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Physical analysis of the diatomic “chemical” energy components

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Abstract. The recent “chemical energy component analysis” permits the total energy of a molecule to be presented approximately but to good accuracy as a sum of atomic and diatomic energy contributions. Here the diatomic energy components are further decomposed into terms of different physical origin: electrostatics (in point-charge approximation and the distributed charge corrections), exchange effects, diatomic overlap and atomic basis extension terms. This analysis may provide us with a deeper insight into the factors influencing both the chemical bonds and the nonbonded interatomic interactions.

Keywords: Energy component analysis – Energy decomposition – Diatomic energy components – Analysis of exchange interactions – Overlap interactions

1 Introduction

Recently we have proposed [1, 2] a “chemical energy component analysis” (CECA) for the a posteriori analysis of the results obtained in quantum chemical calculations performed by using the standard linear combination of atomic orbitals (LCAO) formalism (atom-centered basis sets). By introducing a projective integral expansion technique, the total self-consistent-field (SCF) energy of the molecule can be decomposed approximately but to good accuracy into a sum of atomic and diatomic energy contributions [1]:

$$E \approx \sum_{\mathrm{A}} E_{\mathrm{A}} + \sum_{\mathrm{A<B}} E_{\mathrm{AB}} \quad . \tag{1}$$

(The decomposition is exact for diatomics.) A similar decomposition of the total SCF energy into one- and two-center terms can be performed [3] exactly in the framework of Bader’s topological “atoms-in-molecules” (AIM) formalism [4]. It has also been shown [3] that there is a formal mathematical mapping between the energy decomposition schemes valid in the LCAO and AIM theories, which permitted an independent re-derivation of the CECA expressions [3].[1] It is to be noted that our AIM energy component analysis [3,5] has nothing in common either with Bader’s decomposition of the total energy into the sum of atomic components only, by using a local virial theorem [4], or with the attempt of Sierraalta and Frenking [6] to introduce diatomic energy components on the basis of the former.

The CECA analysis targets those basic aspects of chemical bonding which can usually be sufficiently well described at the SCF level of the theory. It seems a rather useful tool permitting us to interpret the results of ab initio calculations in chemical terms: one can identify the chemical bonds, distinguish between attractive and repulsive situations for the nonbonded atoms, discover distant secondary bondings, etc. (For the first application of CECA to a practical problem we refer to Ref. [7]. Generalization to correlated wave functions is also in progress.)

It is to be stressed that the energy components in Eq. (1) represent static parameters which correspond to the system at a given geometry. Therefore the diatomic energy components characterize the interaction of a given pair of atoms in the molecule, but cannot be directly related to the bond dissociation energies. In the CECA scheme the diatomic energy components corresponding to the chemically bonded atoms are large negative numbers; at the same time the mono-atomic energies are usually significantly higher than the free-atom energies, in accord with our qualitative notion of “promotion” of atoms taking place during the bond formation. The CECA results of studying both strong and weak inter-

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[1] Although the AIM energy decomposition is exact in principle, one cannot avoid some numerical errors in its practical realization [5], because the actual computation of the AIM energy components requires a great number of sixfold numerical integration to be performed. These large-scale numerical integrations are very expensive and such calculations are feasible for small systems only. As opposed to this, the CECA calculations are rather cheap and can easily be performed by using our program [2]

actions indicate that the final energetic effects are usually obtained from a delicate balance of terms of different sign. A given interaction gives rise to a relatively large leading term acting in one direction (e.g. the energy decrease due to the bonding) which is almost compensated by several others of opposite sign (as increase of atomic energy components). This permits us to identify the sources even of finer resulting effects, as the primary factors appear "magnified" in the CECA analysis.

The numerical values of the energy components do not, however, give us any direct information about the physical nature of interactions which are responsible for them. The one-center energy terms reflect the promotion as the bonds are formed, but otherwise seem not to represent a direct chemical interest. (Of course, they may also appear to be worthy of some further analysis in the future.) At the same time, the inspection of the diatomic energy contributions of the CECA scheme shows that they consist of several terms of quite different character.

The aim of the present paper is to decompose the diatomic energy components of the CECA scheme [1] into a sum of terms describing different types of interactions and to consider a few numerical examples of this more detailed energy component analysis. Because the projective integral expansion used in CECA can be viewed as a symmetrized version of a similar technique applied in the "chemical Hamiltonian approach" [8], the energy components discussed later exhibit close similarities with those which were proposed in Ref. [8] but have never been computationally realized.

2 Decomposition of the diatomic SCF energy components

We start from the atomic and diatomic energy components E_{A} and E_{AB} given in Ref. [1], which are valid for single determinant (restricted or unrestricted Hartree–Fock) wave functions; we only change somewhat the order of the terms (real basis functions and orbital coefficients are assumed):

$$\begin{aligned} E_{\mathrm{A}} = {} & \sum_{\nu,\tau\in \mathrm{A}} B^{\mathrm{A}}_{\nu\tau} h^{\mathrm{A}}_{\tau\nu} + \frac{1}{2} \sum_{\kappa,\rho,\tau,\eta\in \mathrm{A}} (\tau\kappa|\eta\rho) \\ & \times \left(B^{\mathrm{A}}_{\kappa\tau} B^{\mathrm{A}}_{\rho\eta} - C^{\alpha\mathrm{A}}_{\kappa\eta} C^{\alpha\mathrm{A}}_{\rho\tau} - C^{\beta\mathrm{A}}_{\kappa\eta} C^{\beta\mathrm{A}}_{\rho\tau} \right) \end{aligned} \tag{2}$$

and

$$\begin{aligned} E_{\mathrm{AB}} = {} & \frac{Z_{\mathrm{A}} Z_{\mathrm{B}}}{R_{\mathrm{AB}}} - \sum_{\tau\in \mathrm{AB}} \left(\sum_{\mu\in \mathrm{A}} B^{\mathrm{AB}}_{\mu\tau} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle \right. \\ & \left. + \sum_{\mu\in \mathrm{B}} B^{\mathrm{AB}}_{\mu\tau} \langle\tau| \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} |\mu\rangle \right) \\ & + \sum_{\substack{\kappa\in \mathrm{A} \\ \rho\in \mathrm{B}}} \sum_{\tau,\eta\in \mathrm{AB}} (\tau\kappa|\eta\rho) \Big(B^{\mathrm{AB}}_{\kappa\tau} B^{\mathrm{AB}}_{\rho\eta} - C^{\alpha\mathrm{AB}}_{\kappa\eta} \\ & \times C^{\alpha\mathrm{AB}}_{\rho\tau} - C^{\beta\mathrm{AB}}_{\kappa\eta} C^{\beta\mathrm{AB}}_{\rho\tau} \Big) \\ & + \sum_{\substack{\nu\in \mathrm{A} \\ \mu\in \mathrm{B}}} D_{\mu\nu} \left(h^{\mathrm{A}}_{\mu\nu} - \sum_{\tau\in \mathrm{A}} A^{\mathrm{A}}_{\mu\tau} h^{\mathrm{A}}_{\tau\nu} + h^{\mathrm{B}}_{\mu\nu} - \sum_{\tau\in \mathrm{B}} A^{\mathrm{B}}_{\nu\tau} h^{\mathrm{B}}_{\tau\mu} \right) \\ & + \frac{1}{2} \sum_{\kappa,\rho\in \mathrm{A}} \sum_{\substack{\gamma,\nu\in \mathrm{AB} \\ (\gamma\notin \mathrm{A})\vee(\nu\notin \mathrm{A})}} \left(D_{\kappa\gamma} D_{\rho\nu} - P^{\alpha}_{\kappa\nu} P^{\alpha}_{\rho\gamma} - P^{\beta}_{\kappa\nu} P^{\beta}_{\rho\gamma} \right) \\ & \times \left[(\gamma\kappa|\nu\rho) - \sum_{\tau,\eta\in \mathrm{A}} A^{\mathrm{A}}_{\gamma\tau} A^{\mathrm{A}}_{\nu\eta} (\tau\kappa|\eta\rho) \right] \\ & + \frac{1}{2} \sum_{\kappa,\rho\in \mathrm{B}} \sum_{\substack{\gamma,\nu\in \mathrm{AB} \\ (\gamma\notin \mathrm{B})(\nu\notin \mathrm{B})}} \left(D_{\kappa\gamma} D_{\rho\nu} - P^{\alpha}_{\kappa\nu} P^{\alpha}_{\rho\gamma} - P^{\beta}_{\kappa\nu} P^{\beta}_{\rho\gamma} \right) \\ & \times \left[(\gamma\kappa|\nu\rho) - \sum_{\tau,\eta\in \mathrm{B}} A^{\mathrm{B}}_{\gamma\tau} A^{\mathrm{B}}_{\nu\eta} (\tau\kappa|\eta\rho) \right] \ . \end{aligned} \tag{3}$$

Here Z_{A} is the nuclear charge of atom A and the convention $(11|22)$ is used for the two-electron integrals:

$$(\tau\kappa|\eta\rho) = \int\int \chi_\tau(1)\chi_\kappa(1) \frac{1}{r_{12}} \chi_\eta(2)\chi_\rho(2)\, \mathrm{d}v_1\, \mathrm{d}v_2 \ . \tag{4}$$

Furthermore, $\hat{h}^{\mathrm{A}}$ is the intraatomic part of the one-electron Hamiltonian

$$\hat{h}^{\mathrm{A}} = -\frac{1}{2}\Delta - \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} \ , \tag{5}$$

and notations such as $\mu \in X$ indicate that the summations should be performed for the basis orbitals assigned to subunit X ($X = \mathrm{A}$, B or AB). The different auxiliary matrices are defined as follows. We introduce the usual **P** matrix ("density matrix") for spin σ ($\sigma = \alpha$ or β) expressed through the coefficients of the occupied orbitals as

$$P^{\sigma}_{\mu\nu} = \sum_{i}^{\text{occ.}} C^{\sigma}_{\mu i} C^{\sigma}_{\nu i} \ , \tag{6}$$

and

$$\mathbf{D} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta} \tag{7}$$

is the resulting (spinless) density matrix. Matrices $\mathbf{A}^X$ are defined as

$$A^X_{\lambda\mu} = \sum_{\sigma\in X} S_{\lambda\sigma} S^{-1}_{(X)\sigma\mu} \quad (\mu \in X) \ , \tag{8}$$

with the shorthand $S^{-1}_{(X)\mu\nu} = (\mathbf{S}^{-1}_X)_{\mu\nu}$ for the elements of the inverse overlap matrix corresponding to the one- or diatomic fragment X. It can be shown that they are closely related to the projectors $\hat{P}^X$ on the subspace of orbitals centered on subunit X; actually they represent the projection matrix as applied to the "bra" vectors. Matrices $\mathbf{B}^X$ and $\mathbf{C}^{\sigma X}$ represent a combination of the densities and the projection on the subunit X:

$$B^X_{\mu\nu} = \sum_{\gamma} D_{\mu\gamma} A^X_{\gamma\nu} \qquad (\nu \in X) \ , \tag{9}$$

$$C^{\sigma X}_{\mu\nu} = \sum_{\gamma} P^{\sigma}_{\mu\gamma} A^X_{\gamma\nu} \qquad (\sigma = \alpha, \beta; \quad \nu \in X) \ . \tag{10}$$

The first three terms of Eq. (3) obviously originate from those terms of the Hamiltonian which describe the nuclear–nuclear repulsion, the electron–nuclear attraction and the interelectronic repulsion, respectively. They do not, however, simply correspond to the respective electrostatic interactions but they also reflect different exchange and overlap effects. That means that we can identify these terms as the sum of the electrostatic, overlap and exchange contributions to the diatomic energy component E_{AB}:

$$
\begin{aligned}
&E_{\mathrm{AB}}^{\mathrm{el.stat.}} + E_{\mathrm{AB}}^{\mathrm{exch.}} + E_{\mathrm{AB}}^{\mathrm{overl.}} \\
&\quad = \frac{Z_{\mathrm{A}} Z_{\mathrm{B}}}{R_{\mathrm{AB}}} - \sum_{\tau \in \mathrm{AB}} \left(\sum_{\mu \in \mathrm{A}} B_{\mu\tau}^{\mathrm{AB}} \langle \tau | \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} | \mu \rangle \right. \\
&\qquad \left. + \sum_{\mu \in \mathrm{B}} B_{\mu\tau}^{\mathrm{AB}} \langle \tau | \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} | \mu \rangle \right) \\
&\qquad + \sum_{\substack{\kappa \in \mathrm{A} \\ \rho \in \mathrm{B}}} \sum_{\tau,\eta \in \mathrm{AB}} (\tau\kappa|\eta\rho) \Big(B_{\kappa\tau}^{\mathrm{AB}} B_{\rho\eta}^{\mathrm{AB}} - C_{\kappa\eta}^{\alpha\mathrm{AB}} C_{\rho\tau}^{\alpha\mathrm{AB}} \\
&\qquad - C_{\kappa\eta}^{\beta\mathrm{AB}} C_{\rho\tau}^{\beta\mathrm{AB}} \Big) \ . \qquad (11)
\end{aligned}
$$

In order to separate the electrostatic, exchange and overlap effects from each other, one should distinguish between the overlap integrals originating from the projections by which the different three- and four-center contributions are compressed into the one- and two-center ones and the "true" overlap effects within the diatomic fragment AB. To perform this separation, we proceed in the spirit of Ref. [8], avoiding, however, the use of the somewhat involved "mixed" second quantized formalism applied there.

The electronic charge density is given by the known formula[2]

$$\rho(\vec{r}) = \sum_{\mu,\nu} D_{\mu\nu} \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) \ . \qquad (12)$$

We group the terms of Eq. (12) by atoms A as

$$\rho(\vec{r}) = \sum_{\mathrm{A}} \sum_{\mu \in \mathrm{A}} \sum_{\nu} D_{\mu\nu} \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) \ . \qquad (13)$$

Now we shall approximate $\rho(\vec{r})$ as a sum of "atomic" charge densities $\rho_{\mathrm{A}}(\vec{r})$, expressed by the basis orbitals of the given atom only. To do this, we replace every function $\chi_\nu^*(\vec{r})$ by its projection onto the subspace of the basis functions of the respective atom A:

$$
\begin{aligned}
\chi_\nu^*(\vec{r}) &\Longrightarrow \left[\hat{P}^{\mathrm{A}} \chi_\nu(\vec{r}) \right]^* \\
&= \left[\sum_{\tau,\rho \in \mathrm{A}} S_{(\mathrm{A})\tau\rho}^{-1} \chi_\tau(\vec{r}) \int \chi_\rho^*(\vec{r}\,') \chi_\nu(\vec{r}\,') \mathrm{d}v' \right]^* . \qquad (14)
\end{aligned}
$$

On substituting Eq. (14) into Eq. (13) we get the approximation

$$\rho(\vec{r}) \approx \sum_{\mathrm{A}} \sum_{\mu,\tau,\rho \in \mathrm{A}} \sum_{\nu} D_{\mu\nu} S_{\nu\rho} S_{(\mathrm{A})\rho\tau}^{-1} \chi_\tau^*(\vec{r}) \chi_\mu(\vec{r}) \ . \qquad (15)$$

That is

$$\rho(\vec{r}) \approx \sum_{\mathrm{A}} \rho_{\mathrm{A}}(\vec{r}) \qquad (16)$$

with

$$\rho_{\mathrm{A}}(\vec{r}) = \sum_{\mu,\tau \in \mathrm{A}} B_{\mu\tau}^{\mathrm{A}} \chi_\tau^*(\vec{r}) \chi_\mu(\vec{r}) \ . \qquad (17)$$

One can see that the "atomic" charge density $\rho_{\mathrm{A}}(\vec{r})$ defined here also enters the electron–nuclear attraction and the Coulombic part of the electron–electron repulsion terms of the one-center CECA energy components (Eq. 2) derived [1, 3] originally in a different manner.

As it is easy to see, the "atomic" charge densities $\rho_{\mathrm{A}}(\vec{r})$ integrate to Mulliken's gross atomic populations on the respective atoms, as a consequence of the equality $\langle \hat{P}^{\mathrm{A}} \chi_\nu | \chi_\mu \rangle = \langle \chi_\nu | \hat{P}^{\mathrm{A}} \chi_\mu \rangle = \langle \chi_\nu | \chi_\mu \rangle$ if $\mu \in \mathrm{A}$.[3] Therefore, the function $\sum_{\mathrm{A}} \rho_{\mathrm{A}}(\vec{r})$ represents an approximation to the true $\rho(\vec{r})$ which conserves the total electronic charge of the molecule – a property extremely important from the point of view of the overall electrostatic balance.

Now, by computing the electrostatic interaction of the two nuclei and that of the "atomic" charge densities $\rho_{\mathrm{A}}(\vec{r})$ and $\rho_{\mathrm{B}}(\vec{r})$ with each other and with the nuclear charges Z_{B} and Z_{A}, respectively, we obtain the electrostatic term of the interatomic energy component:

$$
\begin{aligned}
E_{\mathrm{AB}}^{\mathrm{el.stat.}} = \frac{Z_{\mathrm{A}} Z_{\mathrm{B}}}{R_{\mathrm{AB}}} &- \sum_{\mu,\tau \in \mathrm{A}} B_{\mu\tau}^{\mathrm{A}} \langle \tau | \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} | \mu \rangle - \sum_{\mu,\tau \in \mathrm{B}} B_{\mu\tau}^{\mathrm{B}} \langle \tau | \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} | \mu \rangle \\
&+ \sum_{\tau,\kappa \in \mathrm{A}} \sum_{\eta,\rho \in \mathrm{B}} B_{\tau\kappa}^{\mathrm{A}} B_{\eta\rho}^{\mathrm{B}} (\tau\kappa|\eta\rho) \ . \qquad (18)
\end{aligned}
$$

Comparing Eq. (18) with Eq. (11), one can see that they contain the same nuclear repulsion, while the terms connected with electron–nuclear repulsion exhibit some differences: in Eq. (18) the limits of summation are restricted to one atom, and the diatomic coefficient matrix $\mathbf{B}^{\mathrm{AB}}$ of Eq. (11) is replaced by one of its atomic counterparts $\mathbf{B}^{\mathrm{A}}$ or $\mathbf{B}^{\mathrm{B}}$. (As discussed later, these differences can be attributed to the overlap effects.) Similar analogy can be observed between the last term in Eq. (18), describing interatomic electron–electron repulsion (Coulombic interaction) and the respective term in Eq. (11). In the latter equation, however, there are also terms containing matrices $\mathbf{C}^{\alpha\mathrm{AB}}$ and $\mathbf{C}^{\beta\mathrm{AB}}$; these originate from the exchange part of the Hartree–Fock energy. We need also to obtain the "pure" interatomic exchange energy component $E_{\mathrm{AB}}^{\mathrm{exch.}}$ which is separated out of overlap effects and can be put into correspondence with the Coulombic term in Eq. (18). For that reason we introduce similar restrictions on the summation indices as we have for the terms describing electron–nuclear attraction and Coulombic interactions, and replace matrices $\mathbf{C}^{\sigma\mathrm{AB}}$

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[2] For greater clarity of the derivations, here we admit the case of complex basis orbitals

[3] A well-known drawback of Mulliken's populations is their significant basis dependence. Nevertheless, Mulliken's gross population has a privileged importance, being the only population concept which is consistent with the internal mathematical structure of the atom-centered finite basis (LCAO) formalism: Mulliken's gross population represents the expectation value of the operator of atomic population, which has been defined in the second quantized framework [8]

with their atomic counterpart $\mathbf{C}^{\sigma \mathrm{A}}$ or $\mathbf{C}^{\sigma \mathrm{B}}$, similarly to the case of matrices $\mathbf{B}^{X}$ in the electrostatic terms:

$$E_{\mathrm{AB}}^{\text{exch.}} = -\sum_{\kappa,\tau\in \mathrm{A}} \sum_{\rho,\eta\in \mathrm{B}} (\tau\kappa|\eta\rho)\left(C_{\kappa\eta}^{\alpha \mathrm{B}} C_{\rho\tau}^{\alpha \mathrm{A}} + C_{\kappa\eta}^{\beta \mathrm{B}} C_{\rho\tau}^{\beta \mathrm{A}}\right) \ . \qquad (19)$$

This definition of the interatomic exchange component has been discussed in more detail elsewhere [9]. It can also be obtained by subjecting the diatomic part of the two-electron exchange density [10] (the diagonal element of the exchange part of the second-order density matrix) to an analysis quite similar to that which was given earlier for the one-electron density $\rho(\vec{r})$.

Extracting the electrostatic and exchange components Eqs. (18) and (19) from the right-hand side of Eq. (11), we obtain the overlap contributions to the diatomic energy component E_{AB} as

$$\begin{aligned} E_{\mathrm{AB}}^{\text{overl.}} = &-\sum_{\tau\in \mathrm{AB}} \left(\sum_{\mu\in \mathrm{A}} B_{\mu\tau}^{\mathrm{AB}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle + \sum_{\mu\in \mathrm{B}} B_{\mu\tau}^{\mathrm{AB}} \langle\tau| \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} |\mu\rangle \right) \\ &+ \sum_{\mu,\tau\in \mathrm{A}} B_{\mu\tau}^{\mathrm{A}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle - \sum_{\mu,\tau\in \mathrm{B}} B_{\mu\tau}^{\mathrm{B}} \langle\tau| \frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}} |\mu\rangle \\ &+ \sum_{\substack{\kappa\in \mathrm{A} \\ \rho\in \mathrm{B}}} \sum_{\tau,\eta\in \mathrm{AB}} (\tau\kappa|\eta\rho) \\ &\times \left(B_{\kappa\tau}^{\mathrm{AB}} B_{\rho\eta}^{\mathrm{AB}} - C_{\kappa\eta}^{\alpha \mathrm{AB}} C_{\rho\tau}^{\alpha \mathrm{AB}} - C_{\kappa\eta}^{\beta \mathrm{AB}} C_{\rho\tau}^{\beta \mathrm{AB}} \right) \\ &- \sum_{\kappa,\tau\in \mathrm{A}} \sum_{\eta,\rho\in \mathrm{B}} (\tau\kappa|\eta\rho) \\ &\times \left(B_{\kappa\tau}^{\mathrm{A}} B_{\rho\eta}^{\mathrm{B}} - C_{\kappa\eta}^{\alpha \mathrm{B}} C_{\rho\tau}^{\alpha \mathrm{A}} - C_{\kappa\eta}^{\beta \mathrm{B}} C_{\rho\tau}^{\beta \mathrm{A}} \right) \ . \qquad (20) \end{aligned}$$

It is easy to see that all terms of Eq. (20) are indeed due to the interatomic overlap: they either contain a diatomic differential overlap of the type $\chi_\mu(\vec{r})\chi_\nu(\vec{r})$; $\mu \in \mathrm{A}$, $\nu \in \mathrm{B}$, in the one- or two-electron integrals, or the interatomic elements of the inverse overlap matrix $\mathbf{S}_{(\mathrm{AB})}^{-1}$, or differences such as $S_{(\mathrm{AB})\mu\nu}^{-1} - S_{(\mathrm{A})\mu\nu}^{-1}$; $\mu, \nu \in \mathrm{A}$ between the intraatomic elements of the diatomic and intraatomic inverse overlap matrices, which are also due to the nonzero interatomic block of the overlap matrix.

As we have seen, the energy component $E_{\mathrm{AB}}^{\text{overl.}}$ is the remainder of approximating Eq. (11) by the sum of Eqs. (18) and (19). For moderated basis sets with pronounced atomic character (like the 6-31G** basis used in the examples presented later) it reflects well the influence of the interatomic overlap on the bond formation and on the nonbonded interactions. At the same time, with the improvement of the basis on each atom, the sum (15) of atomic densities $\rho_{\mathrm{A}}(\vec{r})$ approximates better and better the total charge density $\rho(\vec{r})$, and a similar tendency should be observed for the exchange density, too.[4] As a consequence, the overlap energy component Eq. (20) should tend to zero as the atomic basis sets approach completeness. This conclusion is in line with the fact that it is hardly of meaning to speak about some specific interatomic overlap effects in the cases when the basis set is so large that one can approximate well a basis orbital centered on one atom as a linear combination of those centered on a neighbouring one.

In order to see how $E_{\mathrm{AB}}^{\text{overl.}}$ diminishes with improving basis sets, we should turn to the use of projection operators, and observe that the right-hand side of Eq. (20) can be expressed via the differences $\hat{P}^{\mathrm{AB}}\chi_\gamma - \hat{P}^{\mathrm{A}}\chi_\gamma$, where $\hat{P}^{\mathrm{A}}$ and $\hat{P}^{\mathrm{AB}}$ are the projection operators on the subspaces of basis orbitals belonging to atom A and to the diatomic fragment AB, respectively. In fact, matrices $\mathbf{B}^{\mathrm{A}}$ and $\mathbf{B}^{\mathrm{AB}}$ represent combinations of the density matrix $\mathbf{D}$ with the matrices $\mathbf{A}^{\mathrm{A}}$ and $\mathbf{A}^{\mathrm{AB}}$ closely related to the projection operators $\hat{P}^{\mathrm{A}}$ and $\hat{P}^{\mathrm{AB}}$, respectively. Thus, for instance, the sum of terms

$$-\sum_{\tau\in \mathrm{AB}} \sum_{\mu\in \mathrm{A}} B_{\mu\tau}^{\mathrm{AB}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle + \sum_{\mu,\tau\in \mathrm{A}} B_{\mu\tau}^{\mathrm{A}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle \qquad (21)$$

entering Eq. (20) can be rewritten as

$$\begin{aligned} &-\sum_{\gamma} \sum_{\mu\in \mathrm{A}} D_{\mu\gamma} \left(\sum_{\tau\in \mathrm{AB}} A_{\gamma\tau}^{\mathrm{AB}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle - \sum_{\tau\in \mathrm{A}} A_{\gamma\tau}^{\mathrm{A}} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle \right) \\ &= -\sum_{\gamma} \sum_{\mu\in \mathrm{A}} D_{\mu\gamma} \left(\sum_{\tau,\sigma\in \mathrm{AB}} S_{\gamma\sigma} S_{(\mathrm{AB})\sigma\tau}^{-1} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle \right. \\ &\quad \left. - \sum_{\tau,\sigma\in \mathrm{A}} S_{\gamma\sigma} S_{(\mathrm{A})\sigma\tau}^{-1} \langle\tau| \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\mu\rangle \right) \\ &= -\sum_{\gamma} \sum_{\mu\in \mathrm{A}} D_{\mu\gamma} \langle \left(\hat{P}^{\mathrm{AB}} \chi_\gamma - \hat{P}^{\mathrm{A}} \chi_\gamma \right) | \frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}} |\chi_\mu\rangle \ . \qquad (22) \end{aligned}$$

Obviously, the orbitals χ_γ centered on atom A gives vanishing contribution to the sum in Eq. (22), because $\hat{P}^{\mathrm{AB}}\chi_\gamma = \hat{P}^{\mathrm{A}}\chi_\gamma = \chi_\gamma$ for the case when $\gamma \in \mathrm{A} \subset \mathrm{AB}$. If $\gamma \notin \mathrm{A}$, but the orbital χ_γ can be sufficiently well approximated by its projection $\hat{P}^{\mathrm{A}}\chi_\gamma$ on the orbitals of atom A, then the difference between its projection $\hat{P}^{\mathrm{AB}}\chi_\gamma$ and $\hat{P}^{\mathrm{A}}\chi_\gamma$ on the diatomic and on the atomic basis sets, respectively, quickly becomes negligible. This means that $E_{\mathrm{AB}}^{\text{overl.}}$ diminishes as the atomic basis sets increase.

Although $E_{\mathrm{AB}}^{\text{overl.}}$ decreases with improving basis sets, we think that its significance is more than simply being a finite basis correction term. One usually attributes important chemical meaning to the interatomic overlap, when discussing bond formation semiqualitatively in terms of (possibly distorted) atomic minimal basis sets. (That is essentially the level of abstraction on which we are able to visualize chemical bonding.) We hope that the consideration of the energy component $E_{\mathrm{AB}}^{\text{overl.}}$ permits us to quantify these very important conceptual considerations by combining the present analysis with the notion of the effective minimal atomic basis set which was introduced by one of us [11, 12].

The remaining terms of the diatomic energy component Eq. (3) – i.e. those which do not enter the right-hand-side of Eq. (11) – are apparently of basis set extension (finite basis correction) character. As discussed in some detail in Refs. [1, 3], the origin of these terms is the following. When computing the one-center energy components of the CECA scheme, functions such as $\hat{h}^{\mathrm{A}}\chi_\nu$ $(\nu \in \mathrm{A})$ and $\frac{1}{r_{12}}\chi_\kappa(1)\chi_\rho(2)$ $(\kappa, \rho \in \mathrm{A})$ are projected

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[4] We are indebted to the referees whose questions motivated us to perform the analysis that follows

onto the atomic subspace, i.e., only their intraatomic components $\hat{P}^{\mathrm{A}}\hat{h}^{\mathrm{A}}\chi_{\nu}$ and $\hat{P}^{\mathrm{A}}(1)\hat{P}^{\mathrm{A}}(2)\frac{1}{r_{12}}\chi_{\kappa}(1)\chi_{\rho}(2)$, respectively, are taken into account. The differences between the two-center integrals $\langle\chi_{\mu}|\hat{h}^{\mathrm{A}}|\chi_{\nu}\rangle$ ($\nu \in \mathrm{A}$, $\mu \in \mathrm{B}$) and $\langle\chi_{\gamma}(1)\chi_{\nu}(2)|\frac{1}{r_{12}}|\chi_{\kappa}(1)\chi_{\rho}(2)\rangle$ ($\kappa, \rho \in \mathrm{A}$; $\gamma, \nu \in \mathrm{AB}$) and their approximate one-center expansions $\langle\chi_{\mu}|\hat{P}^{\mathrm{A}}\hat{h}^{\mathrm{A}}|\chi_{\nu}\rangle = \sum_{\tau\in\mathrm{A}} A^{\mathrm{A}}_{\mu\tau}\hat{h}^{\mathrm{A}}_{\tau\nu}$ and $\langle\chi_{\gamma}(1)\chi_{\nu}(2)|\hat{P}^{\mathrm{A}}(1)\hat{P}^{\mathrm{A}}(2)\frac{1}{r_{12}}\chi_{\kappa}(1)\chi_{\rho}(2)\rangle = \sum_{\tau,\eta\in\mathrm{A}} A^{\mathrm{A}}_{\gamma\tau} A^{\mathrm{A}}_{\nu\eta}\langle\chi_{\tau}(1)\chi_{\eta}(2)|\frac{1}{r_{12}}|\chi_{\kappa}(1)\chi_{\rho}(2)\rangle$, respectively, would vanish only if the basis set on atom A were complete – then $\hat{P}^{\mathrm{A}}$ would be the identity operator. As this is not the case in practice, there appear some basis extension contributions to the diatomic energy components:

$$\begin{aligned}
E^{\text{bas.ext.}}_{\mathrm{AB}} &= \sum_{\substack{\nu\in\mathrm{A}\\ \mu\in B}} D_{\mu\nu}\left(h^{\mathrm{A}}_{\mu\nu} - \sum_{\tau\in\mathrm{A}} A^{\mathrm{A}}_{\mu\tau}h^{\mathrm{A}}_{\tau\nu} + h^{\mathrm{B}}_{\mu\nu} - \sum_{\tau\in\mathrm{B}} A^{\mathrm{B}}_{\nu\tau}h^{\mathrm{B}}_{\tau\mu}\right)\\
&\quad + \frac{1}{2}\sum_{\kappa,\rho\in\mathrm{A}}\ \sum_{\substack{\gamma,\nu\in\mathrm{AB}\\ (\gamma\notin\mathrm{A})\vee(\nu\notin\mathrm{A})}} \left(D_{\kappa\gamma}D_{\rho\nu} - P^{\alpha}_{\kappa\nu}P^{\alpha}_{\rho\gamma} - P^{\beta}_{\kappa\nu}P^{\beta}_{\rho\gamma}\right)\\
&\quad \times \left[(\gamma\kappa|\nu\rho) - \sum_{\tau,\eta\in\mathrm{A}} A^{\mathrm{A}}_{\gamma\tau}A^{\mathrm{A}}_{\nu\eta}(\tau\kappa|\eta\rho)\right]\\
&\quad + \frac{1}{2}\sum_{\kappa,\rho\in\mathrm{B}}\ \sum_{\substack{\gamma,\nu\in\mathrm{AB}\\ (\gamma\notin\mathrm{B})\vee(\nu\notin\mathrm{B})}} \left(D_{\kappa\gamma}D_{\rho\nu} - P^{\alpha}_{\kappa\nu}P^{\alpha}_{\rho\gamma} - P^{\beta}_{\kappa\nu}P^{\beta}_{\rho\gamma}\right)\\
&\quad \times \left[(\gamma\kappa|\nu\rho) - \sum_{\tau,\eta\in\mathrm{B}} A^{\mathrm{B}}_{\gamma\tau}A^{\mathrm{B}}_{\nu\eta}(\tau\kappa|\eta\rho)\right] \ . \qquad (23)
\end{aligned}$$

It may be worth performing a further analysis of the electrostatic energy component (Eq. 18). Following Ref. [8], we may treat separately the asymptotic part of the two-center integrals $\langle\chi_{\tau}|\frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}}|\chi_{\mu}\rangle$ for $\tau, \mu \in \mathrm{A}$ and $(\tau\kappa|\eta\rho)$ for $\tau, \kappa \in \mathrm{A}$; $\eta, \rho \in \mathrm{B}$, corresponding to the large distances between atoms A and B. It is easy to see that for large interatomic separations R_{AB} one has

$$\langle\chi_{\tau}|\frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}}|\chi_{\mu}\rangle \approx \frac{Z_{\mathrm{B}}S_{\tau\mu}}{R_{\mathrm{AB}}} \qquad (24)$$

and

$$(\tau\kappa|\eta\rho) \approx \frac{S_{\tau\kappa}S_{\eta\rho}}{R_{\mathrm{AB}}} \ . \qquad (25)$$

By using Eqs. (24) and (25) one obtains after trivial algebra the electrostatic energy component Eq. (18) in the point-charge approximation as

$$E^{\text{el.st.point}}_{\mathrm{AB}} = \frac{1}{R_{\mathrm{AB}}}(Z_{\mathrm{A}} - Q_{\mathrm{A}})(Z_{\mathrm{B}} - Q_{\mathrm{B}}) \ , \qquad (26)$$

where

$$Q_{\mathrm{A}} = \sum_{\mu\in\mathrm{A}}\sum_{\gamma} D_{\mu\gamma}S_{\gamma\mu} \qquad (27)$$

is Mulliken's gross atomic population on atom A.

Components $E^{\text{el.st.point}}_{\mathrm{AB}}$ account for the global electrostatic balance in the molecule. The remainder of the approximations in Eqs. (24) and (25) is, of course, significant for the small and intermediate interatomic separations, and gives rise to the terms describing the deviation from the point-like charge distribution on the individual atoms:

$$\begin{aligned}
E^{\text{el.st.dev.}}_{\mathrm{AB}} &= -\sum_{\mu,\tau\in\mathrm{A}} B^{\mathrm{A}}_{\mu\tau}\left(\langle\tau|\frac{Z_{\mathrm{B}}}{r_{\mathrm{B}}}|\mu\rangle - \frac{Z_{\mathrm{B}}S_{\tau\mu}}{R_{\mathrm{AB}}}\right)\\
&\quad - \sum_{\mu,\tau\in\mathrm{B}} B^{\mathrm{B}}_{\mu\tau}\left(\langle\tau|\frac{Z_{\mathrm{A}}}{r_{\mathrm{A}}}|\mu\rangle - \frac{Z_{\mathrm{A}}S_{\tau\mu}}{R_{\mathrm{AB}}}\right)\\
&\quad + \sum_{\tau,\kappa\in\mathrm{A}}\sum_{\eta,\rho\in\mathrm{B}} B^{\mathrm{A}}_{\tau\kappa}B^{\mathrm{B}}_{\eta\rho}\left[(\tau\kappa|\eta\rho) - \frac{S_{\tau\kappa}S_{\eta\rho}}{R_{\mathrm{AB}}}\right] \ . \qquad (28)
\end{aligned}$$

In the classical quantum chemical literature terms of such type were often called "penetration" ones. According to the experience gained to date, this energy component decreases quickly with the distance and starting approximately from the second bonding sphere, the electrostatic interaction can be fairly well approximated by its point-charge component.

A similar separate treatment of the terms corresponding to the point-charge approximation is also possible for the exchange components Eq. (19). As discussed in Ref. [13], the diatomic exchange energy component in the point-charge approximation is proportional to the bond order index between the atoms in question:

$$E^{\text{exch.point}}_{\mathrm{AB}} = -\frac{1}{2}\frac{B_{\mathrm{AB}}}{R_{\mathrm{AB}}} \ , \qquad (29)$$

with

$$B_{\mathrm{AB}} = 2\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}}\left[(\mathbf{P}^{\alpha}\mathbf{S})_{\mu\nu}(\mathbf{P}^{\alpha}\mathbf{S})_{\nu\mu} + (\mathbf{P}^{\beta}\mathbf{S})_{\mu\nu}(\mathbf{P}^{\beta}\mathbf{S})_{\nu\mu}\right] \qquad (30)$$

being the bond order index of atoms A and B. (We note that bond order indices are also computed by the program APOST [2].)

It is known that the Coulomb and exchange parts of the electron–electron interaction energy are well-defined (unitary invariant) quantities separately only if the so-called self-repulsion terms are included; this is the case if one calculates the energy by using density matrices. As a consequence, by applying these formulae in the particular case of the H_2^+ ion, one gets "two-electron" contributions to both Eq. (18) and Eq. (19), which compensate each other, of course. At the same time, Eq. (30) gives a bond order exactly equal to 0.5 for that ion.

We mention that there is a formal similarity between our energy decomposition scheme and that used in the so-called "symmetry-adapted perturbation theory" (SAPT) of intermolecular interactions [14]. However, our treatment does not start from the solutions of the individual atoms as SAPT does and, as a consequence, the terms have quite different nature. In particular, exchange between overlapping closed-shell species usually leads to repulsion, while the Hartree–Fock exchange we are considering gives a negative contribution to the total electronic energy and its interatomic components are also predominantly negative.

3 Illustrative calculations

All the different diatomic energy component values of the ethane, ethylene, acetylene and diborane molecules, except the very small interactions between the terminal hydrogen atoms in diborane, which are connected to different boron atoms, are contained in Tables 1, 2, 3 and 4. (For the hydrocarbons studied, some of the vicinal H–H interactions are significantly larger than those observed in diborane.) The standard 6-31G** basis set was used throughout.

Inspecting the tables, one can draw several conclusions. First of all, the diatomic energy contributions corresponding to chemical bonds are dominated by the negative exchange energy components constituting nearly half of them. This stresses again the intimate connection between the covalent bonding and the quantum mechanical exchange phenomenon (antisymmetry of the wave function) already known from the analysis of bond order indices [10, 13]. The remaining three energy components (electrostatics, overlap and basis extension corrections) are also negative and of roughly similar magnitude – the electrostatic component being usually the largest among them. For bonds, the electrostatic contribution comes almost entirely from the "penetration" term describing deviation of the charge distribution from the pointlike one. This is not surprising, of course, if one considers the bonds as being formed by (hybrid) atomic orbitals oriented towards each other; it is obvious that their electrostatic effect cannot be approximated by point charges placed at the nuclei. (The values obtained in the point-charge electrostatic approximation are small, and is some cases even positive, i.e. they can have the opposite sign to that of the whole electrostatic energy component.)

The case of the boron–boron interaction in diborane should be mentioned separately. It behaves quite similarly to that of the "half bonds" between the bridge hydrogen atoms and either of the borons. This is fully in line with the analytical result [15], according to which the existence of each three-center two-electron B–H–B bond generates a bond order of 0.25 between the limiting

Table 1. Diatomic energy components (au) of the ethane molecule computed by using the 6-31G** basis set

Component	C–C	C–H	H–H geminal	H–H vicinal	C–H vicinal
E_{AB}	−0.5991	−0.6045	0.0157	0.0036 (2×) −0.0007 (1×)	0.0097
Electrostatic	−0.1407	−0.1500	0.0010	0.0020 (2×) 0.0015 (1×)	−0.0085
Point charge	0.0388	−0.0182	0.0038	0.0026 (2×) 0.0021 (1×)	−0.0091
Dev. point. ch.	−0.1795	−0.1318	−0.0027	−0.0006 (2×) −0.0007 (1×)	0.0006
Exchange	−0.3353	−0.3305	0.0016	0.0000 (2×) −0.0004 (1×)	0.0025
Point charge	−0.1675	−0.2382	0.0015	0.0001 (2×) −0.0004 (1×)	0.0015
Dev. point. ch.	−0.1678	−0.0923	0.0001	0.0000 (2×) 0.0000 (1×)	0.0010
Overlap	−0.0957	−0.0878	0.0149	0.0014 (2×) −0.0007 (1×)	0.0166
Basis ext.	−0.0274	−0.0361	−0.0018	0.0002 (2×) −0.0010	−0.0010

Table 2. Diatomic energy components (au) of the ethylene molecule computed by using the 6-31G** basis set

Component	C–C	C–H	H–H geminal	H–H vicinal	C–H vicinal
E_{AB}	−1.0915	−0.6109	0.0176	0.0045 0.0003	0.0124
Electrostatic	−0.2786	−0.1504	0.0018	0.0028 0.0019	−0.0078
Point charge	0.0260	−0.0159	0.0047	0.0035 0.0028	−0.0082
Dev. point. ch.	−0.3046	−0.1345	−0.0028	−0.0007 −0.0009	0.0004
Exchange	−0.6237	−0.3321	0.0016	−0.0001 −0.0004	0.0030
Point charge	−0.3958	−0.2398	0.0013	−0.0001 −0.0005	0.0017
Dev. point. ch.	−0.2279	−0.0923	0.0002	0.0000 0.0000	0.0013
Overlap	−0.1414	−0.0904	0.0162	0.0022 −0.0006	0.0206
Basis ext.	−0.0478	−0.0380	−0.0020	−0.0004 −0.0005	−0.0033

Table 3. Diatomic energy components (au) of the acetylene molecule computed by using the 6-31G** basis set

Component	C–C	C–H	H–H vicinal	C–H vicinal
E_{AB}	−1.7607	−0.5641	0.0059	−0.0243
Electrostatic	−0.5343	−0.1346	0.0072	−0.0146
Point charge	0.0243	−0.0273	0.0087	−0.0129
Dev. point. ch.	−0.5587	−0.1073	−0.0016	−0.0018
Exchange	−0.9846	−0.3043	−0.0004	−0.0057
Point charge	−0.7117	−0.2236	−0.0004	−0.0037
Dev. point. ch.	−0.2729	−0.0807	0.0000	−0.0019
Overlap	−0.1886	−0.0848	−0.0005	0.0039
Basis ext.	−0.0532	−0.0405	−0.0004	−0.0079

Table 4. Diatomic energy components (au) of the diborane molecule computed by using the 6-31G** basis set. (H_{br} and H_{term}. denote hydrogen atoms in the bridge and terminal positions, respectively.)

Component	B–H_{br}	B–H_{term}	B–B	H_{br}–H_{br}	H_{br}–H_{term}	H_{term}–H_{term}
E_{AB}	−0.2790	−0.5173	−0.2266	0.0253	0.0044	0.0057
Electrostatic	−0.0571	−0.1344	−0.0307	−0.0002	−0.0002	0.0005
Point charge	−0.0015	−0.0029	0.0050	0.0002	0.0004	0.0007
Dev. point. ch.	−0.0556	−0.1314	−0.0357	−0.0005	−0.0005	−0.0002
Exchange	−0.1425	−0.2978	−0.1296	−0.0034	0.0006	0.0005
Point charge	−0.0957	−0.2218	−0.0700	−0.0041	0.0006	0.0005
Dev. point. Ch.	−0.0467	−0.0760	−0.0597	0.0007	0.0000	0.0000
Overlap	−0.0577	−0.0665	−0.0412	0.0240	0.0041	0.0050
Basis ext.	−0.0218	−0.0186	−0.0252	0.0050	−0.0001	−0.0003

boron atoms, which involves an attractive exchange interaction between the boron atoms [1]. The present result give further support to this picture.[5]

The situation is quite different for nonbonded atoms. For atoms which are sufficiently close, (e.g. geminal H–H, vicinal C–H interactions of ethane and ethylene, all the H–H interactions of diborane which are included in the table) the dominating effect is the positive overlap repulsion, while the other components are much less and can be of either sign.

A third type of interactions is that between more distant atoms. The interactions of vicinal pairs of hydrogen atoms are either negligible, partly as a consequence of compensation between different effects, or are dominated by the electrostatic energy component, which – in turn – is not very far from the value obtained in the point charge approximation. This latter observation indicates that for most truly long range problems it will probably be sufficient to conserve only the leading Coulomb interactions between the effective atomic point charges. However, preliminary results indicate that intramolecular hydrogen bonds, or the attractive C–H... O interactions such as those reported in Ref. [7], exhibit much more diverse behavior; these more complex problems will be discussed elsewhere.

All the calculations were performed by using the moderate, well-balanced 6-31G** basis set having a pronounced atomic character. Finally we discuss briefly the basis dependence of some quantities important from the point of view of the method. Some data for the ethane molecule calculated by using different basis sets are displayed in Table 5: the total SCF energies, the result obtained by approximating the energy by the sum of one- and two-center components E_A and E_{AB}, and the sums of the absolute values of the overlap and basis extension energy components. Every quantity was calculated at the minimum of the geometry corresponding to the given basis set; the basis sets are ordered according to the optimized energies obtained. One can see that for the basis sets investigated, the error of the approximate energy decomposition does not exhibit any systematic change for the basis sets considered. (The selection of basis sets was limited by the fact that program APOST [2] does not actually handle f or g functions.) Thus the error in Eq. (1) can be considered as "white noise" having no physical significance [1]. The sum of the absolute values of the overlap energy components decreases monotonically (with a single minor exception) with the decrease of the total energy, while the basis extension terms exhibit a maximum-type behavior characteristic for the basis set superposition error known from the theory of intermolecular interactions: the sum of the absolute values of the basis extension terms first increases with the improvement of the basis set and then starts to decrease. Obviously, at very large basis sets only the electrostatic and exchange energy

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[5] It is to be noted, however, that in the AIM framework the B–B interaction has been found to be strongly repulsive [5]. This discrepancy should be attributed to some defects of the AIM description of this rather peculiar system: the AIM analysis of diborane was not possible by using the 6-31G** basis because of the bad location of the bond critical points, and the 6-31G* basis was used instead [5] – obviously still with problematic results. The present CECA results are practically not influenced by such a change in the basis set applied. We also note that the energy decomposition based on the virial theorem also gave a considerable negative boron–boron energy contribution. (Such a decomposition is applicable in stationary points only and utilizes the fact that the kinetic energy operator has only one and two-center integrals. It is as accurate as the virial theorem is fulfilled – for diborane in the 6-31G** basis the virial ratio was 1.9988.)

Table 5. Some quantities characterizing the basis set dependence of the method calculated for the ethane molecule

Basis set	Self-consistent-field energy	Sum of one- and two-center energy components	Sum of absolute values of overlap energy components	Sum of absolute values of basis extension energy components
4-31G	−79.115933	−79.135601	1.467463	0.081833
6-31G	−79.197572	−79.208639	1.398243	0.068657
6-311G	−79.211802	−79.205658	1.211679	0.067432
6-31G*	−79.228755	−79.242279	1.157352	0.165937
6-31G**	−79.238235	−79.248922	0.822349	0.264644
6-31++G**	−79.238860	−79.232905	0.740889	0.267424
6-311G**	−79.251708	−79.236252	0.400110	0.195686
6-311++G**	−79.251935	−79.239413	0.427612	0.194903
6-311++G(2d,2p)	−79.257004	−79.237449	0.277484	0.025893

components of the diatomic energy components will survive. (As already noted, the overlap energy components may be attributed a physical meaning for moderate basis sets of atomic character but not for truly large basis sets.)

4 Conclusions

The recent CECA permits the total energy of a molecule to be presented approximately but to good accuracy as a sum of atomic and diatomic energy contributions [1]. Here the diatomic energy components are further decomposed into terms of different physical origin: electrostatics (in the point-charge approximation and the distributed charge corrections), exchange effects, diatomic overlap and atomic basis extension terms. This analysis may provide deeper insight into the factors influencing both the chemical bonds and the nonbonded interatomic interactions.

The illustrative calculations performed for some simple model systems are in good agreement with the chemical expectations. The diatomic interaction of the chemically bonded atoms is dominated by the exchange energy contribution constituting about half of the respective energy components; the other three energy contributions are also negative and of comparable value. The interaction of non-bonded atoms which are sufficiently close to each other, like geminal hydrogens, is dominated by repulsive overlap energy components. Atoms at larger distances, if they have any considerable resulting interaction at all, exhibit mostly electrostatic effects, which can be estimated semiquantitatively on the basis of the simplest point-charge approximation.

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References

1. Mayer I (2000) Chem Phys Lett 332: 381
2. Mayer I, Hamza A (2000) APOST, version 1.0. http://occam.chemres.hu/programs or (ftp://)kvk.chemres.hu
3. Mayer I, Hamza A (2001) Theor Chem Acc 105: 360
4. Bader RFW (1990) Atoms in molecules: a quantum theory. Oxford University Press, Oxford
5. Salvador P, Duran M, Mayer I (2001) J Chem Phys 115: 1153
6. Sierraalta A, Frenking G (1997) Theor Chim Acta 95: 1
7. Bikádi Z, Keresztúri G, Holly S, Egyed O, Mayer I, Simonyi M (2001) J Phys Chem A 105: 3471
8. Mayer I (1983) Int J Quantum Chem 23: 341
9. Mayer I, Hamza A (2003) Int. J. Quantum Chem 92: 174
10. Mayer I (2003) Simple theorems, proofs, and derivations in quantum chemistry. Kluwer/Plenum, New York (in press)
11. Mayer I (1995) Chem Phys Lett 242: 499
12. Mayer I (1996) J Phys Chem 100: 6249
13. (a) Mayer I (1983) Chem Phys Lett 97: 270; (b) Addendum (1985) Chem Phys Lett 117: 396
14. Jeziorski B, Moszynski R, Szalewicz K (1994) Chem Rev 94: 1887, and references therein
15. Mayer I (1989) J Mol Struct (THEOCHEM) 186: 43