

Energy partitioning for “fuzzy” atoms

P. Salvador^{a)}

Department of Chemistry and Institute of Computational Chemistry, University of Girona, 17071 Girona, Spain

I. Mayer

Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

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The total energy of a molecule is presented as a sum of one- and two-atomic energy components in terms of “fuzzy” atoms, i.e., such divisions of the three-dimensional physical space into atomic regions in which the regions assigned to the individual atoms have no sharp boundaries but exhibit a continuous transition from one to another. By proper definitions the energy components are on the *chemical energy scale*. The method is realized by using Becke’s integration scheme and weight function permitting very effective numerical integrations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1646354]

I. INTRODUCTION

The most important result of a quantum chemical calculation is the total energy of the molecular system; however, being a single number, it carries little immediate chemical information. In order to get connections with genuine chemical concepts, one may use the wave functions or density matrices, and calculate quantities like atomic charges¹ and bond order indices.² An alternative avenue is to decompose the total molecular energy (exactly or approximately) into a sum of atomic and diatomic energy components, which will reflect the different intramolecular interactions in a natural way. Similar to the calculation of quantities like bond orders, such an energy analysis may be performed either in the Hilbert space of the atomic orbitals³ (by identifying the atom with its nucleus and the atomic orbital basis orbitals assigned to it) or in the three-dimensional (3D) physical space in which the molecule is situated. Schemes of Hilbert space analysis are simple and convenient for use, but do not possess any limits for large basis sets. To accomplish a scheme of an analysis in the physical space, one has to assign (at least in some sense, see the following) a part of the 3D space to every atom. Such a decomposition of the physical space into “atomic domains” (and sometimes domains corresponding to the so-called “non-nuclear attractors”) is most often accomplished by using Bader’s “Atoms in Molecules” (AIM) theory.⁴ Bader also presents the molecular energy as a sum of purely atomic contributions, on the basis of applying the virial theorem to every atomic domain, which is usually fulfilled with a relatively good accuracy in the practical calculations. Recently we have shown that in the AIM framework the total self-consistent field (SCF) energy can be presented exactly as a sum of mono- and diatomic energy components.⁵ This decomposition scheme has been realized by performing the necessary numerical integrations in our previous work;⁶ it gave quite convincing results in good qualitative agreement⁷ with those of the Hilbert-space de-

composition in Ref. 8. Unfortunately, the complex form of the AIM domains makes these calculations extremely CPU-demanding. The point is that every two-electron integral over the molecular integrals should be decomposed into integrals over their pieces cut to the individual domains. In order to get a modest but acceptable accuracy, we had to use about 40 000 points per atomic domain. Therefore, the number of operations necessary to perform the energy decomposition of a small molecule exceeded 10^{10} , thus we had to use super-computing facilities.

Although there is some work devoted to reduce the computational cost of the two-electron integration on disjunct domains,^{9,10} we propose an alternative scheme of 3D energy decomposition, which is based on the use of “fuzzy atoms.” It is expected to be affordable in practical calculations and, as it will be seen, it has the advantage that permits a special modification of the formalism, by which one gets the energy components on the *chemical energy scale*. The application of the present approach may be especially advantageous in the “pure” density functional theory (DFT) framework.

II. THEORY

A. “Fuzzy” atoms

Probably “fuzzy” atoms have been first used by Hirshfeld¹¹ for calculating effective atomic charges in molecules by using the so-called “stockholders” scheme. In this scheme one introduces for each atom A and every point \mathbf{r} of the 3D space a non-negative continuous weight function $w_A(\mathbf{r})$, measuring to what degree the given point of space can be considered to belong to atom A. Thus the weight functions should satisfy the conditions

$$w_A(\mathbf{r}) \geq 0 \quad (1)$$

and

$$\sum_{A=1}^{N_{\text{atoms}}} w_A(\mathbf{r}) \equiv 1 \quad (2)$$

^{a)}Electronic mail: pedro.salvador@udg.es

in every point of the 3D space. Thus “fuzzy” atoms do not have any sharp boundaries but exhibit a continuous transition from one to another. This is to a great extent in agreement with the classical chemical notions of *shared electrons* requiring that some electronic charge should belong simultaneously to a pair of chemically bonded atoms. As electron density is a continuous function in the 3D space, sharing of electrons is possible if one assumes a sort of sharing of the physical space, too.

Actually Hirshfeld used for calculating the weight function $w_A(\mathbf{r})$ the ratio of the charge density of the free atom to that of the “promolecule” (assembly of noninteracting atoms placed at the positions of the nuclei in the actual molecule), but that is essentially irrelevant for our considerations solely based on conditions (1) and (2) above.

The populations of the “fuzzy” atoms can be introduced by inserting condition (2) into the normalization integral of the electron density

$$\begin{aligned} N &= \int \rho(\mathbf{r}) dv \\ &\equiv \int \sum_{A=1}^{N_{\text{atoms}}} w_A(\mathbf{r}) \rho(\mathbf{r}) dv \\ &\equiv \sum_{A=1}^{N_{\text{atoms}}} \int w_A(\mathbf{r}) \rho(\mathbf{r}) dv \\ &= \sum_{A=1}^{N_{\text{atoms}}} Q_A \end{aligned} \quad (3)$$

leading to the natural definition

$$Q_A = \int w_A(\mathbf{r}) \rho(\mathbf{r}) dv \quad (4)$$

of the atomic electron populations. Most recently^{12,13} we have proposed to insert condition (2) into the normalization integral twice. As a result, one may consider the electron population Q_A as an analogue of Mulliken’s “gross” atomic population, and present it as a sum of “net” and “overlap” populations q_{AA} and q_{AB} as

$$Q_A = q_{AA} + \sum_{B \neq A} q_{AB} \quad (5)$$

with

$$q_{AA} = \int \rho(\mathbf{r}) w_A^2(\mathbf{r}) dv, \quad (6)$$

and

$$q_{AB} = \int \rho(\mathbf{r}) w_A(\mathbf{r}) w_B(\mathbf{r}) dv, \quad (7)$$

respectively. Obviously, the overlap population q_{AB} measures how much electronic charge may be considered as belonging to both atoms A and B, *simultaneously*. We shall mention that the AIM theory represents a limiting case of the above formalism with the weight functions $w_A(\mathbf{r})$ equal to either one or zero. However, no parameter like overlap population may be introduced in the AIM framework, as in the

AIM case Eq. (7) leads to $q_{AB} \equiv 0$. [In the AIM case either $w_A(\mathbf{r})$ or $w_B(\mathbf{r})$ can differ from zero in a given point, but not both.¹⁴]

In what follows we shall first show that a quite similar technique permits one to decompose the total SCF energy into atomic and diatomic contributions in quite straightforward manner. Then we shall get an improvement of this simple energy decomposition scheme by subjecting the kinetic energy terms to a procedure analogous to that used above for the introduction of the overlap densities. This permits one to get energy components which are on the *chemical energy scale*. Both the “simple” and “improved” schemes will be illustrated by a number of examples, calculated by using Becke’s integration scheme and weight functions,¹⁵ permitting very effective numerical integrations.

B. The “simple” energy decomposition scheme

Let us consider the total SCF energy expressed in terms of molecular orbitals

$$\begin{aligned} E &= \sum_{A < B}^{N_{\text{atoms}}} \frac{Z_A Z_B}{R_{AB}} + 2 \sum_{i=1}^{n_{\text{occ}}} \int \varphi_i^*(\mathbf{r}) \hat{h} \varphi_i(\mathbf{r}) dv \\ &\quad + \sum_{i,j=1}^{n_{\text{occ}}} \int \int \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} [2 \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \\ &\quad - \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)] dv_1 dv_2. \end{aligned} \quad (8)$$

[The restricted Hartree–Fock (RHF) case will be explicitly treated, generalization to the unrestricted Hartree–Fock one is trivial.]

Now, by using Eq. (2) we may write

$$\begin{aligned} \int \varphi_i^*(\mathbf{r}) \hat{h} \varphi_i(\mathbf{r}) dv &= \int \sum_{A=1}^{N_{\text{atoms}}} w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \hat{h} \varphi_i(\mathbf{r}) dv \\ &= \sum_{A=1}^{N_{\text{atoms}}} \int w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \hat{h} \varphi_i(\mathbf{r}) dv \\ &= - \sum_{A=1}^{N_{\text{atoms}}} \int w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \\ &\quad \times \left(\frac{1}{2} \Delta + \sum_{B=1}^{N_{\text{atoms}}} \frac{Z_B}{r_B} \right) \varphi_i(\mathbf{r}) dv \\ &= - \sum_{A=1}^{N_{\text{atoms}}} \int w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \\ &\quad \times \left(\frac{1}{2} \Delta + \frac{Z_A}{r_A} \right) \varphi_i(\mathbf{r}) dv \\ &\quad - \sum_{\substack{A,B=1 \\ (A \neq B)}}^{N_{\text{atoms}}} \int w_A(\mathbf{r}) |\varphi_i(\mathbf{r})|^2 \frac{Z_B}{r_B} dv. \end{aligned} \quad (9)$$

Similarly

$$\begin{aligned}
& \int \int \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) dv_1 dv_2 \\
&= \int \int \sum_{A=1}^{N_{\text{atoms}}} w_A(\mathbf{r}_1) \sum_{B=1}^{N_{\text{atoms}}} w_B(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \\
&\quad \times \frac{1}{r_{12}} \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) dv_1 dv_2 \\
&= \sum_{A,B=1}^{N_{\text{atoms}}} \int \int w_A(\mathbf{r}_1) w_B(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \\
&\quad \times \frac{1}{r_{12}} \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) dv_1 dv_2. \quad (10)
\end{aligned}$$

Thus the SCF (RHF) total energy can be written as

$$E = \sum_A^{N_{\text{atoms}}} E_A + \sum_{A<B}^{N_{\text{atoms}}} E_{AB}, \quad (11)$$

where

$$\begin{aligned}
E_A &= -2 \sum_{i=1}^{n_{\text{occ}}} \int w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \left(\frac{1}{2} \Delta + \frac{Z_A}{r_A} \right) \varphi_i(\mathbf{r}) dv \\
&\quad + \sum_{i,j=1}^{n_{\text{occ}}} \int \int w_A(\mathbf{r}_1) w_A(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \\
&\quad \times \frac{1}{r_{12}} [2\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) - \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)] dv_1 dv_2 \quad (12)
\end{aligned}$$

and

$$E_{AB} = \frac{Z_A Z_B}{R_{AB}} + \varepsilon_{AB} + \varepsilon_{BA} \quad (13)$$

with

$$\begin{aligned}
\varepsilon_{AB} &= -2 \sum_{i=1}^{n_{\text{occ}}} \int w_A(\mathbf{r}) |\varphi_i(\mathbf{r})|^2 \frac{Z_B}{r_B} dv \\
&\quad + \sum_{i,j=1}^{n_{\text{occ}}} \int \int w_A(\mathbf{r}_1) w_B(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \\
&\quad \times [2\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) - \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)] dv_1 dv_2. \quad (14)
\end{aligned}$$

The expression of ε_{BA} can be obtained from ε_{AB} by interchanging A and B everywhere.

In agreement with the discussion above, the decomposition corresponding to the AIM domains^{5,6} can be obtained from these expressions as a special case, by assuming that in the domain of atom A the corresponding $w_A = 1$ and all the other w_B 's are zero.

C. The "improved" energy decomposition scheme

By inspecting the above expressions, one may see that the kinetic energy operator enters only the one-center (atomic) energy component. It is, however, well known^{16,17} that the kinetic energy plays a complex role in the chemical bond formation, and the kinetic energy component *along a*

chemical bond has a great importance. This contradiction with our physical picture may be resolved by using identity (2) once more, and writing

$$\begin{aligned}
& \int w_A(\mathbf{r}) \varphi_i^*(\mathbf{r}) \Delta \varphi_i(\mathbf{r}) dv \\
&\equiv \int w_A(\mathbf{r}) \sum_B^{N_{\text{atoms}}} w_B(\mathbf{r}) \varphi_i^*(\mathbf{r}) \Delta \varphi_i(\mathbf{r}) dv \\
&= \sum_B^{N_{\text{atoms}}} \int w_A(\mathbf{r}) w_B(\mathbf{r}) \varphi_i^*(\mathbf{r}) \Delta \varphi_i(\mathbf{r}) dv. \quad (15)
\end{aligned}$$

Now, terms containing $w_A(\mathbf{r}) w_B(\mathbf{r})$ with $A \neq B$ should be moved to the diatomic energy components, and the atomic component will contain $w_A^2(\mathbf{r})$. Thus we obtain the expressions of our "improved" energy decomposition scheme:

$$E = \sum_A^{N_{\text{atoms}}} E'_A + \sum_{A<B}^{N_{\text{atoms}}} E'_{AB}, \quad (16)$$

where

$$\begin{aligned}
E'_A &= -2 \sum_{i=1}^{n_{\text{occ}}} \int w_A^2(\mathbf{r}) \varphi_i^*(\mathbf{r}) \frac{1}{2} \Delta \varphi_i(\mathbf{r}) dv \\
&\quad - 2 \sum_{i=1}^{n_{\text{occ}}} \int w_A(\mathbf{r}) |\varphi_i(\mathbf{r})|^2 \frac{Z_A}{r_A} dv \\
&\quad + \sum_{i,j=1}^{n_{\text{occ}}} \int \int w_A(\mathbf{r}_1) w_A(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \\
&\quad \times \frac{1}{r_{12}} [2\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) - \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)] dv_1 dv_2 \quad (17)
\end{aligned}$$

and

$$\begin{aligned}
E'_{AB} &= \frac{Z_A Z_B}{R_{AB}} + \varepsilon_{AB} + \varepsilon_{BA} \\
&\quad - 4 \sum_{i=1}^{n_{\text{occ}}} \int w_A(\mathbf{r}) w_B(\mathbf{r}) \varphi_i^*(\mathbf{r}) \frac{1}{2} \Delta \varphi_i(\mathbf{r}) dv. \quad (18)
\end{aligned}$$

Expression (14) does not change.

The above regrouping of the kinetic energy terms has been found necessary to get the energy components on the chemical energy scale.¹⁸ No similar transformation is possible in the AIM framework, for the same reasons as discussed in connection with the absence of the overlap density.

III. ILLUSTRATIVE CALCULATIONS

A. Computational details

We have implemented Becke's method of multicenter numerical integration¹⁵ which reduces the integration over the whole 3D space to the sum of integrations over the individual atoms. For that reason he introduces a non-negative weight factor of every center in every point of space, such that it is equal to the one on the respective nucleus and decreases by the distance. The division of the space between different atoms is performed on the basis of the ratio of their empirical atomic radii. The weight factors corresponding to

the different atoms sum to one in every point—in other words, the weight factors satisfy Eqs. (1) and (2) above and can, therefore, directly be utilized in our energy decomposition scheme, too. Furthermore, Becke's scheme¹⁵ uses Chebyshev's integration for the radial part and Lebedev's quadrature¹⁹ of the angular part for every atomic subproblem. We have downloaded the routine for performing Lebedev quadrature from Ref. 20. Most recently we have used the same integration scheme for calculating overlap populations, bond orders, and valences within the "fuzzy" atoms framework.^{12,13}

The kinetic and electron-nuclear attraction terms involve only one-electron numerical integration, so the respective one- and two-center energy contributions can easily be computed. However, for the Coulomb and exchange terms costly double [i.e., six-dimensional (6D)] integrations are necessary. In order to reduce the computational cost of these 6D integrations, it is very important to use the smallest number of grid points per atom yet ensuring a good accuracy. As discussed above, our previous energy partition in the framework of AIM theory required a large atomic grid (about 40 000 points per atom) due to the complex topology of the atomic basin. It was necessary at that work to use supercomputer facilities in order to compute the numerous pairwise interactions between the atoms.

We have observed that the two-electron terms, in particular the exchange ones, are the main source of error. (A modest grid of 30 radial and 110 angular points per atom has been found sufficient to reproduce the molecular kinetic energy and the electron-nuclear attraction with a very good accuracy.) The largest problem comes from the electrons at positions close in space: if we use the same grid for the integration over the coordinates of both electrons, then we are forced to discard the points where $\mathbf{r}_1 = \mathbf{r}_2$. To solve this difficulty, we have used for integration over the two electrons two identical grids which were, however, rotated with respect to each other along the angle φ of spherical coordinate system in such a way that the points of one grid are roughly halfway between the points of another. In this manner we could obtain an acceptable overall accuracy with a grid consisting of 40 radial and 146 angular points for each atom. (In some cases like sulfur, we have increased the radial grid to 50 points). For the 146 point angular grid of Lebedev integration, the rotation of the second grid along angle φ constituted 0.229 rad (13.12°).

For a typical molecule, the computational cost of the exchange contribution normally represents more than 90% of the overall computational cost. This is because, according to Eqs. (12) and (14), one must perform a double integration for each pair of molecular orbitals. On the contrary, the Coulomb part can be calculated at once by integrating the electron density. Therefore, our method seems especially suitable for the "pure" DFT exchange–correlation functionals (i.e., those not containing the Hartree–Fock exchange) where the double integration of this type of contribution is avoided.

The test calculations presented in the following used the simplest set of weight functions: that originally proposed by Becke for performing numerical integration by and making use of the empirical atomic radii. (As already noted, it satis-

TABLE I. One- and two-center energy components (a.u.) obtained for selected molecules by using the "simple" energy decomposition scheme and 6-31G(*d,p*) basis set.

Molecule	Atom	$E(A)$	Atomic pair	$E(A,B)$
H ₂	H	-0.4477	H,H	-0.2360
N ₂	N	-53.9935	N,N	-0.9569
HF	H	-0.3679	H,F	-0.3163
	F	-99.3293		
CO	C	-37.4171	C,O	-0.9550
	O	-74.3691		
SO	S	-397.1004	S,O	-0.9223
	O	-74.2489		
SO ₂	S	-396.6782	S,O	-0.9726
	O	-74.2853		
SO ₃	S	-396.2293	S,O	-0.9713
	O	-74.3019		
NH ₃	N	-53.9834	N,H	-0.3193
	H	-0.4116		
H ₂ O	O	-74.4748	O,H	-0.3740
	H	-0.3954		
CH ₄	C	-37.3747	C,H	-0.2784
	H	-0.4222		
C ₂ H ₆	C	-37.3201	C,C	-0.3912
	H	-0.4161	C,H	-0.2722
C ₂ H ₄	C	-37.3108	C,C	-0.6102
	H	-0.4172	C,H	-0.2736
C ₂ H ₂	C	-37.3109	C,C	-0.8078
	H	-0.4175	C,H	-0.2707
C ₆ H ₆	C	-37.2563	C,C	-0.4803
	H	-0.4128	C,H	-0.2677
B ₂ H ₆	B	-24.3012	B,H _{br}	-0.1573
	H _{br}	-0.3566	B,H _t	-0.2751
	H _t	-0.4106	B,B	-0.1952

fies conditions (1) and (2) necessary for that purpose.) Following Becke's recipe, we used the Slater–Bragg effective atomic radii²¹ and accepting his suggestion, we increased the radius of hydrogen to the value 0.35 Å. However, for fluorine we used the value 0.9 Å, representing the average of the covalent and ionic radii. For further details we refer to our recent work¹² in which bond orders and valences of "fuzzy" atoms are calculated. Our program uses as sole input the "formatted checkpoint file" generated in a GAUSSIAN run. For interfacing parts of the program APOST⁵ have been adapted. Each one- and two-center contribution can be calculated independently, so that one can obtain relatively quickly the relevant or interesting energy contributions of a molecular system without computing all the contributions. We have made available our program for downloading.²²

B. Results of calculations

Tables I–III contain some results obtained by the above two variants of the energy partitioning in terms of "fuzzy atoms" for one basis set for the "simple" decomposition scheme and for two different basis sets for the "improved" one. In all calculations the geometries were fully optimized for the given basis set.

Table I gathers the results for a number of molecules calculated at the SCF level by using the "simple" energy decomposition scheme. The values for the two-center components correlate reasonably well with the relative bond

TABLE II. One- and two-center energy components, atomic promotion energies with respect to the atomic ROHF energies, and error of integration Δ for selected molecules obtained by using the "improved" energy decomposition scheme and 6-31G(*d,p*) basis set.

Molecule	Atom	E_A (a.u.)	ΔE_A (kcal/mol)	Atomic pair	E_{AB} (a.u.)	E_{AB} (kcal/mol)	Δ (kcal/mol)
H ₂	H	-0.4881	6.4	H,H	-0.1553	-97.5	-0.1
N ₂	N	-54.3761	3.9	N,N	-0.1916	-120.2	0.1
HF	H	-0.4248	46.1	H,F	-0.2042	-128.1	-1.2
	F	-99.3846	-14.3				
CO	C	-37.7757	-61.9	C,O	-0.2343	-147.0	-2.1
	O	-74.7313	29.9				
SO	S	-397.3916	50.7	S,O	-0.349	-219.0	-6.1
	O	-74.531	155.6				
SO ₂	S	-397.3339	86.9	S,O	-0.3166	-198.7	-12.6
	O	-74.6131	104.1				
SO ₃	S	-397.2011	170.2	S,O	-0.3211	-201.5	-12.6
	O	-74.627	95.4				
NH ₃	N	-54.2064	110.4	N,H	-0.1713	-107.5	0.2
	H	-0.4848	8.4				
H ₂ O	O	-74.6635	72.5	O,H	-0.1849	-116.0	0.2
	H	-0.4891	5.7				
CH ₄	C	-37.6074	43.8	C,H	-0.1627	-102.1	1.8
	H	-0.4788	12.2				
C ₂ H ₆	C	-37.5973	50.1	C,C	-0.1777	-111.5	0.4
	H	-0.4722	16.3				
C ₂ H ₄	C	-37.6182	37.0	C,C	-0.2243	-140.8	-1.6
	H	-0.4747	14.8				
C ₂ H ₂	C	-37.6429	21.5	C,C	-0.2588	-162.4	-1.0
	H	-0.4759	14.0				
C ₆ H ₆	C	-37.6138	39.74	C,C	-0.1796	-112.7	-3.3
	H	-0.4692	18.22				
C ₆₀	C	-37.5775	62.5	C,C(6,6)	-0.1723	-108.1	
		C,C(5,6)	-0.1557	-97.7			
		B ₂ H ₆	B	-24.4826	23.1	B,H _{br}	-0.1117
	H _{br}	-0.4032	59.6	B,H _t	-0.1836	-115.2	
	H _t	-0.4564	26.3	B,B	-0.1025	-64.3	

strengths. For instance, the C–C contributions of ethane, ethylene, and acetylene gradually increase. However, the actual numbers are too large in absolute value to be directly compared with the energy changes of chemical interest. These exaggerated two-center energies are compensated with the one-center terms showing very large promotion energies with respect to the isolated atoms. These values are comparable to those obtained within the AIM framework,⁶ except for diborane where AIM partitioning predicted strong repulsion between the two B atoms. (A similar behavior of the one- and two-center contributions has also been observed in the older Hilbert-space energy component analysis.⁸)

On the other hand, the "improved" energy decomposition scheme (in which part of the kinetic energy is given a two-center character analogously to the overlap population) shows energy contributions on the *chemical energy scale*. The respective results are collected in Tables II and III. Inspection of the results indicates that they are in better agreement with the actual bond strengths and do not depend much on the basis set, while basis set dependence may be a serious problem for other methods based on the analysis on the Hilbert space. Furthermore, the good trends obtained with the previous method are also observed and improved. For instance, the increasing bond strength of the series C–H, N–H, O–H, and F–H is reproduced with both basis sets. (The ac-

tual values for the large basis set are -102.7, -109.8, -121.1, and -130.6 kcal/mol, respectively.) The promotion energies defined with respect to the atomic ROHF energies are, in general, within the chemical scale. (They reflect also partial ionization effects, which can give some negative energy contributions on the electron-receiving atoms and positive ones on those losing electrons; in sum intramolecular ionization may be expected to be slightly energy-consuming.) Since it is sometimes difficult to properly choose the atomic reference state, we expect this term to be of chemical interest only when comparing the same atoms in different environments (provided that the same basis set and method is used).

The error of the overall integration (difference between the sum of all one- and two-center contributions computed numerically and the exact SCF energy) is, in general, of the order of 1–5 kcal/mol, which may be considered negligible. Higher errors were obtained for systems containing sulfur atoms. Integration with a larger radial grid helped to reduce this error, which was, indeed, almost entirely originating from the one-center sulfur energy.

As discussed in Ref. 12, other weight functions can also be used, as long as conditions (1) and (2) are fulfilled. As the simplest possibility, we plan to adjust in some systematic manner the effective atomic radii of the atoms which were

TABLE III. One- and two-center energy components, atomic promotion energies with respect to the atomic ROHF energies, and error of integration Δ for selected molecules obtained by using the "improved" energy decomposition scheme and 6-311++G(d,p) basis set.

Molecule	Atom	E_A (a.u.)	ΔE_A (kcal/mol)	Atomic pair	E_{AB} (a.u.)	E_{AB} (kcal/mol)	Δ (kcal/mol)
H ₂	H	-0.4890	6.8	H,H	-0.1547	-97.1	-0.2
N ₂	N	-54.3884	4.3	N,N	-0.1964	-123.2	0.8
HF	H	-0.4206	49.7	H,F	-0.2081	-130.6	-1.3
	F	-99.4260	-18.6				
CO	C	-37.8000	-72.0	C,O	-0.2310	-145.0	-0.9
	O	-74.7409	38.4				
SO	S	-397.3712	78.2	S,O	-0.3582	-224.8	34.8
	O	-74.5436	162.2				
SO ₂	S	-397.3222	109.0	S,O	-0.3247	-203.8	-23.9
	O	-74.6206	113.9				
SO ₃	S	-397.1996	185.9	S,O	-0.3296	-206.8	-20.7
	O	-74.6311	107.3				
NH ₃	N	-54.2096	116.5	N,H	-0.1749	-109.8	0.2
	H	-0.4863	8.5				
H ₂ O	O	-74.6700	82.9	O,H	-0.1930	-121.1	1.0
	H	-0.4922	4.8				
CH ₄	C	-37.6133	45.1	C,H	-0.1636	-102.7	-1.1
	H	-0.4792	12.9				
C ₂ H ₆	C	-37.6022	52.1	C,C	-0.1784	-111.9	1.8
	H	-0.4727	17.0				
C ₂ H ₄	C	-37.6243	38.2	C,C	-0.2280	-143.1	-1.1
	H	-0.4746	15.8				
C ₂ H ₂	C	-37.6527	20.4	C,C	-0.2643	-165.9	1.6
	H	-0.4736	16.5				
C ₆ H ₆	C	-37.6155	43.13	C,C	-0.1828	-114.7	-0.7
	H	-0.4692	19.21				
B ₂ H ₆	B	-24.4935	21.1	B,H _{br}	-0.1087	-68.2	-6.0
	H _{br}	-0.4077	57.8	B,H _t	-0.1813	-113.8	
	H _t	-0.4562	27.4	B,B	-0.0996	-62.5	

not determined by Slater aiming at such detailed numerical studies. One may expect, for instance, that slightly different effective radii could be used for the carbon atoms in the sp^3 , sp^2 , and sp hybrid states, or possibly even for primary, secondary, etc., sp^3 carbons.

We have also tried to apply Hirshfeld's original idea of using weight functions based on the promolecule densities. According to our experience, the decomposition using Hirshfeld-type weights has several drawbacks that prevent us from recommending their use. The numerical integrations by using Hirshfeld weights are much less accurate and/or much more expensive. Furthermore, the numerical values obtained were also discouraging because with the "simple" decomposition scheme both the one- and two-center energy components are exaggerated while with the "improved" scheme one-center energy components lower than -0.5 a.u. are systematically obtained for the hydrogen atoms. The problems are obviously connected with the significant value of the Hirshfeld's weight function of a given nucleus in the vicinity of the others. This means that the atoms are not "well cut," i.e., do not indeed represent domains of the 3D space with a central part assigned to a given atom and an external part with "fuzzy" boundaries. This is especially the case for hydrogen atoms lacking any core shells.

IV. SUMMARY

The total energy of a molecule is presented as a sum of one- and two-atomic energy components in terms of "fuzzy"

atoms, i.e., such divisions of the three-dimensional physical space into atomic regions in which the regions assigned to the individual atoms have no sharp boundaries but exhibit a continuous transition from one to another. By proper definitions the energy components are on the *chemical energy scale*. The method is realized by using Becke's integration scheme and weight function permitting very effective numerical integrations. The results are in good agreement with the chemical picture of molecules and exhibit small basis dependence.

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