

## Electron Localization Function at the Correlated Level: A Natural Orbital Formulation

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**Abstract:** In this work we present a 2-fold approximation for the calculation of the electron localization function (ELF) which avoids the use of the two-particle density (2-PD). The first approximation is used for the calculation of the ELF itself and the second one is used to approximate pair populations integrated in the ELF basins. Both approximations only need the natural orbitals and their occupancies, which are available for most methods used in electronic structure calculations. In this way, methods such as CCSD and MP2 can be used for the calculation of the ELF despite the lack of a pertinent definition of the 2-PD. By avoiding the calculation of the 2-PD, the present formulation provides the means for routine calculations of the ELF in medium-size molecules with correlated methods. The performance of this approximation is shown in a number of examples.

### 1. Introduction

In a recent work,<sup>1</sup> we described in detail a correlated version of the Electron Localization Function (ELF) initially proposed by Becke and Edgecombe<sup>2</sup> for Hartree–Fock (HF) wave functions. This correlated version, derived from the analysis of the pair functions performed independently by one of us<sup>3</sup> and by Kohout and co-workers,<sup>4–7</sup> has been implemented in the ToPMoD package.<sup>8</sup> The correlated ELF requires the calculation of the laplacian of the same-spin pair functions, i.e.,

$$\nabla_{\mathbf{r}_2}^2(\pi^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2))|_{\mathbf{r}_2=\mathbf{r}_1} \quad (1)$$

while the covariance analysis of the electron population implies the evaluation of the integrated pair densities  $\bar{N}^{\alpha\alpha}(\Omega)$ ,  $\bar{N}^{\alpha\beta}(\Omega)$ , and  $\bar{N}^{\beta\beta}(\Omega)$ . Unfortunately, the numerical complexity of the exact approach, which considers the correlated two-particle density (2-PD), limits the use of the correlated ELF population analysis to small systems. Several applications of the ELF include analysis of organometallic complexes,<sup>9</sup> aromaticity analysis,<sup>10–12</sup> electronic structure studies along the IRC,<sup>13,14</sup> and

the mechanism analysis in electrocyclic reactions.<sup>15,16</sup> Such analyses involve large molecules for which the calculation of the 2-PD is beyond reasonable cost.

It is possible to lower the numerical complexity of the calculation of the ELF as well as that of the pair populations by expressing the 2-PD in terms of natural geminals.<sup>17,18</sup> This strategy is, however, rather difficult to implement because the determination of the natural geminals requires the full diagonalization of a very large matrix. Approximate expressions of the 2-PD using the first-order reduced density matrix (1-RDM) or the natural spin orbitals have recently been derived in the framework of the density matrix functional theory.<sup>19–25</sup> The aim of the present work is to investigate the ability of these latter expressions to calculate reliable values of the correlated localization functions and of the integrated pair density.

### 2. Natural Spin-Orbital Expression of the Reduced Two-Particle Density

The 2-PD is defined as follows:<sup>26</sup>

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{N(N-1)} \Psi(x_1, x_2, x_3, \dots, x_N) \Psi^*(x_1, x_2, x_3, \dots, x_N) dx'' d\sigma_1 d\sigma_2 \quad (2)$$

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$$= \langle \Psi | \hat{\pi}(\mathbf{r}_1, \mathbf{r}_2) | \Psi \rangle \quad (3)$$

$$= \pi^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \quad (4)$$

In eq 2  $dx''$  indicates that the integration is performed over the space and spin coordinates of all electrons but two. The 2-PD operator appearing in eq 3 is as follows:

$$\hat{\pi}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r}_i - \mathbf{r}_1) \delta(\mathbf{r}_j - \mathbf{r}_2) \quad (5)$$

Finally in eq 4,  $\pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2)$  and  $\pi^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$  represent the probability densities of finding one electron of spin  $\sigma$  at  $\mathbf{r}_1$  and another at  $\mathbf{r}_2$ , this latter of spin  $\sigma$  and  $\sigma'$ , respectively, regardless the position of the other  $N - 2$  electrons.<sup>26</sup> The calculation of the ELF expression only needs of the same-spin 2-PD,  $\pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2)$ . The Pauli principle prescribes the following:

$$\pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) = 0 \quad (6)$$

and with the electron–electron cusp condition, it provides the following:<sup>27</sup>

$$\nabla_{\mathbf{r}_2} \pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) |_{\mathbf{r}_2=\mathbf{r}_1} = 0 \quad (7)$$

whereas  $\pi^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_1)$  is usually greater than zero.<sup>28</sup> The original definition of the ELF by Becke<sup>2</sup> assumed eq 6, while a recent formulation,<sup>3</sup> which takes the first-non vanishing term of Taylor expansion of the 2-PD assumes both eqs 6 and 7 (it is worth noting that proper choice of the reference point or spherical averaging immediately provides eq 7). In exact wave functions, both conditions come from the antisymmetry of the wave function and are fulfilled by the *exact* 2-PD.<sup>27</sup> Therefore, we also need the approximate expression of the 2-PD used in the calculation of the ELF to fulfill these properties.

The integrated pair densities over the whole space should yield the following:

$$\bar{N}^{\sigma\sigma} = \iint \pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \bar{N}^{\sigma}(\bar{N}^{\sigma} - 1) \quad (8)$$

$$\bar{N}^{\sigma\sigma'} = \iint \pi^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \bar{N}^{\sigma} \bar{N}^{\sigma'} \quad (9)$$

These pair densities are used to calculate the covariance matrix of the electron population in the ELF basins. If we use an approximate expression of the 2-PD to calculate these quantities, then it should fulfill these sum rules in order to obtain a meaningful distribution of the  $N$  electrons among the ELF basins.

For a linear expansion of the wave function, the 2-PD distribution can be expressed on the basis of the molecular orbitals:

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ijkl} \Gamma_{ij}^{kl} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) \quad (10)$$

where the  $\Gamma_{ij}^{kl}$  coefficients obey symmetry and antisymmetry relationships:

$$\Gamma_{ij}^{kl} = \Gamma_{ji}^{lk} = \Gamma_{kl}^{ij} = \Gamma_{lk}^{ji} \quad (11)$$

$$= -\Gamma_{ij}^{lk} = -\Gamma_{ji}^{kl} = -\Gamma_{kl}^{ji} = -\Gamma_{lk}^{ij} \quad (12)$$

These relationships are independent of the type of spinorbitals (canonical or not, provided they are orthonormal) and, in particular, they are valid for natural spinorbitals. Taking advantage of the symmetry and antisymmetry of the coefficients, eq 10 can be rewritten as follows:

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_{ijkl}' \Gamma_{ij}^{kl} (\varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) - \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_l(\mathbf{r}_1) \varphi_k(\mathbf{r}_2)) \quad (13)$$

where the prime indicates that the symmetry relations have been implicitly taken into account in the coefficients in order to restrict the sum to the independent ones. However, insofar as eq 3 is used to evaluate the pair functions, it is not advantageous to use natural orbitals instead of the canonical ones and an approximate expression of  $\pi(\mathbf{r}_1, \mathbf{r}_2)$  is highly desirable in order to reduce its computational cost.

Such approximations are derived from a general expression of  $\pi(\mathbf{r}_1, \mathbf{r}_2)$  in terms of the 1-RDM elements  $\rho(\mathbf{r}_1, \mathbf{r}_2)$ , i.e.,

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1) + \lambda_2(\mathbf{r}_1, \mathbf{r}_2) \quad (14)$$

According to Kutzelnigg and Mukherjee,<sup>21</sup> the three contributions appearing in eq 14 respectively correspond to the full Coulomb interaction, the exchange interaction, and the correlation correction (the latter two are usually called exchange-correlation contribution, which we shall denote by XC). The natural orbital expressions for the Coulomb and exchange interaction terms involve sums over only two indices, whereas the exact correlation contribution is much more complicated. This latter is however expected to be small and therefore several approximate expressions in terms of the natural orbitals  $\varphi_i$  and their occupancies  $n_i$  have been proposed.

1. The HF like approximation for the exchange-correlation part (HF-XC hereafter) assumes,

$$\lambda_2(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (15)$$

which yields the following NO expression of the 2-PD,

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \sum_j n_i n_j (\varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) - \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)) \quad (16)$$

This approximation obviously satisfies the symmetry and antisymmetry relationships between coefficients and fulfills the requirements of eqs 6 and 7. However, it violates the sum rule (eq 8) because the HF-like exchange-correlation part (second term in the rhs of eq 14) only integrates to  $-N^{\sigma}$  for monodeterminantal wave functions.

2. Goedecker and Umrigar<sup>20</sup> have proposed an expression (GU functional):

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \sum_{j \neq i} n_i n_j \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) - \sqrt{n_i n_j} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \quad (17)$$

which satisfies neither the antisymmetry requirements nor the sum rules. It corresponds to a correlation correction of the form,

$$\lambda_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \sum_{j \neq i} (n_i n_j - \sqrt{n_i n_j}) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \quad (18)$$

3. Buijse and Baerends's first approximation<sup>22,25</sup> (BB functional), which was previously derived by Müller,<sup>19</sup> removes the restriction in the inner sum of the GU functional in order to preserve the sum rules.

$$\lambda_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \sum_{j, i} (n_i n_j - \sqrt{n_i n_j}) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \quad (19)$$

Holas<sup>29</sup> has recently generalized the GU functional, giving a restriction-free summation which also preserves the sum rule. Gritsenko et al.<sup>23</sup> have proposed several corrections (BBCn functional) in order to improve the performance of the BB expression in the calculation of the potential energy curve. All these corrections integrate to zero and therefore the sum rules are satisfied. Unfortunately, the antisymmetry requirements remain violated.

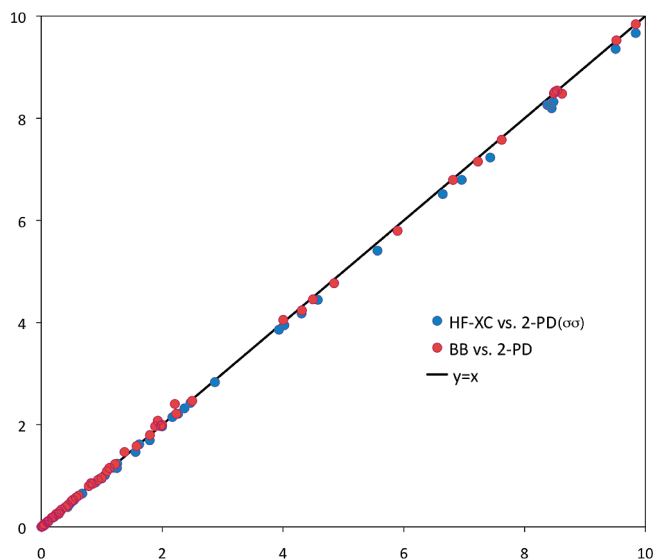
4. The last formula recently published by Piris<sup>24</sup> is close to the GU approximation:

$$\begin{aligned} \pi(\mathbf{r}_1, \mathbf{r}_2) = & \sum_i \sum_{j \neq i} n_i n_j \varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \\ & - \sqrt{n_i n_j} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \quad (20) \\ & - \sum_i^{nco} \sum_{j \neq i}^{nco} \sqrt{(1 - n_i)(1 - n_j)} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \end{aligned}$$

In eq 20, *nco* denotes the number of HF occupied orbitals. Indeed this formula satisfies none of the requirements.

On the one hand, the evaluation of the ELF function requires the 2-PD and its gradient to be identically zero for  $\mathbf{r}_1 = \mathbf{r}_2$ , conditions only fulfilled by the HF-XC. In order to calculate the basin pair populations, the approximate formula must obey the sum rules and therefore only the BB or BBCn expression can be retained. There is no approximation suitable for all of the steps in the calculation of the ELF and basin properties. Therefore, in practice, one has to use these two different approximations of the 2-PD: HF-XC is used for the calculation of the ELF values (which yield the ELF basins), whereas BB is used for the calculation of pair populations within the ELF basins (which provide the covariance matrix). It is worth mentioning that a natural-orbital formulation of the ELF equivalent to the first approximation presented here (HF-XC) was suggested in the past by Savin and co-workers (see footnote in ref 30) and more recently by Kohout.<sup>5</sup>

These approximations have been used in the past to approximate the 2-PD in the calculation of the electron sharing indices (ESI) integrated in atomic basins.<sup>31</sup> In Figure



**Figure 1.** Comparison of ESI (red) and ESI<sup>σσ</sup> (blue) against the BB and HF-XC approximations for the calculation of 2-PD. The atomic basins correspond to Bader's QTAIM ones.<sup>32</sup> From data in ref 31.

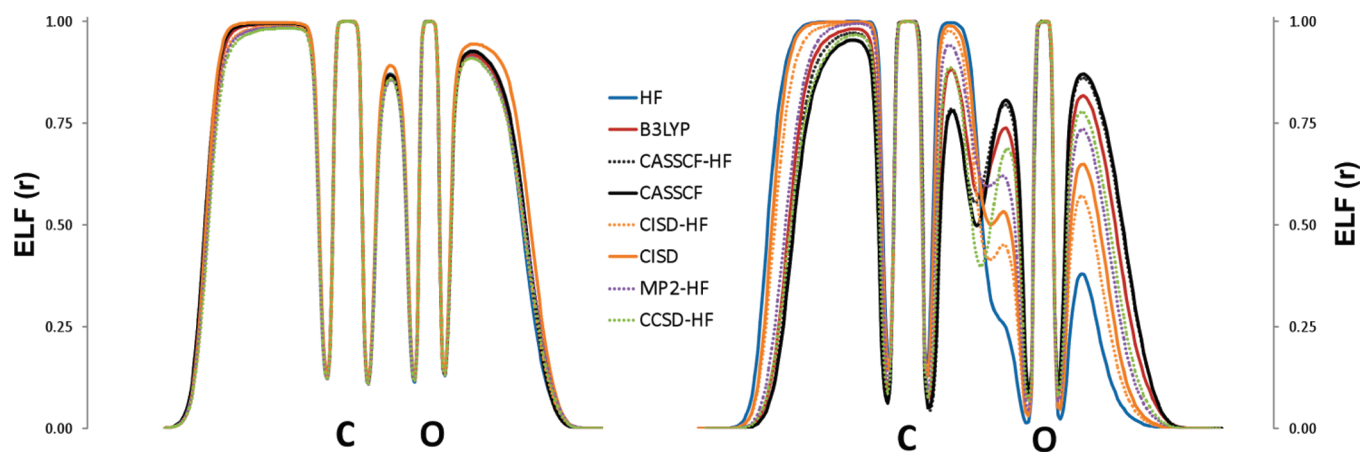
1, we show the differences between the *exact*-ESI and those approximated with BB, and the same-spin ESI (which is calculated from the same-spin 2-PD like the ELF) is compared against HF-XC approximation. Interestingly, both approximations are very accurate, in particular, the performance of the HF-like approximation to reproduce the same-spin 2-PD is very satisfactory.

In addition, the aforementioned approximations for the 2-PD can be used for those cases where one cannot obtain the 2-PD. This is the case of, for example, MP2 or CCSD, for which the pair density cannot be calculated as an expectation value, eq 3. In general, variational methods do not suffer this problem, however, it is worth mentioning the case of a truncated configuration interaction (CI) expansion (such as CID or CISD),<sup>33</sup> for which Hellman–Feynman theorem is not fulfilled and thus there are two density representations, the relaxed (obtained as an energy derivative) and the unrelaxed one (obtained as an expectation value), the latter being the only *N*-representable and the one used in the present work.

### 3. Computational Details

In this work, we have performed HF, DFT, MP2, CCSD, CISD, and CASSCF calculations. Namely, the DFT calculations in this work are performed with Kohn–Sham formalism, and building up an approximate HF-like pair density. For all correlations calculated, we have used HF-XC and BB approximations and the exact 2-PD when possible (CISD, CASSCF).

All calculations were performed with the Gaussian03 program<sup>34</sup> using Pople's 6-311+G(2df,2p) basis set with Cartesian d and f orbitals. From the same program the coefficients of the expansion for both CISD and CASSCF were obtained and used by an own program<sup>35</sup> to construct the  $\Gamma$  matrix in eq 10. Only the expansion coefficients with values above  $10^{-8}$  were taken, and contributions to the values



**Figure 2.** Profile of the electron localization function along the internuclear axis of the carbon monoxide molecule (left:  $R = 1.123$  Å; right:  $R = 2.0$  Å) for the different methods studied.

of density and pair density above  $10^{-12}$  a.u. have been considered. The wave function together with the  $\Gamma$  matrix were read by our own modification of the ToPMoD package of programs<sup>36</sup> to calculate the ELF with both BB and the exact 2-PD. The active space in the CASSCF calculation was composed of the bonding and antibonding valence orbitals and the lone pairs where appropriate. The only exception to this rule is  $F_2$ , for which the experimental bond length<sup>37</sup> (1.412 Å) could not be reproduced with the present active space<sup>38</sup> (1.460 Å) and it was increased with four orbitals with  $\pi$ -symmetry and prominent 3p character (two bonding and the antibonding counterparts) to obtain a satisfactory agreement with experimental bond length (1.417 Å). The number of grid points in the ELF calculations depends on the size of the molecule. A 3D box containing the molecule within 5 Å to the limits of the box is constructed. The number of points are distributed in each of the edges in such a way that they are separated 0.1 Å from each other. For example, in the case of water molecule at the B3LYP level, the number of grid points is  $100 \times 128 \times 110$ .

#### 4. Numerical Validation

Figure 2 illustrates how the HF-XC approximation works for the different methods. The calculations have been carried out on the carbon monoxide molecule for two internuclear separations.

At the equilibrium distance, all functions yield results in very good agreement. At a larger C–O distance, 2 Å, the effects of the electron correlation are more important: at all levels, the curve presents a secondary maximum between C and O; the only exception is HF, where we can appreciate a shoulder. CISD, CISD-HF (i.e., CISD with the 2-PD constructed using the CISD NOs, see eq 16), and MP2-HF improve HF, but exhibit only a small minimum. This can be attributed to the small amount of electron correlation introduced by these methods. CCSD-HF and B3LYP qualitatively reproduce the topological features of the CASSCF localization function. However, they tend to underestimate the function value at the secondary maximum in the C–O bonding region, as well as at the attractor of the V(O) basin

**Table 1.** Populations and Same Spin Pair Populations of the CO Localization Basins Calculated with the Exact CASSCF Pair Function (Exact) and with Buijse and Baerends (BB) Approximation

$\Omega$	$\bar{N}_{\Omega}$		$\bar{N}_{\Omega\Omega}^{\text{SS}}$	
	exact	BB	exact	BB
C(C)	2.07	2.07	0.15	0.15
C(O)	2.10	2.10	0.22	0.22
V(C,O)	3.13	3.10	1.60	1.53
V(C)	2.50	2.51	0.68	0.66
V(O)	4.19	4.22	2.99	2.98

on the right side. Interestingly, CASSCF-HF curve mimics the CASSCF one.

Table 1 shows that the pair populations calculated with the Buijse and Baerends pair function are very close to the exact CASSCF pair function ones. Surprisingly, there are some small deviations for the populations themselves which might be due to numerical round off in both the natural orbitals and the exact pair function determinations.

#### 5. Results

In order to assess how the HF-XC and BB approximation work in the ELF, we have chosen a set of molecules,  $NH_3$ ,  $CO_2$ ,  $H_2O$ ,  $CO$ ,  $CN^+$ ,  $NO^+$ ,  $N_2$ ,  $H_2O_2$ , and  $F_2$ , which have been calculated using a plethora of methods: HF, B3LYP, MP2, CISD, CCSD, and CASSCF. The data has been divided in three groups of molecules: those with small electron-correlation effects, Table 2, species with moderate electron-correlation influence, Table 3, and molecules showing larger electron-correlation effects, Table 4.

First of all, let us analyze the basin populations. Basin populations are calculated through integration of the electron density into the ELF basins. Thus, these numbers are only affected by HF-XC approximation in the calculation of the ELF basins. In those cases where electron correlation affects the electron population, such as  $CO_2$  or the molecules in Tables 3 and 4, the HF-XC approach gives values close to the *exact* expression. The larger differences in the populations with respect to CASSCF values are found for CISD, MP2-BB, and CISD-BB. Interestingly, in those cases where CISD values differ most from the CASSCF ones, HF-XC usually



**Table 2.** Set of Molecules Showing Small Electron-Correlation Effects: NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O

		HF	B3LYP	MP2-BB	CISD-BB	CISD	CCSD-BB	CASSCF-BB	CASSCF
NH <sub>3</sub>	$r_{NH}$	0.998	1.013	1.011	1.008	1.008	1.011	1.022	1.022
	$\angle$ HNH	108.2	107.5	107.1	107.1	107.1	106.9	105.1	105.1
	V(N)	2.10	2.16	2.14	2.15	2.18	2.15	2.21	2.19
	$\sigma^2(N)$	0.92	0.95	0.87	0.87	0.87	0.86	0.94	0.94
	V(N,H)	1.93	1.91	1.91	1.91	1.90	1.91	1.89	1.90
H <sub>2</sub> O	$\sigma^2(N,H)$	0.75	0.76	0.68	0.68	0.72	0.67	0.71	0.74
	$r_{OH}$	0.940	0.961	0.959	0.954	0.954	0.957	0.962	0.962
	$\angle$ HOH	106.4	105.2	104.2	104.8	104.8	104.5	104.7	104.7
	V(O)	2.23	2.28	2.27	2.27	2.28	2.28	2.26	2.25
	$\sigma^2(O)$	1.04	1.06	0.98	0.98	0.99	0.97	1.03	1.01
CO <sub>2</sub>	V(H,O)	1.71	1.66	1.68	1.68	1.67	1.67	1.69	1.69
	$\sigma^2(H,O)$	0.79	0.79	0.71	0.71	0.75	0.70	0.75	0.78
	$r_{CO}$	1.136	1.161	1.170	1.152	1.152	1.161	1.164	1.164
	V(O)	5.71	5.18	5.19	5.21	5.22	5.22	5.25	5.20
	$\sigma^2(O)$	1.39	1.42	1.19	1.22	1.38	1.18	1.25	1.36
	V(C,O)	2.15	2.67	2.67	2.64	2.63	2.63	2.60	2.66
	$\sigma^2(C,O)$	1.19	1.38	1.28	1.28	1.47	1.26	1.32	1.38

**Table 3.** Set of Isoelectronic Molecules with Moderate Electron-Correlation Effects: CO, CN<sup>-</sup>, NO<sup>+</sup>, and N<sub>2</sub>

		HF	B3LYP	MP2-BB	CISD-BB	CISD	CCSD-BB	CASSCF-BB	CASSCF
CO	$r_{CO}$	1.103	1.125	1.136	1.121	1.121	1.127	1.132	1.132
	V(C)	2.37	2.54	2.58	2.47	2.49	2.50	2.51	2.50
	$\sigma^2(C)$	0.66	0.77	0.65	0.59	0.70	0.56	0.67	0.71
	V(C,O)	3.28	3.04	3.08	3.15	2.96	3.10	3.10	3.13
	$\sigma^2(C,O)$	1.44	1.40	1.29	1.31	1.33	1.29	1.36	1.41
CN <sup>-</sup>	V(O)	4.16	4.24	4.16	4.20	4.37	4.22	4.22	4.19
	$\sigma^2(O)$	1.39	1.41	1.17	1.19	1.29	1.16	1.27	1.33
	$r_{CN}$	1.152	1.171	1.189	1.169	1.169	1.176	1.186	1.186
	V(N)	3.30	3.49	3.50	3.42	3.52	3.44	3.47	3.44
	$\sigma^2(N)$	1.20	1.26	1.02	1.04	1.16	1.00	1.10	1.16
NO <sup>+</sup>	V(N,C)	3.86	3.46	3.41	3.62	3.46	3.56	3.51	3.54
	$\sigma^2(N,C)$	1.52	1.47	1.32	1.36	1.39	1.33	1.43	1.48
	V(C)	2.64	2.83	2.91	2.76	2.82	2.80	2.83	2.83
	$\sigma^2(C)$	0.87	0.98	0.79	0.76	0.89	0.73	0.84	0.89
	$r_{NO}$	1.026	1.057	1.083	1.051	1.051	1.059	1.065	1.065
N <sub>2</sub>	V(N)	2.65	2.85	2.98	2.79	2.83	2.83	2.86	2.85
	$\sigma^2(N)$	0.87	0.91	0.81	0.77	0.90	0.75	0.83	0.89
	V(N,O)	3.57	3.15	2.98	3.25	3.09	3.18	3.14	3.17
	$\sigma^2(N,O)$	1.49	1.42	1.27	1.33	1.34	1.31	1.37	1.42
	V(O)	3.62	3.82	3.85	3.77	3.91	3.79	3.81	3.79
	$\sigma^2(O)$	1.29	1.35	1.08	1.11	1.24	1.08	1.15	1.22
N <sub>2</sub>	$r_{NN}$	1.066	1.091	1.113	1.088	1.088	1.096	1.103	1.103
	V(N)	2.96	3.17	3.24	3.11	3.18	3.14	3.17	3.15
	$\sigma^2(N)$	1.05	1.13	0.92	0.92	1.04	0.90	0.97	1.02
	V(N,N)	3.89	3.49	3.31	3.60	3.48	3.52	3.48	3.52
	$\sigma^2(N,N)$	1.53	1.48	1.31	1.36	1.42	1.34	1.42	1.48

gives values closer to those given by CASSCF; see, for instance, CO or V(O) basin in NO<sup>+</sup>. Although this finding is to be regarded to some extent as fortuitous, the significance of this fact must not be overlooked. As a particularly difficult molecule, one may mention F<sub>2</sub> for which B3LYP or CISD attribute a large population to the bonding basin. It is noteworthy that CCSD and CASSCF-BB populations are quite close to the exact CASSCF values. In general, the HF-XC performs very satisfactorily, and the differences found in the populations are mostly attributed to the amount of electron-correlation introduced by the method rather than to the approximation used for the calculation of the 2-PD. It is noteworthy that in the performance of B3LYP; in all cases, with the exception of F<sub>2</sub>, the populations obtained are very close to CASSCF. The ELF topology of N<sub>2</sub> and F<sub>2</sub> was recently reviewed by Bezugly et al.<sup>39</sup> using HF and MRCI

methods. However, no population analysis was performed in this study.

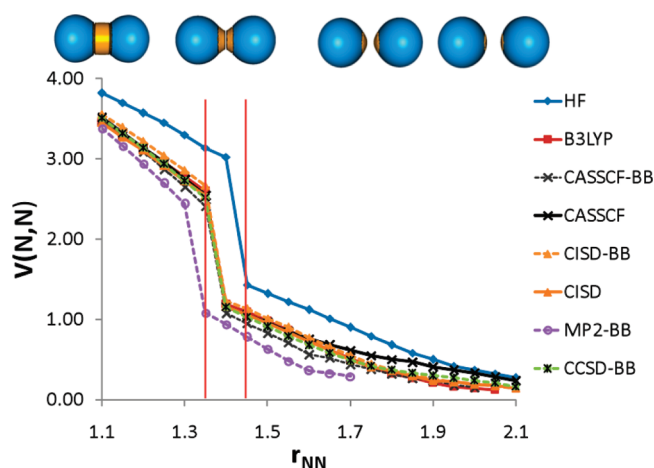
In the following, we will analyze the performance of BB-approximation by comparing the values of the variance of the electron population within the ELF basin,  $\sigma^2$ . One should take into account that these values are also affected by the HF-XC approximation, used to calculate the basin boundaries, and therefore one anticipates further differences than those found in the case of the electron populations.

The values of  $\sigma^2$  are sensibly smaller for the methods that use an approximate 2-PD in the calculation of the variance, even for those molecules not much affected by electron correlation. The fact that the variance is lower with the BB-approximation was already observed in QTAIM partition of the molecular space. See ref 31, where  $\lambda(A)$  was shown to be usually larger with the BB-approximation. Since  $\sigma^2(A)$

**Table 4.** Molecules with Large Electron-Correlation Effects: H<sub>2</sub>O<sub>2</sub> and F<sub>2</sub><sup>a</sup>

		HF	B3LYP	MP2-BB	CISD-BB	CISD	CCSD-BB	CASSCF-BB	CASSCF
H <sub>2</sub> O <sub>2</sub>	$r_{OO}$	1.385	1.448	1.449	1.417	1.417	1.439	1.467	1.467
	$r_{OH}$	0.942	0.966	0.965	0.954	0.954	0.961	0.968	0.968
	$\angle \text{HOO}$	103.2	100.8	99.8	101.5	101.5	100.7	99.8	99.8
	$\angle \text{HOOH}$	112.0	114.9	115.4	113.3	113.3	114.1	114.0	114.0
	$V(\text{H},\text{O})$	1.75	1.69	1.69	1.71	1.70	1.70	1.68	1.70
	$\sigma^2(\text{H},\text{O})$	0.78	0.78	0.71	0.71	0.75	0.70	0.72	0.77
	$V(\text{O},\text{O})$	0.81	$2 \times 0.30$	$2 \times 0.28$	0.67	0.67	$2 \times 0.30$	$2 \times 0.28$	0.60
	$\sigma^2(\text{O},\text{O})$	0.60	0.53	0.47	0.50	0.51	0.51	0.50	0.48
	$V(\text{O})$	2.37	2.45	2.46	2.42	2.43	2.45	2.46	2.44
	$\sigma^2(\text{O})$	1.04	1.08	0.98	0.98	1.03	0.97	1.04	1.05
F <sub>2</sub>	$r_{FF}$	1.326	1.395	1.396	1.368	1.368	1.392	1.417	1.417
	$V(\text{F})$	6.53	6.63	6.66	6.60	6.62	6.62	6.66	6.72
	$\sigma^2(\text{F})$	0.99	0.98	0.76	0.81	0.92	0.75	0.77	0.86
	$V(\text{F},\text{F})$	0.57	$2 \times 0.25$	$2 \times 0.17$	$2 \times 0.19$	$2 \times 0.23$	$2 \times 0.18$	$2 \times 0.19$	$2 \times 0.15$
	$\sigma^2(\text{F},\text{F})$	0.46	0.45	0.28	0.32	0.41	0.30	0.31	0.29

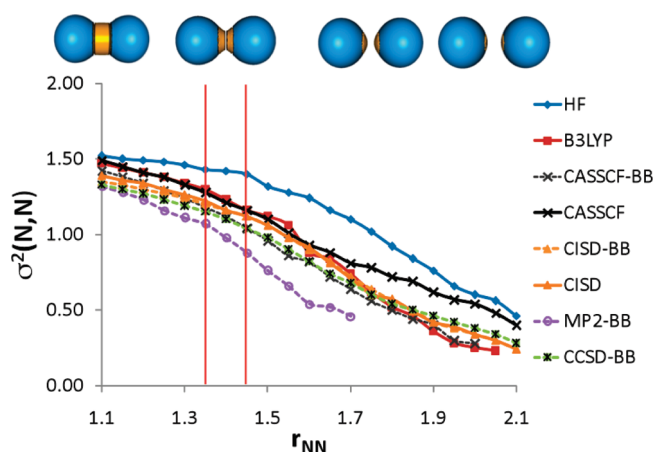
<sup>a</sup> If a given method splits the bonding basin into two basins, then for the sake of comparison, the population variance is given for the basin resulting of merging the two bonding basins.



**Figure 3.** The population of the bonding basin of N<sub>2</sub> along the dissociation curve. When the basin splits into two, only the population of one of them is represented.

$= N(A) - \lambda(A)$ , and populations are almost invariant, one expects BB-approximated  $\sigma^2$  values to be smaller than the exact ones. If we compare the values of CISD, CISD-BB, CCSD-BB, and CASSCF-BB against the values of CASSCF, then we conclude that CISD performs best closely followed by CASSCF-BB, CISD-BB, and CCSD-BB. Although CISD-BB and CCSD-BB perform similarly, it is surprising that CISD-BB is systematically better than CCSD-BB. It indicates that BB-approximation is not particular fortunate in the case of CCSD. Not unexpectedly, MP2 overcorrects HF results, in line with the well-known fact that MP2 overestimates correlation.<sup>40,41</sup> On the other hand, B3LYP results are very good, performing close to CASSCF-BB, with only some exceptions for those systems where the influence of electron-correlation is more notorious, and the adequacy of B3LYP functional for the correct description of both the geometry and the electronic structure is questionable.

Finally, we have calculated the ELF along the dissociation curve of N<sub>2</sub>. Figures 3 and 4 show the change in the bonding basins population and variance, respectively, along the reaction path. Upon dissociation, the bonding basin is split into two basins, which are later absorbed by the lone-pair basin to form a spherical basin corresponding to the valence



**Figure 4.** The variance of the population of the bonding basin of N<sub>2</sub> along the dissociation curve. As the molecule stretches the lone-pair basin absorbs the bonding basin.

shell of N atom. In general, all methods give a similar population along the reaction path with the exception of HF and MP2 which split the bonding basin too late and too early, respectively. In addition, at the MP2 level the bonding basin is absorbed by the lone-pair much sooner (at 1.7 Å). By analyzing the variance of this bonding basin, we reach a similar conclusion. Only after 1.7 Å appreciable differences between CASSCF and the other methods are encountered. On this point and further, CCSD-BB and CISD perform slightly better than the rest.

## 6. Conclusions

In this work we have presented a 2-fold approximation for the calculation of the ELF which avoids the use of the two-particle density (2-PD). The approximation only needs the natural orbitals and their occupancies, which are available for most methods used in electronic structure calculations. In this way, methods such as CCSD and MP2 can be used for the calculation of the ELF despite the lack of a pertinent definition of the 2-PD. The first approximation (HF-XC) relies on the single-determinant approximation for the calculation of the 2-PD and it is used for the calculation of the ELF itself (such approximation was suggested in the past<sup>5,30</sup>). The performance of this approximation is extremely

good, as shown in a number of examples. The second approximation is used for the calculation of pair densities integrated in the ELF basins. It also relies on both natural orbitals and occupancies, but uses a different expression due to Müller and popularized by Baerends and Buijse. The performance of this approximation is also very convincing for CASSCF calculations but systematically underestimates the values of the variance for CCSD calculations. B3LYP exhibits a performance close enough to the approximate CASSCF, except for those molecules where B3LYP is an inappropriate choice for the description of system. The present formulation avoids the calculation of the 2-PD, thus providing the means for routine calculations of the ELF for medium-size molecules with correlated methods.

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