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Diatomic interaction energies in the topological theory of atoms in molecules

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Summary. A partitioning of the *ab initio* total energy into one-center and two-center terms is proposed. The partitioning scheme is developed using the auxiliary function $\tilde{L}(2, 1; 1, 2) = \gamma(2, 1)\gamma(1, 2)$ and the topological theory of atoms in molecules. It is shown that this scheme can be used at theoretical levels beyond Hartree–Fock. The numerical results indicate that the two-center terms follow the experimental trend of the dissociation energies for a series of related compounds.

Key words: Electron density – Binding energy – Interaction energy – Topological theory – Charge density

1 Introduction

The theory of atoms in a molecule developed by Bader et al. [1–3] has been used extensively since it first appeared in the literature. This theory has the advantage that the interactions of the atoms in a molecule can be properly described without using artificial orbital localization schemes. Fundamental chemical concepts, such as the Lewis acid–base model, can be extracted from this theory. Useful chemical concepts such as Fukui indices, covalent bond orders and atomic valence indices have recently been developed by Cioslowski et al. [4, 5] and by Mayer et al. [6].

Mayer et al. [6] have developed a method for determining bond orders and atomic valence indices in the context of the topological theory. Their numerical results are in quite good agreement with those obtained by Cioslowski's approach [4]. The starting point in Mayer's formalism is the second-order density matrix from which not only bond orders but also the diatomic interaction energy can be obtained.

The idea of partitioning the total energy into one- and two-center terms was developed in the early semi-empirical methods as a tool for analysing chemical bonds. Ruedenberg [7] carried out an analysis of the energy of the molecular system using density matrices. Pople [8] pointed out, in the context of the semi-empirical CNDO method, that the total energy of a molecular system can be expressed *exactly* in one- and two-center terms, since in the semi-empirical methodologies the three- and four-center integrals do not exist. Clementi [9] and Fischer [10] proposed that the two-center energy components are related to the strength of a chemical bond. Since different approximations are used in the semi-empirical methods there is no unique scheme for the energy partition, and several partitioning schemes have been proposed in the literature depending on the nature of the semi-empirical method employed. Fischer and Kollmar [10] developed an energy partitioning scheme for CNDO, Dewar [11] for the MINDO method and Ruette et al. [12] for the MINDO/SR approach.

Kollmar [13] developed a partitioning scheme for the *ab initio* Hartree–Fock energy, based on a partition of the Hilbert space spanned by the atomic basis functions. Unfortunately, different values for the one- and two-center terms are obtained depending on whether a non-orthogonalized or an orthogonalized basis set is used. All these schemes (*ab initio* or semi-empirical) are based on the attractive idea that the total energy of a molecule can be decomposed as a summation of monoatomic (one-center) and diatomic (two-center) terms, and that the two-center terms can be related to the strength of the chemical bonds.

One of the drawbacks of such partitioning of the total energy is the fact that they are not invariant under a unitary transformation of the basis set. On the other hand, in the framework of the topological theory, the molecular properties are defined in such a way that they are *invariant* under a unitary transformation. The aim of this work is to develop a partitioning scheme in the spirit of the topological theory of atoms in molecules. For this purpose we have developed equations to obtain the diatomic interaction energies within the framework of Bader's theory of atoms in a molecule. The new definitions for the one- and two-center terms could, in principle, be used not only at the Hartree–Fock level but also with correlated *ab initio* methods. It will be shown that within the same level of approximation (HF or MP2) the numerical results are consistent.

2 Theory

One begins with the first-order density matrix $\gamma(\mathbf{1},\mathbf{2})$ written in terms of the canonical or natural spin orbitals, $\psi_i(\boldsymbol{x},\boldsymbol{s}) = \phi_i(\boldsymbol{x})\sigma(\boldsymbol{s})$, and the occupation numbers $\lambda_i(\alpha)$ and $\lambda_i(\beta)$ for α and β electrons:

$$\gamma(\mathbf{1},\mathbf{2}) = \sum_i \lambda_i(\alpha)\psi_i(\mathbf{1},\alpha)\psi_i^*(\mathbf{2},\alpha) + \lambda_i(\beta)\psi_i(\mathbf{1},\beta)\psi_i^*(\mathbf{2},\beta). \tag{1}$$

From Eq. (1) the auxiliary function $\tilde{L}(\mathbf{2},\mathbf{1};\mathbf{1},\mathbf{2}) = \gamma(\mathbf{2},\mathbf{1})\gamma(\mathbf{1},\mathbf{2})$ can be constructed, which was proposed by Mayer et al. [6] as the starting point in their definition of bond order. Integration of the function $\tilde{L}$ carried out over the spatial and spin coordinates, $\mathrm{d}\boldsymbol{X}_1 = \mathrm{d}\boldsymbol{x}_1\mathrm{d}\boldsymbol{s}_1$, gives for a Hartree–Fock single-determinant wave function the total number of electrons N:

$$N = \iint \mathrm{d}\boldsymbol{X}_1\,\mathrm{d}\boldsymbol{X}_2\,\tilde{L}(\mathbf{2},\mathbf{1};\mathbf{1},\mathbf{2}). \tag{2}$$

In case of a single-determinant wave function, $\tilde{L}$ is the exchange part of the second-order density matrix. As shown by Bader [3], the double integration of $\tilde{L}$ in a given atomic basin determines in this case the extent to which electrons are either localized or delocalized in the basin. Note that in the case of a correlated wave function the integration does not give N. Now consider the Laplacian of the electron density of a Hartree–Fock wave function, which is related to the function

$\tilde{L}$ by means of the equation

$$\frac{1}{4}\nabla^2\rho(\mathbf{1}) = \frac{1}{4}\int \mathrm{d}s_1\,\mathrm{d}X_2\,\nabla_1^2\tilde{L}(\mathbf{2},\mathbf{1};\mathbf{1},\mathbf{2}). \tag{3}$$

It follows that

$$\iint \mathrm{d}X_1\,\mathrm{d}X_2\,\nabla_1^2\tilde{L}(\mathbf{2},\mathbf{1};\mathbf{1},\mathbf{2}) = 0. \tag{4}$$

From the definition of $\tilde{L}$ and Eq. (4), the following identity can be obtained:

$$\frac{1}{2}\iint \mathrm{d}X_1\,\mathrm{d}X_2\,\nabla_1\gamma(\mathbf{1},\mathbf{2})\,\nabla_1\gamma(\mathbf{2},\mathbf{1}) = -\frac{1}{4}\iint \mathrm{d}X_1\,\mathrm{d}X_2[\gamma(\mathbf{2},\mathbf{1})\,\nabla_1^2\gamma(\mathbf{1},\mathbf{2}) + \gamma(\mathbf{1},\mathbf{2})\,\nabla_1^2\gamma(\mathbf{2},\mathbf{1})]. \tag{5}$$

The two sides of Eq. (5) are equivalent expressions for $G(\mathbf{1})$ and $K(\mathbf{1})$ of the electronic kinetic energy:

$$G(\mathbf{1}) = \frac{1}{2}\int \mathrm{d}s_1\,\mathrm{d}X_2\,\nabla_1\gamma(\mathbf{1},\mathbf{2})\,\nabla_1\gamma(\mathbf{2},\mathbf{1}), \tag{6}$$

$$K(\mathbf{1}) = -\frac{1}{4}\int \mathrm{d}s_1\,\mathrm{d}X_2[\gamma(\mathbf{2},\mathbf{1})\,\nabla_1^2\gamma(\mathbf{1},\mathbf{2}) + \gamma(\mathbf{1},\mathbf{2})\,\nabla_1^2\gamma(\mathbf{2},\mathbf{1})]. \tag{7}$$

Here $G(\mathbf{1})$ and $K(\mathbf{1})$ are used in the same way as in the theory of atoms in molecules, where it is shown that the integration of $G(\mathbf{1})$ and $K(\mathbf{1})$ gives identical values if the integration is carried out in the space of the atomic basins as well as in the total space [1, 3]. In Bader's theory the electronic potential energy density $V(\mathbf{r})$ can be expressed, for a stationary state, in terms of the Laplacian of the electronic density and the kinetic energy density $G(\mathbf{r})$. Using Eqs. (3), (6) and the local form of the virial theorem [1, 3], the electronic potential energy density can be written as

$$V(\mathbf{1}) = \frac{1}{4}\int \mathrm{d}s_1\,\mathrm{d}X_2\,\nabla_1^2\tilde{L}(\mathbf{2},\mathbf{1};\mathbf{1},\mathbf{2}) - \int \mathrm{d}s_1\,\mathrm{d}X_2\,\nabla_1\gamma(\mathbf{1},\mathbf{2})\,\nabla_1\gamma(\mathbf{2},\mathbf{1}). \tag{8}$$

In the theory of *atoms in a molecule* the electronic energy, $E(\mathrm{A})$, of an atom A in a molecule in its ground-state equilibrium geometry, is written as

$$E(\mathrm{A}) = T(\mathrm{A}) + V(\mathrm{A}), \tag{9}$$

where

$$T(\mathrm{A}) = K(\mathrm{A}) = \int_{\Omega\mathrm{A}} \mathrm{d}\mathbf{x}_1 K(\mathbf{1}) = G(\mathrm{A}) = \int_{\Omega\mathrm{A}} \mathrm{d}\mathbf{x}_1 G(\mathbf{1}) \tag{10}$$

and

$$V(\mathrm{A}) = \int_{\Omega\mathrm{A}} \mathrm{d}\mathbf{x}_1\,V(\mathbf{1}). \tag{11}$$

The integration is carried out over the atomic basin of atom A. In order to calculate the diatomic interaction energies, Eq. (9) is taken as the starting point. Using Eq. (7) and integrating over the atomic basis of atom A one obtains for the kinetic energy of atom A,

$$T(\mathrm{A}) = K(\mathrm{A}) = \int_{\Omega\mathrm{A}} \mathrm{d}\mathbf{x}_1 K(\mathbf{1}) = -\frac{1}{2}\int_{\Omega\mathrm{A}} \mathrm{d}X_1 \sum_{\mathrm{B}} \int_{\Omega\mathrm{B}} \mathrm{d}X_2\,\gamma(\mathbf{1},\mathbf{2})\,\nabla_1^2\gamma(\mathbf{2},\mathbf{1}). \tag{12}$$

To simplify the notation let us introduce the following definition which holds for Hartree–Fock and correlated wave functions:

$$\eta_{ij} = \lambda_i(\alpha)\lambda_j(\alpha) + \lambda_i(\beta)\lambda_j(\beta). \tag{13}$$

Using Eqs. (1), (12) and (13), $T(\mathrm{A})$ can be written as

$$T(\mathrm{A}) = \sum_{\mathrm{B}}\sum_{i,j} -\frac{1}{2}\eta_{ij}\langle\phi_i|\nabla^2\phi_j\rangle_{\mathrm{A}}\langle\phi_i|\phi_j\rangle_{\mathrm{B}}. \tag{14}$$

In a similar way, an equation for the electronic potential energy density of atom A $V(\mathrm{A})$ can be derived using Eqs. (1), (8) and (11):

$$V(\mathrm{A}) = \sum_{\mathrm{B}}\sum_{i,j}\frac{1}{2}\eta_{ij}[\langle\phi_i|\nabla^2\phi_j\rangle_{\mathrm{A}} - \langle\nabla\phi_i|\nabla\phi_j\rangle_{\mathrm{A}}]\langle\phi_i|\phi_j\rangle_{\mathrm{B}}. \tag{15}$$

Let us now introduce two more definitions:

$$\tilde{T}_{ij}(\mathrm{A}) = -\tfrac{1}{2}\langle\phi_i|\nabla^2\phi_j\rangle_{\mathrm{A}} \tag{16}$$

and

$$\tilde{V}_{ij}(\mathrm{A}) = \tfrac{1}{2}[\langle\phi_i|\nabla^2\phi_j\rangle_{\mathrm{A}} - \langle\nabla\phi_i|\nabla\phi_j\rangle_{\mathrm{A}}]. \tag{17}$$

Using Eqs. (16) and (17), the electronic energy of an atom in a molecule can be written as

$$E(A) = \sum_{\mathrm{B}}\sum_{i,j}\eta_{ij}(\tilde{T}_{ij}(\mathrm{A}) + \tilde{V}_{ij}(\mathrm{A}))\langle\phi_i|\phi_j\rangle_{\mathrm{B}} = \sum_{\mathrm{B}}\sum_{i,j}\eta_{ij}\tilde{E}_{ij}(\mathrm{A})S_{ij}(\mathrm{B}), \tag{18}$$

where

$$\tilde{T}_{ij}(\mathrm{A}) + \tilde{V}_{ij}(\mathrm{A}) = \tilde{E}_{ij}(\mathrm{A}) \tag{19}$$

and

$$S_{ij}(\mathrm{B}) = \int_{\Omega\mathrm{B}} \mathrm{d}V\,\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r}) \tag{20}$$

In order to calculate the diatomic interaction energy, Eq. (18) must be split into monoatomic and diatomic terms:

$$E(\mathrm{A}) = \sum_{i,j}\eta_{ij}\tilde{E}_{ij}(\mathrm{A})S_{ij}(\mathrm{A}) + \sum_{\mathrm{B}\neq\mathrm{A}}\sum_{i,j}\eta_{ij}\tilde{E}_{ij}(\mathrm{A})S_{ij}(\mathrm{B}). \tag{21}$$

The first term in Eq. (21) is a one-center or monoatomic term and contains only those contributions to the energy due to an atom interacting with its own electrons:

$$\varepsilon_{\mathrm{A}} = \sum_{i,j}\eta_{ij}\tilde{E}_{ij}(\mathrm{A})S_{ij}(\mathrm{A}). \tag{22}$$

The energy ε_{A} is related to the energy change of atom A when it is bonded to other atoms. If we have only one isolated atom, Eq. (22) is the total energy of the atom.

The second term in Eq. (21) is a two-center term and gives the *interaction energy* of the electrons with atom A, weighted by the molecular overlap of the atom B. In order to obtain a *diatomic interaction energy* which is related to two centers, it is necessary to add the weighted *interaction energy* of the electrons with the second center (atom B). Therefore, the *diatomic interaction energy between atom A and B*, $\mathrm{DI_{AB}}$, is defined as

$$\mathrm{DI_{AB}} = \sum_{i,j} \eta_{ij} \tilde{E}_{ij}(\mathrm{A}) S_{ij}(\mathrm{B}) + \sum_{i,j} \eta_{ij} \tilde{E}_{ij}(\mathrm{B}) S_{ij}(\mathrm{A}). \tag{23}$$

The total Hartree–Fock energy (E_T) of a molecule is therefore given by

$$E_\mathrm{T} = \sum_\mathrm{A} E(\mathrm{A}) = \sum_\mathrm{A} \varepsilon_\mathrm{A} + \sum_\mathrm{A} \sum_{\mathrm{B}>\mathrm{A}} \mathrm{DI_{AB}}. \tag{24}$$

It is important to point out that, even though Eqs. (14) and (15) hold only for a Hartree–Fock wave function, the definitions given by Eqs. (22) and (23) could, in principle, be used with correlated wave functions provided that the sum of the one- and two-center terms gives the total energy of the system.

Molecules containing only two atoms constitute a special case. Since it is possible to derive an equation for the bond energy of the molecule using the diatomic interaction term, the binding energy BE of a diatomic molecule AB is then given by

$$\mathrm{BE} = E_\mathrm{T} - \varepsilon_\mathrm{AO} - \varepsilon_\mathrm{BO} + \mathrm{ZPE} = \mathrm{DI_{AB}} + \varepsilon_\mathrm{A} + \varepsilon_\mathrm{B} - \varepsilon_\mathrm{AO} - \varepsilon_\mathrm{BO} + \mathrm{ZPE}. \tag{25}$$

Here ε_AO and ε_BO are the total energies of the *free* atoms A and B. ZPE is the zero-point vibrational energy of the molecule.

3 Methodology

All calculations were performed at the HF level of theory using Gaussian 92 [14]. For the diatomic molecules, geometry optimizations were also carried out at the MP2 level. The atomic overlap matrices, as well as all other atomic integrals, were done using the programs EXTREME and PROAIM [15]. For H, C, N, O and F a 6-31G* basis set [16] and for P a 6-311G** basis set [17] were employed. In the case of diatomic molecules, the 6-311G** basis sets [17] were used. Effective Core Potentials (ECP) from Stoll et al. [18] with an uncontracted (1111/11111/1) valence basis sets were used for Cl, Br and I, unless other contraction schemes be specified. The atomic orbital exponents of the Cl atom were optimized in order to obtain better values for the $\mathrm{Cl_2}$ molecule. The original set of exponents presented difficulties when the dissociation energy was calculated. The new set of exponents (basis set B) is reported in Table 1 together with the original values (basis set A). No optimization was done for the most diffuse *p* and *d* functions. The covalent bond orders were calculated using the Angyan, Loos and Mayer formalism [6].

4 Results and discussion

In Table 2 we report the numerical values of the diatomic bond properties of $\mathrm{C_2H}_n$ ($n = 2, 4, 6$), as well as for $\mathrm{N_2X_4}$ (X = H, O and F) compounds. The $\mathrm{DI_{AB}}$ values follow the same trend as the bond orders and the experimental binding energies. The high absolute values for $\mathrm{DI_{AB}}$ are due to the fact that these terms are related to the *total* energy of the molecule which is quite high. According to Eq. (24), the $\mathrm{DI_{AB}}$ term is that part of the total molecular energy which is distributed into the bond. Since different molecules have different *total* energies but may have similar binding energies, the numerical values of $\mathrm{DI_{AB}}$ can be used in a comparative way only. For

Table 1. Exponents for the Cl atomic basis

Original basis set **A**	Optimized basis set **B**
s-type	
14.0730760000	13.9997243570
2.3315650000	2.2988888732
0.5071000000	0.5346775169
0.1824330000	0.1959095423
p-type	
3.3531290000	2.7276884237
0.7856860000	1.2865793960
0.2674540000	0.5647098646
0.0782750000	0.2647896940
0.0154770000	0.0154770000
d-type	
0.5000000000	0.5000000000

Table 2. Diatomic properties at the HF/6-31G** level. Values at MP2/6-31G** are given in parentheses. Bond distance (R_{AB}), Bond order (B_{AB}), Diatomic interaction energy (DI_{AB}) and experimental binding energy (BE)

Molecule	Bond A–B	R_{AB} [Angs.]	B_{AB}	DI_{AB} [au]	Experimental BE_{AB}[a] [kcal/mol]
C_2H_2	C–C	1.186 (1.186)	2.863 (2.712)	−3.838 (−3.656)	230
	C–H	1.057 (1.057)	(0.979) (0.972)	−0.994 (−0.962)	
C_2H_4	C–C	1.317 (1.317)	1.889 (1.828)	−2.575 (−2.487)	173
	C–H	1.075 (1.075)	0.982 (0.965)	−0.995 (−0.957)	
	H–H	1.829 (1.829)	0.040 (0.037)	−0.043 (−0.041)	
C_2H_6	C–C	1.540 (1.540)	0.997 (0.966)	−1.355 (−1.314)	88
	C–H	1.085 (1.085)	0.968 (0.956)	−0.987 (−0.953)	
	H–H	1.746 (1.746)	0.047 (0.042)	−0.035 (−0.033)	
N_2H_4	N–N	1.410	1.227	−2.313	59.03
	N–H	0.985	0.780	−0.944	
	H–H	1.731	0.018	−0.023	
N_2F_4	N–N	2.249	0.748	−1.354	21.03
	N–F	1.313	1.0678	−2.691	
	F–F	2.050	0.158	−0.756	
N_2O_4	N–N	1.580	0.700	−1.166	13.70
	N–O	1.166	1.732	−3.976	
	O–O	2.139	0.333	−1.179	

[a] Experimental values from Ref. [19]

example, the DI_{AB} value for the N–N bond in N_2F_4 is equal to the DI_{AB} value for C–C in C_2H_6, but the experimental binding energies are quite different. For a series of related compounds such as C_2H_n ($n = 2, 4, 6$) or N_2X_4 (X = H, F, O) the DI_{AB} terms show the same order as the binding energies.

Table 3. Diatomic properties for polyatomic molecules at the HF level. Bond distance (R_{AB}), Bond order (B_{AB}), diatomic interaction energy (DI_{AB}) and experimental binding energies (BE)[a]

Molecule	Bond A–B	R_{AB} [Angs.]	B_{AB}	DI_{AB} [au]	Experimental BE_{AB}[b] [kcal/mol]
H_2O	H–O	0.943	0.623	−0.927	119
	H–H	1.506	0.007	−0.012	
PCl_3	P–Cl	2.116	0.891	−1.295	78
	Cl–Cl	3.244	0.142	−0.213	
PBr_3	P–Br	2.280	0.980	−1.226	63
	Br–Br	3.523	0.147	−0.1823	
PI_3	P–I	2.530	1.081	−1.110	44
	I–I	3.946	0.141	−0.141	
HCN	N–C	1.133	2.232	−3.865	
	C–H	1.059	0.923	−0.957	
	N–H	2.192	0.087	*−0.127*	
TS	N–C	1.169	1.857	−3.344	
C–H–N	C–H	1.152	0.503	−0.498	
	N–H	1.468	0.492	*−0.486*	
CNH	N–C	1.155	1.675	−3.014	
	C–H	2.138	0.021	−0.048	
	N–H	0.984	0.649	*−0.825*	

[a] Basis set: H, C N and O 6-31G**, P 6-311G*, Cl (basis set A), Br and I (31/311/1) valence basis set ECP from Ref. [18]

[b] Experimental values from Ref. [19]

In addition to testing the DI_{AB} values at the HF level, we also consider its application at the correlated MP2 level (see Table 2). The calculations were carried out using the same geometries as those obtained at the HF level. When correlated wave functions are used, the bond orders tend to decrease. This result was previously reported [6] for the N_2 molecule. This decrease is also observed for the diatomic interaction energy. Nevertheless, the order is the same as at the HF level, i.e. $DI_{CC}(C_2H_2) > DI_{CC}(C_2H_4) > DI_{CC}(C_2H_6)$. This result shows that the DI_{AB} values calculated at a correlated level can be used with a certain confidence, taking into account that in the correlated case the function $\tilde{L}$ (**2**, **1**; **1**, **2**) is an auxiliary function that has no direct physical meaning.

The order of the DI_{AB} values correlates for a related set of molecules with the experimental bond energies better than the bond orders. This becomes obvious from the calculated results for PX_3 (Table 3). The bond orders B_{AB} increase from $PCl_3 < PBr_3 < PI_3$, while the DI_{AB} values and the P–X bond energies show the reverse trend. The diatomic interaction energies depend on the atoms involved in the interactions much more than the bond orders do. Table 3 shows that the B_{AB} values for the halogen–halogen interactions are very similar, while the DI_{AB} values are quite different. It is not possible to compare the magnitude of DI_{AB} for quite different molecules. For example, the energy for the P–I bond ($DI_{PI} = -1.110$) is higher than the corresponding value of H–O ($DI_{HO} = -0.927$) in H_2O, but the bond energy for P–I is lower than for H–O.

In order to test the capability of the DI_{AB} values to describe chemical changes during a chemical reaction, the proton transfer reaction from HCN to CNH was studied. Table 3 shows that the DI_{CH} values become smaller from the initial state (HCN, $DI_{CH} = -0.957$) to the final state (CNH, $DI_{CH} = -0.048$), reaching a mean value of -0.498 in the transition state (TS). On the other hand, the DI_{NH} value increases from -0.127 to -0.825. The DI_{XH} ($X = C, N$) value decreases as the distance R_{XH} increases. The DI_{CC} values show that the interaction between C and N atoms is a minimum in the CNH molecule. This is reasonable, because in CNH there is only a carbon–nitrogen double bond, while in HCN there is a triple bond. These results demonstrate that the diatomic interaction energies (DI_{AB} values) are capable of describing the chemical changes along a reaction path in a reasonable way.

Table 4 shows that the one-center energy values (ε_A) are lower in absolute value than Bader's atomic values, because Bader's term includes not only the atomic energy, but also part of the interatomic interaction energy. Table 4 shows that there is a strong loss of energy of the atoms ($\Delta\varepsilon > 0$; $\Delta\varepsilon = \varepsilon_A - \varepsilon_{A0}$) when they form molecules. This is the reason why the $DI_{CC}(C_2H_6)$ and $DI_{NN}(N_2F_4)$ values are equal, while the binding energies are quite different (see Table 2). The energetic change of the N atom when forming the N_2F_4 molecule ($\Delta\varepsilon = 4.072$) is greater than the change that takes place at the C atom ($\Delta\varepsilon = 2.961$) for the formation of the C_2H_6 molecule. Since the binding energy is a global value that involves not only the breaking of the bonds but the necessary energy to bring the atoms from the initial electronic state to the final electronic state (ground-state free atoms), these changes have to be taken into account. For comparison, the MP2 values are included in Table 4. Although the magnitudes of ε_A(MP2) and ε_{A0}(MP2) are greater than the corresponding HF values, the difference between them ($\Delta\varepsilon$) is not very large.

Table 5 shows that in the PX_3 ($X = $ Cl, Br, I) series, the halogen atoms lose energy ($\varepsilon_A > \varepsilon_{A0}$) while the P atom gains energy ($\varepsilon_A > \varepsilon_{A0}$). It is interesting to note that while Bader's atomic energies for the carbon atom in HCN and CHN (TS) are quite similar, the ε_A are different. The ε_A value for the C atom in the TS is higher in magnitude than in the HCN molecule, because the loss of the diatomic interaction energy (see Table 3) of the C–H and C–N moieties is partially gained by the C atom. This type of interaction cannot be described using Bader's atomic energies, because they include not only the atomic energy but also part of the interaction energy.

Finally, in Table 6 we report numerical results for some diatomic molecules optimized at the HF and MP2 levels. The calculated binding energies, BE, include the ZPE corrections which are listed in Table 7. At the MP2 level the calculated binding energies are closer to the experimental values than the HF values. It is interesting to note that in some cases the magnitude of DI_{AB}(MP2) is lower than the magnitude of DI_{AB}(HF), although the BE values at MP2 are always higher than the BE values calculated at the HF level (see Table 6). This comes from the simultaneous change of the interaction energies DI_{AB} and the atomic energy values (see Eq. (25)).

5 Summary and conclusion

We summarize the features of this work as follows:

(A) The total Hartree–Fock energy of a molecule can be written as

$$E_T = \sum_{A} \varepsilon_A + \sum_{A} \sum_{B>A} DI_{AB},$$

Table 4. Atomic properties for C_2H_n and N_2X_4 molecules at the HF level. Atomic net charge (Q_A), atomic valence index (V_A), monoatomic energy (ε_A), free atom energy (ε_{A0}) and energy difference ($\Delta\varepsilon$)

Molecule	Atom A	Q_A	V_A	ε_A	Bader's atomic energy	ε_{A0}	$\Delta\varepsilon$
C_2H_2	C	−0.121	3.914	−35.156	−37.842	−37.677	2.521
		(−0.116)	(3.752)	(−35.412)	(−37.987)	(−37.737)	(2.325)
	H	+0.121	1.054	−0.227	−0.569	−0.498	0.271
		(+0.116)	(1.044)	(−0.225)	(−0.558)	(−0.498)	(0.273)
C_2H_4	C	+0.082	3.985	−34.894	−37.725	−37.677	2.783
		(+0.027)	(3.880)	(−35.205)	(−37.925)	(−37.737)	(2.532)
	H	−0.041	1.109	−0.289	−0.647	−0.498	0.209
		(−0.013)	(1.085)	(−0.273)	(−0.619)	(−0.498)	(0.225)
C_2H_6	C	+0.230	4.011	−34.716	−36.629	−37.677	2.961
		(+0.115)	(3.957)	(−35.088)	(−37.887)	(−37.737)	(2.649)
	H	−0.077	1.124	−0.303	−0.663	−0.498	0.195
		(−0.038)	(1.098)	(−0.281)	(−0.629)	(−0.498)	(0.217)
N_2H_4	N	−0.882	2.845	−52.127	−54.690	−54.382	2.255
	H	+0.441	0.833	−0.107	−0.4344	−0.498	0.391
N_2F_4	N	+0.810	3.064	−50.310	−53.602	−54.382	4.072
	F	−0.405	1.343	−97.626	−99.749	−99.362	1.736
N_2O_4	N	+0.868	4.379	−48.871	−53.871	−54.382	5.511
	O	−0.433	2.277	−72.196	−74.074	−74.779	2.583

[a] Basis sets: all 6-31G**. MP2 values in parentheses

Table 5. Atomic properties for some polyatomic molecules at the HF level[a]. Atomic net charge (Q_A), atomic valence index (V_A), monoatomic energies (ε_A). Bader's energies and free atom energies (ε_{A0})

Molecule	Atom A	Q_A	V_A	ε_A	Bader's atomic energy	ε_{A0}
H_2O	O	−1.239	1.246	−74.0477	−75.3346	−74.7790
	H	+0.620	0.630	−0.0549	−0.3445	−0.4983
PCl_3	P	+1.470	2.674	−363.6784	−366.4058	−340.7073
	Cl	−0.488	1.178	−5.6097	−6.2055	−14.7309
PBr_3	P	+1.137	2.939	−362.5872	−365.2554	−340.7073
	Br	−0.379	1.274	−4.4537	−4.9719	−13.1217
PI_3	P	+0.536	3.246	−360.6644	−363.1811	−340.7073
	I	−0.177	1.364	−3.2920	−3.7234	−11.1761
HCN	N	−1.479	2.318	−53.5850	−55.2938	−54.3823
	C	+1.287	3.154	−34.1413	−37.0480	−37.6771
	H	+0.192	1.009	−0.2022	−0.5353	−0.4983
TS C–H–N	N	−1.338	2.350	−53.5469	−55.3148	−54.3823
	C	+1.058	2.360	−34.7857	−37.0190	−37.6771
	H	+0.282	0.996	−0.1358	−0.4610	−0.4983
CNH	N	−1.813	2.324	−53.7803	−55.6270	−54.3823
	C	+1.226	1.696	−35.1275	−36.8785	−37.6771
	H	+0.587	0.670	−0.0654	−0.3545	−0.4983

[a] Basis set: H, C, N and O: 6-31G**, P 6–311G*, Cl (basis set A), Br and I (31/311/1) valence basis set ECP from Ref. [18]

Table 6. Diatomic properties. Bond distance (R_{AB}), bond order (B_{AB}), diatomic interaction energy (DI_{AB}), experimental and calculated binding energies (BE) at the MP2 level[a]

Molecule	Bond A–B	$R_{AB}^{(2)}$ [Angs.]	B_{AB}	DI_{AB} [au]	Calculated BE [kcal/mol]	Experimental BE[b] [kcal/mol]
H_2	H–H	0.738 (0.735) *0.742*	0.992 (1.000)	−0.5750 (−0.5662)	94.30 (76.76)	*103.25*
N_2	N–N	1.120 (1.071) *1.098*	2.834 (3.039)	−5.7381 (−6.2716)	215.20 (106.41)	*225.07*
CO	C–O	1.137 (1.040) *1.128*	1.757 (1.591)	−3.6984 (−3.3228)	255.74 (169.37)	*256.2*
Cl_2	Cl–Cl	2.010 (1.991) 1.988	1.276 (1.327)	−3.3797 (−3.0089)	56.56 (24.25)	*57.3*
Br_2	Br–Br	2.310 (*2.286*) *2.284*	1.283 (*1.338*)	−2.9002 (*− 2.7257*)	42.45 (*13.23*)	*45.45*
I_2	I–I	2.723 (2.695) *2.666*	1.270 (1.325)	−2.3938 (−2.5016)	35.33 (10.84)	*35.60*

[a] HF values in parentheses. Basis sets: H, N, C, O 6-311G**, Br and I (1111/11111/1) valences basis set ECP. Cl Basis set **B**.

[b] Values in italic are from ref. [19].

Table 7. Atomic properties for some diatomic molecules at the MP2 level. Atomic net charge (Q_A), atomic valence index (V_A), monoatomic energies (ε_A), free atom energies (ε_{A0}), zero-point energies (ZPE) and energy differences ($\Delta\varepsilon_A$)[a]

Molecule	Atom A	Q_A	V_A	ε_A [au]	ε_{A0} [au]	ZPE [kcal/mol]	$\Delta\varepsilon_A$
H_2	H	0.000	0.993	−0.2926	−0.4998	6.481	2.2072
		(0.000)	(1.000)	(−2.2831)	(−0.4998)	(6.566)	(0.2167)
N_2	N	0.000	2.834	−51.8019	−54.4970	3.110	2.6951
		(0.000)	(3.039)	(−51.3502)	(−54.3981)	(3.909)	(3.0479)
CO	O	−1.093	1.758	−74.0634	−74.9426	3.043	0.8792
		(−1.330)	(1.591)	(−74.3206)	(−74.8035)	(3.481)	(0.4847)
	C	1.093	1.758	−35.3581	−37.7649		2.4068
		(1.330)	(1.591)	(−35.1263)	(−37.6891)		(2.5628)
Cl_2	Cl	0.000	1.276	−13.1732	−14.8173	0.859	1.6441
		(0.000)	(1.327)	(−13.2165)	(−14.7009)	(0.913)	(1.4844)
Br_2	Br	0.000	1.283	−11.8106	−13.2265	0.476	1.4159
		(0.000)	(1.338)	(−11.7734)	(−13.1253)	(0.508)	(1.3519)
I_2	I	0.000	1.270	−10.0959	−11.2644	0.309	1.1688
		(0.000)	(1.325)	(−9.9376)	(−11.1795)	(0.329)	(1.2419)

[a] HF values in parentheses. Basis sets: H, N, C, O 6-311G**, Br and I (1111/11111/1) valences basis set ECP. Cl basis set **B**

where A and B run over atoms, and the DI_{AB} term is the interaction energy between atoms A and B. ε_A is the atomic energy of the atom A.

(B) The interaction energy DI_{AB} is related to the important chemical concept of bond energy, albeit not directly. For example, the binding energy for a diatomic molecules is given by

$$BE = E_T - \varepsilon_{A0} - \varepsilon_{B0} + ZPE = DI_{AB} + \varepsilon_A + \varepsilon_B - \varepsilon_{A0} - \varepsilon_{B0} + ZPE,$$

where ε_{A0} and ε_{B0} are the total energy of the *free* atoms A and B, and ZPE is the zero-point vibrational energy.

(C) In the theory of atoms in a molecule, the total energy of a molecule is given by

$$E_T = \sum_A E_A$$

where the terms E_A are the atomic energies of the atoms in the molecule. It is not possible therefore, to know which part of E_A belongs to the atom itself and which part is related to the interatomic interactions.

(D) Equation (24) shows how the *total energy* of a given molecule is distributed among atoms (ε_A) and atom pairs (DI_{AB}).

(E) The value of DI_{AB} can be used to compare the trends of the bond strengths for a family of related compounds such as C_2H_n ($n = 2, 4, 6$) or N_2X_4 ($X = O, F, H$).

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