach if one also conserves the diatomic components of that function – the additional terms obtained in this manner should obviously be assigned to the two-center energy contributions. These terms describe the effects of the basis extension from the atoms to the diatomic fragments and should have a decreasing importance as the basis set on each atom improves.

It is easy to see that one has the equality

$$\langle \varphi_i | \hat{L}^A \varphi^A_j \rangle = \langle \varphi_i | \hat{P}^A \hat{L}^A \varphi^A_j \rangle + \sum_{\substack{B \\ B \neq A}} \Big(\langle \varphi^B_i | \hat{L}^A \varphi^A_j \rangle - \langle \varphi^B_i | \hat{P}^A \hat{L}^A \varphi^A_j \rangle \Big) \ . \tag{31}$$

The first term on the right-hand side of this expression is the one-center term formed according to the mapping (Eq. 19) and it was already included in the one-center energy component (Eq. 25), while the second represents the sum of the diatomic basis extension terms discussed earlier. (The term with $B = A$ is omitted as it would vanish according to the properties of the projectors.) By applying this result to the intraatomic Hamiltonian as well as its two-electron analogue, one obtains E_{AB} with several additional terms:

$$\begin{aligned}
E_{AB} = &- \sum_{\tau\in AB} \left(\sum_{\mu\in A} B^{AB}_{\mu\tau} \langle \chi_\tau | \frac{Z_B}{r_B} | \chi_\mu \rangle + \sum_{\mu\in B} B^{AB}_{\mu\tau} \langle \chi_\tau | \frac{Z_A}{r_A} | \chi_\mu \rangle \right) \\
&+ \sum_{\vartheta\in A} \sum_{\rho\in B} \sum_{\mu,\nu\in AB} [\chi_\mu \chi_\nu | \chi_\vartheta \chi_\rho] \left(B^{AB}_{\vartheta\mu} B^{AB}_{\rho\nu} - \frac{1}{2} B^{AB}_{\vartheta\nu} B^{AB}_{\rho\mu} \right) + \frac{Z_A Z_B}{R_{AB}} \\
&+ \sum_{\mu\in A} \sum_{\nu\in B} D_{\mu\nu} \left(h^A_{\nu\mu} - \sum_{\tau\in A} A^A_{\nu\tau} h^A_{\tau\mu} \right) + \sum_{\mu\in B} \sum_{\nu\in A} D_{\mu\nu} \left(h^B_{\nu\mu} - \sum_{\tau\in B} A^B_{\nu\tau} h^B_{\tau\mu} \right) \\
&+ \frac{1}{2} \sum_{\kappa,\rho\in A} \sum_{\substack{\gamma,\nu\in AB \\ (\gamma\notin A)\vee(\nu\notin A)}} \left(D_{\kappa\gamma} D_{\rho\nu} - \frac{1}{2} D_{\kappa\nu} D_{\rho\gamma} \right) \left([\chi_\gamma \chi_\nu | \chi_\kappa \chi_\rho] - \sum_{\tau,\eta\in A} A^A_{\gamma\tau} A^A_{\nu\eta} [\chi_\tau \chi_\eta | \chi_\kappa \chi_\rho] \right) \\
&+ \frac{1}{2} \sum_{\kappa,\rho\in B} \sum_{\substack{\gamma,\nu\in AB \\ (\gamma\notin B)\vee(\nu\notin B)}} \left(D_{\kappa\gamma} D_{\rho\nu} - \frac{1}{2} D_{\kappa\nu} D_{\rho\gamma} \right) \left([\chi_\gamma \chi_\nu | \chi_\kappa \chi_\rho] - \sum_{\tau,\eta\in B} A^B_{\gamma\tau} A^B_{\nu\eta} [\chi_\tau \chi_\eta | \chi_\kappa \chi_\rho] \right)
\end{aligned} \tag{32}$$

This is the formula for the two-atomic energy contribution used in the recently introduced "chemical energy component analysis" [2, 3]. (The one-center contributions coincide with Eq. 25) This scheme [2, 3] permits one to express the total molecular energy approximately but to good accuracy as a sum of atomic and diatomic contributions, the computation of which requires the use of one- and two-center integrals only. This analysis is a very promising tool, as it is able to give us insight into the fine details of the different intramolecular interactions; in particular, one can get much more information about the nonbonded interactions than is provided by other tools such as bond order indices or overlap populations.

6 Conclusions

It is shown that the molecular energy calculated at the SCF level can be strictly expressed as a sum of one-and two-atom energy components in the framework of Bader's topological theory of AIM. By introducing the LCAO mapping of the AIM integrals, at first one gets a relatively simple expression already derived in a different framework [6]. Although this expression served as a background for defining the useful bond order indices, it is not particularly accurate as an energy decomposition scheme, at least for moderate basis sets. By introducing an extension of the integral approximation scheme in such a manner that all two-center integrals are conserved, one arrives at the expressions of the recently proposed "chemical energy component analysis" [2, 3], which permits one to express the total molecular energy approximately but to good accuracy as a sum of atomic and diatomic contributions and provides an insight into the fine details of the different intramolecular interactions.

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