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Use of Pseudopotential Theory to Study Molecular Structure. The Phosphorus Halides

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The theory of ab initio pseudopotential SCF methods is applied to the four PX_3 phosphorus halides. The geometries, force constants, orbital energies, Mulliken populations, and dipole moments are calculated using a minimum Slater basis set. Detailed comparisons are made with experiment where possible and, in the case of PF_3, with a conventional SCF calculation.

Introduction

There has recently been considerable interest in the use of pseudopotential methods to perform *ab initio* valence-only SCF calculations. We have found in a previous study[1] that the theoretical problems in treating systems with more than one valence electron may be successfully overcome in the case of free atoms and homonuclear diatomic molecules. The present work is the first attempt to extend this method to polyatomic molecules and, in addition to study some of the properties of the pseudo wave functions.

The phosphorus halide series—PF_3, PCl_3, PBr_3, and PI_3—is of considerable chemical interest and, with exception of PI_3, has been extensively studied experimentally. Treating such a series of congeners allows the effect of increasing atomic size of the constituent atoms on molecular properties to be determined. In this paper, we first briefly review the theory and computational methods. The electron distribution of PF_3 as described by a Mulliken population analysis is calculated and compared with conventional SCF results. The calculated equilibrium geometries, force constants, and dipole moments of all four halide molecules are then reported. These are found to be in generally good agreement with the experimental values.

Method

The object of pseudopotential methods is to replace a conventional Hamiltonian operator, in this case the closed-shell Fock operator

$$\mathrm{F}\phi_i = [T + U + \sum_{j}^{\mathrm{occ}} (2J_j - K_j)]\phi_i \tag{1}$$

where i and j represent the set of all occupied orbitals, with a pseudo-Fock operator of the form

$$\mathrm{F}'\chi_i = [T + U + \sum_{j}^{\mathrm{valence}} (2J_j - K_j) + V]\chi_i \tag{2}$$

The j's now include only a subset of the occupied orbitals, usually the "valence" orbitals. The remaining occupied orbitals, the "core" orbitals, are not solved for explicity, but their presence is made known to the valence orbitals through the pseudopotential function V. χ_i is a pseudo wave function that is essentially identical with ϕ_i in the valence region but indeterminate in the core region, that is, near the nuclei. In practice, use of a pseudo wave function to determine molecular properties offers a very great computational advantage, since the basis set used to describe χ_i may be much smaller than a conventional Hartree–Fock calculation would require, and also the pseudopotential V may be chosen to include only one-electron terms. It has the inherent disadvantages that properties of the wave function near the nuclei cannot be determined nor can one-electron properties which emphasize the importance of integration over the wave function near the nuclei.

There are two contributions to V: a localized repulsive potential to simulate the electrostatic interaction of the core and valence electrons and a nonlocal potential due to the orthogonality constraints. For the first term we use a model potential function of the form $\sum_A \mathrm{f}(r_A)/r_A$ where r_A is the distance from nucleus A. We will further assume that

$$\langle\chi_i^B\left|\frac{\mathrm{f}(r_A)}{r_A}\right|\chi_j^C\rangle \begin{cases} = \langle\chi_i^B\left|\dfrac{(1 - e^{-\alpha_A r_A})N_c^A}{r_A}\right|\chi_j^C\rangle \\ \quad \text{for A = B or A = C} \\ = \langle\chi_i^B\left|\dfrac{N_c^A}{r_A}\right|\chi_j^C \\ \quad \text{for A} \neq \text{B and A} \neq \text{C} \end{cases} \tag{3}$$

where N_c^A is the number of core electrons on nucleus A and α_A is a parameter determined from atomic calculations. The rationale for using this function has been discussed in an earlier paper.[1] We replace the orthogonality constraint with the Phillips–Kleinman term[2] for each atom

$$\sum_{A}^{\mathrm{atoms}} \sum_{c}^{N_c^A/2} |\phi_c^A\rangle(\epsilon_v - \epsilon_c^A)\langle\phi_c^A| \tag{4}$$

where ϵ_c^A and ϕ_c^A are the core eigenvalues and eigenfunctions of the operator F for atom A. Finally we invoke the frozen core approximation; i.e., the core parameters α_A, ϵ_c^A, and ϕ_c^A are taken to be properties of the free atom and independent of the molecular environment. ϵ_v is then the lowest valence eigenvalue of eq 2, found iteratively. The pseudopotential (or effective potential) V is thus the sum of expressions 3 and 4. We refer to this specific embodiment of pseudopotential theory as the NOCOR method, for neglect of core orbitals.

The theoretical problems in using a pseudopotential of this form for many-electron systems are well-known.[3] Nonetheless we have found it to be approximately valid in may cases, particularly for atoms. Determination of the strengths and weaknesses of this approximation, as well as the pseudopo-

Table I. Valence-Shell Orbital Energies of PF_3 Compared with Measured Ionization Energies (Values in eV)

	Orbital energies		Ionization energies (exptl)	Δ (d – no d)[a]	
	Full SCF	NOCOR		Full SCF	NOCOR
$8a_1$	−9.15	−9.81	12.31	0.24	0.27
6e	−13.70	−14.05	15.91	−1.27	−1.16
$1a_2$	−13.34	−13.77	16.50	−0.47	−0.36
5e	−15.14	−15.46	17.45	−1.54	−1.32
$7a_1$	−17.35	−17.63	18.54	−0.89	−0.79
4e	−17.53	−17.73	19.42	−1.06	−0.95
$6a_1$	−21.44	−21.39		−0.25	−0.15
3e	−41.90	−40.08		−0.80	−0.73
$5a_1$	−43.56	−41.64		−0.48	−0.35

[a] A sixfold set of d orbitals was allowed to the phosphorus atom.

tential method as a whole, in molecular calculations is thus the intent of the present study.

Calculations

The closed-shell pseudo-Hartree–Fock equations for the phosphorus halides were solved using gaussian basis sets. The core orbitals and orbital energies were taken from minimum Slater basis set atomic calculations[4] using the atom-optimized exponents of Clementi and Raimondi,[5] except for the F, Cl, and P atoms, for which atom-optimized gaussian orbitals were used.[6] The valence basis functions in each case were also taken from ref 5. The Slater functions were then each expanded into a set of three gaussians. For the phosphorus d orbitals, a single set of cartesian gaussian functions with an exponent of 0.35 was used.[7] Finally the $f(r_A)$ function was expanded into a set of six gaussians. The computation time was 15 min per molecular configuration using a XDS Sigma 7 computer (comparable to an IBM 360/50), and it was found to be essentially the same for each molecule.

Results and Discussion

A. Comparison of NOCOR with Full SCF Calculations for PF_3. Since the expense of a full SCF minimum basis set calculation on phosphorus trifluoride is not prohibitive, a minimum Slater basis analysis was made (with and without d functions on the phosphorus) for the PF_3 molecule using exactly the same description of the valence orbitals and with the commensurate description of the core orbitals. That is, an atom-optimized minimum-basis set was used, each Slater function expanded into a set of three gaussian functions. Here this basis was also used for the core functions. The orbital energies resulting from this full-core calculation are compared with those of the equivalent NOCOR approximation (both with and without the manifold of d orbitals) in Table I, where the corresponding experimental ionization energies[8] are also reported. Note that the full SCF and NOCOR calculations agree well with each other but give only an approximate fit to the negative of the respective ionization energies.

Hillier and Saunders[8] have also reported the results of a modified minimum Slater calculation of the electronic structure of PF_3, using d orbitals. In this case the basis set was caused to be unbalanced so as to give a good fit of the energy of orbital $8a_1$ (12.68 eV) to the negative of experimental ionization energy of this orbital. However, raising the value of this orbital energy also leads to an increase in the energies of the other orbitals as compared to a minimum Slater calculation, so that the correspondence between the calculation and experimental data showed little improvement for the other orbitals for which experimental ionization energies are available. Note that the modified basis set of Hillier and Saunders may be used in a NOCOR calculation to the same end.

The difference between the orbital energies of the d and the no-d calculation are shown in the last two columns of Table I for the full-core and NOCOR results, respectively. Since these differences are generally in agreement to 0.1 eV, it appears that the NOCOR approximation applies to the (spd) description of the molecule about as well as it does to the (sp) description. In Table II, values for the change in total energy and in its components upon allowing d orbitals are compared for the full SCF and the NOCOR representations. In spite of the fact that the total energy for the full SCF representation is considerably larger than the value obtained from an identical mathematical treatment of the valence orbitals alone in the NOCOR calculation, the change in the energy, ΔE, upon allowing d-orbital participation is very close. Note that the change in the total energy is small compared to the changes in kinetic and nuclear attraction terms, as would be expected from first-order perturbation theory.[9] The difference between ΔE's of the three components of the total energy calculated by the NOCOR and full SCF methods reflect the form of eq 2, in which the core–valence two-electron potential is assumed to be represented by the $f(r_A)$ term of the one-electron potential. Table III shows a detailed comparison between the Mulliken population analysis of the conventional SCF calculation and the corresponding NOCOR results for PF_3. Both the population and (with the exception of the phosphorus 3s–fluorine 2s overlap), the effect of the d orbitals are well reproduced by the NOCOR approximation.

Table II. Energy Changes[a] upon Allowing d Orbitals to the Phosphorus Atom of PF_3

Energy	ΔE (d – no d)	
	Full SCF	NOCOR
Total	−0.35	−0.31
Kinetic	−2.31	−1.76
One-electron potential	+2.33	+1.90
Two-electron potential	−0.36	−0.45

[a] Values in atomic units (au).

Table III. Valence Basis-Function Populations of PF_3[a]

Phosphorus orbital	Fluorine orbital		Population	
			Full SCF	NOCOR
	2s	Gross	1.9271	1.9104
			(1.9602)	(1.9553)
	2p		5.1773	5.1853
			(5.3147)	(5.2937)
3s			1.8325	1.8100
			(1.6002)	(1.6010)
3p			2.3536	2.3166
			(2.6310)	(2.6438)
3d			0.5502	0.5860
			(0)	(0)
3s	2s	Overlap	−0.0812	−0.0891
			(−0.0974)	(−0.0888)
3s	2p		+0.0759	+0.0566
			(+0.0597)	(+0.0493)
3p	2s		−0.0533	−0.0373
			(−0.0902)	(−0.0749)
3p	2p		−0.3481	+0.3874
			(+0.3868)	(+0.4025)
3d	2s		+0.0271	+0.0497
			(0)	(0)
3d	2p		+0.3952	+0.3077
			(0)	(0)

[a] Values without phosphorus d-orbital participation given in parentheses.

As a final comparison between conventional SCF and NOCOR results, we present in Figure 1 the total electron densities in the valence orbitals of PF_3 as calculated from the NOCOR and full SCF methods. In these plots the vertical distance is a measure of the electron density; the other two directions define distances in a plane containing the C_{3v} axis and one F atom. The direction of view is down the C_{3v} axis, the P atom being nearer the forward edge of the plots. Both

Table IV. Mulliken Populations Calculated by the NOCOR Method for the Phosphorus Halides[a]

	P gross charge		P–X overlap population	
	With d[b]	Without d	With d	Without d
PF_3	0.29 (0.31)	0.78 (0.82)	0.66 (0.62)	0.29 (0.26)
PCl_3	0.21	0.42	0.64	0.44
PBr_3	0.21	0.30	0.53	0.40
PI_3	−0.16	−0.04	0.57	0.46

[a] Full SCF Values in parentheses. [b] A sixfold set of d orbitals was allowed to the phosphorus.

Table V. Equilibrium Bond Lengths (in A)

	Present work	Expt		Present work	Expt
PF_3	1.686	1.563 ± 0.002[a]	PBr_3	2.373	2.220 ± 0.003[c]
PCl_3	2.204	2.0426 ± 0.0005[b]	PI_3	2.597	2.43 ± 0.04[d]

[a] E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, **33**, 460 (1970). [b] G. Cazzoli, *ibid.*, **52**, 37 (1974). [c] K. Kuchitsu, T. Shibata, A. Yokozeki, and C. Matsumura, *Inorg. Chem.*, **10**, 2584 (1971). [d] P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950).

Table VI. Force Constants for Symmetric Bond Stretching[a] (in mdyn/A^2)

	Present work	Expt		Present work	Expt
PF_3	5.19	6.23 ± 0.13[b]	PBr_3	2.83	2.18[d]
PCl_3	3.52	3.11 ± 0.16, 3.48 ± 0.30[c]	PI_3	2.47	1.2[e]

[a] With respect to the internal symmetry coordinate. [b] See footnote *a*, Table V. [c] See footnote *b*, Table V. [d] See footnote *c*, Table V. [e] H. Stammreich, R. Forneris, and Y. Tavares, *J. Chem. Phys.*, **25**, 1278 (1956).

Table VII. Equilibrium X-P-X Bond Angles (in deg)

	Present work	Expt[a]		Present work	Expt[a]
PF_3	97.0	96.9 ± 0.7	PBr_3	101.9	101.0 ± 0.4
PCl_3	101.6	100.1 ± 0.02	PI_3	104.4	102 ± 2

[a] See footnotes to Table V.

Table VIII. Force Constants for Angular Symmetric Bending[a] (in mdyn/radian^2)

	Present work	Expt[b]		Present work	Expt[b]
PF_3	2.05	1.96 ± 0.04	PBr_3	1.41	1.47
PCl_3	1.79	1.54	PI_3	1.35	1.06

[a] With respect to the internal symmetry coordinate. [b] See footnotes to Table VI.

calculations are dominated by a concentration of charge in the valence shell of the fluorine atom, along with diffuse bonding and lone-pair contributions from the phosphorus. The full SCF results must contain a complicated antinodal structure near each nucleus in order for the SCF valence wave functions to be orthogonal to the core functions. The NOCOR wave functions do not have this constraint but are instead forced to decrease smoothly in the core region. Note that the full SCF and NOCOR electron densities are virtually identical in the valence regions of the molecule, that is, at points in space not too near the nuclei. However, the lack of antinodal structure in the NOCOR valence orbitals leads to an enhancement of the electron density of these valence orbitals in the core region (when a full electron pair is allowed to each orbital, as in these calculations). This effect shows up clearly in a slightly increased height at the top of the charge concentration around the fluorine for the NOCOR as compared to the full SCF calculation.

B. Intercomparison of the Phosphorus Halides. To show how the electronic structure of PF_3 compares with that of the other phosphorus halides, we summarize in Table IV the gross Mulliken charges on phosphorus and the P–X overlap population. Also given is the effect of allowing the participation of d orbitals on the phosphorus. The results of the NOCOR calculation are once more found to be in reasonable agreement with the full SCF results for PF_3. Note that the iodine in PI_3 appears to be electron donating with respect to the phosphorus and that allowing d character[10] to the phosphorus leads to an increasing amount of charge feedback from the halogen to the phosphorus in the series PBr_3, PCl_3, and PF_3, in accord with the increasing σ-electron-withdrawing character of the Br, Cl, and F atoms.

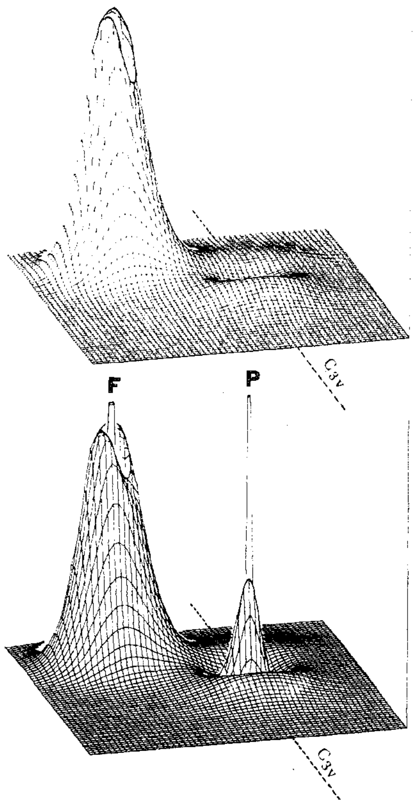

Figure 1. Cross-sectional electron density plots of the total valence shell of phosphorus trifluoride. The basal plane of each graph contains the phosphorus atom and one of the fluorine atoms and passes through the C_{3v} axis of the molecule; the vertical elevation at any point is proportional to the electron density at that point. The top plot shows the results from the NOCOR calculation and the bottom one shows results from the equivalent full SCF calculation.

Table IX. Dipole Moments (in Debyes)

	NOCOR	Expt		NOCOR	Expt
PF_3	0.52 (0.51)[a]	1.03[b]	PBr_3	0.32	0.61[d]
			PI_3	0.06	0.00[e]
PCl_3	0.63	0.78[c]			

[a] Full SCF value. [b] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21**, 308 (1953). [c] U. Grassi, *Nuovo Cimento*, **10**, 3 (1933). [d] K. Suenga and A. Kotera, *Nippon Kagaku Zasshi*, **70**, 116 (1949). [e] M. G. Malone and A. L. Ferguson, *J. Chem. Phys.*, **2**, 99 (1934).

Finally, it is of interest to compare the physical properties predicted by the NOCOR method, i.e., using a minimum basis set, with the known experimental values. In Tables V–IX we report the equilibrium geometries, force constants, and dipole moments of the four phosphorus halides. Three general conclusions may be drawn from these results: (1) bond lengths are consistently overestimated by 0.12–0.17 Å; (2) bond angles and bending force constants are determined more accurately than the corresponding bond lengths or stretching force constants; in particular the very slight increase in the bond angle on going from compounds of lighter to heavier elements is correctly predicted; (3) the results are somewhat more accurate for compounds of the lighter than of the heavier elements.

It is important to note that in all cases, the quantities calculated by our method are quite comparable in accuracy to those that would be expected from a comparable full SCF calculation. This finding is in accord with our previous study of the series of group 4 homonuclear, diatomic molecules.[1] The cost advantage of the pseudopotential method may be estimated on the assumption that the computation time increases as the fourth power of the size of the basis set. This means that an exactly equivalent full SCF computation for PF_3 would take about 5 times longer than the pseudopotential computation, whereas, for PI_3, the increase in time would be around 1300-fold!

Conclusions

The NOCOR method is found to give results that agree well with equivalent full SCF calculations for the PF_3 molecule and that compare usefully with experiment for all of the phosphorus halides. These results plus our previous findings[1] on the group IV diatomics indicate that the NOCOR method is appropriate for obtaining useful information for inorganic compounds which because of the large number of electrons involved were previously inaccessible to SCF calculations.

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Registry No. PF_3, 7783-55-3; PCl_3, 7719-12-2; PBr_3, 7789-60-8; PI_3, 13455-01-1.

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Hydrogen-1, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Spectral Studies of Some Phenyl- and Perflurorphenyl-Substituted Aminophosphines and Aminophosphonium Salts

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^1H, ^{13}C, and ^{31}P NMR data have been acquired for the aminophosphine $(i\text{-}C_3H_7)NHP(C_6H_5)_2$, **1**, the new aminophosphines $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, **2**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2$, **3**, and the new aminophosphonium salts, $(i\text{-}C_3H_7)NHP(C_6H_5)_2(CH_3)I$, **4**, $(i\text{-}C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4$, **5**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2(CH_3)BF_4$, **6**. Particular interest is associated with the following aspects of the NMR data: (1) the appearance and solvent dependence of the chemical shifts of the amino proton resonances, (2) the long-range (five-bond) coupling between the ortho fluorines of the C_6F_5 groups and the phosphonium methyl protons of **5** and **6**, and (3) the nonidentical *P*–N–C–*C* couplings in **2** and **5**.

The stereochemistry of aminophosphines[2] and related compounds[3] is a subject which is eliciting increasing attention. The focal points of these studies comprise the frequent occurrence of planar nitrogenous geometries, the electronic character of the P–N linkage, and the trends in the P–N torsional barriers. The aminophosphines $(i\text{-}C_3H_7)NHP(C_6H_5)_2$,[4] **1**, $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, **2**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2$, **3**, and the aminophosphonium salts $(i\text{-}C_3H_7)NHP(C_6H_5)_2(CH_3)I$, **4**, $(i\text{-}C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4$, **5** and $(i\text{-}C_3H_7)NHP(C_6F_5)_2(CH_3)BF_4$, **6**, which are described in the present work were synthesized as precursors to the corresponding iminophosphoranes. However, during routine characterization of these compounds by ^1H, ^{13}C, and ^{31}P NMR spectroscopy certain interesting spectral features were revealed such that separate publication of this aspect appeared to be warranted. The points of emphasis in the present paper are (1) the appearance and solvent dependence of the chemical shifts of the amino proton resonances, (2) the long-range (five-bond) coupling between the ortho fluorines of the C_6F_5 groups and the phosphonium methyl protons of **5** and **6**, and (3) the nonidentical *P*–N–C–*C* couplings in **2** and **5**.

Experimental Section

Isopropylaminodiphenylphosphine, **1**, was prepared according to the method of Hart and Sisler.[4]

Preparation of Pentafluorophenylmagnesium Bromide. To a flame-dried apparatus consisting of a 250-ml round-bottomed flask equipped with a mechanical stirrer and a Claisen head topped by a dropping funnel with a gas inlet adapter were added 5.35 g (0.22 g-atom) of magnesium turnings and 60 ml of dried ether. The flask and its contents were cooled to −15° prior to adding 49.4 g (0.20 mol) of pentafluorobromobenzene in 60 ml of dried ether from the dropping funnel to the stirred reaction mixture. A dry N_2 atmosphere was maintained throughout the reaction. After 2 hr of stirring (during which time the mixture was allowed to warm to 0°) the reaction mixture was transferred back into the dropping funnel in preparation for the synthesis of the phenyl(pentafluorophenyl)halophosphine mixture.

Preparation of Phenyl(pentafluorophenyl)halophosphine Mixture.