Theor Chem Acc (2002) 107:362–371
DOI 10.1007/s00214-002-0356-8

Theoretical Chemistry Accounts

Regular article

The calculation of electron localization and delocalization indices at the Hartree–Fock, density functional and post-Hartree–Fock levels of theory

Jordi Poater, Miquel Solà, Miquel Duran, Xavier Fradera

Institut de Química Computacional and Departament de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain

Received: 13 February 2002 / Accepted: 24 April 2002 / Published online: 18 June 2002
© Springer-Verlag 2002

Abstract. Localization, $\lambda(A)$, and delocalization indices, $\delta(A,B)$, as defined in the atoms in molecules theory, are a convenient tool for the analysis of molecular electronic structure from an electron-pair perspective. These indices can be calculated at any level of theory, provided that first- and second-order electron densities are available. In particular, calculations at the Hartree–Fock (HF) and configuration interaction (CI) levels have been previously reported for many molecules. However, $\lambda(A)$ and $\delta(A,B)$ cannot be calculated exactly in the framework of Kohn–Sham (KS) density functional theory (DFT), where the electron-pair density is not defined. As a practical workaround, one can derive a HF-like electron-pair density from the KS orbitals and calculate approximate localization and delocalization indices at the DFT level. Recently, several calculations using this approach have been reported. Here we present HF, CI and approximate DFT calculations of $\lambda(A)$ and $\delta(A,B)$ values for a number of molecules. Furthermore, we also perform approximate CI calculations using the HF formalism to obtain the electron-pair density. In general, the approximate DFT and CI results are closer to the HF results than to the CI ones. Indeed, the approximate calculations take into account Coulomb electron correlation effects on the first-order electron density but not on the electron-pair density. In summary, approximate DFT and CI localization and delocalization indices are easy to calculate and can be useful in the analysis of molecular electronic structure; however, one should take into account that this approximation increases systematically the delocalization between covalently bonded atoms, with respect to the exact CI results.

Key words: Localization index – Delocalization index – Topological analysis – Electron-pair density – Density functional theory

Correspondence to: X. Fradera
e-mail: xavier@iqc.udg.es

1 Introduction

The quantum theory of atoms in molecules (AIM) has gained popularity in the last decade as a rigorous method for molecular structure analysis [1]. The AIM theory provides a solid framework for partitioning a molecule into its constituent atoms. Accordingly, every molecular property can be partitioned into atomic contributions. The basis for the definition of atoms in a molecule is the one-electron density or charge density, $\rho(\mathbf{r})$, which is a quantum observable and amenable to experimental determination by means of X-ray crystallography. Thus, in principle, the AIM theory can be applied to the analysis of electron densities obtained from experiment or calculated at any level of theory. In practice, it has been mostly used for the analysis of charge densities calculated by using ab initio quantum mechanical methods; however, in recent years, there has been increasing interest in the analysis of experimental charge densities [2].

Following the AIM theory, an atomic basin is defined as a region in real space bound by zero-flux surfaces in $\rho(\mathbf{r})$ or by infinity [1]. Usually, each basin contains an atomic nucleus, which acts as a topological attractor for the basin; thus, each basin can be assigned to one of the atoms in a molecule. This partitioning scheme ensures that each of the atomic subsystems behaves as a proper open system [1]. Moreover, the atomic contributions to any molecular property can be calculated by integrating through the atomic basins. For instance, the electron population of an atom A is defined as follows,

$$N(A) = \int_A \rho(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{1}$$

where the subscript A indicates that the integration has to be carried out only through the space corresponding to the atomic basin of the atom A. The summation of all the atomic electron populations in a molecule yields the number of electrons, N.

Even though the AIM theory is based on the topographical analysis of the one-electron density, the

second-order of electron-pair density, $\Gamma(\mathbf{r_1}, \mathbf{r_2})$, contains relevant information on the distribution of the electrons between the atoms in a molecule [3, 4, 5]. Knowledge of the electron-pair density allows the electron localization and delocalization indices to be defined [6],

$$\lambda(A) = -2D_2(A,A) + N(A)N(A) \ , \tag{2}$$

$$\delta(A,B) = -4D_2(A,B) + 2N(A)N(B) \ , \tag{3}$$

where $D_2(A,A) = \int_A \Gamma(\mathbf{r_1}, \mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$ and $D_2(A,B) = \int_{A,B} \Gamma(\mathbf{r_1}, \mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} + \int_{B,A} \Gamma(\mathbf{r_1}, \mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$.

$D_2(A,A)$ corresponds to the probability of having two electrons in the basin of atom A, while $D_2(A,B)$ is the probability of having an electron in the basin of atom A at the same time that there is another electron in the basin of atom B. Actually, the calculation of localization and delocalization indices as defined in Eqs. (2) and (3) corresponds to a partition of the exchange–correlation density,

$$\Gamma_{XC}(\mathbf{r_1}, \mathbf{r_2}) = 2\Gamma(\mathbf{r_1}, \mathbf{r_2}) - \rho(\mathbf{r_1})\rho(\mathbf{r_2}) \ , \tag{4}$$

between atoms and pairs of atoms. At the Hartree–Fock (HF) level, $\Gamma_{XC}(\mathbf{r_1}, \mathbf{r_2})$ accounts for the exchange or Fermi correlation between electrons [7]. At higher levels of theory, $\Gamma_{XC}(\mathbf{r_1}, \mathbf{r_2})$ also includes Coulomb correlation effects. Thus, $\lambda(A)$ is related to the amount of correlation between electrons in atom A, while $\delta(A,B)$ relates to the correlation between electrons in atoms A and B. Since $\Gamma_{XC}(\mathbf{r_1}, \mathbf{r_2})$ must integrate to the negative of the number of electrons in the system, $-N$, the summation of all the localization and delocalization indices in a molecule must be equal to N.

$D_2(A,A), D_2(A,B), \lambda(A)$, and $\delta(A,B)$ values for a small set of diatomic molecules at the HF level of theory are reported in Table 1. For homonuclear molecules, the two atoms are denoted A and A', i.e., the delocalization index is $\delta(A,A')$. It is interesting to compare these values with those corresponding to the noninteracting atoms. Consider, for instance, two H atoms at infinite separation. D_2(H, H) is zero for each of the H atoms because there is only one electron and no electron pairs in each basin, while D_2(H, H′) is 1, which corresponds to an interatomic electron pair with infinite interelectronic distance (one electron in each basin). Then, following Eqs. (2) and (3), $\lambda(H) = 1$, and $\delta(\mathrm{H}, \mathrm{H}') = 0$, i.e. there is one electron localized in each H atom and no electron delocalization between the two atoms. The situation is different for the H_2 molecule. At the HF level, the two electrons are in a σ orbital that is delocalized between the two atoms, and each electron has a 50% probability of being in each atom. Since there is no correlation between two electrons of unlike spin at the HF level, the probability that both electrons are in one of the two basins is $D_2(\mathrm{H}, \mathrm{H}) = 0.5 \times 0.5 = 0.25$. Accordingly, the probability of one electron being in H and the other in H′ is $D_2(\mathrm{H}, \mathrm{H}') = 2 \times 0.5 \times 0.5 = 0.5$, where the factor 2 accounts for the two possible ways of putting two electrons in two atoms: H(1)H′(2) and H(2)H′(1). Using these values, one obtains $\lambda(\mathrm{H}) = 0.5$ and $\delta(\mathrm{H}, \mathrm{H}') = 1$ (Table 1). The formation of the N_2 molecule also leads to a decrease in the number of interatomic electron pairs, 47.48, with respect to the 49 pairs that can be formed between the isolated atoms. At the HF level, $\lambda(N)$ and $\delta(N, N')$ are 5.48 and 3.04.

The CO molecule has 42.68 interatomic electron pairs. This value can be compared to the number of electron pairs that are formed between two isolated C and O atoms (48) and between two C^+ and O^- ions (45). $\delta(\mathrm{C}, \mathrm{O})$ is 1.57, significantly lower than $\delta(N, N')$ in N_2, because the polarity of the bond leads to an inequal sharing of the three electron pairs between the C and O atoms. Finally, for the LiF molecule, $D_2(\mathrm{Li}, \mathrm{F})$ is 20.39, very close to the value of 20 for the isolated Li^+ and F^- ions. In comparison, two isolated neutral Li and F atoms form 27 interatomic electron pairs. $\delta(\mathrm{Li}, \mathrm{F})$ is rather low (about 0.2), in agreement with the ionic character of the bond.

According to the results just discussed here and in previous articles [6, 8, 9], the localization index, $\lambda(A)$, gives the number of electrons that are localized in atom A. For any atom, the localization index is always smaller than or equal to the atomic population. Actually, the ratio 100 $[\lambda(A)/N(A)]$ is the percentage of electron localization in atom A. It can reach 100% only for isolated atoms. In practice, values close to 100% are obtained for atoms which have only closed-shell interactions with their neighbors. The delocalization index, $\delta(A,B)$, corresponds to the number of electrons delocalized or shared between the atoms A and B. High values of $\delta(A,B)$ are usually obtained for pairs of bonded atoms with open-shell interactions. The actual values of $\delta(A,B)$ depend on the order and polarity of the bond between the two atoms. For polyatomic molecules, it is worth remarking that delocalization indices between nonbonded atoms, although generally small, can be of chemical significance in some cases [6, 8, 9].

Equations (2), (3) and (4) are completely general and can be used at any level of theory, provided that the first and second-order density functions are known. In particular, most of the current theoretical ab initio methods express the molecular wavefunction in terms of molecular orbitals (MOs). Then $\lambda(A)$ and $\delta(A,B)$ can be expressed as

$$\lambda(A) = -2\sum_{i,j,k,l} D_{ijkl}S_{ij}(A)S_{kl}(A) + N(A)^2 \ , \tag{5}$$

Table 1. Atomic populations, N, integrated values of the electron pair-density, D_2, localization λ, and delocalization, δ , indices for the H_2, N_2, LiF, and CO molecules at the Hartree–Fock (*HF*) level. Results from Ref. [6]

molecule	atom	N(A)	D_2(A,A)	D_2(A,B)	λ(A)	δ(A,B)
H_2	H	1.000	0.250	0.500	0.500	1.000
N_2	N	7.000	21.761	47.479	5.479	3.042
LiF	Li	2.060	1.136	20.387	1.971	0.178
	F	9.940	44.447		9.851	
CO	C	4.647	8.865	42.677	3.860	1.574
	O	9.354	39.463		8.567	

$$\delta(A,B) = -4\sum_{i,j,k,l} D_{ijkl}S_{ij}(A)S_{kl}(B) + 2N(A)N(B) \ , \qquad (6)$$

respectively, where $\{D_{ijkl}\}$ are density matrix elements for the second-order density matrix in a MO base, and $\{S_{ij}(A)\}$ are overlaps between MOs, integrated within the basin of atom A. The four-index summations in Eqs. (5) and (6) run over all the occupied MOs in the molecule. These equations can also be expressed in terms of basis functions,

$$\lambda(A) = -2\sum_{\mu,\nu,\lambda,\sigma} D_{\mu\nu\lambda\sigma}S_{\mu\nu}(A)S_{\lambda\sigma}(A) + N(A)^2 \ , \qquad (7)$$

$$\delta(A,B) = -4\sum_{\mu,\nu,\lambda,\sigma} D_{\mu\nu\lambda\sigma}S_{\mu\nu}(A)S_{\lambda\sigma}(B) + 2N(A)N(B) \ , \qquad (8)$$

$\{D_{\mu\nu\lambda\sigma}\}$ are density matrix elements for the second-order density matrix in an atomic orbital base, and $\{S_{\mu\nu}(A)\}$ are overlaps between basis functions, integrated within the basin of atom A.

At the HF level of theory, the electron-pair density can be expressed in terms of the one-electron density matrix [10],

$$\Gamma(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{2}\begin{vmatrix} \rho(\mathbf{r_1},\mathbf{r_1}) & \rho(\mathbf{r_1},\mathbf{r_2}) \\ \rho(\mathbf{r_2},\mathbf{r_1}) & \rho(\mathbf{r_2},\mathbf{r_2}) \end{vmatrix} \ . \qquad (9)$$

Then, the expressions for the localization and delocalization indices at the restricted HF level for closed-shell molecules can be written as [6],

$$\lambda(A) = 2\sum_{i,j}\left[S_{ij}(A)\right]^2 \ , \qquad (10)$$

$$\delta(A,B) = 4\sum_{i,j} S_{ij}(A)\,S_{ij}(B) \ . \qquad (11)$$

At the HF level of theory, the localization and delocalization indices reduce to Wiberg indices [11] if the integrations over atomic basins are replaced by a Mulliken-like partitioning in Hilbert space [12, 13].

Localization and delocalization indices have been calculated for a number of molecules at the HF and configuration interaction (CI) levels of theory [6, 8, 9, 12, 13, 14, 15, 16, 17]. The evolution of the localization and delocalization indices during the course of several reactions has been studied [8], as well as the effects of solvation on the electron-pairing patterns of several molecules [15]. Although most of the calculations reported correspond to closed-shell molecules, this kind of analysis can be extended easily to open-shell molecules [16]. In general, it has been found that at the HF level the results obtained from the AIM analysis are generally consistent with the qualitative predictions of the simple Lewis model [18], especially for diatomic molecules; however, the results obtained at the CI level of theory are quite different from the HF ones. In general, for pairs of atoms forming covalent bonds, $\delta(A,B)$ values calculated at the CI level are significantly lower than the HF ones, especially for nonpolar covalent bonds. In contrast, for pairs of atoms with closed-shell bonds (ionic or van der Waals) or nonbonded atoms, the HF and CI results are very similar [6]. From a physical point of view, the HF method accounts only for exchange or Fermi correlation, which is the main driving force towards the pairing of electrons of different spin [3, 4, 5]. Post-HF methods, such as CI, also take into account Coulomb correlation, which considers the instantaneous repulsion between electrons of any spin, thus disrupting the pairing of α and β electrons in covalent bonds.

In addition to the calculation of $\lambda(A)$ and $\delta(A,B)$ as defined here, there exist other approaches for studying the localization or delocalization of electrons in molecules. The best known is the electron localization function (ELF) [19], which can be used to locate the regions of maximal electron localization in real space. Actually, both approaches are complementary. A recent study has found that the delocalization index correlates with the electron population in the bonding region as determined from the topological analysis of ELF [20]. Furthermore, it is worth saying that the concept of electron delocalization can be extended to include three-center electron delocalization [21], which has been used to characterize three-center bonding [22]; however, third-order electron densities are needed for this kind of analysis, which precludes its use at post-HF levels of theory.

Recently, several authors have used the HF expressions of $\lambda(A)$ and $\delta(A,B)$ (Eqs. 10, 11) with Kohn–Sham (KS) orbitals obtained with density functional theory (DFT) methods [23, 24, 25, 26, 27]. From a practical point of view, in the cases where HF calculations are available for comparison [26], the DFT results obtained in this way are very close to the HF ones. In general, the only difference is that electron delocalization between covalently bonded atoms increases slightly at the DFT level of theory [26]. This is at variance with the results reported in Ref. [6], where it was shown that consideration of Coulomb correlation at the CI level generally leads to a significant decrease in the electron delocalization between covalently bonded atoms. From a theoretical point of view, using Eqs. (10) and (11) with KS wavefunctions obtained by means of DFT methods is questionable, because it assumes that the electron-pair density at the DFT level of theory can be constructed using the same formalism valid at the HF level. However, since there is not yet a practical way to obtain molecular electron-pair densities in DFT methods [28], this is the only feasible approach at the moment for the calculation of approximate localization and delocalization indices at the DFT level.

The aim of this work is to analyze the effects of introducing electron correlation at several levels of theory on the atomic populations and on localization and delocalization indices. In particular, special attention is paid to the approximate results obtained at the DFT level of theory. For such a purpose, systematic calculations of $\lambda(A)$ and $\delta(A,B)$ for a number of representative molecules using the HF, DFT, and CI methods were performed. At the DFT level of theory, where the electron-pair density is not available, the HF expressions, Eqs. (10) and (11), were used to calculate approximate localization and delocalization indices. At the CI level of theory, two different approaches were used for the calculation of localization and delocaliza-

tion indices. First, Eqs. (7) and (8) and the CI electron-pair density were used to obtain $\lambda(A)$ $\delta(A,B)$ indices, taking explicitly into account all the correlation effects present in the CI wavefunction. Second, Eqs. (10) and (11) and the natural orbitals (NOs) generated in the CI calculation were used to obtain approximate localization and delocalization indices, in the spirit of the approximate DFT calculations reported in the literature [23, 24, 25, 26, 27]. The comparison of the exact and approximate results at the CI level of theory will allow the validity of using the HF equations for the electron-pair density in the context of DFT and ab initio post-HF calculations to be assessed.

2 Methods

The present work is focused on the study of three series of molecules: diatomic systems, hydrides, and polyatomic molecules. HF and CI with singles and doubles excitations results were taken from Ref [6]. DFT calulations with the B3LYP functional were carried out for all the molecules, using the Gaussian 98 [29] and Aimpac [30] packages. At the three levels of theory, the 6-311 + + G(2d,2p) basis sets was used for the hydride molecules and H_2, while the 6-311G(2d) basis set was used for He_2 and Ar_2, and the 6-311 + G(2d) basis set for the rest of the diatomic molecules. The 6-31G* basis set was used for CO_2, SO_2, and SO_3, and the 6-31G** basis set was used for C_2H_4, C_2H_6, and B_2H_6. Molecular geometries were completely optimized at all levels of theory.

The atomic populations and the localization and delocalization indices at the HF and CI levels correspond to the results reported in Ref. [6]. Approximate DFT and CI indices were calculated by using the HF expressions in Eqs. (10) and (11) with the KS orbitals and the NOs obtained at the DFT and CI levels of theory, respectively. For the approximate CI calculations, the occupations of the NOs are replaced by the occupations obtained at the HF level of theory: for a closed-shell molecule with N electrons, the first $N/2$ NOs are considered doubly occupied and the rest are considered as empty. In fact, the only difference between the exact HF calculations and the approximate DFT and CI calculations is in the set of orbitals that is actually used in each calculation; therefore, in relation to the calculation of $\lambda(A)$ and $\delta(A,B)$ values, the three cases can be considered as HF calculations. Thus, HF(DFT) and HF(CI) are used to denote the approximate DFT and CI calculations, respectively. Note that the HF and DFT orbital occupations are identical, but different from the CI NO occupations; thus, the atomic populations calculated with the HF(CI) approximation are different from the exact CI populations.

The accuracy of the integrations was assessed by ensuring that the integrated Laplacian in each atomic basin was close to zero. Furthermore, for each molecule, both the summation of all the atomic populations and the summation of all the localization and delocalization indices must yield the number of electrons in the molecules. The error in these summations was smaller than 10^{-4} au for the diatomic molecules and hydrides and smaller than 10^{-3} au for all the polyatomic molecules.

3 Results

The AIM analysis was carried out for three series of molecules: a series of diatomic molecules (Table 2), a series of second-row hydride molecules (Table 3), and a set of small polyatomic molecules (Table 4). The atomic populations and the localization and delocalization indices calculated with four different approaches (see earlier) are gathered in Tables 2–4. Atomic units are used in Tables 1–4 and throughout the text.

3.1 Diatomic molecules

The results for the series of diatomic molecules are collected in Table 2. For the heteronuclear molecules, the atomic charges are related to the polarity of the

Table 2. Atomic populations, N, localization, λ, and delocalization, δ , indices for a series of diatomic molecules at different levels of theory: HF, configuration interaction with singles and doubles excitation (*CI*), and approximate density functional theory (*DFT*) and CI by using the HF expressions, called HF(DFT) and HF(CI), respectively

		N(A)				λ(A)				δ(A,B)			
molecule	atom	HF[a]	DFT	CI[a]	HF(CI)	HF[a]	HF(DFT)	CI[a]	HF(CI)	HF[a]	HF(DFT)	CI[a]	HF(CI)
H_2	H	1.000	1.000	1.000	1.000	0.500	0.500	0.575	0.500	1.000	1.000	0.849	1.000
N_2	N	7.000	7.000	7.000	7.000	5.479	5.477	5.891	5.478	3.042	3.046	2.219	3.044
F_2	F	9.000	9.000	9.000	9.000	8.358	8.361	8.498	8.364	1.283	1.279	1.005	1.273
LiF	Li	2.060	2.079	2.067	2.066	1.971	1.969	1.973	1.971	0.178	0.221	0.193	0.190
	F	9.940	9.921	9.932	9.935	9.851	9.810	9.838	9.840				
CO	C	4.647	4.853	4.794	4.749	3.860	3.946	4.072	3.904	1.574	1.814	1.443	1.690
	O	9.354	9.147	9.206	9.251	8.567	8.240	8.484	8.406				
CN^-	C	5.227	5.512	5.434	5.368	4.121	4.286	4.490	4.204	2.210	2.451	1.888	2.328
	N	8.773	8.488	8.566	8.632	7.668	7.262	7.621	7.468				
NO^+	N	5.525	5.857	5.803	5.725	4.323	4.529	4.837	4.445	2.405	2.656	1.934	2.559
	O	8.475	8.143	8.197	8.275	7.273	6.815	7.231	6.995				
He_2	He			2.000	2.000			1.9981	1.9982			0.0038	0.0037
Ar_2	Ar			18.000	18.000			17.9935	17.9927			0.0130	0.0145

[a] From Ref. [6]

Table 3. Atomic populations, N, localization λ, and delocalization, δ , indices for a series of diatomic molecules at different levels of theory: HF, CI, and approximate DFT and CI by using the HF expressions, called HF(DFT) and HF(CI), respectively

		N(A)				λ(A)				δ(A,B)				
molecule	atom	HF[a]	DFT	CI[a]	HF(CI)	HF[a]	HF(DFT)	CI[a]	HF(CI)	pair	HF[a]	HF(DFT)	CI[a]	HF(CI)
LiH	**Li**	2.088	2.111	2.097	2.093	1.990	1.991	1.993	1.990	**Li,H**	0.197	0.241	0.208	0.207
	H	1.911	1.889	1.902	1.907	1.812	1.768	1.798	1.804					
BeH_2	**Be**	2.275	2.336	2.299	2.289	2.003	2.014	2.021	2.005	**Be,H**	0.272	0.322	0.279	0.283
	H	1.862	1.832	1.850	1.856	1.681	1.621	1.664	1.667	**H,H'**	0.090	0.101	0.093	0.094
BH_3	**B**	2.886	3.166	3.027	3.028	2.131	2.234	2.256	2.178	**B,H**	0.503	0.621	0.515	0.562
	H	1.704	1.611	1.657	1.657	1.306	1.173	1.272	1.246	**H,H'**	0.145	0.127	0.128	0.133
CH_4	**C**	5.825	5.961	5.955	5.932	3.861	3.993	4.310	3.964	**C,H**	0.982	0.984	0.823	0.984
	H	1.048	1.010	1.011	1.017	0.486	0.453	0.519	0.462	**H,H'**	0.044	0.043	0.054	0.042
NH_3	**N**	8.048	7.957	7.995	8.029	6.706	6.578	6.819	6.678	**N,H**	0.894	0.919	0.784	0.900
	H	0.651[b]	0.681	0.668	0.657	0.185	0.200	0.243	0.188	**H,H'**	0.018	0.021	0.034	0.019
H_2O	**O**	9.254	9.111	9.156	9.198	8.638	8.402	8.543	8.544	**O,H**	0.616	0.709	0.613	0.654
	H	0.372	0.444	0.422	0.401	0.061	0.085	0.106	0.070	**H,H'**	0.007	0.010	0.019	0.008
FH	**F**	9.779	9.721	9.738	9.754	9.580	9.475	9.521	9.536	**F,H**	0.398	0.491	0.435	0.438
	H	0.221	0.279	0.262	0.246	0.022	0.034	0.044	0.027					

[a] From Ref. [6]
[b] Value corrected from Ref. [6]

bond. For each molecule, the magnitude of the charges increases in the order HF > HF(CI) > CI > DFT. The differences between the HF and DFT atomic populations or charges are between 0.2 and 0.3 for CO, NO^+ and CN^-, and only about 0.02 for LiF. These trends are in agreement with the well-known fact that, in general, the HF method overestimates the degree of ionicity of covalent bonds.

The molecular description provided by means of the atomic populations is complemented by the localization and delocalization indices. In particular, the interatomic delocalization index depends on the polarity and order of the bond. At the HF level, the covalent apolar molecules H_2, N_2, and F_2, have $\delta(A,A')$ values of 1.00, 3.04, and 1.28, respectively. In contrast, the ionic LiF molecule exhibits a $\delta(\mathrm{Li,F})$ value of 0.18. In between, the polar covalent molecules, NO^+, CN^-, and CO, exhibit $\delta(A,B)$ values of 2.41, 2.21, and 1.57, respectively. Localization indices in diatomic molecules depend on the atomic populations and delocalization indices and do not afford more relevant information.

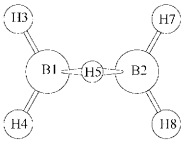
The $\lambda(A)$ and $\delta(A,B)$ values obtained with the HF(DFT) and HF(CI) methods are very close to the HF results. For instance, for the H_2 molecule, the results are exactly the same at the three levels of theory, a consequence of H_2 having only one doubly occupied symmetric orbital [6, 16]. For the N_2, F_2, and LiF molecules, the differences between the $\lambda(A)$ and $\delta(A,B)$ values calculated with the HF method and the HF(DFT) and HF(CI) approximations are below 0.05. Electron correlation effects are stronger in covalent molecules. In all cases, both the HF(DFT) and the HF(CI) delocalization indices increase with respect to the HF level. The HF(DFT) approximation yields the largest $\delta(A,B)$ values for the covalent polar molecules, with differences between 0.2 and 0.3 with respect to the HF results.

The results obtained at the CI level of theory are significantly different from the HF ones. The most remarkable trend is that delocalization indices corresponding to pairs of atoms with shared interactions are systematically lower at the CI level. For instance, for the H_2 molecule, $\delta(\mathrm{H,H'})$ is 1.0 and 0.8 at the HF and CI levels of theory, respectively. At the HF level, there is actually no correlation between the two electrons of different spin occupying the same orbital. For the HF(DFT) and HF(CI) calculations, the shape of the only occupied MO changes with respect to the HF calculations, but the two electrons continue to be uncorrelated and perfectly delocalized between the two atoms, with $\delta(\mathrm{H,H'})$ equal to 1 [6, 16]. In contrast, the CI level of theory takes into account the instantaneous correlation between electrons of different spin. In this case, the interelectron repulsion leads to a greater localization of the electrons and a decrease in $\delta(\mathrm{H,H'})$.

The same reasoning can be applied to the N_2 and F_2 molecules. The $\delta(\mathrm{N,N'})$ values are about 3.0 for the HF, HF(CI), and HF(DFT) calculations and 2.22 at the CI levels, while the $\delta(\mathrm{F,F'})$ values are 1.28 and 1.01 at the HF and CI levels, respectively. For the covalent polar molecules, consideration of Coulomb correlation at the CI level also leads to a lowering of the interatomic delocalization indices, in spite of the decrease in charge transfer with respect to the HF level. In fact, the

Table 4. Atomic populations, N, localization, λ, and delocalization, δ , indices for a series of polyatomic molecules at different levels of theory: HF, CI, and approximate DFT and CI by using the HF expressions, called HF(DFT) and HF(CI), respectively

a		N(A)				λ(A)				δ(A,B)				
molecule	atom	HF[a]	DFT	CI[a]	HF(CI)	HF[a]	HF(DFT)	CI[a]	HF(CI)	pair	HF[a]	HF(DFT)	CI[a]	HF(CI)
CO_2	C	3.243	3.698	3.518	3.441	2.187	2.363	2.443	2.257	C,O	1.056	1.336	1.075	1.184
	O	9.378	9.151	9.241	9.279	8.660	8.271	8.547	8.491	O,O	0.380	0.425	0.313	0.392
SO_2	S	13.212	13.696	13.448	13.396	11.947	12.220	12.251	12.045	S,O	1.265	1.476	1.196	1.351
	O	9.394	9.152	9.276	9.302	8.585	8.196	8.533	8.438	O,O	0.352	0.435	0.290	0.377
SO_3	S	11.745	12.516	12.052	11.985	10.299	10.698	10.610	10.409	S,O	0.963	1.212	0.961	1.051
	O	9.418	9.161	9.316	9.338	8.660	8.242	8.595	8.532	O,O	0.275	0.314	0.240	0.280
C_2H_4[b]	C	5.920	6.002	5.969	5.955	3.927	4.010	4.356	3.963	C,C	1.889	1.914	1.422	1.897
	H	1.040	0.999	1.016	1.022	0.486	0.451	0.519	0.471	C,H	0.981[c]	0.972	0.843[c]	0.979
										C,H'	0.066[c]	0.063	0.061[c]	0.064
										H,H	0.040	0.038	0.053	0.038
										H,H'(c)	0.008[c]	0.008	0.021	0.007
										H,H'(t)	0.013[c]	0.015	0.018	0.013

b		N(A)				λ(A)				δ(A,B)				
molecule	atom	HF[a]	DFT	CI[a]	HF(CI)	HF[a]	HF(DFT)	CI[a]	HF(CI)	pair	HF[a]	HF(DFT)	CI[a]	HF(CI)
C_2H_6[b]	C	5.763	5.910	5.847	5.824	3.755	3.891	3.892	3.810	C,C	0.988	1.012	0.825	0.997
	H	1.079	1.030	1.051	1.059	0.518	0.476	0.492	0.500	C,H	0.966	0.966	0.913	0.967
										C,H'	0.044	0.042	0.075	0.043
										H,H	0.046	0.040	0.043	0.044
										H,H'(g)	0.004[c]	0.004	0.008	0.004
										H,H'(a)	0.012[c]	0.013	0.022	0.012
B_2H_6	B	2.881	3.108	2.993	2.945	2.103	2.167	2.207	2.119	B_1,B_2	0.047	0.078	0.033	0.055
	H_3	1.699	1.622	1.660	1.676	1.257	1.008	1.235	1.226	B_1,H_3	0.473	0.558	0.477	0.498
	H_5	1.719	1.647	1.685	1.701	1.103	1.153	1.100	1.075	B_1,H_5	0.264	0.321	0.282	0.281
										B_1,H_7	0.017	0.023	0.009	0.019
										H_3,H_4	0.134	0.118	0.120	0.130
										H_5,H_6	0.237	0.213	0.194	0.232
										H_3,H_5	0.116	0.105	0.103	0.114
										H_3,H_7(c)	0.011	0.011	0.021	0.011
										H_3,H_8(t)	0.015	0.018	0.017	0.016

[a] From Ref. [6]
[b] (C,H) and (C,H') refer to the pairs formed by a carbon and its bonded hydrogen and a carbon and the hydrogen bonded to the other carbon, respectively. (H,H') refers to a pair formed by two hydrogens bonded to the same carbon and (H,H') to pairs formed by hydrogens bonded to different carbons. For C_2H_4, c and t refer to the pair of hydrogens being in cis or trans positions and C_2H_6, g and a refer to the pair of hydrogens being in gauche or anti positions
[c] Value corrected from Ref. [6]

effects of electron correlation of $\delta(A,B)$ are inversely proportional to the polarity of the bond: the differences between the HF and CI delocalization increase along the CO, CN^-, NO^+, and N_2 series (Table 2).

The differences between the HF and CI results are minimal for the LiF molecule. Indeed, $\delta(\mathrm{Li,F})$ is marginally larger at the CI level (0.19) than at the HF level (0.18). The He_2 and Ar_2 molecules are not bound at the HF and DFT levels of theory. At the CI level, $\delta(\mathrm{He,He'})$ and $\delta(\mathrm{Ar,Ar'})$ are 0.004 and 0.013, respectively. Similar results are obtained at the HF(CI) level. In general, Coulomb correlation appears to have little effect on the interatomic delocalization for pairs of atoms with ionic or van der Waals bonding (closed-shell interactions).

The results discussed so far correspond to molecular geometries completely optimized at each level of theory. Indeed, the same trends are obtained if the calculations are performed at the experimental geometry for each molecule (results not reported).

3.2 Hydrides

The results for the second-row hydrides are collected in Table 3. According to the atomic charges and the $\delta(X,H)$ values at the HF level, the molecules in this series can be ordered as LiH, BeH_2, FH, BH_3, H_2O, NH_3, and CH_4 with respect to the decreasing polarity of the X–H bond, where X is a second-row atom. The C–H bonds in CH_4 are very close to perfect apolar covalency, with $\delta(C,H)$ close to 1 and small atomic charges on the C and H atoms. In the other extreme, LiH , BeH_2, and FH provide good examples of strongly polar X–H interactions. The corresponding delocalization indices are $\delta(\mathrm{Li,H}) = 0.20$, $\delta(\mathrm{Be,H}) = 0.27$, and $\delta(\mathrm{F,H}) = 0.40$. The H atoms in LiH and BeH_2 exhibit charges of about −0.9, while the H atom in FH bears a charge of 0.78. Finally, BH_3, H_2O, and NH_3 are good examples of molecules with moderately polar X–H bonds. The corresponding $\delta(X,H)$ values are 0.50, 0.61, and 0.89, respectively, while the N(H) charges are −0.70, 0.63, and 0.59, respectively. As for the localization indices, the $\lambda(X)$ and $\lambda(H)$ values are closely related to the atomic populations and delocalization indices.

The general trends along the hydride series discussed in the preceding paragraph are preserved at all the levels of theory; however, the method of calculation has significant effects on the numerical values. The effects of electron correlation in the atomic populations are similar to those found in the preceding section; thus, for all the molecules, the degree of charge transfer between the central atom and the H atoms decreases in the order HF > HF(CI) $\geqslant$ CI > DFT. The effects of electron correlation are more important for the molecules with polar covalent bonds (BeH_2, BH_3, NH_3, H_2O). For these molecules, the differences between the N(H) values calculated at the HF and DFT levels are between 0.03 and 0.09.

When comparing the HF, HF(DFT), and HF(CI) results, the $\delta(X,H)$ values appear to be inversely proportional to the degree of charge transfer at each level of theory. Accordingly, $\delta(X,H)$ increases in the direction HF < HF(CI) < HF(DFT), while $\lambda(X)$ and $\lambda(H)$ follow closely the trends in the atomic populations. In general, the differences between the three methods are small, and the maximal difference between the HF and HF(DFT) results is 0.12 for $\delta(B,H)$ in BH_3. When comparing the HF and CI results, the trends are very dependent on the molecule. For the molecules with strong polar bonds (LiH, BeH_2, FH), $\delta(X,H)$ increases slightly at the CI level. For H_2O, the interatomic delocalization is practically identical at the two levels of theory. Finally, for CH_4 and NH_3, $\delta(X,H)$ decreases at the CI level of theory. As for the localization indices, the CI results are generally similar to the HF(CI) and HF(DFT) ones; however, $\lambda(X)$ and $\lambda(H)$ are larger at the CI level for BH_3, CH_4, NH_3, and H_2O.

H–H′ interactions are also possible for molecules with more than one H atom. In general , the $\delta(H,H')$ values are quite small, especially for positively charged H atoms. Furthermore, similar results are obtained with the four methods of calculation employed; however, it is interesting to remark that, for the H_2O and NH_3 molecules, electron correlation effects increase the delocalization between the H atoms. For instance, for the H_2O molecule, $\delta(H,H')$ is 0.007, 0.008, and 0.019 at the HF, HF(CI), and CI levels, respectively.

3.3 Polyatomic molecules

The results for several small polyatomic molecules are gathered in Table 4. In general, the AIM analysis becomes more complex in this case, because the number of interatomic interactions grows geometrically with the number of atoms. While electronic delocalization between distant atoms is generally small, in some cases, the delocalization indices between nonbonded atoms can be significant. Furthermore, the results obtained with the AIM theory for these molecules are often difficult to interpret with the Lewis model, even at the HF level of theory. Indeed, a recent study [22] points out that three-center bonding should be taken into account in order to describe electron localization and delocalization in these molecules. The characterization of three-center bonding in Ref. [22] was carried out by means of a three-center bond index, which is a generalization of the delocalization index; however, these calculations are not yet possible at post-HF levels of theory [21] and have not been considered in the present study. Indeed, the discussion will focus on the differences between localization and delocalization indices calculated at several levels of theory. A more detailed explanation of the electron-pair characteristics of these molecules can be found in previous works [6, 22].

Actually, C_2H_4 and C_2H_6 are the only molecules for which the AIM description at the HF level is fully consistent with the Lewis picture. The atomic charges on the C and H atoms of both molecules are very low, for all the methods of calculation. The HF-based methods yield $\delta(\mathrm{C,H})$ values close to 1.0 for both molecules and $\delta(\mathrm{C,C})$ values close to 1.0 and 1.9 for ethane and ethene, respectively. The delocalization indices between nonbonded atoms are smaller than 0.1 and apparently with little chemical significance. In all cases,the differences between the HF, HF(CI), and HF(DFT) results are minimal. In contrast, electron correlation effects at the CI level are significant. For ethane, $\delta(\mathrm{C,C})$ and $\delta(\mathrm{C,H})$ are 0.83 and 0.91, respectively, at the CI level. For ethene, the CI values for $\delta(\mathrm{C,C})$ and $\delta(\mathrm{C,H})$ are 1.42 and 0.84.

CO_2, SO_2, and SO_3 exhibit strong positive charges at the central atoms. For instance, at the HF level, the charges at the central atom are 2.76, 2.79 and 4.26, for CO_2, SO_2, and SO_3, respectively, whereas the charges at the O atoms are −1.38, −1.39, and −1.41, respectively, In spite of the large charge transfer, the delocalization indices between bonded atoms are high: 1.06, 1.27, and 0.96 for CO_2, SO_2, and SO_3, respectively. In addition, the three molecules exhibit $\delta(O,O')$ values ranging between 0.28 and 0.38. These results are quite difficult to interpret in terms of the Lewis model. For instance, for the CO_2 molecule, the atomic charges are more in

agreement with the ionic structure, $O^- - C^{2+} - O^-$, than with the canonical one, O = C = O; however, the value of $\delta(C,O)$ larger than 1 does not suit well to a single bond between two highly charged atom. Similar problems arise for SO_2 and SO_3. In addition, delocalization between terminal O atoms cannot be taken into account with the Lewis model. As usual, the atomic charges decrease in the direction HF > HF(CI) > CI > DFT for CO_2, SO_2, and SO_3, while all the delocalization indices increase as HF < HF(CI) < HF(DFT). The delocalization indices at the CI level are consistently lower than those calculated with the HF(CI) approximation. In particular, the HF and CI $\delta(X,O)$ values (X = C,S) in the three molecules are very similar, and the $\delta(O,O)$ values are lower at the CI level compared to HF.

At the HF level, the atomic populations and the localization and delocalization indices for the B and terminal H atoms in B_2H_6 are very close to those obtained for BH_3 (Table 3). $\delta(B,H)$ is larger for the terminal H atoms than for the bridge H atoms. Interestingly, the electron delocalization between the two bridge H atoms is significantly larger (0.24) than between the two B atoms (0.05). Indeed, this fact has been used to question the three-center, two-electron B–H–B bonding model for this molecule [6]. As expected, the degree of charge transfer between the B and the terminal and bridge H atoms decreases as HF > HF(CI) $\geq$ CI > DFT. For the bonded atom pairs, the delocalization index increases in the direction HF < HF(CI) < HF(DFT). At the CI level, $\delta(B_1,H_3)$ is practically equivalent to the HF value, while $\delta(B_1,H_5)$ is very similar to the HF(CI) value. In general, interatomic delocalization between H atoms decreases as HF > HF(CI) > DFT, while the opposite trend is found for the B–B delocalization. These trends can be related to the decrease in charge transfer from B to H atoms at post-HF or DFT levels of theory. For all the nonbonded atom pairs, electron correlation at the CI level leads to a significant decrease in the interatomic delocalization with respect to the HF value.

4 Discussion

The results presented here allow some general conclusions on the effects of Coulomb electron correlation on first and second-order electron densities to be drawn from the point of view of the AIM analysis. Comparative studies between atomic populations and localization and delocalization indices at the HF and CI levels of theory have already been reported in the literature [6]. Here, we focus on the HF(CI) and HF(DFT) approximations in comparison to HF and CI. The differences between HF, HF(CI), and CI can be used to analyze the effects of electron correlation on the localization and delocalization indices in terms of one- and two-electron effects. In principle, Coulomb correlation effects on $\rho(\mathbf{r})$ are considered to some degree in the HF(CI) and CI methods, while effects on $\Gamma(\mathbf{r_1},\mathbf{r_2})$ are taken into account only with the CI method. As for the HF(DFT) method, there is not a corresponding DFT method with a correct two-electron density for comparison; however, since HF(DFT) calculations have often been reported in the literature [23, 24, 25, 26, 27], it is of interest to compare the HF, HF(DFT), and CI methods, in order to analyze which kinds of electron correlation effects are actually taken into account with the HF(DFT) method. This comparison is carried out separately for each kind of interatomic interaction.

1. Covalent nonpolar open-shell interactions. In this case, there is practically no transfer of charge between the two atoms and the effect of electron correlation on the atomic populations is null or negligible at any level of theory. Furthermore, all the HF-based methods give practically the same values for the localization and delocalization indices. However, at the CI level of theory, electrons are more localized in each atomic basin, and the electron delocalization indices decrease significantly. This is a genuine two-electron effect, since neither HF(CI) nor HF(DFT) are able to reproduce this trend.
2. Covalent polar open-shell interactions. Polar interactions imply some degree of charge transfer between the two atoms. Consideration of electron correlation at the HF(CI), CI, or DFT levels generally leads to a decrease in the charge transfer with respect to the HF method. This decrease in charge transfer also leads to a slight increase in the interatomic delocalization for the HF(CI) and HF(DFT) methods; however, at the CI level this effect is opposed by the increase in the electron–electron repulsion. For pairs of atoms with moderately polar bonds, the CI delocalization indices are generally lower than the HF ones. For strongly polar interactions, the two effects may be of the same magnitude, and then the HF and CI delocalization indices are quite close. Depending on the polarity of the bond, the interatomic delocalization can be larger at the HF or CI levels of theory.
3. Closed-shell interactions. For LiF, the differences between the results obtained with the four methods are small. In particular, the HF(CI) and CI results are very similar for LiF, He_2 and Ar_2, revealing that interatomic $\alpha - \beta$ electron correlation is not important for these kinds of interactions.
4. Nonbonded interactions. Again, all the methods of calculation yield similar results for these kinds of interactions; however, the $\delta(A,B)$ values between distant atoms may increase slightly at the CI level.

5 Conclusions

In general, the results presented here confirm that a proper account of electron correlation is important for the correct description of atomic interactions from the point of view of electron localization and delocalization indices. The HF method consistently overestimates strongly the interatomic delocalization between bonded atoms with open-shell interactions compared to the CI method. In contrast, qualitatively good results are obtained at the HF level for closed-shell or nonbonded

interactions, for which the interatomic correlation is small.

Some of the differences between the HF and CI results can be attributed to the effects of Coulomb electron correlation in the one-electron density. It is well known that HF generally exaggerates the transfer of charge between bonded atoms. The HF(CI) and HF(DFT) methods produce lower transfers of charge, but do not take into account instantaneous Coulomb correlation, leading to larger interatomic delocalization between covalently bonded atoms with respect to HF. Finally, CI also takes into account properly correlation effects between electrons of different spin, leading to a significant decrease in the interatomic delocalization with respect to HF.

In general, the HF(DFT) and HF(CI) results are very similar, with the only difference being that at the DFT level the transfer of charge is generally smaller and the interatomic distances are also larger. Indeed, neither of the two methods accounts explicitly for the Coulomb electron–electron correlation, at least with reference to the calculation of localization and delocalization indices. In fact, although Coulomb correlation effects are included to some extent on the one-electron density [31], they are not directly taken into account in the two-electron density calculated using the HF formalism.

At present, there is not a practical method for the rigorous calculation of localization and delocalization indices at the DFT level of theory; therefore, the use of the HF formalism with the KS orbitals is the only practical way to obtain localization and delocalization indices at this level of theory. Actually, several studies have been published reporting calculations of approximate DFT localization and delocalization indices [23, 24, 25, 26, 27]. These results show that the approximate indices provide useful chemical insight, and that they can be applied routinely to the analysis of relatively large molecules; however, it is important to be aware that Coulomb electron correlation is not fully considered in these kinds of calculations. From a practical point of view, it has to be taken into account that HF(DFT) indices consistently overestimate the electron delocalization between covalently bonded atoms. Taking these limitations into account, HF(DFT) indices can be considered as a convenient tool for the analysis of molecular electron-pair structure at the DFT level.

In principle, the calculation of $\lambda(A)$ and $\delta(A,B)$ indices can be performed exactly at correlated levels of theory, such as CI, Møller–Pleset perturbation theory, coupled-cluster, etc. However, correlated two-electron densities are difficult to obtain from the available software packages for ab initio calculations; thus, the calculation of approximate localization and delocalization indices could be considered as a good alternative in these cases. However, there are other definitions of electron-sharing indices or bond-order indices that are closely related to the delocalization index [32, 33, 34]. These expressions take into account the occupations of the NOs at post-HF levels of theory and could be valuable for the calculation of approximate localization and delocalization indices at post-HF levels of theory. Further work on this subject is being carried out in our laboratory.

Acknowledgements. Financial help was provided by the spanish DGES project no. PB98-0457-C02-01. J.P. thanks the Department d'Universitats, Recerca i Societat de la Informació (DURSI), of the Generalitat de catalunya for a doctoral fellowship (no. 2000FI-00582). M.S. is indebted to the DURSI for financial support through the Distinguished University Research Promotion 2001.

References

1. Bader RFW (1990) Atoms in molecules: a quantum theory. Clarendon, Oxford
2. Koritsanzsky TS, Coppens P (2001) Chem Rev 101: 1583
3. Bader RFW, Stephens ME (1975) J Am Chem Soc 97: 7391
4. Bader RFW, Streitweser A, Neuhaus A, Laidig KE, Speers P (1996) J Am Chem Soc 118: 4959
5. Bader RFW, Johnson S, Tang TH, Popelier PLA (1996) J Phys Chem 100: 1598
6. Fradera X, Austen MA, Bader RFW (1999) J Phys Chem A 103: 304
7. McWeeny R (1976) Methods of molecular quantum mechanics, 2nd edn. Academic, London
8. Poater J, Solà M, Duran M, Fradera X (2001) J Phys Chem A 105: 2052. Erratum, ibid 106 (2002) 4794
9. Bader RFW, Matta CF (2001) J Inorg Chem 40: 5603
10. (a) Lowdin PO (1955) Phys Rev 97: 1474; (b) Lowdin PO (1955) Phys Rev 97: 1509; (c) Lowdin PO (1955) Phys Rev 97: 1490
11. Wilberg KB (1968) Tetrahedron 24: 1083
12. Ponec R, Uhlik F (1997) J Mol Struct (THEOCHEM) 391: 159
13. Ponec R, Carbó-Dorca R (1999) Int J Quantum Chem 72: 85
14. Bader RFW, Bayles D (2000) J Phys Chem A 104: 5579
15. Poater J, Solà M, Duran M, Fradera X (2001) J Phys Chem A 105: 6249
16. Fradera X, Solà M (in press)
17. Poater J, Solà M, Robles J, Duran M, Fradera X (2002) In: Sen KD (ed) Reviews in modern quantum chemistry: a celebration of the contributions of R. G. Parr World Scientific, Singapore, pp 831–870
18. Lewis GN (1916) J Am Chem Soc 38: 762
19. Silvi B, Savin N (1994) Nature 371: 683
20. Chesnut DB, Bartolotti LJ (2000) Chem Phys 257: 175
21. Bochicchio R, Lain L, Torre A, Ponec R (2000) J Math Chem 28: 83
22. Bochicchio R, Ponec R, Lain L, Torre A (2000) J Phys Chem A 104: 9130
23. Dobado JA, Martinez Garcia H, Molina Molina J, Sundberg MR (2000) J Am Chem Soc 122: 1144
24. El-Bergmi R, Dobado JA, Portal D, Molina Molina J (2000) J Comput Chem 21: 322
25. Dobado JA, Molina Molina J, Uggla R, Sundberg MR (2000) Inorg Chem 39: 2831
26. Kar T, Ángyán JG, Sannigrahi AB (2000) J Phys Chem A 104: 9953
27. Chesnut DB (2001) Chem Phys 271: 9
28. Baerends EJ (2001) Phys Rev Lett 87: 133004
29. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Milliam Jm, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomeli C, Adamo C, Clifford S, Ocheterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowki J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Pislorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith TA, AL-Laham MA,

Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pole JA (1998) Gaussian 98. Gaussian, Pittsburgh, PA
30. Biegler-König FW, Bader RFW, Tang TH (1982) J Comput Chem 3: 317
31. (a) Solà M, Mestres J, Carbó R, Duran M (1996) J Chem Phys 104: 636 (b) Wang J, Eriksson LA, Boyd RJ, Shi Z, Johnson BG (1994) J Phys Chem 98: 1844; (c) Wang J, Shi Z, Boyd RJ, Gonzalez C (1994) J Phys Chem 98: 6988
32. (a) Fulton RL (1993) J Phys Chem 97: 7516; (b) Fulton RL, Mixon ST (1993) J Phys Chem 97: 7530
33. Ángyán JG, Loos M, Mayer I (1994) J Phys Chem 98: 5244
34. Ángyán JG, Rosta E, Surján PR (1999) Chem Phys Lett 299: 1