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On the Connection between Probability Density Analysis, QTAIM, and VB Theory

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Supporting Information

The supporting information is broken down in the same subsections as the 'Results and Discussion' section of the article.

SI.1 Starting Simple: the Ionic Contribution in H_2

- The normalization factor of the VB wave function is given in Equation 1:

$$N_{\mathrm{H}_2}^{\mathrm{VB}} = \sqrt{\frac{s^2+1}{[1-2\eta\,(1-\eta)]\,(s^2+1)+4\eta\,(1-\eta)\,s}} \tag{1}$$

- Note, that σ_u^2 cannot be obtained by varying η in the described VB ansatz: σ_u^2 is only given in the limit of $\eta \to \pm\infty$ or as a linear combination (eg. of $\eta = 1$ and $\eta = -1$).

SI.2 Ionic Contributions in Single Bonds

SI.2.1 Homoatomic Bonds

Table 1 Energies calculated with the expanded TZPae basis

		Energy (E_h)	
Molecule	HF	VBSCF(2,2)	CASSCF(2,2)
H−H	−1.13262188	−1.14996878	−1.15069983
H_3C-CH_3	−79.25958227	−79.26417295	−79.27517642
H_2N-NH_2	−111.21896718	−111.22033175	−111.24266371
HO−OH	−150.83305499	−150.86210147	−150.87990568
F−F	−198.75903975	−198.81831197	−198.83396493

- For the EDF weights, it should be noted, that there are not only the covalent and singly ionic partitions. However, the probabilities of the neglected partitions add to a maximum of 3.2% for the CAS wave function of ethane, see Table 2. The sum is lower for all other molecules.

Table 2 Partitions of ethane. Partitioning with the unions of the methyl groups Bader basins

Partition	(9,9)	(10,8)	(8,10)	(11,7)	(7,11)	(6,12)	(12,6)	(5,13)	(13,5)
Probability (%)	52.1	22.4	22.4	1.6	1.6	≈ 0.05	≈ 0.05	≈ 0.001	≈ 0.001

Table 3 Ionic contribution according to different definitions

			Ionic	weight	(%)		
Molecule	WF	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA	EDF
H−H	VB	14.3	48.4	4.4	1.8	6.6	42.3
	CAS					11.3	41.6
H_3C-CH_3	VB	29.7	45.1	21.2	12.6	11.6	44.2
	CAS					0.0	44.7
H_2N-NH_2	VB	30.8	40.6	22.4	15.9	19.3	43.0
	CAS					17.6	43.7
HO−OH	VB	26.2	31.9	17.2	14.4	18.1	38.5
	CAS					17.4	38.7
F−F	VB	22.0	26.0	13.6	12.1	15.7	33.9
	CAS					15.1	34.2

SI.2.2 Heteroatomic Bonds

Table 4 Energies calculated with the expanded TZPae basis. The numbers of active electrons and orbitals for the VBSCF calculations are given as 'ae' and 'ao' respectively

		Energy (E_h)	
Molecule	(ae,ao)	HF	VBSCF
BH_3	(6,6)	−26.40030526	−26.43781390
CH_4	(8,8)	−40.21338321	−40.27572262
NH_3	(6,6)	−56.21968378	−56.27134130
H_2O	(4,4)	−76.05863609	−76.09284712
HF	(2,2)	−100.06144919	−100.07712258
HCl	(2,2)	−460.09058044	−460.09934668

Table 5 Ionic contribution according to different definitions

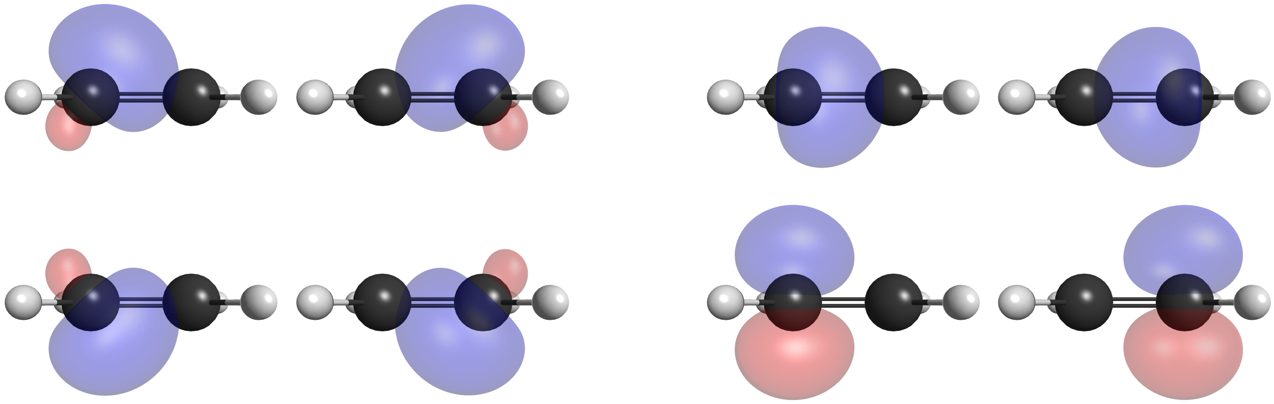
			Ionic	weight	(%)	
Molecule	Structure	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA
BH_3	H^+	6.4	22.1	3.2	0.9	0.0
	H^-	14.1	27.7	10.9	4.8	17.2
CH_4	H^+	13.0	23.5	10.4	4.7	3.8
	H^-	13.8	24.1	13.8	6.9	9.0
NH_3	H^+	21.1	28.4	19.1	11.3	24.0
	H^-	9.0	18.5	8.4	3.6	3.0
H_2O	H^+	32.4	36.7	33.8	23.4	43.2
	H^-	3.0	12.2	2.0	0.8	0.4
HF	H^+	42.5	44.0	51.5	38.0	60.4
	H^-	0.5	7.8	0.0	0.0	0.0
HCl	H^+	25.3	31.7	25.0	14.9	18.0
	H^-	5.3	15.1	1.6	0.9	1.6

SI.3 Double Bonds

SI.3.1 Ethylene

Table 6 Energies calculated with the expanded TZPae basis

		Energy (E_h)	
WF	1 str.	3 strs.	full
τ VB	−78.02970725	−78.08512592	−78.101836964
σ-π VB	−78.04339120	−78.08755209	−78.101836822
MO	−78.06119750		−78.115385820



(a) τ VB orbitals

(b) σ-π VB orbitals

Fig. 1 For both sets of VB orbitals, the active orbitals are labelled 1-4 clockwise, starting top-left.

Table 7 VB weights for three structure VB wave functions, using the orbitals labelling of Figure 1. The two spin-coupled pairs of active orbitals are given for each structure

				Weight	(%)		
WF	Pair 1	Pair 2	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA
	1,2	3,4	74.8	66.6	84.4	88.0	99.9
τ	1,1	3,3	12.6	16.7	7.8	6.0	0.1
	2,2	4,4	12.6	16.7	7.8	6.0	0.1
	1,2	3,4	78.3	72.3	87.5	89.5	
σ-π	1,1	3,3	10.9	13.9	6.2	5.2	
	2,2	4,4	10.9	13.9	6.2	5.2	

Table 8 Partition weights for the full τ VB wave function

			Weight	(%)		
Partitions	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA	EDF
(8,8)	65.7	48.8	80.4	85.9	100.0	44.9
(7,9)+(9,7)	36.0	46.1	19.3	14.0	0.0	48.0
(6,10)+(10,6)	-1.7	5.1	0.3	0.1		6.9

- All partition weights in Table 8 except for the EDF one can be retrieved by summation of the respective entries in Table 9.

Table 9 VB weights for the full τ VB wave function, using the orbitals labelling of Figure 1. The two spin-coupled pairs of active orbitals and the partition are given for each structure

				Weight	(%)		
Pair 1	Pair 2	Partition	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA
1,2	3,4	(8,8)	56.0	30.1	54.6	77.4	97.1
1,1	2,3	(8,8)	0.0	0.0	0.0	0.0	
1,1	2,4	(9,7)	0.0	0.4	0.0	0.0	
1,1	3,4	(9,7)	9.0	11.1	4.8	3.5	
2,2	1,3	(7,9)	0.0	0.4	0.0	0.0	
2,2	1,4	(8,8)	0.0	0.0	0.0	0.0	
2,2	3,4	(7,9)	9.0	11.1	4.8	3.5	
3,3	1,2	(7,9)	9.0	11.1	4.8	3.5	
3,3	1,4	(8,8)	0.0	0.0	0.0	0.0	
3,3	2,4	(7,9)	0.0	0.4	0.0	0.0	
4,4	1,2	(9,7)	9.0	11.1	4.8	3.5	
4,4	1,3	(9,7)	0.0	0.4	0.0	0.0	
4,4	2,3	(8,8)	0.0	0.0	0.0	0.0	
1,1	2,2	(8,8)	0.1	0.1	0.9	0.1	
1,1	3,3	(8,8)	7.3	7.0	8.8	3.4	1.4
1,1	4,4	(10,6)	-0.8	2.5	0.1	0.1	
2,2	3,3	(6,10)	-0.8	2.5	0.1	0.1	
2,2	4,4	(8,8)	7.3	7.0	8.8	3.4	1.4
3,3	4,4	(8,8)	0.1	0.1	0.9	0.1	
2,3	1,4	(8,8)	-5.2	4.5	6.4	1.5	

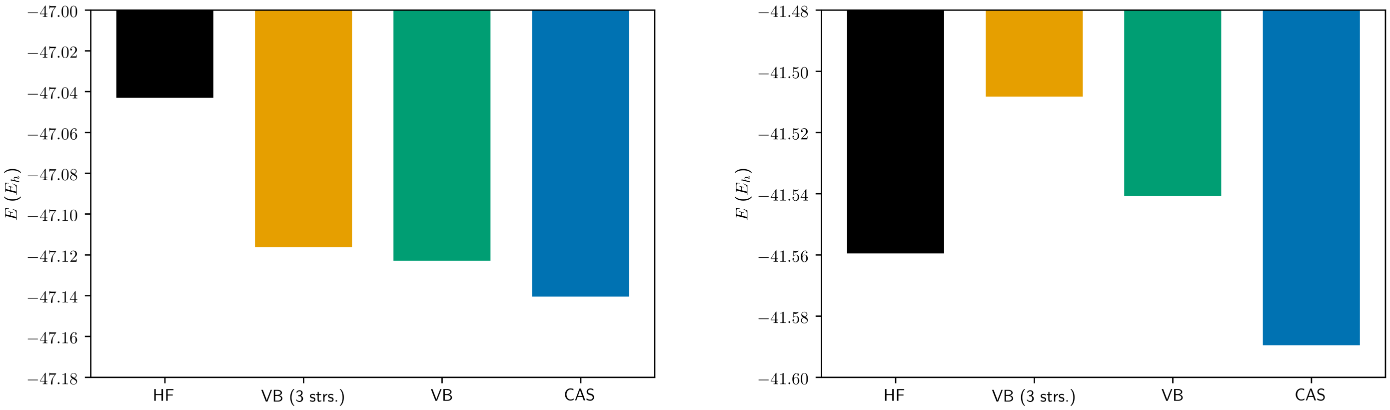
- Note, that for the σ-π wave function the assignment of the PDA attractors to the structures is not possible, see the Figures in the Article. Yet, if the attractors are assigned to the τ structures, the weights are identical to those of the full τ wave function.

Table 10 VB weights for the full σ-π VB wave function, using the orbitals labelling of Figure 1. The two spin-coupled pairs of active orbitals and the partition are given for each structure

				Weight	(%)	
Pair 1	Pair 2	Partition	Chirg.-Couls.	Löwdin	Inverse	Renorm.
1,2	3,4	(8,8)	57.2	30.4	59.2	79.0
1,1	2,3	(8,8)	0.0	0.0	0.0	0.0
1,1	2,4	(9,7)	0.0	0.0	0.0	0.0
1,1	3,4	(9,7)	7.8	7.5	3.8	3.6
2,2	1,3	(7,9)	0.0	0.0	0.0	0.0
2,2	1,4	(8,8)	0.0	0.0	0.0	0.0
2,2	3,4	(7,9)	7.8	7.5	3.8	3.6
3,3	1,2	(7,9)	10.2	15.6	6.4	3.4
3,3	1,4	(8,8)	0.0	0.0	0.0	0.0
3,3	2,4	(7,9)	0.0	0.0	0.0	0.0
4,4	1,2	(9,7)	10.2	15.6	6.4	3.4
4,4	1,3	(9,7)	0.0	0.0	0.0	0.0
4,4	2,3	(8,8)	0.0	0.0	0.0	0.0
1,1	2,2	(8,8)	0.0	0.0	0.4	0.0
1,1	3,3	(8,8)	6.4	6.1	7.2	3.0
1,1	4,4	(10,6)	-0.8	2.6	0.2	0.1
2,2	3,3	(6,10)	-0.8	2.6	0.2	0.1
2,2	4,4	(8,8)	6.4	6.1	7.2	3.0
3,3	4,4	(8,8)	0.0	0.0	0.5	0.0
2,3	1,4	(8,8)	-4.2	6.0	4.7	0.8

SI.3.2 Ozone and Sulfur Dioxide

- The energies of four wave functions are compared in Figure 2 and Table 11 for both, ozone and sulfur dioxide.



(a) ozone

(b) sulfur dioxide

Fig. 2 Method comparison by energies for the 1,3-dipoles ozone and sulfur dioxide.

Table 11 Energies of ozone and sulfur dioxide calculated with the BFD-VTZ basis (ie. with ECPs)

		Energy (E_h)		
Molecule	HF	VB (3 strs.)	VB	CAS
O_3	−47.04309464	−47.11626590	−47.122964372	−47.14046885
SO_2	−41.55955596	−41.50832933	−41.540845058	−41.58957229

- The energies of the ozone wave functions follow the expected trend HF $>$ VB(3str.) $>$ VB(full) $>$ CAS.
- However, for sulfur dioxide, even the full VB wave function does not reach the Hartree-Fock accuracy. To understand this result, the ‘physical’ differences between VBSCF(4,3) and CASSCF(4,3) have to be discussed a bit more in-depth: the three active orbitals in CASSCF can be written as linear combinations of three atomic orbitals each, which seems to be in agreement with VBSCF. Yet, expanding the CAS wave function into atomic orbitals does not give the VB wave function, since these atomic orbitals are optimized for each molecular orbital individually. This additional variational freedom of the CAS wave function is related—but not equal—to the variational advantage of the BOVB method by Hiberty and Shaik.[1] Eventually, this additional freedom is inherent in the HF wave function as well—though to a lesser degree. Thus, while the energetic order for sulfur dioxide seems troublesome at first, it does not hinder the comparison and interpretation.

Table 12 VB weights for different ozone wave functions. Labels are taken from Braïda et al.[2]

			Weight	(%)		
WF	Structure	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA
VB (3 strs.)	**D**	70.4	69.4	75.5	76.2	90.2
	$\mathbf{Z_1} + \mathbf{Z_2}$	29.6	30.6	24.6	23.8	9.6
VB (full)	**D**	65.4	64.4	75.6	73.4	88.2
	$\mathbf{Z_1} + \mathbf{Z_2}$	31.4	31.3	23.1	25.3	11.3
	$\mathbf{Z_3} + \mathbf{Z_4}$	1.9	2.1	1.0	1.0	0.1
	MI	1.3	2.2	0.3	0.3	0.0
CAS	**D**					87.3
	$\mathbf{Z_1} + \mathbf{Z_2}$					12.1
	$\mathbf{Z_3} + \mathbf{Z_4}$					0.1
	MI					0.0
HF	**D**					7.3
	$\mathbf{Z_1} + \mathbf{Z_2}$					47.2
	$\mathbf{Z_3} + \mathbf{Z_4}$					7.3
	MI					38.1

Table 13 VB weights for different sulfur dioxide wave functions. Labels are taken from Braïda et al.[2]

			Weight	(%)		
WF	Structure	Chirg.-Couls.	Löwdin	Inverse	Renorm.	PDA
VB (3 strs.)	**D**	34.7	35.3	30.2	31.8	13.3
	$\mathbf{Z_1} + \mathbf{Z_2}$	65.3	64.7	69.8	68.2	86.7
VB (full)	**D**	19.3	19.7	22.0	18.6	
	$\mathbf{Z_1} + \mathbf{Z_2}$	58.4	55.0	60.0	63.6	0.1
	$\mathbf{Z_3} + \mathbf{Z_4}$	1.0	2.8	0.2	0.2	
	MI	21.2	22.5	17.8	17.6	99.9
CAS	**MI**					100.0
HF	**MI**					100.0

References

1 P. C. Hiberty and S. Shaik, *Theor. Chem. Acc.*, 2002, **108**, 255–272.

2 B. Braïda, S. E. Galembeck and P. C. Hiberty, *J. Chem. Theory Comput.*, 2017, **13**, 3228–3235.