N–O and P–O bond nature in hypervalent compounds. Is Bader analysis basis set and geometry independent?

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1 Introduction

The nature of the P-O bond has been extensively studied over the years, and reviewed recently by Gilheany[1]. From these works, discussions in the P-O bond nature exist among three different alternatives:

- one σ bond and two π back-bonds (negative hyperconjugation).
- one σ bond and three π back-bonds.
- three Ω (banana) bonds.

In our group, results from the topological analysis of electron density, using an accurate enough wavefunction, described the P-O bond as:
a polar single σ-bond for which the length is determined mainly by electrostatic interactions.[2]
In this communication, the dependence of the Bader analysis[5] against the quality of the basis set and geometries will be discussed, at the different theoretical levels. The study has been performed for **1** H_3PO, **2** F_3PO, **3** H_3NO, **4** F_3NO compounds. In addition, the Bader analysis was performed at different values of the P-O bond length. The results presented in this communication prove that the Bader analysis is basis set and geometry independent, if the system is well described.

2 Methodology

All calculations have been carried out using the Gaussian 94 package of programs[3]. The HF, B3LYP and MP2(full) levels were used together with the 6-31G, 6-31G*, 6-311G*, 6-311+G*, 6-311++G(3d,2p) basis sets. Bader analyses have been performed by the AIMPAC series of programs[4] using the wavefunction as input, as described in *"Atoms in Molecules Theory"* [5, 6].

3 Level/Basis Set Dependence

In Table I the X–O distance is listed, at the different theoretical levels, for **1**-**4**. As can be seen the inclusion of polarization functions are essential. The changes on X–O (X=P,N) bonds for **1**-**4** are mainly independent of the basis, if polarization functions exist.

The main description of the $\rho(r)$ topology is summarized in Fig. 1, for **1**-**4** at the B3LYP/6-31G and 6-311++G(3d,2p) levels. The description for the different levels is totally equivalent to those presented for B3LYP, and all the representations including polarization functions are also equivalent.

Table I X–O bond length (Å) for **1**–**4** at the different theoretical levels.

basis	HF	B3LYP	MP2
1 (H_3PO)			
6-31G	1.622	1.624	1.622
6-31G*	1.464	1.494	1.497
6-311G*	1.458	1.488	1.486
6-311+G*	1.461	1.492	1.491
6-311++G(3d,2p)	1.452	1.480	1.486
2 (F_3PO)			
6-31G	1.540	1.558	1.551
6-31G*	1.425	1.456	1.458
6-311G*	1.416	1.448	1.446
6-311+G*	1.418	1.450	1.449
6-311++G(3d,2p)	1.411	1.440	1.443
Exptl. [1]	1.436		
3 (H_3NO)			
6-31G	1.531	1.451	1.490
6-31G*	1.376	1.344	1.361
6-311G*	1.371	1.351	1.354
6-311+G*	1.369	1.365	1.360
6-311++G(3d,2p)	1.361	1.352	1.353
4 (F_3NO)			
6-31G	1.203	1.189	1.182
6-31G*	1.172	1.169	1.164
6-311G*	1.162	1.155	1.149
6-311+G*	1.165	1.154	1.147
6-311++G(3d,2p)	1.164	1.153	1.147
Exptl. [1]	1.159		

4 Geometry Dependence

To test the validity of the Bader analysis against the geometrical variation, full topological analysis of $\rho(r)$ for the equilibrium geometry was compared to different geometries in which the PO bond was changed from 1.6 to 2.0Å. Table II summarized the BCP properties against bond length variation. The graphical representation of the Bader analysis at different bond lengths is depicted in Fig. 2. The overall topological analysis is invariant with large bond lengths modifications (1.492-1.7Å). Larger variation move ρ from oxygen to phosphorus. The case with a very long distance between P and O resembles vdW interaction. The ρ and $\nabla^2(\rho)$ values follow these changes (see Table II).

Table II. Variation of $(\rho(r))$ and $\nabla^2(\rho(r))$ with the P–O length.

P–O	$\rho(r)$	$\nabla^2(\rho(r))$
1.492	0.225	1.331
1.60	0.188	0.586
1.70	0.164	0.100
1.80	0.144	-0.159
1.90	0.123	-0.065
2.00	0.103	0.018

Table III: Bader's atomic charges for **1**-**4** at the different theoretical levels.

basis	HF	B3LYP	MP2	HF	B3LYP	MP2
1 (H_3PO)		@P			@O	
6-31G	2.34	1.94	2.13	-1.21	-1.07	-1.14
6-31G*	3.45	2.94	3.11	-1.60	-1.43	-1.46
6-311G*	3.35	2.79	2.97	-1.55	-1.38	-1.41
6-311+G*	3.34	2.77	2.94	-1.55	-1.39	-1.40
6-311++G(3d,2p)	3.43	2.91	3.10	-1.57	-1.41	-1.43
2 (F_3PO)		@P			@O	
6-31G	3.36	2.86	3.01	-1.18	-1.01	-1.05
6-31G*	4.13	3.77	3.87	-1.58	-1.42	-1.45
6-311G*	3.97	3.58	3.68	-1.54	-1.36	-1.40
6-311+G*	3.97	3.56	3.66	-1.54	-1.36	-1.39
6-311++G(3d,2p)	4.01	3.66	3.74	-1.55	-1.38	-1.40
3 (H_3NO)		@N			@O	
6-31G	-0.64	-0.46	-0.46	-0.53	-0.59	-0.63
6-31G*	-0.58	-0.41	-0.46	-0.66	-0.64	-0.69
6-311G*	-0.53	-0.38	-0.43	-0.66	-0.64	-0.69
6-311+G*	-0.54	-0.41	-0.45	-0.68	-0.67	-0.71
6-311++G(3d,2p)	-0.51	-0.36	-0.41	-0.70	-0.65	-0.69
4 (F_3NO)		@N			@O	
6-31G	1.05	0.84	0.86	-0.35	-0.22	-0.15
6-31G*	1.45	1.13	1.17	-0.46	-0.34	-0.32
6-311G*	1.39	1.08	1.13	-0.47	-0.33	-0.33
6-311+G*	1.38	1.07	1.12	-0.47	-0.32	-0.32
6-311++G(3d,2p)	1.45	1.13	1.17	-0.48	-0.33	-0.32

5 Conclusions

- As it is shown elsewhere, polarization functions are essential in the overall description.
- The overall Bader analysis is invariant with the level/basis set chosen, if polarization functions are included.
- Geometrical variations (ca. 0.2Å) give similar Bader description for the PO bond nature.

All the above let us to describe the X–O bond as: *a polar single σ-bond for which the length is determined mainly by electrostatic interactions.*

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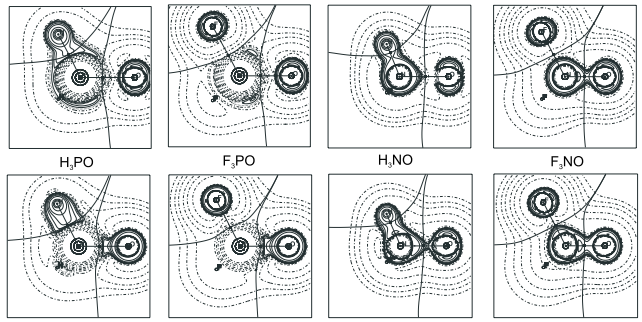

Fig. 1: Contour maps of $\nabla^2\rho(r)$ for **1**-**4** at the B3LYP/6-31G (above) and B3LYP/6-311++G(3d,2p) (below)

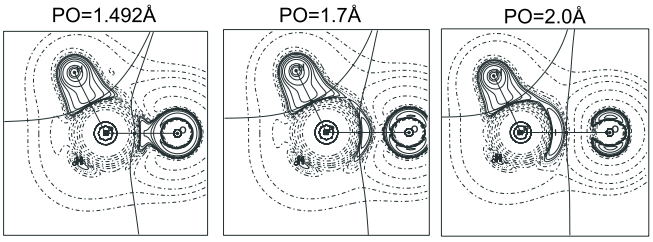

Fig.2 B3LYP/6-311+G* contour map of $\nabla^2\rho(r)$, at different P-O distances for H_3PO

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