

# Electron Localization and Delocalization in Open-Shell Molecules

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*Received 11 February 2002; Accepted 16 May 2002*

**Abstract:** Localization and delocalization indices derived in the framework of the quantum Atoms in Molecules theory have recently been used to analyze the electron-pair structure of closed-shell molecules. Here we report calculations of localization and delocalization indices for open-shell molecules at the Hartree-Fock (HF) level. Several simple doublet and triplet radical molecules are studied. In general, interatomic delocalization between bonded atoms is heavily dependent on the order and polarity of the bond. Unpaired electrons also have a significant effect on the interatomic delocalization indices. Indeed, for many radicals, the analysis of the spin components reveals that the interatomic delocalization is very different for  $\alpha$  and  $\beta$  spin electrons in many cases. In general, at the HF level, the results can be rationalized in terms of orbital contributions. However, the definition of localization and delocalization indices is completely general, and they could be calculated at any level of theory, provided that the one- and two-electron densities are available.

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**Key words:** electron localization; electron delocalization; open-shell; topological analysis; electron-pair density; non-nuclear attractor; Atoms in Molecules theory

## Introduction

The Atoms in Molecules Theory (AIM)<sup>1</sup> defines the atoms in a molecule from the topological analysis of the molecular electron density,  $\rho(\mathbf{r})$ . Briefly, an atomic basin is a region in real space bounded by zero-flux surfaces in the electron density or by infinity. Properties of an atom, such as the electron population,  $N(A)$ , can be calculated by integration through the corresponding basin. By using the electron-pair density,  $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ , one can define a localization index,  $\lambda(A)$ , which corresponds to the number of electrons localized in an atom  $A$ , and a delocalization index,  $\delta(A, B)$ , which is the number of electrons delocalized between two atoms,  $A$  and  $B$ .<sup>2</sup> The concepts of localized and delocalized electrons can be related to the concepts of shared and nonshared electrons, respectively, in the Lewis model.<sup>3</sup> However, the analysis in terms of  $\lambda(A)$  and  $\delta(A, B)$  is based in the physical observables  $\rho(\mathbf{r})$  and  $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ .<sup>2</sup>

Recently, localization and delocalization indices have been used extensively to analyze a number of closed-shell molecules at the Hartree-Fock (HF) and configuration interaction (CI) levels of theory.<sup>2,4–13</sup> In general, the HF method exaggerates the interatomic delocalization between covalently bonded atoms, with respect to CI. Localization and delocalization indices have been calculated also from Kohn-Sham orbitals obtained in the framework of the density functional theory (DFT).<sup>14–20</sup> However, the

electron-pair density used in these calculations is obtained by using the HF approximation with the Kohn-Sham orbitals. Thus, the DFT results reported in refs. 14–20 consider electron correlation beyond the HF level only indirectly.<sup>21</sup> Localization and delocalization indices have also been applied successfully to the analysis of several reactions<sup>4</sup> and to the description of solvent effects in several molecules and in the Menshutkin reaction.<sup>5</sup>

So far, calculations of  $\lambda(A)$  and  $\delta(A, B)$  or related quantities for open-shell molecules have been very scarce. MacDougall and Bader<sup>22</sup> have computed atomic properties of carbenes and silylenes in triplet states, including percentages of localization [ $100 N(A)/\lambda(A)$ ] for selected atoms. Recently, Chesnut and Bartolotti<sup>23</sup> have calculated delocalization indices for the triplet state of a charge resonance complex. The aim of the present contribution is

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Contract/grant sponsor: Spanish DGES; contract/grant number: PB98-0457-C02-01

Contract/grant sponsor: Departament d'Universitats, Recerca i Societat de la Informació of the Generalitat de Catalunya (M.S.)

This article includes Supplementary Material available from the authors upon request or via the Internet at <ftp://ftp.wiley.com/public/journals/jcc/suppmat/23/1347> or <http://www.interscience.wiley.com/jpages/0192-8651/suppmat/v23.1347.html>

to calculate localization and delocalization indices for a number of representative radical molecules in doublet and triplet spin states, and to analyze in detail the contributions of the  $\alpha$  and  $\beta$  spin electrons to  $\lambda(A)$  and  $\delta(A,B)$ .

## Methods

Restricted open shell HF (ROHF) and unrestricted HF (UHF) wave functions were calculated for a number of diatomic and triatomic neutral radical molecules using the GAUSSIAN98 package.<sup>24</sup> The spin multiplicity considered was 2 (doublet) for BeH, BO, CH, CN, NO<sub>2</sub>, CNO, OH, and C<sub>2</sub>H, and 3 (triplet) for CH<sub>2</sub>, HNC, NF, NH, O<sub>2</sub>, and PH. The 6-311++G(2d,2p) basis set<sup>25</sup> was used for all the calculations, and the molecular geometries were completely optimized in all cases. The topological analysis of the electron densities and the atomic integrations were performed using the AIMPAC package.<sup>26</sup> In the CH, OH, and OCN systems, the electron density loses the linear symmetry because the  $\pi_x$  and  $\pi_y$  orbitals have different occupations at the ROHF and UHF levels. These symmetry problems could be solved by means of CASSCF calculations. However, the breaking of symmetry does not have a major influence on the electron-pairing patterns of these two molecules, and we have preferred to keep the ROHF and UHF levels of theory throughout.

At any level of theory, localization and delocalization indices can be defined in terms of the one- and two-electron densities:

$$\lambda(A) = - \int_A (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) d\mathbf{r}_1 d\mathbf{r}_2 \quad (1)$$

$$\delta(A, B) = -2 \int_A \int_B (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

respectively. The integrations in the equations above were carried out through one or two atomic basins, as indicated. At the HF level of theory, these equations reduce to the following:<sup>2</sup>

$$\lambda(A) = \sum S_{ij}(A)^2 \quad (3)$$

$$\delta(A, B) = 2 \sum S_{ij}(A)S_{ij}(B) \quad (4)$$

where the summations run over all the pairs of molecular spin-orbitals (MSOs) of the molecule, and  $\{S_{ij}(A)\}$  are overlaps of pairs of MSOs within the basin of atom A. Eqs. (3) and (4) are applicable to restricted HF (RHF), ROHF, and UHF wave functions. Taking into account that overlaps between  $\alpha$  and  $\beta$  MSOs are zero, the separation of  $\alpha$  and  $\beta$  contributions to the  $\lambda(A)$  and  $\delta(A,B)$  indices is straightforward. Note that the  $\alpha$  and  $\beta$  components are exactly equivalent at the RHF level, but not at the ROHF and UHF levels. Furthermore, for linear or planar molecules, the contributions of groups of orbitals belonging to different symmetry groups can also be calculated.<sup>2,4</sup>

For every atom in a molecule, the electron population and the  $\{S_{ij}(A)\}$  elements were obtained at the ROHF and UHF levels of

theory. Then, localization and delocalization indices were calculated using eqs. (3) and (4). Furthermore, the  $\alpha$  and  $\beta$  spin contributions were also calculated, as well as the contributions of different symmetry groups. The precision of all the calculations was ensured by checking that both the sum of the atomic populations and the sum of all the localization and delocalization indices yielded the number of electrons in each molecule with good accuracy. Errors in the summations are less than 0.002 for all the molecules. au are used throughout the article.

## Results and Discussion

Table 1 shows the ROHF results for all the molecules, including the contributions of the  $\alpha$  and  $\beta$  spin components. The contributions of the orbitals in each symmetry group are also detailed in Table 1. All the linear molecules are considered with  $C_{\infty v}$  symmetry, and their orbitals are divided into  $\sigma$  and  $\pi$  sets, with the  $\pi$  set including the  $\pi_x$  and  $\pi_y$  orbitals. The nonlinear molecules exhibit  $C_{2v}$  or  $C_s$  symmetry; however, only the  $C_s$  subgroup can be used for the orbital analysis (the partition of the localization and delocalization indices into orbital contributions requires that all the overlaps between orbitals belonging to different groups are zero within each atomic basin<sup>2</sup>). Thus, orbitals in all the nonlinear molecules are separated into those that are symmetric ( $a'$ ) and antisymmetric ( $a''$ ) with respect to the molecular plane. Similar results are obtained using the UHF method, except for molecules that suffer from heavy spin contamination at the UHF level (CN, HNC, and C<sub>2</sub>H). Thus, results at the UHF level are reported only for these three molecules. UHF results for the rest of molecules are included as supplementary material.

### Hydrides

The series of hydride molecules BeH, CH, NH, OH, and PH can be used to show how the polarity of the X—H bond is reflected in the atomic populations and localization and delocalization indices ( $X = \text{Be, C, N, O, P}$ ). For instance, interatomic charge transfer is very low for the CH radical, and the  $\delta(\text{C,H})$  value is about 1.0. Thus, the C—H bond in this molecule can be considered as apolar covalent. Similar considerations apply to CH<sub>2</sub>. In turn, the X—H bonds in the rest of hydride molecules appear to be polarized to some extent. For the BeH and PH radicals, there is a transfer of charge from the heavy atom to the H, whereas the NH and OH molecules exhibit positive charges on the H atom. The N—H bond in NH appears to be only slightly polar, with a charge of +0.33 on the H atom and a  $\delta(\text{N,H})$  value close to 1 (0.94). In contrast, BeH and OH exhibit a considerable degree of charge transfer and relatively low interatomic delocalization. Finally, the PH radical, although having a charge of −0.58 on H, exhibits a  $\delta(\text{P,H})$  value of 1.13. The fact that  $\delta(\text{P,H})$  is larger than 1 means that the no-bonding valence electrons in the P atom are somewhat delocalized to the H atom (*vide infra*).

The comparison of the  $\alpha$  and  $\beta$  components of the atomic populations and localization and delocalization indices (see Table 1) gives further insight on the detailed electron-pair structure of these molecules. Thus, considering that there are always more  $\alpha$  than  $\beta$  electrons, the atomic populations reveal that  $\alpha$  spin density

is accumulated preferentially in the heavy atom. This trend is valid for the doublet (BeH, CH, OH) and for the triplet radicals (NH, PH, CH<sub>2</sub>). In all cases, there is also some excess of  $\alpha$  electrons in the basins of the H atoms. However, the differences between  $\alpha$  and  $\beta$  electron populations in H atoms are smaller than 0.08 for all the molecules except PH, where the difference is 0.13.

The CH, NH, and OH molecules have six  $\sigma$  electrons, plus one, two, and three  $\pi$  electrons, respectively. The overlap between orbitals of  $\sigma$  and  $\pi$  symmetry is null. Therefore, at the ROHF level of theory, the  $\alpha$  and  $\beta$  contributions to the  $\sigma$  group are totally equivalent for these molecules, and the open-shell character is given only by the  $\pi$  electron(s). For the three molecules, the  $\pi$  electrons are strongly localized in the heavy atom.  $\pi$  electron populations in the H atoms are rather low, while the corresponding localization indices are practically zero. Values for  $\delta^\pi(X, H)$  are also quite low. For CH and NH,  $\delta^\pi(X, H)$  has only  $\alpha$  character, while for OH,  $\delta^\pi(X, H)$  gathers the contributions from two  $\alpha$  and one  $\beta$  electrons. In all cases, the  $\alpha$  component of the interatomic delocalization is slightly larger than the  $\beta$  one.

CH<sub>2</sub> has seven  $a'$  and one  $a''$  electrons; therefore, the  $\alpha$  and  $\beta$  contributions are not equivalent for any of the two symmetry groups. Indeed, the  $\alpha$  spin density in both the  $\sigma$  and  $\pi$  sets is localized mainly in the C atom. The interatomic  $\delta(C, H)$  delocalization has basically  $a'$  character (in plane), with a small  $a''$  (out of plane) contribution. In the  $a'$  set, both  $\alpha$  and  $\beta$  electrons make similar contributions to  $\delta(C, H)$ : 0.52 and 0.48 for  $\alpha$  and  $\beta$  electrons, respectively. The  $a''$  set only includes an  $\alpha$  electron, which is localized mainly in the C atom, and it has little influence on  $\delta(C, H)$ . The delocalization between the two H atoms,  $\delta(H, H')$ , is also very small.

Finally, PH has a group of 10  $\sigma$  electrons with closed-shell character, plus six  $\pi$  electrons (four  $\alpha$ , two  $\beta$ ). The first two  $\pi$  orbitals, which are doubly occupied, are nonbonding core orbitals centered in the P atom. Therefore, the electrons in these orbitals are totally localized in the P atom (see, for instance, the localization and delocalization values for the  $\beta$   $\pi$  electrons). The last two  $\pi$  orbitals, which are singly occupied, are also nonbonding and centered in the P atom, and have nonbonding valence character. However, the  $\alpha$  electrons in these orbitals are not completely localized into the P basin. Altogether, the  $\sigma$  and  $\pi$  electrons contribute 0.88 and 0.25, respectively, to  $\delta(P, H)$ .

### Nonhydrides

O<sub>2</sub> is the only diatomic homonuclear molecule analyzed, and therefore is the only example of an apolar covalent interaction. Each of the two O atoms has 4.5  $\alpha$  and 3.5  $\beta$  electrons, respectively. The  $\sigma$  density has closed-shell character in this molecule, and the  $\sigma$  interatomic delocalization is 1.04, corresponding to a perfectly delocalized electron pair plus some small contribution from electrons in nonbonding orbitals. The two  $\beta$  electrons with  $\pi$  symmetry are also perfectly shared between the two atoms. Together, they contribute exactly 1.00 to  $\delta(O, O')$ . In contrast, the interatomic delocalization of the four  $\alpha$  electrons with  $\pi$  symmetry is only 0.26. The orbital model provides the explanation for the differences in the delocalization of the  $\alpha$  and  $\beta$  electrons. For each of the  $\pi_x$  and  $\pi_y$  sets, there is an  $\alpha$  electron in a bonding orbital and

another one in an antibonding orbital, plus a  $\beta$  electron in a bonding orbital:

$$\pi_x(2)\pi_y(2)\pi_x^*(1)\pi_y^*(1).$$

In the framework of the MO theory, there is no overlap between spin-orbitals of different symmetry, or between spin-orbitals of different spin. Accordingly, neither of the  $\beta$  electrons in the  $\pi_x$  and  $\pi_y$  bonding orbitals interact directly with other electrons and they are perfectly delocalized between the two O atoms. In contrast, for each of the  $\pi_x$  and  $\pi_y$  symmetry groups, the mutual repulsion between the  $\alpha$  electrons in the bonding and antibonding orbitals leads to a high localization of these  $\alpha$  electrons. The effect of the unpaired electrons can be evaluated by removing one electron in a  $\pi_y^*$  orbital from O<sub>2</sub> to yield the doublet O<sub>2</sub><sup>+</sup> cation. Note that the electron density of O<sub>2</sub><sup>+</sup> loses the linear symmetry at the ROHF level of theory. However, this level of theory is enough for assessing the effects of the unpaired electrons in  $\delta(O, O')$ . The O—O distance in the cation is shorter, in agreement with the removal of an electron from an antibonding orbital, and the interatomic delocalization becomes larger (2.67), compared to O<sub>2</sub> (2.29). However, it is worth noting that the increase in  $\delta(O, O')$  is due to the only  $\alpha$  electron with  $\pi_y$  symmetry that remains in O<sub>2</sub><sup>+</sup>. This electron is perfectly delocalized between the two O atoms and contributes 0.5 to the interatomic delocalization. In contrast, the two electrons in the  $\pi_x$  and  $\pi_x^*$  orbitals contribute 0.14, as in the neutral O<sub>2</sub> molecule. Altogether, the delocalization of the  $\pi$ - $\alpha$  electrons is larger in O<sub>2</sub><sup>+</sup> (0.64) than in O<sub>2</sub> (0.26). Eventually, the removal of a second electron to produce O<sub>2</sub><sup>2+</sup> would lead to a delocalization of 0.5 also for the remaining  $\pi_x$  electron, and a delocalization of 2.0 for the four  $\pi$  electrons together. At this point, it is interesting to mention that the bonding or antibonding character of a given MO cannot be directly related to high or low interatomic delocalization for the electrons in this orbital. For instance, back of the envelope calculations for the H<sub>2</sub> molecule in the ground state [ $\sigma_g(2)$ ] and in the doubly excited singlet state [ $\sigma_u^*(2)$ ] show that, at the HF level,  $\delta(H, H')$  is 1.0 in both cases (see Appendix A). For the ground-state H<sub>2</sub>, the decrease in  $\delta(H, H')$  at the CI level is due to the interaction between the  $\sigma_g$  and  $\sigma_u^*$  orbitals, not to the antibonding character of the  $\sigma_u^*$  orbital. In general, at the HF level, an isolated bonding or antibonding orbital will contribute to the electron delocalization between the atoms where this orbital extends, with the actual degree of electron delocalization depending on the electronegativities of the two atoms. Orbitals with nonbonding or lone-pair character will not contribute appreciably to the interatomic delocalization, unless they are very extended in space (see the PH molecule above). Finally, interactions between electrons in orbitals belonging to the same symmetry group and having significant overlap lead to a marked decrease in interatomic delocalization (for instance, the  $\pi_x$  and  $\pi_x^*$  orbitals in O<sub>2</sub>).

The triplet NF molecule is isoelectronic to O<sub>2</sub>, but the bond between the N and F atoms is strongly polar, with a transfer of charge of 0.43 electrons from N to F. The spin density population is much higher in the N atom (1.82) than in the F one (0.18). There is a  $\sigma$  electron pair that is unequally shared between the two atoms [ $\delta^\sigma(N, F) = 0.84$ ]. Furthermore, the interatomic delocalization is

**Table 1.** ROHF/6-311G++(2d,2p) Populations and Localization and Delocalization Indices (in bold) and Spin and Symmetry Components of These Quantities (in plain text).

Molecule	Symmetry	Atom (A)	N(A)				$\lambda(A)$			Pair (A, B)	$\delta(A, B)$		
			Total	$\alpha$	$\beta$	$\alpha - \beta$	Total	$\alpha$	$\beta$		Total	$\alpha$	$\beta$
BeH (D) <sup>a</sup>	Total	Be	<b>3.129</b>	2.029	1.100	0.929	<b>2.913</b>	1.907	1.006	Be, H	<b>0.431</b>	0.244	0.187
	Total	H	<b>1.872</b>	0.971	0.900	0.071	<b>1.656</b>	0.850	0.807				
CH (D) <sup>a</sup>	Total	C	<b>5.981</b>	3.471	2.510	0.961	<b>5.434</b>	3.179	2.255	C, H	<b>1.094</b>	0.584	0.510
	$\sigma$		5.020	2.510	2.510	—	4.510	2.255	2.255		1.020	0.510	0.510
	$\pi$		0.961	0.961	—	0.961	0.924	0.924	—		0.075	0.075	—
	Total	H	<b>1.019</b>	0.529	0.490	0.039	<b>0.472</b>	0.237	0.235				
	$\sigma$		0.980	0.490	0.490	—	0.470	0.235	0.235				
	$\pi$		0.039	0.039	—	0.039	0.002	0.002	—				
NH (T) <sup>a</sup>	Total	N	<b>7.325</b>	4.647	2.678	1.969	<b>6.854</b>	4.396	2.458	N, H	<b>0.942</b>	0.502	0.440
	$\sigma$		5.356	2.678	2.678	—	4.916	2.458	2.458		0.880	0.440	0.440
	$\pi$		1.969	1.969	—	1.969	1.938	1.938	—		0.062	0.062	—
	Total	H	<b>0.675</b>	0.353	0.322	0.031	<b>0.204</b>	0.102	0.102				
	$\sigma$		0.644	0.322	0.322	—	0.204	0.102	0.102				
	$\pi$		0.031	0.031	—	0.031	0.000	0.000	—				
OH (D) <sup>a</sup>	Total	O	<b>8.621</b>	4.808	3.813	0.995	<b>8.307</b>	4.648	3.659	O, H	<b>0.629</b>	0.320	0.309
	$\sigma$		5.640	2.820	2.820	—	5.344	2.672	2.672		0.592	0.296	0.296
	$\pi$		2.982	1.988	0.994	0.994	2.963	1.976	0.987		0.037	0.024	0.013
	Total	H	<b>0.379</b>	0.192	0.187	0.005	<b>0.064</b>	0.032	0.032				
	$\sigma$		0.360	0.180	0.180	—	0.064	0.032	0.032				
	$\pi$		0.018	0.012	0.006	0.006	0.000	0.000	0.000				
CH <sub>2</sub> (T) <sup>b</sup>	Total	C	<b>6.086</b>	3.961	2.126	1.835	<b>5.026</b>	3.376	1.650	C, H	<b>1.060</b>	0.584	0.476
	a'		5.155	3.029	2.126	0.903	4.159	2.509	1.650		0.996	0.520	0.476
	a''		0.931	0.931	—	0.931	0.867	0.867	—		0.064	0.064	—
	Total	H	<b>0.957</b>	0.520	0.437	0.083	<b>0.405</b>	0.216	0.189		<b>0.043</b>	0.022	0.021
	a'		0.922	0.485	0.437	0.048	0.404	0.215	0.189		0.041	0.020	0.021
	a''		0.034	0.034	—	0.034	0.001	0.001	—		0.002	0.002	—
PH (T) <sup>a</sup>	Total	P	<b>14.422</b>	8.144	6.278	1.866	<b>13.858</b>	7.800	6.059	P, H	<b>1.128</b>	0.689	0.439
	$\sigma$		8.556	4.278	4.278	—	8.118	4.059	4.059		0.878	0.439	0.439
	$\pi$		5.866	3.866	2.000	1.866	5.741	3.741	2.000		0.250	0.250	0.000
	Total	H	<b>1.578</b>	0.856	0.722	0.134	<b>1.014</b>	0.511	0.502				
	$\sigma$		1.444	0.722	0.722	—	1.004	0.502	0.502				
	$\pi$		0.134	0.134	0.000	0.134	0.009	0.009	0.000				
O <sub>2</sub> (T) <sup>c</sup>	Total	O	<b>8.000</b>	4.500	3.500	1.000	<b>6.853</b>	4.113	2.740	O, O	<b>2.294</b>	0.775	1.519
	$\sigma$		5.000	2.500	2.500	—	4.480	2.240	2.240		1.038	0.519	0.519
	$\pi$		3.000	2.000	1.000	1.000	2.372	1.872	0.500		1.255	0.255	1.000
NF (T) <sup>a</sup>	Total	N	<b>6.575</b>	4.199	2.376	1.823	<b>5.932</b>	3.884	2.049	N, F	<b>1.285</b>	0.631	0.654
	$\sigma$		4.504	2.252	2.252	—	4.082	2.041	2.041		0.846	0.423	0.423
	$\pi$		2.070	1.947	0.123	1.824	1.851	1.843	0.008		0.439	0.208	0.231
	Total	F	<b>9.425</b>	4.801	4.624	0.177	<b>8.782</b>	4.485	4.297				
	$\sigma$		5.496	2.748	2.748	—	5.072	2.536	2.536				
	$\pi$		3.930	2.053	1.877	0.176	3.710	1.949	1.761				
CN (D) <sup>a</sup>	Total	C	<b>4.730</b>	2.808	1.922	0.886	<b>3.469</b>	2.192	1.277	C, N	<b>2.521</b>	1.231	1.290
	$\sigma$		3.475	2.180	1.295	0.885	3.075	1.995	1.080		0.799	0.370	0.429
	$\pi$		1.254	0.627	0.627	—	0.394	0.197	0.197		1.722	0.861	0.861
	Total	N	<b>8.270</b>	4.192	4.078	0.114	<b>7.010</b>	3.577	3.433				
	$\sigma$		5.525	2.820	2.705	0.115	5.126	2.635	2.491				
	$\pi$		2.746	1.373	1.373	0.000	1.884	0.942	0.942				
BO (D) <sup>a</sup>	Total	B	<b>3.406</b>	2.157	1.249	0.908	<b>2.872</b>	1.859	1.013	B, O	<b>1.069</b>	0.596	0.472
	$\sigma$		3.080	1.994	1.086	0.908	2.846	1.846	1.000		0.470	0.297	0.173
	$\pi$		0.326	0.163	0.163	—	0.026	0.013	0.013		0.598	0.299	0.299
	Total	O	<b>9.594</b>	4.843	4.751	0.092	<b>9.059</b>	4.545	4.515				
	$\sigma$		5.920	3.006	2.914	0.092	5.684	2.857	2.827				
	$\pi$		3.674	1.837	1.837	—	3.376	1.688	1.688				
HNC (T) <sup>d</sup>	Total	N	<b>8.244</b>	4.247	3.997	0.250	<b>6.834</b>	3.537	3.297	N, H	<b>0.837</b>	0.437	0.400
	a'		6.828	3.539	3.289	0.250	5.831	3.036	2.795		0.812	0.425	0.387
	a''		1.416	0.708	0.708	—	1.002	0.501	0.501		0.024	0.012	0.012

(continued)

Table 1. (Continued)

Molecule	Symmetry	Atom (A)	N(A)				$\lambda(A)$			Pair (A, B)	$\delta(A, B)$		
			Total	$\alpha$	$\beta$	$\alpha - \beta$	Total	$\alpha$	$\beta$		Total	$\alpha$	$\beta$
NO <sub>2</sub> (D) <sup>b</sup>	Total	H	<b>0.627</b>	0.337	0.291	0.046	<b>0.174</b>	0.100	0.074	N, C	<b>1.984</b>	0.983	1.002
	a'		0.610	0.328	0.282	0.046	0.174	0.100	0.074		1.183	0.582	0.601
	a''		0.018	0.009	0.009	—	0.000	0.000	0.000		0.802	0.401	0.401
	Total	C	<b>5.128</b>	3.416	1.712	1.704	<b>4.101</b>	2.906	1.195	H, C	<b>0.069</b>	0.037	0.032
	a'		4.562	3.133	1.429	1.704	3.941	2.826	1.115		0.059	0.032	0.027
	a''		0.566	0.283	0.283	—	0.160	0.080	0.080		0.010	0.005	0.005
	Total	N	<b>6.145</b>	3.336	2.809	0.527	<b>4.240</b>	2.451	1.789	N, O	<b>1.905</b>	0.885	1.020
	a'		5.267	2.897	2.370	0.527	3.917	2.290	1.627		1.349	0.607	0.742
	a''		0.878	0.439	0.439	—	0.324	0.162	0.162		0.554	0.277	0.277
	Total	O	<b>8.428</b>	4.332	4.096	0.236	<b>7.298</b>	3.813	3.485	O, O	<b>0.355</b>	0.153	0.202
	a'		6.866	3.551	3.315	0.236	6.104	3.216	2.888		0.174	0.063	0.111
	a''		1.562	0.781	0.781	—	1.194	0.597	0.597		0.182	0.091	0.091
OCN (D) <sup>a</sup>	Total	C	<b>3.868</b>	1.974	1.894	0.080	<b>2.458</b>	1.243	1.216	C, N	<b>1.567</b>	0.880	0.687
	$\sigma$		2.952	1.476	1.476	—	2.260	1.130	1.130		0.842	0.421	0.421
	$\pi$		0.915	0.497	0.418	0.079	0.198	0.112	0.086		0.726	0.460	0.266
	Total	N	<b>7.863</b>	4.339	3.524	0.815	<b>6.911</b>	3.812	3.099	C, O	<b>1.252</b>	0.582	0.670
	$\sigma$		5.350	2.675	2.675	—	4.904	2.452	2.452		0.544	0.272	0.272
	$\pi$		2.512	1.663	0.849	0.814	2.007	1.360	0.647		0.708	0.310	0.398
	Total	O	<b>9.269</b>	4.687	4.582	0.105	<b>8.474</b>	4.309	4.165	N, O	<b>0.337</b>	0.174	0.163
	$\sigma$		5.696	2.848	2.848	—	5.398	2.699	2.699		0.052	0.026	0.026
	$\pi$		3.573	1.839	1.734	0.105	3.076	1.610	1.466		0.286	0.148	0.138
	Total	C <sub>1</sub>	<b>5.503</b>	2.776	2.727	0.049	<b>3.644</b>	1.837	1.807	C <sub>1</sub> , C <sub>2</sub>	<b>1.876</b>	0.934	0.943
	a'		3.829	1.939	1.890	0.049	2.944	1.487	1.457		0.445	0.218	0.227
	a''		1.674	0.837	0.837	—	0.700	0.350	0.350		1.432	0.716	0.716
C <sub>2</sub> H (D) <sup>a</sup>	Total	C <sub>2</sub>	<b>5.430</b>	3.171	2.587	0.584	<b>3.982</b>	2.454	1.527	C <sub>1</sub> , H	<b>0.958</b>	0.480	0.478
	a'		3.718	2.315	1.403	0.912	3.249	2.088	1.161		0.922	0.462	0.460
	a''		1.712	0.856	0.856	—	0.732	0.366	0.366		0.036	0.018	0.018
	Total	H	<b>0.851</b>	0.428	0.423	0.005	<b>0.328</b>	0.166	0.162	C <sub>2</sub> , H	<b>0.064</b>	0.031	0.033
	a'		0.809	0.407	0.402	0.005	0.328	0.166	0.162		0.028	0.013	0.015
	a''		0.042	0.021	0.021	—	0.000	0.000	0.000		0.036	0.018	0.018
	Total	NNA	<b>1.217</b>	0.625	0.592	0.033	<b>0.283</b>	0.150	0.133	C <sub>1</sub> , NNA	<b>0.885</b>	0.466	0.420
	a'		0.643	0.338	0.305	0.033	0.200	0.109	0.091		0.405	0.225	0.180
	a''		0.574	0.287	0.287	—	0.082	0.041	0.041		0.480	0.240	0.240
	Total									C <sub>2</sub> , NNA	<b>0.957</b>	0.470	0.487
	a'										0.466	0.224	0.242
	a''										0.492	0.246	0.246
	Total									H, NNA	<b>0.026</b>	0.015	0.012
	a'										0.015	0.009	0.006
	a''										0.012	0.006	0.006

(D) and (T) denote doublet and triplet spin multiplicity, respectively.

<sup>a</sup>C<sub>∞v</sub> molecules.<sup>b</sup>C<sub>2v</sub> molecules (C<sub>s</sub> subgroup used).<sup>c</sup>D<sub>∞h</sub> molecules (C<sub>∞v</sub> subgroup used).<sup>d</sup>C<sub>s</sub> molecules.

0.21 and 0.23 for the four  $\alpha$  and two  $\beta$   $\pi$  electrons, respectively. These values are significantly lower than the ones in O<sub>2</sub>, especially for the  $\beta$   $\pi$  electrons, which are perfectly shared in O<sub>2</sub>. As in the O<sub>2</sub> molecule, the lower delocalization of the  $\alpha$  electrons, compared to the  $\beta$  ones, is due to the repulsion between  $\alpha$  electrons in bonding and antibonding  $\pi$  orbitals.

The bond in the CN doublet radical can be considered as moderately polar. Actually, the transfer of charge from C to N is 0.27 electrons, and the interatomic delocalization is quite high

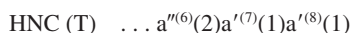
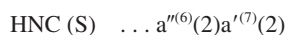
(2.51). The spin density population is 0.89 and 0.11 in the C and N atoms, respectively. The  $\pi$  density has closed-shell character, and it furnishes the major part of the interatomic delocalization (1.72). In turn, the delocalization of the  $\sigma$  electrons is 0.80, with the  $\beta$  electrons being more delocalized (0.43 for four electrons) than the  $\alpha$  ones (0.37 for five electrons). Indeed, the singly occupied  $\sigma$  orbital has partial C—N bonding and C nonbonding character. As in the  $\pi$  electron set of the O<sub>2</sub> molecule, this extra electron helps to increase the localization of the rest of the  $\sigma$



electrons with  $\alpha$  spin. It is interesting to compare the results of the CN doublet radical with those of the closed-shell  $\text{CN}^-$  anion reported in ref. 2. The extra electron in the anion fills the singly occupied  $\sigma$  orbital in the CN radical, but it leads to a strong redistribution of both the  $\sigma$  and  $\pi$  electron densities. With respect to CN, in  $\text{CN}^-$  C increases the  $\sigma$  population by about 0.75 electrons and decreases the  $\pi$  population by about 0.25 electrons. In contrast, the N atom gains about 0.25  $\sigma$  and about 0.25  $\pi$  electrons. The interatomic delocalization is lower in  $\text{CN}^-$  (2.21) than in CN (2.52). In particular,  $\delta^\sigma(\text{C},\text{N})$  is similar in the two molecules (0.80 and 0.73 for CN and  $\text{CN}^-$ , respectively), but  $\delta^\pi(\text{C},\text{N})$  is significantly higher in CN (1.72) compared to  $\text{CN}^-$  (1.48).

The doublet BO radical is isoelectronic with CN. In this case, the bond is more polar, as reflected in the high transfer of charge from B to O (1.59). The unpaired  $\alpha$  electron belongs to the  $\sigma$  subset, and the spin density population is mainly located on the B atom (0.91; for NF, CN, and BO, the spin density goes to the less electronegative atom). With respect to CN, the singly occupied orbital in BO has more lone-pair and less antibonding character. The interatomic delocalization is relatively high (1.07). However, each of the electron pairs involved in the bond is strongly polarized. Thus, the  $\sigma$  and  $\pi$  components of  $\delta(\text{B},\text{O})$  are 0.47 and 0.59, respectively. Interestingly, in contrast with the CN radical, the  $\alpha$   $\sigma$  electrons are more delocalized (0.30) than the  $\beta$  ones (0.17). It appears that, the more the lone-pair character in the unpaired electron, the less it interacts with the rest of the  $\alpha$  electrons.

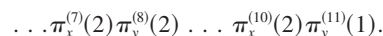
The HNC molecule in the triplet state has an angular geometry, with an HNC angle of  $113.03^\circ$ , in contrast to the ground state linear geometry. There is a considerable transfer of charge from the H and C atoms to the N atom. Thus, charges in the N, H, and C atoms are  $-1.24$ ,  $+0.37$ , and  $+0.87$ , respectively, with the unpaired electrons located mainly in C (1.7) and N (0.25).  $\delta(\text{N},\text{H})$  and  $\delta(\text{C},\text{N})$  are 0.83 and 1.99, respectively. In comparison,  $\delta(\text{N},\text{H})$  and  $\delta(\text{C},\text{N})$  are 0.66 and 1.68, respectively, in the singlet ground state,<sup>4</sup> and  $\delta(\text{C},\text{N})$  is 2.22 in the  $\text{CN}^-$  anion.<sup>2</sup> In the HNC triplet, the  $a''$  electron set has closed-shell character, and the  $a'$  set has open-shell character.  $\delta(\text{N},\text{H})$  and  $\delta(\text{C},\text{H})$  have practically only  $a'$  character, while  $\delta(\text{C},\text{N})$  has significant  $a'$  and  $a''$  components. For the three delocalization indices, the  $\alpha$  and  $\beta$  components are very similar. The first of the two singly occupied orbitals in the HNC triplet is very similar to the singly occupied orbital in the CN doublet (see above), and it has partial bonding and nonbonding character. The second singly occupied orbital has bonding character between the N and H atoms, and antibonding between N and C. It is interesting to compare the singlet and triplet states of the HNC molecule in terms of orbital occupations and its effects on the bond length and interatomic delocalization between C and N. With respect to the singlet-ground state, in the triplet state there is an electron excited from an orbital with partial bonding and nonbonding character,  $a'^{(7)}$  to an antibonding orbital  $a''^{(8)}$ :



This is reflected, for instance, in the C—N distance, which is larger in the triplet state (1.223 Å) than in the singlet (1.154 Å). Interestingly, the atomic overlaps of orbital  $a'^{(8)}$  with the rest of the orbitals with  $a'$  symmetry are rather small, and the net effect of the excitation is an increase in  $\delta(\text{C},\text{N})$  (see Appendix A). In summary, the C—N bond is stronger in the ground singlet state, but the electron delocalization between the C and N atoms is larger in the triplet state.

The bonds in the doublet  $\text{NO}_2$  radical are moderately polar, with charges of  $+0.85$  and  $-0.43$  on the N and O atoms, respectively, and  $\delta(\text{N},\text{O})$  delocalizations of 1.91. These results are in qualitative agreement with the canonical Lewis structures assigned to this molecule. There is significant spin density population in both the N (0.54) and the two O atoms (0.23). The delocalization between the nonbonded atoms is significant (0.36), in agreement with the results reported for similar polyatomic closed-shell molecules ( $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , etc.).<sup>2</sup> The orbital analysis in Table 1 reveals that the  $a''$  component has closed-shell character, and makes a significant contribution to  $\delta(\text{N},\text{O})$  (0.55), but a smaller one than the  $a'$  contribution (1.34). In contrast, the  $a'$  and  $a''$  components in  $\delta(\text{O},\text{O}')$  are similar: 0.17 and 0.18, respectively. Both  $\delta(\text{N},\text{O})$  and  $\delta(\text{O},\text{O}')$  have a slightly larger  $\beta$  component, compared to the  $\alpha$  one. Again, the lower delocalization of the  $\alpha$  electrons can be related to the additional repulsion due to the electron in the singly occupied orbital.

The linear OCN doublet radical exhibits two kinds of polar covalent bonds: O—C and C—N. The charges on the O, C, and N atoms are  $-1.27$ ,  $+2.13$ , and  $-0.86$ , respectively. The spin density population is located mainly on the N atom (0.84). As expected, interatomic delocalization is larger between C and N (1.57) than between C and O (1.25), while delocalization between N and O is not negligible (0.34). The orbital based analysis in Table 1 reveals that the open-shell character is related to the  $\pi$  density.  $\delta(\text{C},\text{N})$  has predominant  $\sigma$  character (0.84, compared to 0.73 for the  $\pi$  component). In contrast, for the two other delocalization indices the  $\pi$  component is larger. Thus, the  $\sigma$  component is 0.54 and 0.05, for  $\delta(\text{C},\text{O})$  and  $\delta(\text{N},\text{O})$ , respectively, while the  $\pi$  component is 0.71 and 0.29, respectively, for  $\delta(\text{C},\text{O})$  and  $\delta(\text{N},\text{O})$ . Interestingly, the  $\alpha$  component is dominant in  $\delta(\text{C},\text{N})$ , while the  $\beta$  component is dominant in  $\delta(\text{C},\text{O})$ , and the  $\alpha$  and  $\beta$  contributions to  $\delta(\text{N},\text{O})$  are similar. An explanation for this fact can be obtained by analyzing the  $\pi$  orbitals in this molecule:



Orbitals 7 and 8 have bonding character between C and O, while 10 and 11 have bonding character between C and N, plus some nonbonding character in O. The unpaired electron in orbital 11 does not disrupt the delocalization of the electrons in orbital 10, which belongs to a different symmetry group. Thus, it leads to an increase of the  $\alpha$  delocalization between C and N. At the same time, it has also some interaction with the  $\alpha$  electrons in orbital 8, leading to a decrease of  $\delta(\text{C},\text{O})$ .

The electron density of the  $\text{C}_2\text{H}$  doublet radical exhibits a non-nuclear attractor (NNA), located between the two carbon atoms. Recently, Pendás et al.<sup>27</sup> have analyzed the occurrence of NNA's in the electron densities of diatomic molecules, clusters,

**Table 2.** UHF/6-311G++(2d,2p) Populations and Localization and Delocalization Indices (in bold) and Spin and Symmetry Components of These Quantities (in plain text) for the Radicals with Higher Spin Contamination.

Molecule	Atom (A)	N(A)				$\lambda(A)$			Pair (A, B)	$\delta(A, B)$		
		Total	$\alpha$	$\beta$	$\alpha - \beta$	Total	$\alpha$	$\beta$		Total	$\alpha$	$\beta$
CN (D) <sup>a</sup>	C	<b>4.847</b>	3.217	1.630	1.587	<b>3.392</b>	2.258	1.134	C, N	<b>2.371</b>	1.378	0.993
	N	<b>8.152</b>	3.783	4.369	-0.586	<b>6.968</b>	3.095	3.873				
HNC (T) <sup>b</sup>	N	<b>8.095</b>	3.890	4.205	-0.315	<b>6.752</b>	3.134	3.618	N, H	<b>0.847</b>	0.448	0.399
	H	<b>0.637</b>	0.358	0.279	0.079	<b>0.183</b>	0.117	0.066		<b>1.837</b>	1.064	0.773
C <sub>2</sub> H (D) <sup>a</sup>	C	<b>5.268</b>	3.752	1.516	2.236	<b>4.319</b>	3.203	1.116	H, C	<b>0.062</b>	0.035	0.027
	C <sub>1</sub>	<b>5.666</b>	2.454	3.212	-0.758	<b>3.905</b>	1.608	2.297	C <sub>1</sub> , C <sub>2</sub>	<b>1.804</b>	0.906	0.898
	C <sub>2</sub>	<b>5.522</b>	3.619	1.903	1.716	<b>4.204</b>	2.922	1.282	C <sub>1</sub> , H	<b>0.967</b>	0.477	0.490
	H	<b>0.851</b>	0.437	0.414	0.023	<b>0.327</b>	0.184	0.143	C <sub>2</sub> , H	<b>0.059</b>	0.021	0.038
	NNA	<b>0.960</b>	0.490	0.470	0.020	<b>0.188</b>	0.099	0.089	C <sub>1</sub> , NNA	<b>0.751</b>	0.309	0.442
									C <sub>2</sub> , NNA	<b>0.771</b>	0.464	0.307
									H, NNA	<b>0.022</b>	0.008	0.014

(D) and (T) denote doublet and triplet spin multiplicity, respectively.

<sup>a</sup>C<sub>∞v</sub> molecules.

<sup>b</sup>C<sub>s</sub> molecules.

and crystals. In general, for any pair of atoms, there is a range of interatomic values that is associated with the presence of an NNA. Thus, the actual occurrence of an NNA between two atoms depends on the interatomic distance at the equilibrium geometry. According to ref. 27, the C—C distance in C<sub>2</sub>H (1.18 Å) is within the range of formation of an NNA between two C atoms. Moreover, the NNA is preserved in calculations at higher levels of theory (QCISD) or with larger basis sets (aug-cc-pvtZ). NNA's have also been found in the related C<sub>2</sub>H<sub>2</sub><sup>8</sup> and SiH<sub>2</sub> molecules.<sup>28</sup> Thus, we considered that the NNA in C<sub>2</sub>H is not a computational artifact. The NNA attractor also has an associated basin, and together they define a pseudoatom, which has to be taken into account for the calculation of localization and delocalization indices. Recently, Madsen et al.<sup>29</sup> have studied the properties of an NNA found in a sodalite crystal doped with an extra Na atom. In that case, the NNA contains approximately an unpaired electron, which is highly delocalized because of the lack of a nuclear attractor in its basin. The population of the NNA in C<sub>2</sub>H is significant (1.22), while the H atom has a population of 0.85, the terminal C<sub>2</sub> atom 5.43, and the central C<sub>1</sub> 5.50. The unpaired electron population is located basically on C<sub>2</sub> (0.91). The localization of the electron density in the NNA is 0.28, only 23.3% of the population, and most of the electron density in the NNA is delocalized towards C<sub>1</sub> (0.89) and C<sub>2</sub> (0.96). Because of the NNA, the two C atoms are not directly bonded, in a topological sense; however,  $\delta(C_1, C_2)$  is still quite high (1.88). Finally,  $\delta(C_1, H)$  is 0.96, consistent with an apolar covalent C—H bond. For all the interatomic delocalization values, the  $\alpha$  and  $\beta$  components are very similar. The orbital analysis reveals that the  $\pi$  component is predominant in  $\delta(C_1, C_2)$  (1.43  $\pi$  vs. 0.45  $\sigma$ ), while the  $\sigma$  and  $\pi$  electrons make practically equivalent contributions to  $\delta(C_1, NNA)$  and  $\sigma(C_2, NNA)$ , and there is no significant  $\pi$  delocalization towards the H atom.

## Comparison of ROHF and UHF Results

Most of the molecules in Table I have little spin contamination at the UHF level. Accordingly, atomic populations, localization and delocalization indices for these molecules are generally very similar at the ROHF and UHF levels of theory. In terms of spin contributions, the UHF method generally leads to only slightly larger differences between the  $\alpha$  and  $\beta$  components, with respect to ROHF. In general, the electron-pair structure as described in terms of localization and delocalization indices is totally equivalent at the two levels of theory (UHF results for all the molecules are available as supplementary material). However, one can expect significant differences between restricted and unrestricted calculations for systems that are not well described at the ROHF or UHF levels. For instance, the singlet H<sub>2</sub> molecule at large internuclear distances is not well described with a restricted wave function (see Appendix B). In turn, many radical molecules exhibit significant spin contamination at the UHF level. It is worth noting that the effect of spin contamination on bonding indices has been discussed in detail by Sannigrahi and coworkers.<sup>30,31</sup>

Here we analyze the effects of spin contamination on CN, C<sub>2</sub>H, and HCN, which are the radicals with higher spin contamination at the UHF level.  $\langle \hat{S} \rangle^2$  for these molecules is 1.082, 1.126, and 2.313, compared to the values of 0.75 and 2 expected for molecules with doublet and triplet multiplicity, respectively. Table 2 gathers the UHF results for these molecules.

In the CN molecule at the UHF level, the C atom has an excess of 1.59  $\alpha$  electrons, while the N atom has an excess of 0.59  $\beta$  electrons. In contrast, at the ROHF level, there is an excess of 0.89 and 0.11  $\alpha$  electrons in the C and N atoms, respectively. Indeed, it is well known that spin contamination generally produces artificially large  $\alpha$  and  $\beta$  spin density populations.<sup>32,33</sup> The UHF results for CN also show a smaller transfer of charge, compared to the

ROHF results, at the same time that the interatomic delocalization decreases, from 2.52 at the ROHF level to 2.37 at the UHF level. Moreover, at the UHF level, the  $\alpha$  electrons are significantly more delocalized than the  $\beta$  ones. In contrast, at the ROHF level,  $\beta$  delocalization is slightly larger than  $\alpha$  delocalization. Similar trends are found for the  $C_2H$  doublet. In this case, at the UHF level, the spin density populations in  $C_1$  and  $C_2$  are 0.76  $\beta$  and 1.72  $\alpha$  electrons, respectively. The molecular topology is the same at the ROHF and UHF levels. As for the triplet HNC radical, the N has 0.32  $\beta$  electrons in excess at the UHF level. Compared to ROHF, the UHF method increases  $\alpha$  delocalization and decreases  $\beta$  delocalization, while the total delocalization indices show little variation between the two levels of theory.

## Conclusions

The calculation of localization and delocalization indices at the UHF and ROHF levels of theory has allowed us to analyze in detail the electron-pair structures of some representative doublet and triplet simple radicals. The main trends found for closed-shell molecules at the RHF level also hold for open-shell molecules. In general, interatomic delocalization between bonded atoms is tightly related to the order and polarity of the bond. Furthermore, for open-shell molecules, it is worth analyzing the separate contributions of  $\alpha$  and  $\beta$  electrons. Atomic populations reveal that, in most cases, the spin density is preferentially localized into one of the atomic basins. Furthermore, in many of the radicals,  $\alpha$  and  $\beta$  electrons exhibit different degrees of interatomic delocalization. In many cases, an excess of  $\alpha$  electrons, with respect to the  $\beta$  ones, leads to a larger localization of the  $\alpha$  electrons, because of the increase in  $\alpha$ - $\alpha$  repulsions. This trend is more clear in molecules like  $O_2$ , where the unpaired  $\alpha$  electrons are located in antibonding orbitals. Actually, the delocalization of the  $\alpha$  electrons can be smaller or larger than the delocalization of the  $\beta$  electrons, depending on the degree of overlap between the bonding and antibonding orbitals.

For most of the molecules studied, the ROHF and UHF results are practically equivalent, except for the fact that UHF takes into account spin polarization, and tends to produce larger differences between the  $\alpha$  and  $\beta$  contributions to the  $N(A)$ ,  $\lambda(A)$ , and  $\delta(A,B)$  values. However, some molecules exhibit significant spin contamination at the UHF level. In these cases, the differences between the ROHF and UHF results tend to be larger.

In summary, localization and delocalization indices have proven to be very useful for the detailed analysis of the electron-pair structure of open-shell molecules. At the ROHF and UHF levels, this analysis is generally in qualitative agreement with the predictions of the Lewis model. However, it must be taken into account that this approach is completely general. Thus, this study could be easily extended to higher levels of theory if the corresponding electron-pair densities are available. We expect that consideration of correlation between electrons of different spin would lead to a general decrease of the interatomic charge transfer and electron delocalization, as in closed-shell molecules.

## Acknowledgments

M. S. is indebted to the Departament d'Universitats, Recerca i Societat de la Informació of the Generalitat de Catalunya for financial support through the Distinguished University Research Promotion 2001.

## Supporting Information

Table S1 gathers atomic populations, localization and delocalization indices, with symmetry and spin components, for all the molecules in Table 1 calculated at the UHF/6-311++G(2d,2p) level.

## Appendix A: Interaction between Bonding and Antibonding Orbitals in Model Systems

The  $H_2$  and  $H_2^-$  molecules provide convenient model systems to analyze the effects of the interactions between bonding and antibonding orbitals in the localization and delocalization indices. We consider the  $H_2$  and  $H_2^-$  molecules at the HF/STO-3G level, using the RHF and ROHF methods for the closed and open-shell species, respectively. In all cases, the combination of the 1s basis functions of the two atoms produces two MO's, one bonding ( $\sigma_g$ ) and one antibonding ( $\sigma_u^*$ ). From now on, we use A and B to refer to the two H atoms in  $H_2$  and  $H_2^-$ , and a and b to refer to the  $\sigma_g$  and  $\sigma_u^*$  orbitals, respectively. Let's consider the following wave functions, three with singlet multiplicity, and one with triplet multiplicity:

$${}^1\Psi_1 = \frac{1}{\sqrt{2}} a(1)a(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \quad (A.1)$$

$${}^1\Psi_2 = \frac{1}{\sqrt{2}} b(1)b(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \quad (A.2)$$

$${}^1\Psi_3 = \frac{1}{2} (a(1)b(2) + a(2)b(1))(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \quad (A.3)$$

$${}^3\Psi_4 = \frac{1}{\sqrt{2}} (a(1)b(2) - a(2)b(1))\alpha(2)\alpha(1) \quad (A.4)$$

Note that two electrons and two MO's allow us to construct two more triplet wave functions, which are equivalent to the one in eq. (A.4). In contrast, for  $H_2^-$ , the use of a minimal basis set only allows for the description of the doublet ground state:

$${}^2\Psi_5 = \frac{1}{\sqrt{3!}} \begin{vmatrix} a(1)\alpha(1) & a(1)\beta(1) & b(1)\alpha(1) \\ a(2)\alpha(2) & a(2)\beta(2) & b(2)\alpha(2) \\ a(3)\alpha(3) & a(3)\beta(3) & b(3)\alpha(3) \end{vmatrix} \quad (A.5)$$

The localization and delocalization indices of these species can be calculated easily using eqs. (3) and (4), taking into account the orbital occupations for each species. The  $D_{\infty h}$  symmetry of these



systems imposes some restrictions on the values of the atomic MO overlaps:

$$S_{aa}(A) = S_{aa}(B) = S_{bb}(A) = S_{bb}(B) = \frac{1}{2} \quad (\text{A.6})$$

$$S_{ab}(A) = S_{ba}(A) = -S_{ab}(B) = -S_{ba}(B) \quad (\text{A.7})$$

with the actual values of  $S_{ab}(A)$  and  $S_{ab}(B)$  depending on the shapes of the  $\sigma_g$  and  $\sigma_u^*$  orbitals in each molecule. Thus, we can express the localization and delocalization indices of each system in terms of  $S_{ab}(A)$  or  $S_{ab}(B)$ . For instance, the derivation of  $\delta(A,B)$  for wave functions 1 to 5 is straightforward.

#### Singlet Ground-State $H_2$

$$^1\delta_1(A, B) = 4S_{aa}(A)S_{aa}(B) = 4\left(\frac{1}{4}\right) = 1 \quad (\text{A.8})$$

#### Doubly-Excited Singlet State $H_2$

$$^1\delta_2(A, B) = 4S_{bb}(A)S_{bb}(B) = 4\left(\frac{1}{4}\right) = 1 \quad (\text{A.9})$$

#### Singly-Excited Singlet State $H_2$

$$^1\delta_3(A, B) = 2(S_{aa}(A)S_{aa}(B) + S_{bb}(A)S_{bb}(B)) = 2\left(\frac{1}{4} + \frac{1}{4}\right) = 1 \quad (\text{A.10})$$

#### Singly-Excited Triplet State $H_2$

$$^3\delta_4(A, B) = 2(S_{aa}(A)S_{aa}(B) + S_{bb}(A)S_{bb}(B) + S_{ab}(A)S_{ab}(B) + S_{ba}(A)S_{ba}(B)) = 2\left(\frac{1}{4} + \frac{1}{4} - 2(S_{ab}(A))^2\right) = 1 - 4(S_{ab}(A))^2 \quad (\text{A.11})$$

#### Doublet Ground-State $H_2^-$

$$^2\delta_5(A, B) = 2(2S_{aa}(A)S_{aa}(B) + S_{bb}(A)S_{bb}(B) + S_{ab}(A)S_{ab}(B) + S_{ba}(A)S_{ba}(B)) = 2\left(2 \cdot \frac{1}{4} + \frac{1}{4} - 2(S_{ab}(A))^2\right) = 1.5 - 4(S_{ab}(A))^2 \quad (\text{A.12})$$

Eqs. (A.8–A.10) show that, at the RHF level, the interatomic delocalization in a singlet  $H_2$  molecule is exactly 1, with no dependence on the basis set, degree of excitation, or internuclear distance. Fulton has obtained similar results for his sharing index, which is equivalent to  $\delta(A,B)$  at the HF level of theory.<sup>34</sup> Indeed, the fact that the occupied orbitals are bonding or antibonding does not have any influence on  $\delta(A,B)$ . In the three singlet wave functions, each of the  $\alpha$  and  $\beta$  electrons, which are not correlated, is perfectly delocalized between the two atoms and contributes 0.5 to the interatomic delocalization. In contrast, for the singly-excited triplet state, the two electrons are mutually correlated, because the Fermi hole is correctly described at the HF level, and this is

reflected in the  $-4(S_{ab}(A))^2$  term in eq. (A.11). If the overlap between the bonding and antibonding orbitals is low,  $\delta(A,B)$  will tend to 1. In contrast, if the overlap is close to the maximal value possible,  $\pm 0.5$ ,  $\delta(A,B)$  will tend to 0. Note that, in the case that both a and b orbitals were bonding (or both antibonding), the term depending on  $S_{ab}(A)$  could be positive.

Finally,  $\delta(A,B)$  for the double  $H_2^-$  also depends on a  $-4(S_{ab}(A))^2$  term, eq. (A.12). It is interesting to compare this system with the  $H_2$  molecule in the singlet ground state, eq. (A.8). The extra electron in  $H_2^-$ , compared to  $H_2$ , has two different effects on  $\delta(A,B)$ . On one hand, an electron in the  $\sigma_u^*$  orbital, on its own, contributes 0.5 to  $\delta(A,B)$ . On the other hand, the extra electron correlates with one same-spin electron in the  $\sigma_g$  orbital, and contributes  $-4(S_{ab}(A))^2$  to  $\delta(A,B)$ . Depending on the degree of overlap between the  $\sigma_g$  and  $\sigma_u^*$  orbitals, the net effect will be an increase or decrease of the interatomic delocalization, with respect to  $H_2$ . At the ROHF/STO-3G level,  $S_{ab}(A)$  is  $\pm 0.48$ , and  $\delta(A,B)$  is 0.59, sensibly lower than in  $H_2$ . Interestingly, the extension of the basis sets decreases the overlap of the two orbitals and leads to a higher delocalization. Thus, at the ROHF/6-311++G(2d,2p) level,  $S_{ab}(A)$  is  $\pm 0.14$ , and  $\delta(A,B)$  is 1.42.

The electronic structure of the  $\pi_x$  electrons in the  $O_2$  doublet is formally equivalent to that of the  $\sigma$  electrons in  $H_2^-$ :  $\pi_x(2)\pi_x^*(1)$ . At the ROHF/6-311++G(2d,2p) level, the atomic overlap between the  $\pi_x$  and  $\pi_x^*$  orbitals is 0.47 in both O atoms. At the same time, both orbitals have zero overlap with the rest of MO's in the molecule. Therefore, one can use eq. (A.12) to calculate the  $\pi_x$  contribution to the interatomic delocalization in  $O_2$ :

$$\delta^{\pi_x}(A, B) = 2\left(2 \cdot \frac{1}{4} + \frac{1}{4} - 2(0.467)^2\right) = 0.628 \quad (\text{A.13})$$

The same applies to the  $\pi_y$  subset.

## Appendix B: Comparison of the UHF and RHF Descriptions of the Dissociation of the $H_2$ Molecule

In Appendix A, it has been pointed out that, at the RHF level, the interatomic delocalization between the two atoms in  $H_2$  is exactly 1 for any interatomic distance. Indeed, it is well known that the RHF method is not capable of describing correctly the dissociation of  $H_2$ . The fact that  $\delta(A,B)$  continues to be 1 at large distances is just another point of view on this subject: the dissociation is not performed correctly because, even at infinite distance, the two electrons continue to be artificially delocalized between the two nuclei. In contrast, the UHF method is able to describe correctly the dissociation of  $H_2$ , at least qualitatively.<sup>35</sup>

It is interesting to compare the RHF and UHF wave functions from the point of view of the electron-pair structure, as reflected in the corresponding delocalization indices. At the RHF level, the two electrons are in the same orbital, and the atomic overlaps of this orbital are exactly 0.5, for any value of the internuclear distance, eq. (A.6) and (A.8). Accordingly, the interatomic delocalization is exactly 1 at any point of the dissociation process. The

UHF method drops the restriction that the two electrons share the same spatial part of the MO, therefore,

$$\delta^{\text{UHF}}(\text{A}, \text{B}) = 2(S_{aa}(\text{A})S_{aa}(\text{B}) + S_{a'a'}(\text{A})S_{a'a'}(\text{B})) \quad (\text{B.1})$$

where  $a$  and  $a'$  are the unrestricted MO's centered on atoms  $\text{A}$  and  $\text{B}$ . Near to the equilibrium distance, one may assume that the spin-orbitals  $a$  and  $a'$  are delocalized between the two atoms, and that  $S_{aa}(\text{A}) \approx S_{aa}(\text{B}) \approx S_{a'a'}(\text{A}) \approx S_{a'a'}(\text{B}) \approx 0.5$ , and  $\delta(\text{A}, \text{B})$  is close to 1. However, as the molecular dissociation proceeds, each of the two orbitals will be progressively localized in one of the nuclei. At infinite distance,  $S_{aa}(\text{A}) = S_{bb}(\text{B}) = 1$ , and  $S_{aa}(\text{B}) = S_{bb}(\text{A}) = 0$ . Therefore,  $\delta(\text{A}, \text{B})$  is exactly zero at the dissociation limit.

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