

# A Study of Basis Set Effects on Structures and Electronic Structures of Phosphine Oxide and Fluorophosphine Oxide

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A variety of basis sets have been used for geometric and electronic structure studies. Electronic effects were measured using integrated spatial electron populations (ISEP). The two largest basis sets used, 6-31G\* and DZ+P, give significantly different results. Use of two *d*-orbital sets (6-31G\*[dd]) or decontraction of the 2*sp* shell on phosphorus has little further effect. *d*-Orbitals on oxygen are required for consistent electronic structure results, and *d*-orbitals on fluorine have a small but significant effect. Use of diffuse functions, required for anions, is not recommended with small basis sets on neutral molecules. Large negative charges ( $\approx -1.5$ ) on oxygen are given by all of the larger basis sets by the ISEP procedure and indicate that the PO bond in these compounds is largely semi-polar. The best simple symbolic representation of phosphine oxide is  $\text{H}_3\text{P}^+ - \text{O}^-$ , rather than  $\text{H}_3\text{P}=\text{O}$ .

## INTRODUCTION

*Ab initio* Hartree-Fock theory is being applied increasingly to a variety of chemical systems including relatively large systems and those with atoms beyond the first row. In our own work on compounds containing second-row elements, it was important to learn what the minimum size basis set is that would give results of reasonably reliable chemical significance. Much of our work has dealt with electronic structures as determined through integrated spatial electron populations (ISEP).<sup>2,3</sup> hence, we were interested in basis set effects not just on geometrical structure, but on electronic structure as well. In this paper we present such a study for phosphine oxide and fluorophosphine oxide using a variety of basis sets.

Phosphine oxide has received a great deal of recent theoretical attention with some studies of basis set effects and of electronic structure analysis of the PO bond, particularly by population analyses and the role of *d*-orbitals. Gordon et al.<sup>4</sup> compared STO-2G\*,<sup>5</sup> and 3-21G\*<sup>6</sup> structures. Bollinger et al.,<sup>7</sup> compared several basis sets with and without *d*-orbitals with phosphine oxide and several substituted derivatives. The present work ex-

tends these studies by including the following basis sets: 3-21G (33-21G for phosphorus)<sup>8</sup>, 3-21G(\*) formed by the addition of six quadratic functions with exponent of 0.47 (later transformed to the canonical five *d*-functions and a single function of *s*-symmetry) to phosphorus.<sup>6</sup> The 3-21G\* basis includes the further addition of quadratic functions to all first row elements, assuming a standard *d*-exponent exponent of 0.80 (derived from the 6-31G\* basis set) and the standard phosphorus *d*-exponent of 0.55. In the 3-21G\* basis an earlier P *d*-exponent of 0.47 was used. Note that the optimized 3-21G\* phosphorus *d*-exponent is 0.523.<sup>9</sup> In the present article all use of the 0.47 exponent will be indicated by the \*' symbol. The 3-21+G and 3-21+G\* bases are formed from the 3-21G and 3-21G\* bases, respectively, by adding a diffuse *sp* shell to all electron-rich centers in the manner prescribed by Schleyer et al.<sup>10</sup> For the present work, this includes oxygen (exponent = 0.0845) and fluorine (exponent = 0.1076). In addition, the exponent of the diffuse functions on oxygen was optimized for  $\text{PH}_3\text{O}$  and found to be 0.1080. The "3-21-21G" basis is formed by decontracting the most diffuse of the three sets of primitive functions that comprise the phosphorus 2*sp* shell, thereby providing a split 2*sp* shell. This decontraction was done to examine the extent to which phosphorus

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*d*-functions compensate for the possible inadequacy of using a single contracted set of functions to describe the  $2sp$  shell in second-row elements. Wallmeier and Kutzelnigg, for example, have pointed out how *d*-orbitals may compensate for deficiencies in the *sp* basis.<sup>11</sup> Finally, "DZ+P" refers to the double-zeta basis sets of Dunning<sup>12</sup> that include polarization functions on all centers. This result was compared to the 6-31G\* basis and to a similar basis set (6-31G\*[dd]) with two *d*-functions on phosphorus having exponents of 0.22 and 0.77. These exponents were taken from Schmidt and Gordon.<sup>13</sup> Programs used include GAMESS,<sup>14</sup> a modified GAUSSIAN80<sup>15</sup> and GAUSSIAN82.<sup>16</sup> Integrated spatial electron populations (ISEP) were calculated with PROJ<sup>17</sup> with numerical integrations in regions of interest demarked by minimum values of the projected density function.<sup>18</sup>

## GEOMETRIES

Geometry results for phosphine oxide are summarized for a variety of basis sets in Table I. In their announcement of the 3-21G

basis set for second row elements, Pople et al. concluded that polarization functions on second row elements are necessary in order to balance the basis set.<sup>6</sup> This conclusion has since been amply demonstrated for phosphine oxide and is clearly seen from the summary in Table I. The P-O bondlength is overestimated by about 0.1 Å using the 3-21G basis. Any addition to the basis set gives an improved geometry. Addition of polarization functions to phosphorus produces a predictably shorter P-O bond; full polarization of both oxygen and phosphorus results in further contraction. A change in the *d*-orbital exponent on phosphorus has a small but significant effect. The effect is clearly demonstrated by comparison of the standard 6-31G\* basis set with the same basis in which the single *d*-set on phosphorus with exponent 0.55 is replaced by two sets having exponents of 0.22 and 0.77 (6-31G\*[dd]). The result is a slight decrease in the PO bondlength of 0.005 Å and a slight increase in PH of 0.003 Å. The planar electron density difference plot in Figure 1 shows that the principal effect of splitting the *d*-shell is to concentrate more electron density at the phosphorus nucleus and in a  $p_\sigma$ -type region around oxygen.

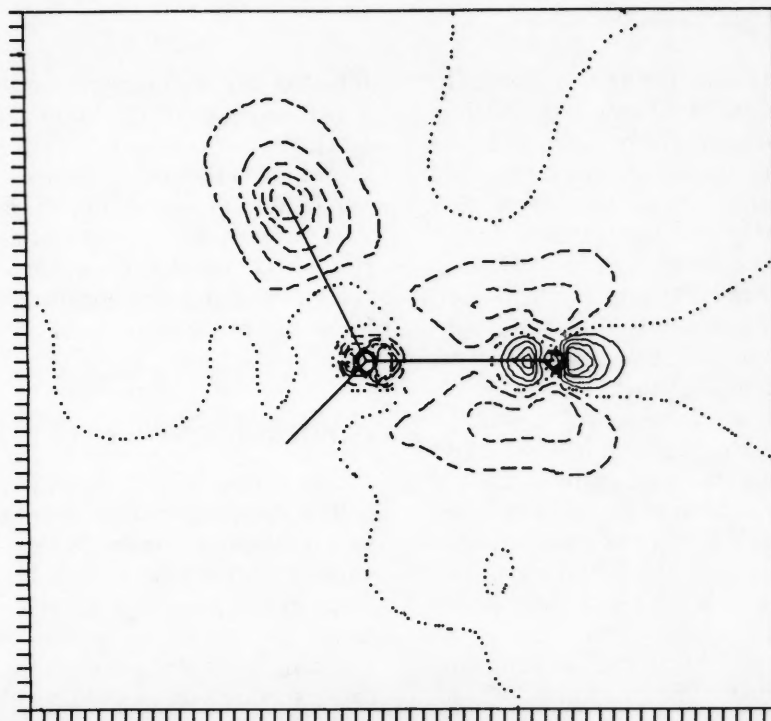


Figure 1. Planar electron density difference plot for phosphine oxide,  $\rho(6-31G*[dd]) - \rho(6-31G^*)$ , at the 6-31G\* geometry for a HPO plane. Oxygen is on the right. Contour levels are from -0.01 to +0.01 by 0.002 e au<sup>-3</sup>.

Table I. A summary of phosphine oxide structures.

Basis Set <sup>a</sup>	Bond Lengths (Å)		Bond Angles (deg.) H-P-O	Dipole Moment D	-E (hartree)
	P-O	P-H			
STO-3G <sup>b,c</sup>	1.656	1.383	118.7		412.35674
STO-2G <sup>*d,e</sup>	1.423	1.386	119.3	3.73 <sup>*</sup>	
3-21G <sup>e</sup>	1.579	1.405	117.2	4.603	415.08303
6-21G <sup>b</sup>	1.587	1.406	117.1		417.06827
DZ <sup>b</sup>	1.605	1.405	116.0		417.18307
3-21G <sup>(*)</sup>	1.482	1.400	117.1	3.903	415.25620
3-21+G <sup>(*)f</sup>	1.497	1.396	116.2	4.921	415.28876
3-21+G <sup>(*)</sup>	1.497	1.396	116.1	4.920	415.28776
3-21-21+G <sup>(*)f</sup>	1.497	1.399	116.0	4.921	415.31830
3-21-21+G <sup>(*)</sup>	1.497	1.397	116.2	4.926	415.31706
3-21G <sup>*f</sup>	1.467	1.400	117.7	3.406	415.28498
3-21G <sup>*</sup>	1.460	1.393	117.76	3.461	415.29613
3-21G <sup>*d,e</sup>	1.470	1.391	117.5		415.20701
3-21G <sup>*d,g</sup>	1.459	1.392	117.76		415.23517
3-21+G <sup>*f</sup>	1.481	1.398	116.5	4.529	415.31663
3-21-21+G <sup>*f</sup>	1.481	1.398	116.5	4.538	415.34593
6-31G <sup>*</sup>	1.464	1.393	116.95	4.176	417.30681
6-31G <sup>*(dd)<sup>h</sup></sup>	1.459	1.396	116.57	3.972	417.31758
DZ+P <sup>i</sup>	1.469	(1.418) <sup>j</sup>	116.5	4.302	417.1976
DZ+P(on P) <sup>b</sup>	1.475	1.387	116.6		417.30637
DZ+P	1.474	1.393	115.8	5.136	417.33419

<sup>a</sup>Prime refers to phosphorus *d*-exponent of 0.47.

<sup>b</sup>Ref. 7.

<sup>c</sup>Carnegie-Mellon Quantum Chemistry Archive, 1985, p. 114.

<sup>d</sup>Ref. 4.

<sup>e</sup>Using the five canonical *d*-orbitals.

<sup>f</sup>Using optimized diffuse exponent on O of 0.1080.

<sup>g</sup>M. W. Schmidt and M. S. Gordon, *Can. J. Chem.*, **63**, 1609–1615 (1985).

<sup>h</sup>Two Cartesian *d*-functions used on P with exponents of 0.22 and 0.77.

<sup>i</sup>Ref. 11.

<sup>j</sup>Assumed value.

<sup>k</sup>6-31G<sup>\*</sup> at the STO-2G<sup>\*</sup> geometry; Ref. 19.

Diffuse functions lengthen both the 3-21G<sup>(\*)</sup> and 3-21G<sup>\*</sup> P-O bonds by 0.015 Å, while decontraction of the 2*sp* shell on phosphorus has no effect on geometry. Unfortunately, the largest basis sets used differ significantly in their results. DZ+P and 6-31G<sup>\*</sup> differ by 0.01 Å in the PO bond-length and 1° in the HPO bond angle. 3-21G<sup>\*</sup> gives a geometry close to the 6-31G<sup>\*</sup> result—certainly no worse than the differences between the largest basis sets.

A similar set of optimizations was done for fluorophosphine oxide, using a less extensive collection of basis sets. Prior optimizations of this structure have been at the STO-2G<sup>\*</sup> and 3-21G<sup>\*19</sup> levels with a partial optimization at DZ+P.<sup>11</sup> The results for the 3-21G-type basis sets are shown in Table II. As before, polarization functions result in contraction of the P-O and P-F bonds, while diffuse functions lengthen these bonds. The gas-phase P-O and P-F bondlengths for trifluorophosphine oxide are 1.436 ± 0.006 Å and 1.524 ± 0.003 Å, respectively,<sup>20</sup> while the corresponding bond-

lengths for difluorophosphine oxide are 1.437 ± 0.006 Å and 1.539 ± 0.003 Å.<sup>21</sup> Extrapolating these values for monofluorophosphine oxide yields a predicted P-O bondlength of 1.44 Å and a P-F bondlength of 1.54–1.55 Å, which is in best agreement with the 3-21G<sup>\*</sup> results. Because of steric factors, the bond angles are not directly comparable for either of these systems.

## ELECTRONIC STRUCTURE

Using the 3-21G<sup>\*</sup> optimized geometries, SCF wavefunctions for phosphine oxide and fluorophosphine oxide were calculated at a variety of basis set levels, and suitable regions of the projected density surfaces were demarked and integrated to give the corresponding fragment populations. Examples of these surfaces for phosphine oxide and fluorophosphine oxide are shown in Figure 2. The resulting fragment populations are shown in Table III.

**Table II.** A summary of fluorophosphine oxide structures.

Basis set	Bond Lengths (Å)			Bond Angles (deg.)			Energy -E, hartree
	P-O	P-F	P-H	F-P-O	H-P-H	H-P-O	
3-21G	1.541	1.615	1.388	114.5	104.1	117.3	513.41776
STO-2G <sup>*a</sup>	1.411	1.484	1.390	118.8			
3-21G( <sup>*'</sup> )	1.462	1.564	1.387	115.0	103.8	117.0	513.64811
3-21+G( <sup>*'</sup> )	1.474	1.590	1.386	114.8	106.8	116.4	513.70340
3-21G <sup>*'</sup>	1.451	1.542	1.389	115.7	103.3	116.9	513.71789
3-21G <sup>*a</sup>	1.450	1.553	1.378	115.2			
3-21+G <sup>*'</sup>	1.462	1.568	1.389	115.1	105.6	116.6	513.37409
DZ+P <sup>b</sup>	1.467	1.578	(1.390) <sup>c</sup>	(117.3) <sup>c</sup>	(105.3) <sup>c</sup>		515.9301

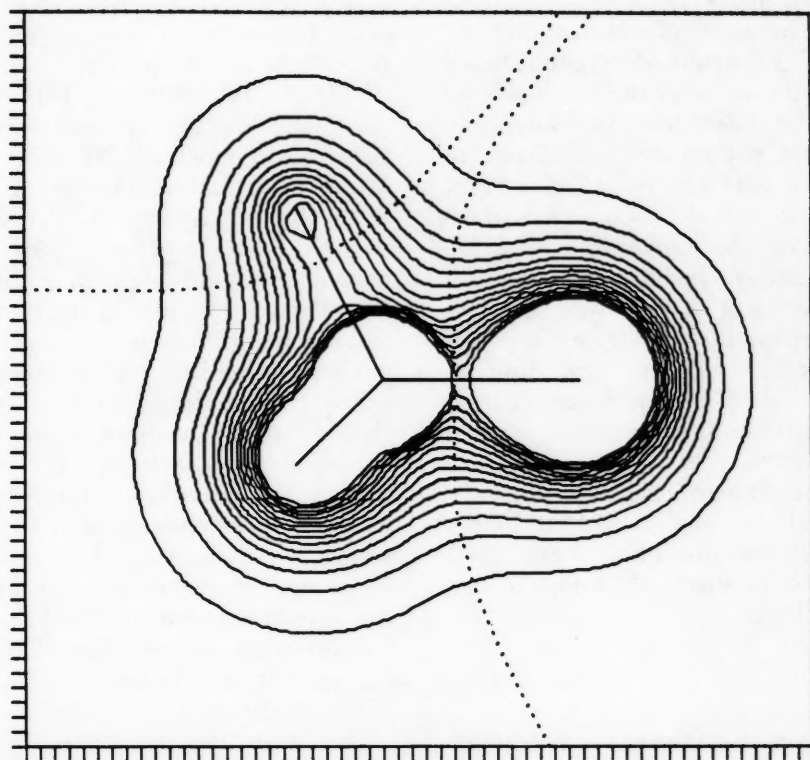
<sup>a</sup>Ref. 19; five *d*-orbitals used.

<sup>b</sup>Ref. 11.

<sup>c</sup>Assumed value.

The minimum density demarcations of such projected functions are approximations to the virial boundaries of R. F. W. Bader;<sup>22</sup> these boundaries are vertical curtains compared to the true virial curved surfaces. Accordingly, the derived integrated populations are only approximations to the true integrations over Bader "basins." The Projection method is used because the integration along one coordinate axis is analytical with Gaussian functions<sup>17</sup> and is faster than a true

Bader integration. Nevertheless, the differences generally involve regions of low electron density and the derived integrated populations from the PROJ approach do not differ much from true Bader integrated populations. In cases such as the present in which the molecule can lie conveniently in a plane, the absolute ISEP values are expected to be reasonable, and differences in such populations as a function of structure or basis set should be even more meaningful.



**Figure 2.** Projection function plot (3-21G<sup>\*</sup>) for phosphine oxide for the H(top)-P-O(right side) plane showing the ISEP demarcation lines (dotted). Contours range from 0.02 to 0.60 by 0.04  $e \text{ au}^{-2}$ . O population: 9.527  $e$ ; H population: 1.102 $e$ .

**Table III.** Integrated Populations (ISEP).

Phosphine Oxide			
Basis Set	Oxygen Population (Electrons)		
3-21G	9.254		
3-21G(*)	9.438		
3-21+G(*)	9.455		
3-21G*'	9.535		
3-21G**	9.527		
3-21+G*'	9.562		
6-31G*	9.533		
6-31G*(dd)	9.531		
DZ+P	9.576		
Fluorophosphine Oxide			
Basis Set	Oxygen Population (Electrons)	Fluorine Population (Electrons)	Dipole Moment (Debye)
3-21G	9.258	9.805	4.229
3-21G(*)	9.451	9.821	3.487
3-21+G(*)	9.471	9.816	4.252
3-21G*'	9.513	9.855	3.132
3-21+G*'	9.535	9.851	3.906
3-21-21G*'	9.514	9.852	3.133
DZ+P	9.537	9.828	4.231

\*H population 1.102 e; net charge on P +1.832.

The resulting population on oxygen in these systems is quite sensitive to basis set effects and particularly the inclusion of *d*-orbitals. The inclusion of polarization functions on both phosphorus and oxygen is found to be necessary in order for the smaller basis sets of the 3-21G\* type to adequately approximate the oxygen populations calculated for phosphine oxide with the 6-31G\*(dd) basis. Changing the *d*-orbital exponent on phosphorus has a small but perceptible effect on the population at oxygen, whereas changes in the basis set have only a relatively small effect on electron populations at fluorine. Polarization functions on oxygen and fluorine increase the populations of both centers. Addition of diffuse functions on oxygen further increases its population, while their addition to the fluorine basis produces a negligible effect. In fluorophosphine oxide, decontraction of the phosphorus 2*sp* shell likewise produces no effect on the populations of oxygen or fluorine.

## DISCUSSION

The best description of the valence region of phosphine oxide is probably given by the 6-31G\*(dd) basis set because the 3*d* orbitals on phosphorus are valence orbitals and their

better description in this basis is probably more important than the better core description of the DZ+P basis. These two rather large basis sets give a disappointingly large difference in calculated dipole moments, 3.97D (6-31G\*[dd]) vs 5.14D (DZ+P), and the ISEP oxygen populations differ by 0.045 electrons (Table III). This difference is larger than that of most other basis set effects. The 3-21G\* type basis sets agree well with the 6-31G\* and 6-31G\*[dd] results in the oxygen ISEP although the computed dipole moments vary substantially with rather small changes in basis set. Use of 6-31G\* increases the density close to the nucleus at the expense of an almost spherically symmetric shell at an intermediate region; however, integration around the oxygen region shows little net change. With relatively small basis sets the dipole moments may be too sensitive a measure of electronic structure to be useful for gauging valence electronic effects. All of the basis set electronic effects are smaller for fluorophosphine oxide. The 3-21G\* type basis set seems to give an adequate representation of this structure and electronic structure.

The large negative charge at oxygen in phosphine oxide suggests that diffuse functions should be important. Addition of such diffuse functions to the 3-21G(\*) basis set (*d*

on P only) results in longer PO bondlengths, whereas the addition of *d*-functions to oxygen gives geometries that are in better agreement with the larger basis results. Addition of *d*-functions to oxygen allows a polarization of the lone-pair electrons so as to minimize electron-electron repulsion. Diffuse functions do not allow this polarization, but instead lower repulsion by increasing the mean radius of the lone-pair orbitals. Because the 3-21G basis set is small, however, these diffuse functions also represent a significant perturbation of the entire valence shell and likewise increase the mean radius of the bonding orbitals, resulting in artificially lengthened bonds. Diffuse functions have an important role in anions but clearly have less utility in compounds that are neutral, even if highly polar. Indeed, with small basis sets on neutral systems, diffuse functions can significantly unbalance the basis set.

Finally, the large negative charges on oxygen given by the ISEP method indicate that the PO bond in these compounds is largely semi-polar. The best simple symbolic representation of phosphine oxide is  $\text{H}_3\text{P}^+ - \text{O}^-$  rather than  $\text{H}_3\text{P}=\text{O}$ . The dipole moment is large but not nearly as large as the dipolar structure would indicate *if the charges were spherically symmetric about the nuclei*. Of course, these charges actually are highly polarized to give the indicated moments.

In conclusion, the 3-21G\* basis set, with polarization functions on all first and second-row elements, provides a good reproduction of both experimental and higher-level theoretical geometries, and adequately reproduces the significant features of electron densities obtained using larger basis sets. The use of diffuse functions does not produce a significant improvement in these neutral molecules; if used without full polarization, diffuse functions can result in distorted geometries. Diffuse functions are recommended for calculations of anions, and then generally, in addition to polarization functions. Finally, decontraction of the 2*sp* shell on phosphorus does not change either population or geometry results, indicating that the shell is sufficiently well-described in its fully contracted form for many purposes.

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