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Partitioning Scheme for the *ab initio* SCF Energy

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As a tool for the interpretation of *ab initio* SCF calculations, an energy partitioning scheme is presented. When performed within an orthogonalized basis, the scheme allows the deduction of well transferable, almost basis independent two-center terms which characterize bond strengths and non-bonded interactions. The results for a large number of molecules are given. The construction of an orthogonal minimal basis (OMBA) from arbitrary basis sets as a generalization of the symmetrical orthogonalization is described. The transferability of Fock matrix elements is discussed. The energy partitioning quantities are related to the corresponding terms obtained with the semi-empirical schemes CNDO and MINDO/3.

Key words: Energy partitioning

1. Introduction

For the semi-empirical methods CNDO [1] and MINDO [2] an energy partitioning scheme was proposed [3, 4] in which the total energy was broken down into one- and two-center terms:

$$E=\sum_{A>B} E_{AB}+\sum_{A} E_{A} \qquad (1)$$

The individual terms were dissected further into their physical components which were for the two-center terms:

$$E^{R}_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B} P_{\mu\nu}h_{\mu\nu}$$

$$E^{K}_{AB}=-\tfrac{1}{2}\gamma_{AB}\sum_{\mu\in A}\sum_{\nu\in B} P^{2}_{\mu\nu}$$

$$E_{AB}^{V}=-P_{A}V_{AB}-P_{B}V_{BA};\quad P_{A}=\sum_{\mu\in A}P_{\mu\mu}$$

$$E_{AB}^{J}=P_{A}\cdot P_{B}\cdot\gamma_{AB}$$

$$E_{AB}^{N}=\frac{Z_{A}\cdot Z_{B}}{R_{AB}}$$

where P denotes the bond order, h the one-electron operator matrix, V_{AB} nuclear electron attraction and γ_{AB} electron–electron repulsion matrix elements. The resonance energy E_{AB}^{R} and the comparatively small contribution of the electron exchange E_{AB}^{K} depend on the bond orders between basis orbitals at the centers A and B and can thus be viewed as the one-electron and the two-electron part of the interference energy [8–11] of the bond A–B. E_{AB}^{V}, E_{AB}^{J}, E_{AB}^{N}, on the other hand, are potential energy terms depending on the charge densities and nuclear charges of the atoms A and B.

The energy partitioning scheme was applied to many organic systems [3–7]. As it turned out, the quantities E_{AB} and E_{AB}^{R} are well transferable between different molecules and their variation reflects observed trends in bond strengths while the potential energy terms cancel to a large extent. In addition, non-bonded interactions characterized by E_{AB} or E_{AB}^{R} made up for the calculated energy differences between the conformers of ethane [3, 6].

The development of a corresponding partitioning for the *ab initio* SCF energy seemed to be desirable. Such a scheme should fulfil the following criteria: it should allow

1) the analysis of bonding and of non-bonded interactions in larger molecules,
2) the characterization of bonds in terms of energy quantities, which should be transferable between different molecules and should depend little on the basis set used,
3) the comparison with the corresponding quantities of semi-empirical methods. Thus, it should enable the analysis of semi-empirical schemes and the tracking down of failures of those methods to their origin in the parametrization or the formula used.

Ab initio energy partitioning schemes reported in the literature so far [9–11] were based on Ruedenberg's theory of bond formation [8]. Moffat and Popkie [9] applied their partitioning method particularly to CN triple bonds. They found that the criteria 1 and 2 were not well satisfied though the sharing penetration energy of similar bonds in different molecules assumed similar values. Driessler and Kutzelnigg [10, 11] partitioned a model energy expression which allowed for left-right correlation. They obtained a consistent picture of the basic principles underlying the formation of a chemical bond [10]. In addition, they studied the conditions under which their energy expression could be reduced to energy formulae which have been applied in some semi-empirical schemes [11].

In the following a partitioning scheme for the *ab initio* SCF energy is presented which is aimed at the fulfilment of the three criteria described above. Our scheme is related to the semi-empirical partitioning method and gives the most consistent results when performed within an orthogonalized atomic orbital basis.

2. The Energy Partitioning Scheme

It is not possible to apply the scheme of the partitioning of the semi-empirical SCF energy to the *ab initio* SCF energy for two reasons:

1) The SCF energy

$$E=\sum_{\mu,\nu} P_{\mu\nu}h_{\mu\nu}+\tfrac{1}{4}\sum_{\mu,\nu} P_{\mu\nu}\sum_{\rho,\sigma} P_{\rho\sigma}\{2(\mu\nu\mid\rho\sigma)-(\mu\rho\mid\nu\sigma)\}\sum_{A>B}\frac{Z_A\cdot Z_B}{R_{AB}} \tag{3}$$

   contains 3- and 4-center terms in the electron repulsion part which cannot be neglected. In the semi-empirical schemes like CNDO and MINDO 3- and 4-center repulsion integrals do not occur (neglect of differential overlap, NDO [12]).

2) As a consequence of the non-orthogonality of the atomic orbital basis the off-diagonal elements $h_{\mu\nu}$ of the one-particle operator contain a considerable amount of potential energy originating even from those nuclei in a molecule which are far away from the orbitals μ and ν. The excellent transferability of the E^R_{AB} values of the semi-empirical methods is a consequence of the fact that in semi-empirical theories the $h_{\mu\nu}$ elements depend only on the orbitals μ and ν and not on the surrounding.

Equivalent to Eq. (3), the total SCF energy of a molecule can as well be written in the form

$$E=\tfrac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(h_{\mu\nu}+f_{\mu\nu})+\sum_{A>B}\frac{Z_A\cdot Z_B}{R_{AB}} \tag{4}$$

where f denotes the Fock matrix.

It can now formally be dissected into one- and two-center terms according to Eq. (1) with

$$E_A=\tfrac{1}{2}\cdot\sum_{\mu,\nu\in A} P_{\mu\nu}(h_{\mu\nu}+f_{\mu\nu})+\tfrac{1}{2}Z_A\cdot\sum_{B\neq A}\frac{Z_B}{R_{AB}} \tag{5}$$

and

$$E_{AB}=\sum_{\mu\in A}\sum_{\nu\in B} P_{\mu\nu}(h_{\mu\nu}+f_{\mu\nu}) \tag{6}$$

In the Eqs. (5) and (6) the three- and four-center electron repulsion integrals of Eq. (3) are contracted to one- and two-center terms via the Fock matrix elements. Within semi-empirical methods for E_{AB} of Eq. (6) the following expression is obtained:

$$E_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B} P_{\mu\nu}h_{\mu\nu}-\tfrac{1}{2}\sum_{\mu\in A}\sum_{\nu\in B} P^2_{\mu\nu}\gamma_{AB}=E^R_{AB}+E^K_{AB} \tag{7}$$

Thus, E_{AB} of Eq. (6) consists within semi-empirical schemes only of the contributions of the resonance energy and of the electron exchange energy (E^K_{AB}) to the bond and does not contain any of the electrostatic energy terms which are absorbed by the one-center terms of Eq. (5). Within CNDO and MINDO, however, the bond-order dependent quantities E^R_{AB} and $E^R_{AB}+E^K_{AB}$ have proven to be well transferable quantities which are characteristic for bond strengths and for non-bonded interactions as well. Hence, one might expect that the two-center energies defined by Eq. (6) and obtained from *ab initio* SCF calculations have the same favorable properties as they had in CNDO and MINDO.

Within *ab initio* the E_{AB} can be dissected further into the following physical components which are

1) the kinetic energy

$$E^T_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B}P_{\mu\nu}T_{\mu\nu} \tag{8}$$

2) the potential energy

$$E^V_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B}P_{\mu\nu}V_{\mu\nu} \tag{9}$$

3) the electron–electron interaction energy

$$E^J_{AB}=\sum_{\mu\in A}\sum_{\nu\in B}P_{\mu\nu}(f_{\mu\nu}-h_{\mu\nu}) \tag{10}$$

Finally, we would like to define the quantity F_{AB} as

$$F_{AB}=E_{AB}+E^J_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B}P_{\mu\nu}f_{\mu\nu} \tag{11}$$

We interpret F_{AB} as the energy of the bond A–B containing as a part of its potential energy essentially the interaction with all other electron pairs as well.

As long as we use Eq. (6) within a non-orthogonal basis we cannot expect the E_{AB} values to be transferable between different molecules since the potential energy terms E^V_{AB} and E^J_{AB} will depend on the surrounding of the bond A–B. However, in the F_{AB} values the different contributions of the potential energy are expected to cancel to some extent. As has been shown by O'Leary *et al.* [13], Fock matrix elements are in fact well transferable between different molecules as long as the same basis is used. The transferability of Fock matrix elements applies also to orthogonalized basis orbitals [13, 14].

In the following we present numerical results for the two-center terms of our energy partitioning scheme applied to
1) non-orthogonal basis sets (Section 4) and to
2) orthogonalized basis sets (Section 8), for which a better cancellation of potential energy contributions can be expected [16].

The discussion in this paper will be restricted to the two-center terms. The one-center terms of Eq. (5) contain atomic energies as well as potential energy contributions originating from distant atoms. Within the partitioning scheme given here, it did not seem to be possible to extract meaningful quantities from the one-center terms.

3. Computational Methods

The *ab initio* SCF program used is based on the integral program developed by Ahlrichs [17]. Three different types of basis sets were used:

1) Minimal basis (MB): A 5.2/2 Gaussian basis contracted to (2,1/1) was used in some of the calculations on hydrocarbons. The optimum exponents and contraction coefficients were obtained from molecular calculations [18].
2) Double zeta basis (DZ): A 7.3/3 Huzinaga basis [19] contracted to (4,1,1,1/2,1) was applied. DZ+D denotes the double zeta basis augmented by a set of *d*-functions at the heavy atoms with an exponent of 1.0.
3) Triple zeta basis (TZ) denotes a Huzinaga 9.5/5 basis contracted to (5,1,1,1,1/3,1,1).

The energy partitioning program was written in FORTRAN. For the construction of the orthogonalized basis a localization procedure was needed. We used a modification of the Edmiston–Ruedenberg method [20]. Depending on the definition of the distance function in the localization procedure we were able to obtain either orthogonalized hybrid orbitals or orthogonalized Cartesian AO's. Since the electron repulsion integrals were not used as the distance function, the localization procedure needed no more computer time than the localization of Boys [15].

For the semi-empirical calculations we used the MINDO/3 method [2] and a modified CNDO procedure which was parametrized for hydrocarbons in order to yield satisfactory heats of atomization and bond lengths [21].

4. Energy Partitioning within a Non-Orthogonal Basis

When an energy partitioning analysis according to the Eqs. (6, 8–11) is performed within a non-orthogonal basis one will expect that the electrostatic terms of a bond E^V_{AB} and E^J_{AB} will depend not only on the bond under consideration but also very much on its surrounding.

In Table 1 the physical components of some standard bonds in several smaller molecules obtained with a double zeta basis are shown. The potential energy contributions E^V_{AB} as well as the total energy of a bond E_{AB} are increasing with an increasing size of the molecule. That is best demonstrated in the table by the behavior of the CH bonds: in absolute value, the E_{CH} value in ethane is about 30% larger than the corresponding value in methane. In Table 2, where the MB values for a number of larger molecules are listed, cases can be found in which these effects are even more pronounced (e.g. E_{CH} in CH_4 vs. E_{CH} in benzene).

Table 1. The physical components of two-center contributions within a non-orthogonal basis (DZ) (values in a.u.)

Type	Length (Å)	Molecule	E^T_{AB}	E^V_{AB}	E^J_{AB}	E_{AB}	F_{AB}
C–H	1.10	CH_4	0.335	−4.089	1.500	−2.352	−0.752
		C_2H_6	0.343	−5.623	2.255	−3.025	−0.770
		C_2H_4	0.335	−5.333	2.102	−2.897	−0.795
		CH_2O	0.297	−5.185	2.031	−2.858	−0.827
	1.06	C_2H_2	0.327	−4.551	1.736	−2.488	−0.752
		HCN	0.312	−4.523	1.702	−2.509	−0.807
N–H	1.02	NH_3	0.372	−4.153	1.504	−2.278	−0.774
O–H	0.96	OH_2	0.316	−4.412	1.664	−2.432	−0.768
F–H	0.92	FH	0.413	−3.657	1.281	−1.963	−0.682
C–C	1.53	C_2H_6	0.306	−5.268	2.158	−2.804	−0.646
C=C	1.33	C_2H_4	0.608	−10.013	4.037	−5.368	−1.331
C≡C	1.20	C_2H_2	1.025	−15.588	6.298	−8.265	−1.968
C≡O	1.13	CO	0.976	−9.332	3.532	−4.824	−1.293
C=O	1.22	CH_2O	0.717	−9.436	3.703	−5.017	−1.314
N≡N	1.10	N_2	1.076	−10.469	3.833	−5.560	−1.727
N–N	1.48	N_2H_4	0.318	−4.740	1.902	−2.520	−0.618
O–O	1.48	O_2H_2	0.344	−3.707	1.462	−1.901	−0.439
F–F	1.42	F_2	0.343	−3.338	1.282	−1.713	−0.429

Table 2. Two-center energies of hydrocarbons within a non-orthogonal basis (MB) (values in a.u.)

Type	Length (Å)	Molecule	$-E_{AB}$	$-F_{AB}$
C≡C	1.20	C_2H_2 acetylene	7.216	1.432
C=C	1.33	C_2H_4 ethylene	5.378	1.066
	1.34	C_3H_6 propene	6.541	1.076
	1.34	C_4H_6 1,3 butadiene	6.988	1.051
	1.32	C_4H_4 cyclobutadiene	7.451	1.103
C⋯C	1.40	C_6H_6 benzene	7.553	0.876
	1.40	$C_3H_3^+$ cyclopropenyl$^+$	4.526	1.006
	1.40	$C_3H_5^+$ allyl$^+$	5.553	1.190
	1.40	$C_2H_5^+$ ethyl$^+$ (class.)	4.121	1.012
	1.40	$C_2H_5^+$ ethyl$^+$ (non-cl.)	4.445	1.182
C–C	1.53	C_2H_6 ethane	3.442	0.640
	1.53	C_3H_6 propene	4.105	0.673
	1.53	C_4H_4 cyclobutadiene	3.931	0.596
	1.52	C_3H_6 cyclopropane	3.559	0.561
	1.51	C_4H_4 tetrahedrane	3.406	0.468
	1.48	C_4H_6 1,3 butadiene	5.062	0.708
C–H	1.10	CH_4 methane	2.257	0.685
	1.10	C_2H_6 ethane	3.021	0.694
	1.10	C_6H_6 benzene	4.700	0.710
	1.10	$C_3H_3^+$ cyclopropenyl$^+$	3.263	0.931
	1.10	$C_2H_5^+$ ethyl$^+$ (non-cl.)	3.042	0.954
	1.10	C_2H_4 ethylene	2.858	0.703
	1.06	C_2H_2 acetylene	2.694	0.727
C⋯H	1.30	$C_2H_5^+$ ethyl$^+$ (non-cl.)	1.240	0.368

In the F_{AB} values, which include the electron repulsion of all the electron pairs, those annoying effects of the potential energy present in the E_{AB} values cancel to a large extent. Thus, the F_{CH} values in methane and in ethane differ by less than 3%. Certainly, the cancellation of the different types of potential energies (nuclear-electron attraction vs. electron repulsion) is not complete. Thus, in the DZ basis the F_{CH} value of the very strong CH bond in acetylene is in its absolute value slightly smaller than that of the CH bond in ethane. Nuclear attraction and electron repulsion cancel to a different extent in neutral molecules and in ions. Thus, the F_{CH} values in cations are about 30% larger than in neutral hydrocarbons. However, also in polar neutral molecules the F_{AB} values are influenced by the charge distribution in the molecule. The F_{CH} value in formaldehyde (CH_2O) is comparatively large because the H atom is bound to a partially positive carbon atom. The relatively small values of F_{OH} in H_2O and of F_{FH} in HF are a consequence of the partial negative charge of the O and the F atom, respectively. The same trend can be seen when the CH bonds in HCN and acetylene are compared.

As the comparison of the Tables 1 and 2 indicates, the F_{AB} values depend also on the basis set. Thus, the double zeta value for F_{CC} (Table 1) in acetylene is about 40% larger than F_{CC} obtained with the minimal basis (Table 2). This behavior is related to the observation of O'Leary *et al.* [13] that Fock matrix elements are sensitive to changes in the basis set.

We conclude that F_{AB} values are satisfactorily transferable between different molecules only as long as the same basis is used and the bonds compared do not differ in their polarity. Some general trends in bond strengths (triple vs. double bonds, etc.) are reproduced by the F_{AB} values. Finally, we note that of the two-center terms, the kinetic energy E_{AB}^{T} and the electron interaction energy E_{AB}^{J} have a positive sign, while only the electron nuclear attraction gives a negative (i.e. bonding) contribution. The components of the actual bonding energy are expected to have just the opposite sign [8, 10]. We will come back to this point in Section 8.1.

5. The Construction of an Orthogonalized Minimal Basis (OMBA)

In the case of a non-orthogonal minimal basis the simplest procedure for obtaining an orthogonalized basis is the well known symmetrical orthogonalization of Löwdin [22] which preserves the transformation properties of the basis and yields an orthogonal basis resembling the initial basis as closely as possible. In the case of more extended basis sets one has to deal with the problem of the contraction of the basis to a minimal basis. For non-orthogonal basis sets a solution of this problem was recently given by Heinzmann and Ahlrichs [23] who proposed the so-called MAO's for a basis independent population analysis. For the construction of an orthogonalized minimal basis (OMBA) we developed a procedure which can be applied also to extended basis sets and which can be viewed as a generalization of the symmetrical orthogonalization. The procedure consists of the following five steps:

1) A trial non-orthogonal minimal basis is constructed (for details see below in this section).

2) The occupied MO's are projected into the trial basis.
3) The orthogonal complement to the projected MO's is constructed in the space of the trial basis.
4) The projected MO's of step 2 are replaced by the original MO's and the orthogonal complement (step 3) is orthogonalized with respect to the MO's. In this step a set of vectors is obtained, the number of which is equal to the number of minimal basis vectors regardless of the size of the actual basis. This set of vectors consists of the occupied MO's and a set of virtual orbitals composed of valence AO's (denoted in the following as virtual valence MO's).
5) The minimal orthogonal basis can now be obtained by a total localization of the vectors constructed in step 4. We decided to localize the core MO's separately in order to avoid any mixing between core and valence AO's (cf. Section 8.5). Preceding the total localization, the occupied and virtual valence MO's are localized separately in order to study the transferability of Fock matrix elements (Section 6).

The contraction coefficients of the trial non-orthogonal minimal basis (step 1) can simply be obtained from the diagonal elements of the bond order matrix. In order to ensure that the basis obtained is approximately covariant with respect to coordinate transformations, the contraction coefficients of the three Cartesian p functions have to be averaged. Alternatively, a trial minimal basis with the correct transformation properties can be constructed using the condition that the trial basis should have maximum overlap with the occupied MO's. The condition reads:

$$W = \sum_j \langle \varphi_j, \chi_k \rangle^2 = \text{maximum for each } k \tag{12}$$

where φ_j are the occupied MO's and the χ_k denote the basis orbitals which are to be constructed. As can be easily derived, the orbitals χ_k are then obtained from the eigenvalue equation

$$A\chi_k = \varepsilon_k \cdot S \cdot \chi_k \tag{13}$$

as the eigenvectors belonging to the largest eigenvalues ε_k where the matrices A and S are defined as follows:

S is the overlap matrix with respect to the original (non-minimal) basis. With the imposed condition that the χ_k should be strictly localized at atomic centers the matrix A is obtained as:

$$A = [SPS]_{\text{blocked}} \tag{14}$$

i.e. in the matrix SPS (where P is the bond order matrix) all elements have to be set to zero which belong to interactions of basis functions located at different atomic centers. Instead of Eq. (14) we rather used:

$$A = S_{\text{blocked}} P_{\text{blocked}} S_{\text{blocked}} \tag{15}$$

The χ_k obtained from Eq. (13) with the matrix A of Eq. (15) maximize the intraatomic part of the overlap between the MO's φ_j and the AO's χ_k. The basis orbitals χ_k are closely related to the MAO's of Heinzmann and Ahlrichs [23].

6. Properties of Localized Occupied and Virtual Valence MO's

From other investigations [24] it is known that Fock matrix elements with respect to localized MO's are well transferable between molecules and depend little on the basis set used. In Section 5 the construction of localized virtual valence MO's was described as an intermediate step in the construction of the OMBA. In Table 3 MO energies (i.e. diagonal Fock matrix elements) of localized occupied and virtual valence MO's are listed. The results show that the MO energies of the virtual orbitals are transferable between molecules as well as those of the occupied MO's. For hydrocarbons the results are given for two different basis sets (DZ and MB). The energies of the occupied MO's seem to depend somewhat less on the basis set than the orbital energies of the virtual MO's, though also the latter differ in general by less than 5% between the two basis sets.

Table 3. Energies of Localized Occupied and Virtual Valence MO's (values in a.u.)

		Occupied	MO's	Virtual	MO's
Type	Molecule	DZ	MB	DZ	MB
C–H	C_2H_2	−0.737	−0.714	0.865	0.785
„	C_2H_4	−0.673	−0.650	0.760	0.717
„	C_2H_6	−0.643	−0.633	0.726	0.694
„	CH_4	−0.641	−0.633	0.717	0.684
N–H	NH_3	−0.750	—	0.696	—
O–H	OH_2	−0.842	—	0.657	—
F–H	FH	−0.950	—	0.615	—
σ–C–C	C_2H_2	−0.998	−0.944	1.376	1.454
„	C_2H_4	−0.841	−0.831	0.993	1.009
„	C_2H_6	−0.675	−0.675	0.668	0.669
π	C_2H_2	−0.405	−0.387	0.295	0.329
„	C_2H_4	−0.376	−0.367	0.221	0.258
„	C_3H_6 propene	—	−0.362	—	0.274
„	C_4H_6 butadiene	—	−0.369	—	0.271
„	c-C_4H_4	—	−0.366	—	0.274
„	c-C_6H_6	—	−0.379	—	0.289
„	N_2	−0.611	—	0.211	—
„	CO	−0.632	—	0.205	—
„	CH_2O	−0.518	—	0.168	—

The transferability of MO energies is of some consequence for the properties of the Fock matrix elements with respect to the OMBA:

Let us consider a non-polar two-center bond for which a localized MO φ_1 and a corresponding virtual MO φ_2 was obtained. Then two OMBA's χ_1 and χ_2 can be written in the form:

$$\chi_1 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$$
$$\chi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2) \tag{16}$$

The Fock matrix elements with respect to the OMBA can then be expressed by the f matrix elements with respect to the localized MO's by the relation

$$f_{11}^{\mathrm{OMBA}} = f_{22}^{\mathrm{OMBA}} = \tfrac{1}{2}(f_{11}^{\mathrm{LMO}} + f_{22}^{\mathrm{LMO}})$$
$$f_{12}^{\mathrm{OMBA}} = \tfrac{1}{2}(f_{11}^{\mathrm{LMO}} - f_{22}^{\mathrm{LMO}}) \tag{17}$$

Since the Fock matrix elements with respect to the LMO's are transferable between different molecules and depend little on the basis set, the Fock matrix elements with respect to the OMBA are expected to have the same desirable properties. In fact, it was shown in previous studies [13, 14] that for hydrocarbons Fock matrix elements with respect to symmetrically orthogonalized basis sets are well transferable between different molecules.

7. Population Analysis within the OMBA

Within any orthogonal basis the sum of the diagonal elements of the bond order matrix is equal to the number of electrons. Thus, a population analysis within the OMBA is very simple and atomic gross populations are obtained as the sum of the corresponding diagonal bond order matrix elements. In Table 4 the populations of hydrogen atoms in different molecules are compared with the corresponding Mulliken [25] populations for two basis sets (MB and DZ). In the case of the minimal basis, the OMBA populations are very similar to the Mulliken populations, while within the DZ basis the net positive charge at the hydrogens is

Table 4. Atomic gross populations of hydrogen atoms in different molecules.

	Mulliken		OMBA	
Molecule and position	MB	DZ	MB	DZ
CH_4	0.94	0.83	0.96	0.89
C_2H_6	0.95	0.82	0.96	0.89
C_2H_4	0.95	0.81	0.96	0.88
C_2H_2	0.93	0.70	0.93	0.78
HCN	—	0.66	—	0.77
$C_2H_5^+$ (non-cl.) α–H bridge	0.81	0.64	0.85	0.74
"	0.79	0.69	0.81	0.76
NH_3	—	0.74	—	0.83
OH_2	—	0.66	—	0.76
FH	—	0.57	—	0.68

considerably smaller when calculated from the OMBA instead of taking it from the Mulliken populations. The OMBA populations depend somewhat less on the basis than the Mulliken populations.

Within an orthogonal basis, also the off-diagonal elements of the bond order matrix have some meaning. In π-theory they were quite generally related to bond strengths and bond lengths [26]. Since we have to deal with bonds in which more than two basis orbitals are participating, individual bond order matrix elements cannot be used for the characterization of a bond. Thus, we calculated the bond order square [41] of a bond according to

$$B_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2 \tag{12}$$

Table 5. Bond order squares with respect to the OMBA for CC and CH bonds obtained from minimal basis SCF calculations

Type	Molecule	$2s$–$2s$	σ (sum)	π	π'	Total
C–C	C_2H_6	0.062	0.992	0.013	0.013	1.018
	Cyclopropane	0.043	0.978	0.012	—	0.990
	Tetrahedrane	0.036	0.750	—	—	0.750
$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$	Benzene	0.111	0.990	0.444	0.017	1.451
C=C	C_2H_4	0.144	0.988	1.000	0.029	2.017
C≡C	C_2H_2	0.277	0.988	1.000	1.000	2.988
C–H	CH_4	0.247	0.992	—	—	0.992
	C_2H_6	0.246	0.984	—	—	0.984
	C_2H_4	0.299	0.980	—	—	0.980
	C_2H_2	0.446	0.984	—	—	0.984
	Cyclopropane	0.291	0.980	—	—	0.980
	Tetrahedrane	0.406	0.974	—	—	0.974
C···H	$C_2H_5^+$ (non-cl.)	0.051	0.474	—	—	0.474

Results for hydrocarbons are listed in Table 5. Single bonds have B_{AB} values of about 1, double bonds of around 2 and triple bonds of about 3. The definition of B_{AB} is related to the definition of bond orders given by Jug [27]. His σ bond order is the square root of the σ part of B_{AB}. Jug then adds the π bond orders separately. Noteworthy are the small s characters found in Table 5 for C–C bonds in strained ring systems like cyclopropane and tetrahedrane. The C–H bonds in these systems have a comparatively large s character. The bond order could be used for an explicit definition of hybridization indices. Since there is not a unique choice for such a definition, this problem is not discussed further in the present paper.

σ bond orders are usually close to one as long as the σ bond is adequately described by a localized two-center MO. If only a multi-center MO is responsible for the formation of a bond, the bond orders become smaller as in the case of the C··H bond in the non-classical ethyl cation, where a B_{AB} value of about 0.47 is obtained. A notable exception seems to be the C–C bond in the tetrahedrane molecule for which we calculate the B_{CC} to be only about 0.75, indicating that in this highly strained system it is no longer possible to construct reasonably well bonding two-center bent bonds. Obviously, the two highest occupied MO's in tetrahedrane are only weakly bonding. In cyclopropane, on the other hand, the bent bonds have still a B_{AB} value of about 1.

We conclude that the OMBA can serve as a basis for population analysis and for the calculation of bond orders which provide useful information about bonding situations in molecules. Though they do not reproduce minor changes in bond strengths (e.g., the B_{CC} values in ethane and in cyclopropane are about the same, though the CC bond in cyclopropane is considerably weaker than in ethane), they have the advantage of being very insensitive towards changes in bond lengths and other minor changes of geometrical parameters.

8. Energy Partitioning within the OMBA

8.1. The Physical Components of the Two-Center Energies

In the case of a one-electron two-center bond (e.g. H_2^+) the bonding energy ΔE within minimal basis is for large distances simply given by

$$\Delta E = (1 - S_{12}) h_{12}^{\mathrm{OAO}} = (1 - S_{12}) E_{12} \tag{19}$$

where S_{12} is the overlap between the two non-orthogonal basis vectors and h_{12}^{OAO} is the one-electron operator matrix element with respect to the corresponding symmetrically orthogonalized basis AO's (which are identical with the OMBA orbitals in this case) and E_{12} is the two-center energy defined in Eq. (6). The relationship (19) may be considered as a justification for the description of bond strengths with two-center energies computed from matrix elements with respect to orthogonalized basis sets.

Let us now consider the interaction of two He atoms, where the bonding and the anti-bonding orbitals are both doubly occupied. Within minimal basis the interaction energy for large distances is given by

$$\Delta E = 2(1 - S_{12}) h_{12}^{\mathrm{OAO}} - 2(1 + S_{12}) h_{12}^{\mathrm{OAO}} = -4 S_{12} h_{12}^{\mathrm{OAO}} \geqslant 0 \tag{20}$$

The E_{12} is zero in this case, since P_{12}^{OAO} vanishes. Quite generally, interaction energies which arise from the penetration of doubly occupied orbitals appear in our scheme in the diagonal elements E_A of Eq. (5) together with all other electrostatic interactions. The ΔE of Eq. (20) represents usually fairly small quantities, since the overlap between electron pairs are comparatively small (<0.25) in normal molecules and the h_{12}^{OAO} is also proportional to S for larger distances.

In Table 6 we have listed the physical components of the two-center contributions according to the Eqs. (8–11) for different types of bonds calculated with the DZ basis. Striking is the fact that the different physical components, kinetic energy, potential energy and electron–electron interaction, have just the opposite sign than they have within the non-orthogonal basis (cf. Table 1). However, it is the sign of the

Table 6. The physical components of two-center contributions within the OMBA (values in a.u., SCF calculations with DZ basis)

Molecule	Bond	E^T_{AB}	E^V_{AB}	E^J_{AB}	$-E_{AB}$	$-F_{AB}$
H_2	H–H	−0.881	0.145	−0.229	0.965	1.195
C_2H_2	C–H	−1.885	1.458	−0.543	0.970	1.513
C_2H_4	,,	−1.705	1.378	−0.527	0.854	1.381
C_2H_6	,,	−1.594	1.242	−0.559	0.843	1.334
CH_4	,,	−1.594	1.152	−0.449	0.891	1.340
NH_3	N–H	−1.789	1.293	−0.456	0.954	1.410
OH_2	O–H	−1.952	1.407	−0.457	1.001	1.458
FH	F–H	−2.135	1.578	−0.461	1.019	1.481
C_2H_2	C≡C total	−5.045	4.100	−1.414	2.360	3.774
	π only[a]	−0.783	0.803	−0.360	0.340	0.700
C_2H_4	C=C total	−3.456	2.753	−0.917	1.620	2.537
	π only	−0.640	0.681	−0.319	0.278	0.597
	π′ only	−0.168	0.179	−0.049	0.038	0.086
C_2H_6	C–C total	−2.201	1.889	−0.559	0.871	1.430
	π only[a]	−0.078	0.085	−0.023	0.016	0.038
N_2H_4	N–N	−2.216	1.996	−0.552	0.772	1.324
O_2H_2	O–O	−1.965	1.904	−0.514	0.575	1.089
F_2	F–F	−2.005	2.051	−0.537	0.491	1.028
N_2	N≡N total	−5.369	3.911	−1.381	2.839	4.220
	π only[a]	−1.002	0.985	−0.403	0.420	0.823
CO	C≡O total	−4.747	3.366	−1.061	2.442	3.502
	π only[a]	−0.848	0.833	−0.316	0.331	0.647

[a] Values refer to one of the two equivalent π contributions.

matrix elements with respect to the orthogonalized basis orbitals which determines whether an energy term yields a bonding or an anti-bonding contribution to a bond. According to Table 6, the kinetic energy E^T_{AB} and the electron–electron interactions E^J_{AB} result in bonding, while the potential energy contributes to the repulsive part of the bond. This result is in accordance to more thorough analyses of the origin of the chemical bond [10, 28, 29]. Goddard *et al.* [29] found that bonding in covalent bonds can be traced back to the "exchange part of the kinetic energy", a quantity which is closely related to the E^T_{AB} with respect to an orthogonalized basis. The negative sign of the off-diagonal elements of the kinetic energy operator with respect to orthogonalized hybrid orbitals was recently discussed by Cook [16].

Since the sum of the diagonal bond order matrix elements within the OMBA is equal to the number of the electrons, the contributions of the potential energy should mainly appear in the diagonal elements of the energy partitioning scheme. If the Mulliken approximation [25] would hold exactly for the potential energy matrix elements with respect to the non-orthogonal basis, the E^V_{AB} with respect to OMBA should vanish [16]. However, as the values given in Table 6 show, the E^V_{AB} values are very large, though the different potential energy contributions cancel to a large extent in the F_{AB} values. The F_{AB} values amount to about 80% of the corresponding E^T_{AB} values.

As it is seen from the Table 6, the kinetic energy E^T_{AB} and the total energy quantities E_{AB} and F_{AB} show a good correlation with bond strengths (cf. Section 8.3), whereas the potential energy contribution E^V_{AB} seems to be influenced by the surrounding (compare CH_4 and C_2H_6), though the effects are much smaller than they were in the non-orthogonal basis (cf. Table 1). As it is well known, the bond strengths decrease considerably in the series CH_3–CH_3, NH_2–NH_2, HO–OH and F–F; the experimental values of the dissociation energies are 88, 71, 51, 37 kcal/mole, respectively [30]. It is interesting that this trend is reproduced by the E_{AB} and the F_{AB} values for these bonds, even though the repulsion of the lone pairs is included in the diagonal terms and gives no contribution to E_{AB} and F_{AB}. The increasing p character of the central bond in the series C_2H_6···F_2 is responsible for the weakening of the bond as reflected by the two-center energy values.

8.2. Dependence of the Two-Center Terms on the Basis Set

Since in *ab initio* SCF calculations usually different basis sets are used, it is important that any quantity which is computed for the purpose of interpretation of the results depends as little as possible on the particular basis set used in the calculation. In Table 7 the two-center terms E_{AB} and F_{AB} are compared for different basis sets:

1) Minimal basis (MB, for hydrocarbons only),
2) Double zeta basis (DZ)
3) DZ+D
4) Triple zeta basis (TZ)

According to the total SCF energy, by far the largest basis improvement is accomplished when going from MB to DZ. In acetylene, for example, the DZ energy

Table 7. Two-Center energies obtained with different basis sets (values in a.u.)

		$-E_{AB}$				$-F_{AB}$			
Bond	Molecule	MB	DZ	DZ+D	TZ	MB	DZ	DZ+D	TZ
H–H	H_2	0.971	0.965	0.960[a]	0.981	1.196	1.195	1.187[a]	1.213
C–H	C_2H_2	0.987	0.970	0.976	0.961	1.462	1.513	1.521	1.497
	C_2H_4	0.907	0.854	0.853	0.856	1.340	1.381	1.384	1.333
	C_2H_6	0.906	0.843	0.841	0.839	1.308	1.334	1.337	1.309
	CH_4	0.929	0.891	0.888	0.878	1.308	1.340	1.340	1.320
N–H	NH_3	—	0.954	0.966	0.955	—	1.411	1.410	1.429
O–H	OH_2	—	1.001	0.995	1.001	—	1.458	1.440	1.498
C–C	C_2H_6	0.997	0.871	0.908	0.889	1.387	1.430	1.449	1.391
C=C	C_2H_4	1.791	1.620	1.671	1.552	2.522	2.537	2.566	2.484
C≡C	C_2H_2	2.612	2.360	2.433	2.259	3.817	3.774	3.829	3.697
N≡N	N_2	—	2.839	3.012	2.791	—	4.220	4.306	4.184
C≡O	CO	—	2.442	2.701	2.393	—	3.502	3.634	3.482
C=O	CH_2O	—	1.836	1.954	1.806	—	2.759	2.821	2.759

[a] DZ+p (exponent 0.65).

is about 0.72 a.u. lower than the MB energy. DZ+D and TZ yield 0.025 and 0.08 a.u. lower energies, respectively, than the DZ basis. When going from MB to DZ, the two-center energies are remarkably stable; for E_{AB} the largest changes amount to about 10%, while the F_{AB} values differ even much less for the two basis sets, at most about 3%. When going from DZ to TZ the two-center terms show variations of not more than 3%. Except for the bonds which contain hydrogen atoms, the two center terms decrease in absolute value with improvement of the basis set, indicating that the basis improvement favors especially the atomic part of the energy. When, however, *d* functions are added to the basis, the E_{XH} and F_{XH} in general change little, while the E_{XX} and F_{XX} values are increasing in absolute value, especially in the case of multiple bonds. By far the largest change is observed in the CO molecule where the increase amounts to about 10% for E_{AB} and about 4% for the F_{AB} value. This shows that the polarization functions are improving especially the bonding region of multiple (π) bonds.

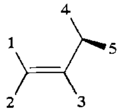
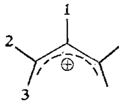
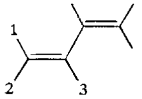
We have seen that in particular the F_{AB} values depend surprisingly little on the basis set used. An energy partitioning analysis seems to be meaningful even if done for a minimal basis calculation only. In addition, F_{AB} values from different molecules may be compared, even if they were obtained from calculations with different basis sets.

8.3. The Transferability of Two-Center Terms

The inspection of the different two-center energy terms (Section 8.1. and Table 6) has revealed that the quantities E^T_{AB}, E_{AB} and in particular F_{AB} show a monotonic variation with bond strength. We have calculated the values of E^T_{AB}, E_{AB} and F_{AB} for a large number of hydrocarbon systems in order to get a comprehensive picture of the different two-center energy terms for a large number of molecules. The results are listed in Table 8.

The analysis of the CH bonds shows that the E_{CH} values, while reproducing some trends correctly (e.g., the CH bond is in acetylene much stronger than in methane), show some dependence on the environment which does not correspond to any changes in bond strengths: for the different CH bonds in 1,3 butadiene, the E_{CH} values differ from each other by up to 5%. In propene, E_{CH} of one of the allylic bonds is about 4% larger than the E_{CH} of one of the olefinic bonds. Finally, the E_{CH} value in benzene is almost 15% smaller in absolute magnitude than the corresponding value in methane. The kinetic energy terms E^T_{AB} and the F_{AB} values give a more consistent picture. In fact, even minor trends are reproduced well: the CH bonds in cyclopropane, cyclobutadiene and in tetrahedrane are stronger than normal sp^3 CH bonds like in methane because of the higher *s* character of the former CH bonds originating from the ring strain. Of the allylic CH bonds in propene, the bond in hyperconjugation to the double bond shows slightly smaller F_{CH} and E^T_{CH} values than the CH bond in the plane of the three carbon atoms. The F_{CH} values for the different CH bonds in butadiene are identical within 0.001 a.u. and differ at most 0.002 a.u. from other normal olefinic CH bonds like in ethylene or in propene.

Table 8. Two-center energies in hydrocarbons (minimal basis; values in a.u.)

Type	Length (Å)	Molecule and position		$-E^T_{AB}$	$-E_{AB}$	$-F_{AB}$
C–H	1.10	CH_4 methane		1.365	0.929	1.308
		C_2H_6 ethane		1.368	0.906	1.308
		C_2H_4 ethylene		1.433	0.907	1.340
		$C_2H_5^+$ ethyl$^+$ (cl.), β ecl.		1.298	0.833	1.202
		other β		1.343	0.867	1.262
				1.412	0.904	1.313
		$C_2H_5^+$ ethyl$^+$ (non-cl.)		1.410	0.896	1.310
		C_3H_6 cyclopropane		1.415	0.886	1.332
		C_3H_6 propene	1	1.433	0.920	1.342
			2	1.433	0.878	1.340
			3	1.442	0.881	1.344
			4	1.372	0.920	1.311
			5	1.364	0.880	1.294
		C_4H_4 tetrahedrane		1.482	0.859	1.367
		C_4H_4 cyclobutadiene		1.494	0.834	1.370
		C_6H_6 benzene		1.457	0.791	1.347
		$C_3H_3^+$ cyclopropenyl$^+$		1.467	0.871	1.337
		$C_3H_5^+$ allyl$^+$	1	1.447	0.868	1.332
			2	1.422	0.881	1.322
			3	1.424	0.924	1.330
		C_4H_6 butadiene	1	1.435	0.916	1.342
			2	1.436	0.871	1.342
			3	1.443	0.881	1.341
	1.06	C_2H_2 acetylene		1.593	0.987	1.462
C···H	1.30	$C_2H_5^+$ ethyl$^+$ (non-cl.)		0.567	0.400	0.718
C–C	1.53	C_2H_6 ethane		1.759	0.997	1.387
		C_3H_6 propene		1.853	0.986	1.431
		C_4H_4 cyclobutadiene		1.643	0.924	1.319
	1.52	C_3H_6 cyclopropane		1.513	0.945	1.272
	1.51	C_4H_4 tetrahedrane		1.377	0.895	1.210
		C_3H_4 cyclopropene		1.493	0.904	1.249
	1.48	C_4H_6 butadiene		2.121	1.071	1.626
C$\overset{\cdots}{-}$C	1.40	C_6H_6 benzene		2.497	1.431	2.035
		$C_3H_3^+$ cyclopropenyl$^+$		2.049	1.307	1.807
		$C_3H_5^+$ allyl$^+$		2.505	1.425	2.053
		$C_2H_5^+$ ethyl$^+$ (cl.)		2.262	1.349	1.836
		$C_2H_5^+$ ethyl$^+$ (non-cl.)		2.097	1.395	1.855
		$C_3H_7^+$ prot. propene		2.117	1.371	1.852
C=C	1.33	C_2H_4 ethylene		2.881	1.791	2.522
	1.34	C_3H_6 propene		2.881	1.731	2.495
		C_4H_6 butadiene		2.831	1.687	2.451
	1.32	C_4H_4 cyclobutadiene		2.734	1.863	2.499
		C_3H_4 cyclopropene		2.665	1.766	2.445
C≡C	1.20	C_2H_2 acetylene		4.316	2.612	3.817

The general trends in bond strengths of the various types of CC bonds are reproduced by the two-center energy components. The ratio of the F_{AB} values for single, double and triple bonds is about 1.0:1.8:2.7. Within the single bonds a marked influence of hybridization (sp^3–sp^3 in ethane vs. sp^3–sp^2 in propene and sp^2–sp^2 in butadiene) and of conjugation can be seen in the two-center terms. The large increase in the two-center terms of the CC single bond in butadiene can partly be attributed to the shortening of that bond to 1.48 Å (cf. Section 8.4). Ring strain leads to a reduction of F_{CC}, E_{CC} and E^T_{CC} values as compared to strain-free systems. This holds for single bonds as well as for double bonds; conjugation of double bonds leads to a reduction of F_{AB} values (butadiene compared to ethylene). The table lists several examples for molecules with C–C bonds which are in between single and double bonds. In these cases a bond length of 1.40 Å was used throughout. Benzene and the allyl cation show about the same F_{CC} values, while the influence of ring strain is reflected in the cyclopropenyl cation. The bonds in the ethyl cations are weaker; they contain only a smaller π contribution which in the case of the classical cation is the consequence of hyperconjugation. The hyperconjugation leads to a weakening of the eclipsed vicinal CH bond as can be seen from the corresponding F_{CH} value.

We conclude that of the two-center energies the F_{AB} and to some extent the E^T_{AB} values are transferable between different molecules and reproduce even minor changes in hybridization and conjugation. Because of the excellent cancellation of far-reaching potential energy contributions in the F_{AB} values, the F_{AB} of corresponding bonds in neutral molecules and in cations are of the same size.

8.4. Dependence of Two-Center Energy Contributions on the Bond Distance

Unlike bond orders, the two-center energy contributions depend strongly on the bond distance. As can be seen from the few examples given in Table 9, a variation of a bond length of 0.05 Å is accompanied by considerable changes in the two-center

Table 9. Dependence of two-center energies on the bond distance (values in a.u.)

						CH-bond		
Type	Molecule	Length (Å)	$-E^T_{CC}$	$-E_{CC}$	$-F_{CC}$	$-E^T_{CH}$	$-E_{CH}$	$-F_{CH}$
C≡C	C_2H_2	1.15	4.575	2.839	4.065	1.599	0.966	1.454
		1.20	4.316	2.612	3.817	1.593	0.987	1.462
		1.25	4.065	2.405	3.586	1.589	1.005	1.469
C=C	C_2H_4	1.28	3.055	1.953	2.695	1.436	0.894	1.334
		1.33	2.881	1.791	2.522	1.433	0.907	1.340
		1.38	2.718	1.645	2.363	1.431	0.918	1.344
C–C	C_2H_6	1.48	1.858	1.094	1.487	1.367	0.898	1.305
		1.53	1.759	0.997	1.387	1.368	0.906	1.308
		1.58	1.669	0.909	1.296	1.369	0.913	1.312
	Butadiene	1.53	1.997	0.969	1.511	1.441	0.889	1.343
	Benzene[a]	1.53	2.042	1.044	1.566	1.453	0.808	1.349

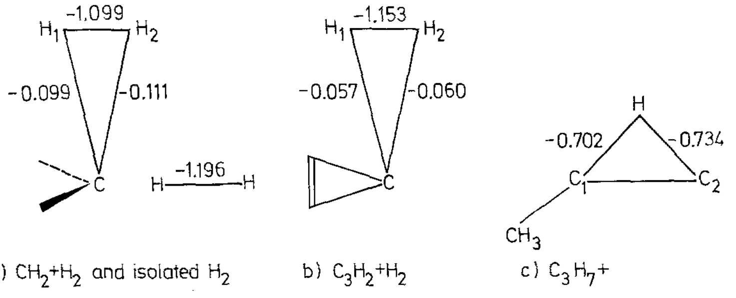
[a] Alternate bonds of 1.53 and 1.34 Å, resp.

terms, which amount to about 6% for the E^T_{AB}, 9% for the E_{AB} and 7% for the F_{AB} values. Thus, one has to be very cautious comparing two-center energies of bonds of different lengths in different molecules. Table 9 gives in addition the results for C–C single bonds of the artificial length of 1.53 Å for butadiene (double bond 1.34 Å) and for benzene (alternate bonds of 1.53 and 1.34 Å). In the case of butadiene a large part of the bond strengthening as observed in Table 8 seems to originate from the bond shortening, though the E^T_{CC} and F_{CC} (not the E_{CC}) values in butadiene are distinctively larger in absolute value than the corresponding values in ethane with the same CC bond length. Owing to the aromatic conjugation in the six-membered ring, the two-center energies in benzene are very large even if the single bonds of the distorted structure with alternate bond lengths are considered.

As one of their important properties, the two-center energy terms depend little on their surrounding and thus they should depend little on the bond lengths of *neighbouring* bonds. In order to check this point, Table 9 lists the two-center terms also of the CH bonds. In fact, the E^T_{CH} and the F_{CH} values vary by about half of one per cent or less when the CC bond length is increased by 0.05 Å.

When studying hypersurfaces of chemical reactions, one has usually to deal with many geometrical parameters which have to be optimized. Because of economic reasons, certain bonds are sometimes restricted to the same length even though they may not be equivalent. The energy partitioning can help in such situations in finding out if the assumption made about the same length of two bonds is reasonable or which of the bonds tends to be shorter than the other. As an illustration, the F_{AB} values which occurred in three such cases are presented in Fig. 1.

In the reaction of the addition of hydrogen to singlet carbenes, the hydrogen molecule approaches the carbene from above and a three-center bond is formed with the "empty" *p* orbital of the carbenic center [31]. We have made the assumption that the two hydrogen atoms of the approaching hydrogen molecule have the same distance to the C atom and selected a point on the hypersurface where that distance is 1.80 Å. The F_{CH} values (Fig. 1a) indicate, however, that the C–H_1 bond is weaker than C–H_2. In fact, the calculations of the hypersurface of the reaction CH_2+H_2 [31, 32] showed that along the optimum reaction path, C–H_1



a) CH_2+H_2 and isolated H_2 b) C_3H_2+H_2 c) C_3H_7+

Fig. 1. F_{AB} values for some systems with non-equivalent bonds of identical length (values in a.u.). [Bond lengths occurring in the systems a) and b): $C–H_1=C–H_2=1.80$ Å, $H_1–H_2=0.74$ Å; $C_1–H=C_2–H=1.30$ Å for system c)]

tends to be longer than C–H_2. The same result is obtained for the addition of hydrogen to cyclopropenylidene C_3H_2 (Fig. 1b) [33], a nucleophilic carbene. Here, the F_{CH} values are much smaller in absolute value than in the case of CH_2+H_2. Correlating with F_{CH}, F_{HH} of the hydrogen molecule in the $C_3H_2+H_2$ system is much closer to the value in the free hydrogen molecule than the F_{HH} in the system CH_2+H_2. Thus, the three-center bond in the system $C_3H_2+H_2$ is very unfavorable and the addition reaction needs according to the calculation of the hypersurface [33] a very large activation energy, whereas the reaction CH_2+H_2 was reported to proceed without any barrier [32].

As a third example, the F_{CH} values of the non-classical CH bonds in protonated propene are shown in Fig. 1c. According to the F_{CH} values, C_2–H is weaker than C_1–H. As the hypersurface of the system shows, the structure with two CH bonds of identical length does not correspond to a local minimum and the H atom is moving over to C_1 forming the more favorable iso-propyl cation. The process was studied in detail with CNDO [34] and the energy partitioning of the protonated structure was used as a demonstration for the polarizing effect exerted by methyl groups on neighboring π-bonds.

8.5. Comparison with Other Orthogonalized Basis Sets

All values for the energy partitioning within orthogonalized basis sets reported in the previous sections refer to the OMBA constructed according to the scheme described in Section 5. There are alternate procedures for the construction of orthogonalized basis sets (cf. Sect. 5) which could be used as the basis for our energy partitioning scheme. For a minimal basis SCF calculation of propene we have compared the energy partitioning results for 5 differently constructed orthogonalized basis sets (Table 10):

1) In our standard procedure, the core molecular orbitals are localized separately and do not contaminate the valence atomic orbitals. The non-orthogonal trial basis (step 1 in Sect. 5) is obtained from the diagonal bond order matrix elements.
2) The non-orthogonal trial basis is obtained from the diagonalization of the blocked *SPS* matrix (Eq. (15)). From the comparison of the results obtained with the basis types (1) and (2) in Table 10 it follows that it is of no relevance which of the two procedures is chosen for the computation of the non-orthogonal trial basis.
3) The core molecular orbitals are not excluded in the localization step (step 5 in Sect. 5) leading to the OMBA. The mixing of core orbitals into the valence atomic orbitals has some effect on the calculated two-center quantities. As expected, the absolute values of E_{AB} and F_{AB} are increasing by a few per cent (cf. basis types (1) and (3) in Table 10).
4) Within a minimal basis, the symmetric orthogonalization of Löwdin [15] can be applied (OAO, basis type (4)). As the comparison with the corresponding OMBA (1*s* not excluded, basis type (3)) shows, the two-center terms for the two basis sets differ very little.

Table 10. Energy partitioning with different orthogonalized basis sets for propene (minimal basis, values in a.u.)

Bond	(1) OMBA $-E_{AB}$	$-F_{AB}$	(2) OMBA (*SPS*) $-E_{AB}$	$-F_{AB}$	(3) OMBA (1*S* incl.) $-E_{AB}$	$-F_{AB}$	(4) OAO $-E_{AB}$	$-F_{AB}$	(5) OSO (1*s* sep.)[a] $-E_{AB}$	$-F_{AB}$
C=C	1.731	2.495	1.730	2.490	1.820	2.603	1.822	2.578	1.964	2.480
π only	0.350	0.610	0.350	0.610	0.350	0.610	0.352	0.610	0.414	0.610
C–C	0.986	1.431	0.992	1.428	1.009	1.465	1.022	1.454	1.150	1.421
C_2–H (olefinic)	0.881	1.344	0.891	1.343	0.894	1.365	0.902	1.355	1.030	1.340
C_3–H (aliph., in plane)	0.920	1.311	0.917	1.306	0.934	1.330	0.930	1.318	1.029	1.303

[a] Partitioning of the valence electron energy only.

5) The core molecular orbitals are excluded in the symmetric orthogonalization and only the valence electron energy is partitioned. In this case, only the F_{AB} values can be compared with corresponding OMBA values (basis type (1)). We conclude from the comparison of basis types (3) and (4) and of the types (5) and (1) that for a minimal basis the construction of the OMBA is virtually identical with a symmetrical orthogonalization. The same conclusion can be reached from the comparison of populations obtained with the two kinds of basis sets.

The principal features of the energy partitioning scheme are not affected by the specific way chosen for the construction of the orthogonalized basis set. The absolute values of the two-center energies show a systematic increase of a few per cent if the core molecular orbitals are not separated from the valence AO's.

9. Non-Bonded Interactions

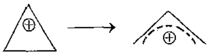
In the Sections 5 and 8 the two-center energies E^T_{AB}, E_{AB} and F_{AB} of chemical bonds were discussed in relation to bond strengths. Thus, it was tacitly assumed that the two-center terms referring to non-bonded interactions were small. For non-bonded interactions between C atoms in hydrocarbon systems the values for E^T_{CC}, E_{CC} and F_{CC} with respect to the non-orthogonal as well as with respect to the OMBA are given in Table 11. Within the non-orthogonal basis the direct overlap between basis functions at non-bonded atoms is fairly small and we might therefore expect the corresponding two-center energies to be small as well. However, as the values of Table 11 show, this is only true for the E^T_{AB} values. Surprisingly large are most of the E_{AB} values owing to large potential energy contributions which, on the other hand, cancel quite well in the F_{CC} values with the notable exception of cyclobutadiene where according to F_{13} a large repulsive 1–3 interaction is present.

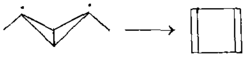
Within the OMBA a more coherent picture of the non-bonded interactions is obtained. Since the orthogonalized basis orbitals are not strictly centered at atoms, the interactions as described by E^T_{CC} are in general somewhat larger than in the case of the non-orthogonal basis, though they are still very small compared to E^T_{CC} bond values. Both the E_{CC} and the F_{CC} values are small as well. The F_{13} values in the allyl cation and in cyclobutadiene are slightly larger. Those attractive interactions have

Table 11. Non-bonded interactions between carbon atoms (minimal basis, values in a.u.)

Molecule	Interaction A–B	Distance (Å)	Non-orthogonal basis			OMBA		
			E^T_{AB}	E_{AB}	F_{AB}	E^T_{AB}	E_{AB}	F_{AB}
Benzene	1–3	2.42	−0.000	0.338	0.065	−0.033	−0.008	−0.018
	1–4	2.80	0.008	0.205	0.023	0.026	−0.004	−0.008
Butadiene	1–3	2.48	0.001	0.246	0.061	−0.032	−0.008	−0.017
	1–4	3.70	−0.001	−0.015	−0.014	−0.001	−0.005	−0.012
Propene	1–3	2.54	0.002	0.196	0.053	−0.029	−0.008	−0.015
Cyclobutadiene	1–3	2.02	−0.027	1.360	0.319	−0.043	−0.023	−0.030
Allyl$^+$	1–3	2.42	−0.005	0.222	0.036	−0.011	−0.024	−0.051

consequences for the hypersurfaces of the two systems: the ring opening of the cyclopropyl cation [35] and the opening of the bicyclobutyl diradical to cyclobutadiene [36]





are allowed [35] processes with little activation energy.

Non-bonded interactions between hydrogen atoms were found to be responsible for the energy differences between conformers when calculated with semi-empirical schemes [3, 6]. These interactions are compared with the corresponding CNDO values in Section 11.

10. The Transferability of Fock Matrix Elements

We have found that the F_{AB} values with respect to orthogonalized basis sets are well transferable between different molecules and depend little on the basis set used in the SCF calculation. For the F_{AB} values with respect to non-orthogonal basis sets, on the other hand, the transferability was found to be more limited: The polarity of the bond, its surrounding and the basis set used in the SCF calculation had considerable influence on the F_{AB} values. Since bond order matrix elements referring to orthogonalized basis sets (cf. Section 17) and referring to non-orthogonal minimal basis sets are also quantities which can be transferred between different molecules, it follows from the definition of the F_{AB} (Eq. (11)) that the transferability properties of the F_{AB} and of the Fock matrix elements are intrinsically connected. The transferability of Fock matrix elements between different molecules was studied by O'Leary *et al.* [13]. The authors proposed a simulated approximate MO theory (SAMO) in which the Fock matrix elements for larger molecules are taken from smaller pattern molecules. The SAMO scheme was originally developed for non-orthogonal basis sets. A corresponding method making use of the transferability of Fock matrix elements with respect to an orthogonalized basis was proposed by Leroy *et al.* [14] for hydrocarbons. In that scheme, the Fock matrix elements occurring in the calculation of a hydrocarbon are simply taken from a collection of averaged Fock matrix elements obtained from SCF calculations on some hydrocarbons. The two schemes were compared by O'Leary *et al.* [13] who found that the Fock matrix elements with respect to a non-orthogonal basis were slightly better transferable than those with respect to the orthogonalized basis. From our results for the F_{AB} values we can deduct the following properties of the Fock matrix elements:

1) Fock matrix elements with respect to the non-orthogonal basis are transferable only within the restriction mentioned above. That is in accordance with the results of O'Leary *et al.*, who found that for the SAMO technique one needs fairly large pattern molecules (with 3 or 4 heavy atoms). Thus, one cannot extract the off-diagonal Fock matrix elements for the CH bond in ethane from a calculation of methane (the F_{CH} values differ by more than 2%, cf. Table 1). Difficulties should also arise when Fock matrix elements of ions are taken from neutral pattern molecules.

2) The transferability of Fock matrix elements with respect to orthogonalized basis sets should be less restricted: since far-reaching potential energy contributions are well cancelled in the off-diagonal Fock matrix elements, the use of much smaller pattern molecules should suffice. According to the F_{CH} values in ethane and in methane (Table 8), one could use Fock matrix elements from methane in a SCF calculation of ethane. Transferring matrix elements between neutral molecules and ions should not pose many problems.

The application of MO schemes based on the transferability of Fock matrix elements should therefore be less complicated for orthogonalized than for non-orthogonal basis sets, though the latter led to more accurate results [13]. We must add that the discussion of this section referred to off-diagonal Fock matrix elements only.

11. Comparison with Semi-Empirical SCF Methods

The semi-empirical methods which are based on the neglect of differential overlap (NDO) [12], like CNDO and MINDO, can be rationalized as being approximate SCF methods referring to orthogonalized basis sets [37–39]. One of the basic provisions of the semi-empirical schemes is that the off-diagonal one-electron as well as the Fock matrix elements depend only on the respective basis orbitals and are not affected by the surrounding. Thus, the transferability of Fock matrix elements and of the F_{AB} values can be viewed as a justification for such semi-empirical methods.

The energy partitioning analysis presented here for *ab initio* SCF was applied in a similar form to modified CNDO [3] and the MINDO [4] energy expressions. The two-center energies obtained from *ab initio* SCF and from the two semi-empirical methods were compared in order to trace back some failures of semi-empirical schemes to their origin in the parametrization or in the formula used. In Table 12, the E_{AB} and F_{AB} values are listed for some molecules calculated with *ab initio* SCF (MB for hydrocarbons and DZ for other compounds), with modified CNDO and with MINDO/3. Though the two-center terms obtained with the three methods are of the same order of magnitude, the semi-empirical energies are in absolute value systematically smaller than the *ab initio* values, with the MINDO/3 terms in all cases being the smallest. Obviously, compared to *ab initio* SCF the semi-empirical off-diagonal Fock matrix elements are too small in absolute value. The semi-empirical diagonal Fock matrix elements, on the other hand, are too negative, such that the MO energies of the occupied bonding orbitals are in reasonable agreement with *ab initio* and with experiment. This disagreement does not pose problems as long as only molecular systems with occupied bonding orbitals are considered. Molecules, however, in which anti- or non-bonding MO's are occupied (like H_2O_2, F_2 etc.) are then with semi-empirical theories (cf. Ref. [11]) predicted to be too stable.

Another disagreement between *ab initio* and semi-empirical methods is observed for the off-diagonal Fock matrix elements between atomic orbitals at the same atom. In *ab initio* SCF these matrix elements are usually close to zero, the corresponding bond order matrix elements are also small and the energy contributions from these

Table 12. Two center energies obtained with *ab initio* SCF, mod. CNDO and MINDO/3 (all values in a.u.)

		Ab initio OMBA[a]		Modified CNDO		MINDO/3	
Bond	Molecule	$-E_{AB}$	$-F_{AB}$	$-E_{AB}$	$-F_{AB}$	$-E_{AB}$	$-F_{AB}$
H–H	H_2	0.971	1.196	0.686	0.961	0.509	0.706
C–H	C_2H_2	0.987	1.462	0.816	1.028	0.607	0.758
	C_2H_4	0.907	1.340	0.763	0.972	0.570	0.722
	C_2H_6	0.906	1.508	0.752	0.964	0.567	0.722
	CH_4	0.929	1.308	0.756	0.970	0.574	0.730
N–H	NH_3	0.954	1.410	—	—	0.641	0.812
O–H	OH_2	1.001	1.440	—	—	0.673	0.845
C≡C	C_2H_2	2.612	3.817	2.075	2.665	1.733	2.165
C=C	C_2H_4	1.791	2.522	1.454	1.828	1.230	1.509
	c-C_3H_4	1.766	2.445	1.429	1.804	1.167	1.439
C–C	C_2H_6	0.997	1.387	0.853	1.023	0.734	0.863
	c-C_3H_6	0.945	1.272	0.798	0.966	0.644	0.776
N≡N	N_2	2.839	4.220	—	—	1.650	2.146
N–N	N_2H_4	0.772	1.324	—	—	0.562	0.709
O–O	O_2H_2	0.575	1.089	—	—	0.680	0.828

[a] MB for hydrocarbons and DZ for other molecules.

interactions are negligible. Quite differently, in CNDO the $f_{\mu\nu}$ elements between two basis functions at the same atom are given by

$$f_{\mu\nu} = -\tfrac{1}{2}P_{\mu\nu}\gamma_{AA} \quad (\mu, \nu \in A)$$

where γ_{AA} is the one-center Coulomb integral which is very large (~ 0.6 a.u. for C). Especially in strained ring systems like cyclopropane large bond orders between $2s$ and $2p$ orbitals at the same C atom are obtained with CNDO. The corresponding (binding) energy contributions which have no counterpart in *ab initio* SCF lead to an unreasonable stabilization of small ring compounds as compared to open chain molecules.

In MINDO/3 the problem of strained systems is partially solved. Here the expression for the off-diagonal one-center Fock matrix elements is

$$f_{\mu\nu} = -\tfrac{1}{2}P_{\mu\nu}\{(\mu\mu \mid \nu\nu) - 3(\mu\nu \mid \mu\nu)\}$$

where the two-electron integrals are treated as parameters. The resulting Fock matrix elements are much smaller in absolute value than in CNDO, though they are still considerably too large.

A third problem of semi-empirical methods is their incapability of reproducing barriers of conformational interconversions. From CNDO calculations on the conformers of ethane [3, 6] it was concluded that the non-bonded interactions between vicinal hydrogen atoms account for the calculated energy differences between conformers. These interactions which are attractive between *trans* hydrogens and repulsive between *cis* hydrogens were shown to have their origin in hyperconjugation of the CH bonds [3]. The two-center terms of the non-bonded

Table 13. Non-bonded interactions of vicinal H atoms in ethane (energy values in 10^{-4} a.u.)

Conformer	Dihedral angle HCCH ′	OMBA (from MB) $E^T_{HH'}$	$E_{HH'}$	$F_{HH'}$	$P_{HH'}$	$f_{HH'}$	Modified CNDO $F_{HH'}$	$P_{HH'}$	$f_{HH'}$	MINDO/3 $F_{HH'}$	$P_{HH'}$	$f_{HH'}$
ecl.	0°	51	27	27	−0.0624	−230	25	−0.0620	−201	10	−0.0623	−81
stagg.	60°	6	3	3	−0.0344	−38	10	−0.0291	−163	3	−0.0193	−79
ecl.	120°	6	0	1	+0.0406	−22	−13	+0.0452	−143	−16	+0.0727	−108
stagg.	180°	2	−12	−10	+0.0796	−61	−25	+0.0853	−149	−31	+0.1203	−129
Σ (ecl.)		191	81	77			2			−64		
Σ (stagg.)		38	−16	−13			−19			−75		
Δ ecl./stagg.		153	97	90			17			11		
ΔE_{SCF} ecl./stagg.				49			24			17		

interactions between the vicinal H atoms in the staggered and in the eclipsed conformer of ethane are listed in Table 13. The $F_{HH'}$ values obtained from *ab initio* SCF, from CNDO, and from MINDO/3 calculations show the same variation with the dihedral angle: attraction for 180° and repulsion for 0°. However, in *ab initio* SCF the sum of the non-bonded interactions favors the staggered over the eclipsed conformation by 0.0090 a.u. while the corresponding values for CNDO and MINDO/3 are only about 0.0017 and 0.0011 a.u., respectively. The calculated rotational barriers show the same trend (0.0049, 0.0024 and 0.0017 a.u., experimental value 0.0047 a.u. [40]).

Obviously, the failure of CNDO and of MINDO/3 in the reproduction of rotational barriers corresponds to an unsatisfactory description of the non-bonded interactions. The corresponding bond order matrix elements, which are also given in Table 13, agree very well for *ab initio* and for mod. CNDO, proving that the hyperconjugation is well described in CNDO and that the error must be located in the Fock matrix elements. Closer inspection of the Fock matrix elements reveals that the difference between the $F_{HH'}$ for *cis* and *trans* hydrogens is too small in the semi-empirical methods. In CNDO and MINDO/3, the one-electron matrix elements $h_{\mu\nu}$ are set proportional to the overlap. A more rapid decrease of the $h_{\mu\nu}$ with the distance should improve rotational barriers calculated with the two semi-empirical schemes.

The examples given in this section show that the energy partitioning procedure can be used as a tool for the analysis of semi-empirical methods and could be helpful in the development of new parametrization schemes.

12. Conclusions

From the results obtained with our energy partitioning scheme the following conclusions can be drawn:

1) Of the two-center energy terms computed within a non-orthogonal basis, only the quantity F_{AB} proved to be of some value. The F_{AB} assume similar values for similar bonds in different molecules as long as the surrounding of the bonds considered are not too different and the same basis is used. The behavior of the F_{AB} terms is in accordance with the known transferability properties of Fock matrix elements.
2) Within the orthogonalized basis sets all two-center energy terms are transferable between different molecules. In particular, the F_{AB} values depend little on the basis set and on the surrounding of a bond and show a monotonic relationship to bond strengths.
3) The F_{AB} terms can also be used for the characterization of non-bonded interactions which can be of interest, since such interactions often determine the shape of a potential hypersurface of a chemical reaction.
4) The dissection of the F_{AB} values into contributions from different basis orbitals can serve interpretational purposes (σ and π bond contributions, *s* character of a bond, etc.).

5) Since the energy partitioning was performed within an orthogonalized basis, it is possible to compare directly energy components with corresponding values obtained from semi-empirical schemes. Such a comparison could help in the design of parametrization schemes as well as in the tracing back of failures of semi-empirical methods to their origin in the parametrization scheme.
6) The orthogonalized minimal basis which can be constructed from non-orthogonal basis sets of arbitrary size can be used for population analysis. Bond orders can be used for the characterization of bond types and for the definition of hybridization indices.

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