# Intermolecular Correlation of Self-Consistent Field Molecular Orbitals. I. *Ab Initio* LCAO–MO–SCF Studies of the $PF_2H$ and $OPF_2H$ Molecules

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**Abstract:** Results from *ab initio* LCAO–MO–SCF calculations carried out in a moderately sized Gaussian basis set, with and without inclusion of atomic d orbitals on the phosphorus, are reported for the molecules $PF_2H$ and $OPF_2H$. It was found that nine of the ten valence-shell molecular orbitals of $PF_2H$ are individually closely related to nine of the thirteen valence-shell molecular orbitals of $OPF_2H$. This close relationship shows up in electronic populations, electron-density plots, and orbital energies. The predominant bonding contributions to each valence-shell molecular orbital have been categorized in terms of $\sigma$ and $\pi$ character. In addition, valence-shell molecular orbitals of $PF_2H$ and $OPF_2H$ are correlated with those of the $PF_3$, $OPF_3$, $PH_3$, and $OPH_3$ molecules, and it is shown that some of these molecular orbitals persist practically unchanged from one molecule to another in this set of related compounds.

As evidenced by the considerable effort that has been put into schemes[1] for the localization of SCF molecular orbitals, it has been quite generally believed that these SCF orbitals are too delocalized for direct interpretation in chemical terms. However, prior *ab initio* SCF studies[2–5] carried out by our group have indicated that SCF molecular orbitals are quite readily interpreted in terms of chemical bonding and that certain of them persist, at least in their general form as indicated by electron-density plots, from molecule to molecule.[2] This intermolecular correlation of SCF molecular orbitals is observed between a pair of molecules wherein an atom of a given group in the periodic table is substituted by another atom[3] from the same group, and we expect that it should also appear in substitution series of molecules, *e.g.*, $MX_iY_{n-i}$ where X and Y are substituents on a central moiety, M, of functionality *n*.

Difluorophosphine, $PF_2H$, and difluorophosphine oxide, $OPF_2H$, were chosen for the calculations reported herein, since these molecules are intermediate members of two closely related substitution series ($X = H$, $Y = F$, and $n = 3$ for M = P or OP) and their geometries have been well characterized by microwave spectroscopy.[6,7] In this paper we shall contrast the molecular orbitals of these two closely related molecules and will also compare them with the molecular orbitals of the end members of their substitution series. It is interesting to note that both difluorophosphine[8] and difluorophosphine oxide[9] are new compounds which were discovered[8,9] in the last few years.

## Calculational Details

The LCAO–MO–SCF computations were carried out with uncontracted Gaussian-type orbitals on a Control Data 6600 computer using the program MOSES[10] and atom-optimized s and p atomic orbitals, as outlined in our recent publications[2–5] dealing with this kind of work. Nine orbital exponents were used to describe the s orbitals of the phosphorus, with five for the p, and either one or none for the d. Likewise for either the fluorine or oxygen, five exponents were used to describe the s orbitals and two to describe the p, whereas for the hydrogen three orbital exponents were used to describe the s orbital. The values of these exponents have been previously published.[3–5,11] The d orbital exponent for phosphorus was chosen to be 0.36 from work carried out on molecular optimization in phosphine[12] and phosphine oxide.[4]

The following bond distances and angles obtained from interpretation of the microwave spectrum of difluorophosphine[6] were used in this study: P–F = 1.582 Å, P–H = 1.412 Å, ∠FPF = 99.0°, and ∠HPF = 96.3°. The values from the microwave study of difluorophosphine oxide[7] are P–F = 1.539 Å, P–H = 1.387 Å, ∠FPF = 99.8°, ∠HPF = 101.9°, and ∠FPO = 116.3°.

## Results and Discussion

**Total and Inner-Orbital Energies.** When d orbitals were allowed to the phosphorus, the total SCF energy was calculated to be −538.42 au for the $PF_2H$ molecule and −612.80 au for the $OPF_2H$ molecule. With d orbitals disallowed, the total SCF energy was calculated to be −538.23 au for the $PF_2H$ and −612.48 au for the $OPF_2H$. In the case of the $PF_2H$ molecule, the nuclear-repulsion energy was found to be +118.02 au, and, for $OPF_2H$, it was +197.03 au.

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The calculated binding energies for these molecules are of considerably greater chemical interest than the total SCF energies since the former deal only with the change in energy, $\Delta E$, involved upon assembling the ground-state atoms into the ground-state molecule. Binding energies for difluorophosphine and difluorophosphine oxide are presented in Table I, where they are compared with values for phosphine and phosphorus trifluoride which were calculated in directly comparable basis sets. If there were a linear change in binding energy across the series of molecules $PH_3$, $PFH_2$, $PF_2H$, $PF_3$, the value of the binding energy of the $PF_2H$ molecule (allowing phosphorus d character) would be 11.34 eV from the binding energies of $PH_3$ and $PF_3$ given in Table I, instead of the directly calculated value of 10.71 eV. Likewise, with no d character being allowed, the extrapolated value for the binding energy of $PF_2H$ is 6.05 eV instead of the directly calculated value of 5.61 eV. Thus, we see that, in either case, the $PF_2H$ molecule is destabilized by about 0.6 eV, probably because of interactions between the fluorine and hydrogen atoms. These interactions seem to be assignable to through-space repulsions rather than, say, to changes induced in the phosphorus lone-pair character. This lone-pair character is quite well amassed into the outermost orbital of these molecules; and the energies for this orbital, as calculated in comparable basis sets involving d character on the phosphorus, are $-10.23$ eV for $PH_3$, $-9.50$ eV for $PF_2H$, and $-9.28$ eV for $PF_3$. Moreover, in all of these cases, this outermost orbital is calculated to be stabilized by about the same amount (0.14 eV) by disallowing d character to the phosphorus.

**Table I.** Binding Energies of Some Related Molecules Calculated in Consistent Basis Sets

| Molecule | Binding energy (using d orbitals), eV[a] | Change upon the incorporation of d orbitals, eV |
|---|---|---|
| $PH_3$ | 7.63 | 1.77 |
| $PF_3$ | 13.20 | 7.06 |
| $PF_2H$ | 10.71 | 5.10 |
| $OPF_2H$ | 13.91 | 8.48 |

[a] This column gives the binding energy for the (951/52/3) basis set minus that for the (95/52/3), where the basis set corresponds to the following ordering of the atoms, when present: P/F, O/H.

The inner molecular orbitals always correspond to only a slight deformation of the respective inner atomic orbitals, and hence they are readily compared from molecule to molecule. Table II shows the inner-orbital energies for difluorophosphine and difluorophosphine oxide as well as for the related molecules, phosphine and phosphorus trifluoride, all of which were calculated in comparable basis sets, allowing d character to the phosphorus. It should be noted in this table that, when going from one given molecule to another, the change in energy for one of the inner phosphorus orbitals is about the same as it is for any of the others. This remarkable consistency in the changes produced in all of the inner-shell orbital energies by rearrangements and/or ionization of the valence electrons have been noted previously in both experimental and theoretical studies.[13,14]

**Table II.** Inner-Shell Orbital Energies for Some Related Molecules Calculated in Consistent Basis Sets

| | Orbital energies[a] in eV | | | |
|---|---|---|---|---|
| | $PH_3$ | $PF_2H$ | $PF_3$ | $OPF_2H$ |
| P "1s"[b] | −2176.8 | −2179.0 | −2179.5 | −2181.8 |
| P "2s" | −205.3 | −207.2 | −207.7 | −209.1 |
| P "2p" | −147.5 | −149.4 | −150.0 | −151.5 |
| F "1s" | | −720.2 | −721.1 | −721.5 |
| O "1s" | | | | −562.0 |

[a] These calculations included d character on the phosphorus. [b] The designation of the orbital corresponds to the atom but is shown in quotation marks since there is a small amount of delocalization which differs from molecule to molecule.

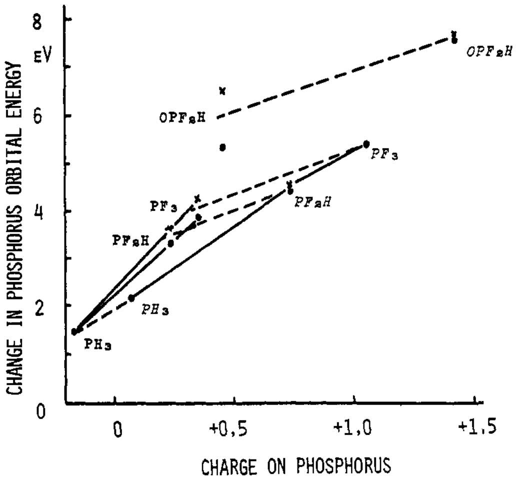

Figure 1. Variation with the charge on the phosphorus (calculated from the Mulliken gross population) of the inner orbital energy for phosphorus in the molecule minus the respective inner orbital energy for the phosphorus atom. The points denoted by x refer to the P "1s" orbital and the solid circles to the P "2s" and "2p" orbitals, unless these are all very close in which case the solid circle refers to all of the phosphorus inner orbitals. The points denoted by the chemical formulas in italics correspond to the calculations with d orbitals disallowed, while the other points on the left-hand side of the graph refer to the inclusion of d orbitals. The dotted lines show the effects of allowing d character to the phosphorus.

In Figure 1, values for the phosphorus inner-orbital energy, as computed for the various molecules of Table II, minus the same inner-orbital energy of the phosphorus atom (calculated in the same basis set) are plotted as a function of the gross atomic charge.[15] It can be seen from this plot that the orbital energy of the phosphorus inner orbitals varies approximately linearly with the electrical charge on the phosphorus across the series of molecules, $PH_3$, $PF_2H$, and $PF_3$. Also, the slopes of the dotted lines show that allowing d character to the phosphorus causes a diminution in the molecular inner-orbital energies concomitant with a drop in the charge on the phosphorus. All of this behavior is in accord with the ideas relating inner-orbital binding energies to atomic charges which are commonly employed in the interpretation of inner orbital photoelectron spectroscopy (ESCA).[16] How-

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**Table III.** Comparison of Valence-Shell Molecular-Orbital Data for $PF_2H$ with That for $OPF_2H$

| Orbitals | | | Electronic populations[a] | | | | | | | Orbital energies, eV |
|---|---|---|---|---|---|---|---|---|---|---|
| Predominant bonding | Symmetry | | Gross atomic | | | | Overlap | | | |
| | $PF_2H$ | $OPF_2H$ | P | F | O | H | P–F | P–O | P–H | |
| (P–F)σ | 6a′ | | 0.339 | 0.833 | | −0.006 | 0.205 | | −0.006 | −44.12 |
| | | *7a′* | *0.378* | *0.806* | *0.014* | *−0.005* | *0.207* | *0.012* | *−0.006* | *−45.71* |
| (P–F)σ | 3a′′ | | 0.224 | 0.888 | | 0.000 | 0.165 | | 0.000 | −43.10 |
| | | *3a′′* | *0.239* | *0.881* | *0.000* | *0.000* | *0.177* | *0.000* | *0.000* | *−44.49* |
| (P–O)σ | | *8a′* | *0.490* | *0.012* | *1.468* | *0.003* | *0.000* | *0.578* | *0.003* | *−36.47* |
| (P–H)σ, P lp | 7a′ | | 0.994 | 0.405 | | 0.196 | 0.048 | | 0.229 | −22.75 |
| | | *9a′* | *0.731* | *0.458* | *0.143* | *0.210* | *0.072* | *0.010* | *0.227* | *−23.10* |
| (P–H)σ, (P–F) | 8a′ | | 0.606 | 0.608 | | 0.179 | 0.129 | | 0.180 | −17.82 |
| | | *10a′* | *0.687* | *0.554* | *0.056* | *0.148* | *0.129* | *0.035* | *0.175* | *−19.43* |
| (P–F)σ, F lp | 4a′′ | | 0.363 | 0.818 | | 0.000 | 0.104 | | 0.000 | −17.32 |
| | | *4a′′* | *0.369* | *0.789* | *0.053* | *0.000* | *0.088* | *0.035* | *0.000* | *−18.90* |
| (P–F)σ, F lp | 9a′ | | 0.452 | 0.774 | | 0.000 | 0.137 | | −0.003 | −17.00 |
| | | *11a′* | *0.294* | *0.775* | *0.156* | *0.000* | *0.134* | *−0.019* | *−0.001* | *−17.96* |
| F lp | 5a′′ | | 0.093 | 0.954 | | 0.000 | 0.057 | | 0.000 | −15.44 |
| | | *5a′′* | *0.131* | *0.926* | *0.017* | *0.000* | *0.074* | *0.012* | *0.000* | *−16.60* |
| F lp | 6a′′ | | 0.034 | 0.983 | | 0.000 | 0.022 | | 0.000 | −14.59 |
| | | *6a′′* | *0.055* | *0.966* | *0.013* | *0.000* | *0.029* | *0.008* | *0.000* | *−15.83* |
| F lp, (P–H)σ | 10a′ | | 0.445 | 0.611 | | 0.332 | 0.029 | | 0.266 | −14.01 |
| | | *12a′* | *0.315* | *0.562* | *0.312* | *0.250* | *0.025* | *0.025* | *0.192* | *−15.54* |
| O lp | | *13a′* | *0.255* | *0.290* | *1.217* | *0.149* | *−0.025* | *0.106* | *0.116* | *−13.42* |
| O lp, (P–O)π | | *7a′′* | *0.298* | *0.118* | *1.466* | *0.000* | *−0.031* | *0.331* | *0.000* | *−11.80* |
| O lp, (P–O)π | | *14a′* | *0.341* | *0.037* | *1.421* | *0.163* | *−0.001* | *0.328* | *0.037* | *−11.65* |
| P lp, (P–H)σ* | 11a′ | | 1.231 | 0.234 | | 0.302 | −0.089 | | −0.135 | −9.51 |

[a] Numbers in italics refer to the $OPF_2H$ molecule, whereas the other numbers refer to the $PF_2H$ molecule. The calculations included d character on the phosphorus.

ever, we have found that in plots similar to Figure 1, where the inner orbital energies and atomic charges from Mulliken populations were calculated in directly comparable basis sets, that approximately linear behavior is only found for closely related series of molecules, such as the set of structures $PH_iF_{3-i}$ for $i = 0, 1, 2, 3$.

**Valence-Shell Molecular Orbitals.** The Mulliken population analyses[15] are reported for the valence-shell molecular orbitals of difluorophosphine and difluorophosphine oxide in Table III, where the respective orbital energies are also presented. From inspection of these populations, it is clear that these valence-shell molecular orbitals, although delocalized, exhibit a dominant feature such as (P–O)σ bonding or perhaps a fluorine lone pair ($F_{lp}$). These predominant bonding characteristics are shown in the first column of Table III. An examination of this table reveals that the population analyses of certain of the molecular orbitals of $PF_2H$ are very similar to those of $OPF_2H$ and these related orbitals are presented in the table as pairs. Thus, orbital 6a′ of $PF_2H$ is seen to be very similar to orbital 7a′ of $OPF_2H$, so that these two orbitals exhibit the same predominant bonding characteristics.

Of the ten valence-shell molecular orbitals of $PF_2H$, nine are found to correlate closely with nine of the thirteen valence-shell molecular orbitals of $OPF_2H$. These nine orbitals are dominated by P–F, P–H, and $F_{lp}$ character. The valence-shell molecular orbitals which are found not to correlate are dominated by characteristics which are not shared between the molecules. These features are the phosphorus and oxygen lone-pair electrons as well as the phosphorus–oxygen bond. Note that, not surprisingly, the energies of the pairs of closely related molecular orbitals are close to each other (see Table III) so that, from inspection of the orbital energies alone, it would be possible to identify the nine pairs of intermolecularly related molecules. Three-dimensional electron-density plots of the kind we have previously reported[2-5] show the close relation within each of these correlated pairs of valence-shell molecular orbitals. Furthermore, the related pairs of orbitals are affected similarly when d orbitals are allowed or disallowed to the basis set. Not surprisingly, allowing d character to the orbitals dominated by the fluorine lone pairs (4a′′, 11a′, 5a′′, and 6a′′ for $OPF_2H$) led to larger changes in the Mulliken population analysis of $OPF_2H$ than of $PF_2H$, with appreciable charge transfer to the phosphorus of the $OPF_2H$ as would be expected for $p_\pi$–$d_\pi$ feedback from the fluorine to the phosphorus. The largest increase in (a) the transfer of charge to the phosphorus as well as in (b) the P–O overlap population, upon allowing d character to the phosphorus, was found for orbital 14a′ of $OPF_2H$—an orbital which is dominated by the oxygen lone pair as well as by P–O π bonding.

*Ab initio* studies[11,12,17] carried out in our laboratory on a given molecule as described in several different basis sets have shown that, over a range of reasonably well-balanced basis sets, the shapes of the electron-density plots of a given orbital are little changed and that this is also true to a somewhat lesser extent for the Mulliken population analyses. Therefore, we have been able to carry out intermolecular valence-shell molecular-orbital corelations between a number of related molecules (including $PF_2H$ and $OPF_2H$) which have been measured in either exactly or approximately comparable basis sets. The resulting correlations are shown in Table IV where the listings are in the order of the orbital energies. Some pairs of orbitals in Table IV are nearly identical and these are connected by double-headed arrows. Likewise, several

(17) I. Absar and J. R. Van Wazer, unreported data on water calculated in the following bases: *a* minimum Slater, *b* extended Slater, larger than a double ζ, *c* (52/2) Gaussian, *d* (73/2) Gaussian, *e* (1052/41) Gaussian.

**Table IV.** Intermolecular Correlation of SCF Delocalized Molecular Orbitals[a]

| Major contribution | $PF_3$ | $OPF_3$ | $PF_2H$ | $OPF_2H$ | $PH_3$ | $OPH_3$ |
|---|---|---|---|---|---|---|
| (P–F)σ | $5a_1$ ⟷ | $6a_1$ | $6a'$ ⟷ | $7a'$ | | |
| (P–F)σ | $3e\ (a_2)$ | $3e\ (a_2)$ | $3a''$ ⟷ | $3a''$ | | |
| (P–F)σ | $3e\ (a_1)$ | $3e\ (a_1)$ | | | | |
| (P–O)σ | | $7a_1$ ⟷ | | $8a'$ ⟷ | | $5a_1$ |
| (P–H)σ, (P–F) | $6a_1$ | $8a_1$ | $7a'$ | $9a'$ | | |
| (P–H)σ, (P–F)σ | | | $8a'$ | $10a'$ ↮ | $4a_1$ | $6a_1$ |
| (P–H)σ | | | | | $2e\ (a_2)$ | $2e\ (a_2)$ |
| (P–H)σ | | | | | $2e\ (a_1)$ | $2e\ (a_1)$ |
| (P–F)σ, F lp | $4e\ (a_2)$ | $4e\ (a_2)$ | $4a''$ ⟷ | $4a''$ | | |
| (P–F)σ, F lp | $4e\ (a_1)$ | $4e\ (a_1)$ | | | | |
| (P–F)σ, F lp | $7a_1$ | $9a_1$ | $9a'$ | $11a'$ | | |
| F lp | $5e\ (a_2)$ | $5e\ (a_2)$ | $5a''$ | $5a''$ | | |
| F lp | $5e\ (a_1)$ | $5e\ (a_1)$ | | | | |
| F lp | $6e\ (a_2)$ | $6e\ (a_2)$ | $6a''$ | $6a''$ | | |
| F lp | $6e\ (a_1)$ | $6e\ (a_1)$ | | | | |
| F lp, (P–H)σ | | | $10a'$ | $12a'$ ↮ | | $6a_1$ |
| F lp | $1a_2$ ⟷ | $1a_2$ | | | | |
| O lp | | $10a_1$ | | $13a'$ ↮ | | $7a_1$ |
| P lp, (P–H)* | $8a_1$ | | $11a'$ | | $5a_1$ | |
| O lp, (P–O)π | $7e\ (a_2)$ | | $7a''$ | | $3e\ (a_2)$ | |
| O lp, (P–O)π | $7e\ (a_1)$ | | $14a'$ | | $3e\ (a_1)$ | |

[a] The double-headed arrows, ⟷, indicate pairs of orbitals that are very closely related, whereas the crossed-off double arrow, ↮, shows orbitals which are poorly related.

pairs are rather distantly related and these pairs are denoted by double-headed arrows with a line through them. Again, inspection of three-dimensional orbital-density plots confirms the relationships based on comparison of the electronic populations of the molecular orbitals.

## Conclusions

Not only are the delocalized molecular orbitals obtained from self-consistent field calculations about as readily understood and interpretable in chemical terms as are the localized orbitals derived[1] from them, but some of the delocalized orbitals appearing in one molecule may reappear with little change in another related molecule. We conclude from the work reported here and from a prior study[2] that there are probably a relatively limited number of SCF delocalized orbitals which are to be found over and over again in common chemical compounds. It should be of great importance to practical chemistry to identify these "molecularly invariant" orbitals so that their properties such as electron binding energies, contributions to the electronic part of the dipole moment, etc., may be intercompared to give a better insight into the electronic structure of matter. Furthermore, an *a priori* prediction as to which of these orbitals will appear in a given molecule and the development of methods for the generation of their specifications without doing any quantum-mechanical calculation is a feasible and worthwhile enterprise toward which we shall direct further efforts.

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