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The Concept of Vacant *d* Orbitals and the Causes of the Differences between the Properties of Nitrogen and Phosphorus Compounds

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Comparison of non-empirical calculations on analogous nitrogen and phosphorus compounds shows that the presence of vacant *d* orbitals in the valence shells of the elements in the Third Period cannot be the real cause of the differences between the properties of nitrogen and phosphorus compounds and that the effects are ultimately determined by the differences between the effective sizes of the valence *s* and *p* orbitals of these elements.
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I. INTRODUCTION

This review discusses the problem which properties of nitrogen and phosphorus atoms determine the fundamental differences between the properties of the compounds of these elements. It begins with a brief account of the properties of isolated nitrogen and phosphorus atoms and their valence states. The discussion is based on the standpoint necessary for developing the subsequent reasoning.

II. NITROGEN AND PHOSPHORUS ATOMS AND THEIR VALENCE STATES

The properties of nitrogen and phosphorus atoms are determined by their positions in Mendeleev's periodic table. The structure of the Table became comprehensible after quantum mechanics had been developed and had yielded the solution of the problem of the hydrogen atom. It was found that the electron in the hydrogen atom can have a discrete (and not continuous as in the classical treatment) series of states whose energy E_n is determined by the principal quantum number n:

$$E_n = -\frac{me^4}{2\hbar^2}\cdot\frac{1}{n^2}; \quad n = 1, 2, 3 \ldots .$$

In addition to the energy, the state of the electron is characterised by its angular momentum, which is determined by the orbital quantum number l:

$$M^2 = \hbar^2 l(l+1); \quad l = 0, 1, 2 \ldots$$

The range of momenta in states with a definite energy is limited:

$$l \leqslant n-1.$$

States with zero angular momentum ($l = 0$) are referred to as *s* states, those corresponding to $l = 1$ are *p* states, those corresponding to $l = 2$ are *d* states, etc. When the *s* states, for which the angular momentum is zero, are excluded, the states are distinguished by the direction of the angular momentum, which is determined by the magnetic quantum number m:

$$M_z = \hbar m; \quad m = 0, \pm 1, \pm 2, \ldots . \pm l.$$

Fig. 1 presents a schematic arrangement of the possible states of the electron in the hydrogen atom. The excited levels of hydrogen are degenerate, i.e. a whole set of different states corresponds to the same energy. The energy levels are degenerate not only as regards direction but also as regards momentum, i.e. the energies of the *s*, *p*, and *d* states are identical.

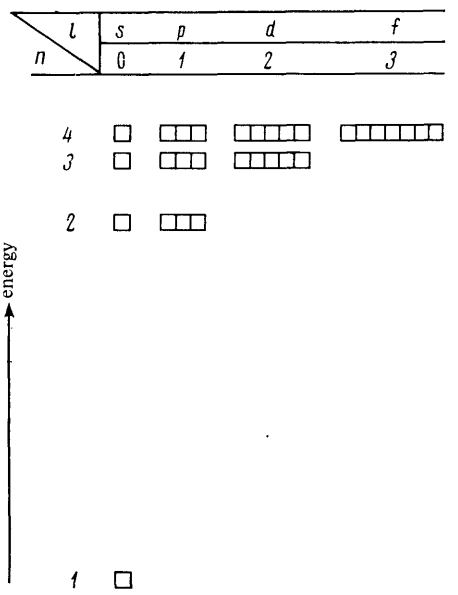


Figure 1. Schematic illustration of the possible electronic states in the hydrogen atom.

If the electrons did not interact, an identical pattern of possible electronic states would persist in a multielectron atom and it would be possible to determine the structure of any atom by filling these states in succession,

taking into account the Pauli principle. In reality electrons repel one another. For example, the 2*s* electron of lithium is not only not attracted to the nucleus, but is actually repelled by the inner 1*s* electrons (Fig. 2), the overall effects of which can be described as shielding of the nucleus—the decrease of the actual nuclear charge to an "effective" charge. The shielding conditions depend on the nature of the electron cloud. The density of the electron cloud in the *s* states is a maximum in the region of the nucleus; this applies not only to the 1*s* state but also to the 2*s* and 3*s* states (Fig. 3*a*). In the *p* states, the density of the electron cloud at the nucleus is zero (Fig. 3*b*) and in the *d* states the density is again zero at the nucleus and increases very slowly (Fig. 3*c*). Accordingly, the shielding of the nucleus by other electrons is much more marked for a *d* electron than for a *p* electron and for the latter it is more marked than for an *s* electron. As a result, the degeneracy as regards momentum is removed: the energies of the *s*, *p*, and *d* electrons are no longer the same. Fig. 4 presents a schematic arrangement of the possible electronic states in a multielectron atom.

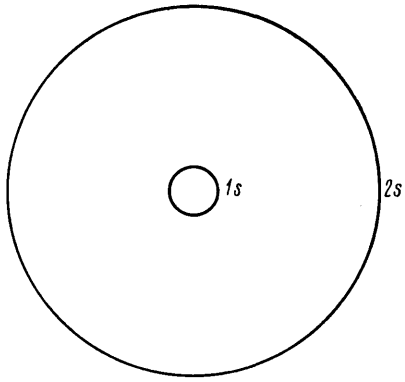


Figure 2. The lithium atom. The radii of the circumferences correspond to the maximum radial densities of the 1*s* and 2*s* electrons[1].

Nitrogen and phosphorus atoms are located in Group V but in the Second and Third Periods. We shall consider how their properties are determined by their positions. We shall begin with the ionisation potential—a property of decisive importance for chemistry (Fig. 5).

Fig. 2 shows that the valence electron of lithium is remote from the nucleus from which it is effectively shielded by the 1*s* electrons and the ionisation potential is therefore very low. In the beryllium atom, the increased nuclear charge is incompletely shielded, and the ionisation potential is greater. Although the nuclear charge has again increased in the boron atom, the additional electron is now located in a *p* orbital for which the shielding is more marked, as a result of which the ionisation potential is smaller than for beryllium. The additional electron in carbon is located in the next vacant *p* orbital and the increased nuclear charge, which is incompletely compensated by shielding, leads to an increase of the ionisation potential; this effect is even greater for nitrogen and in the oxygen atom the additional electron enters a *p* orbital already occupied by an electron. The mutual repulsion of the two electrons in the same orbital is so powerful, that, despite the increased nuclear charge, the ionisation potential of oxygen is smaller than that of nitrogen. Thus the ionisation potential of nitrogen is greater than those of its immediate neighbours—not only carbon but also oxygen:

	C	N	O
I, eV	11.256	14.53	13.614

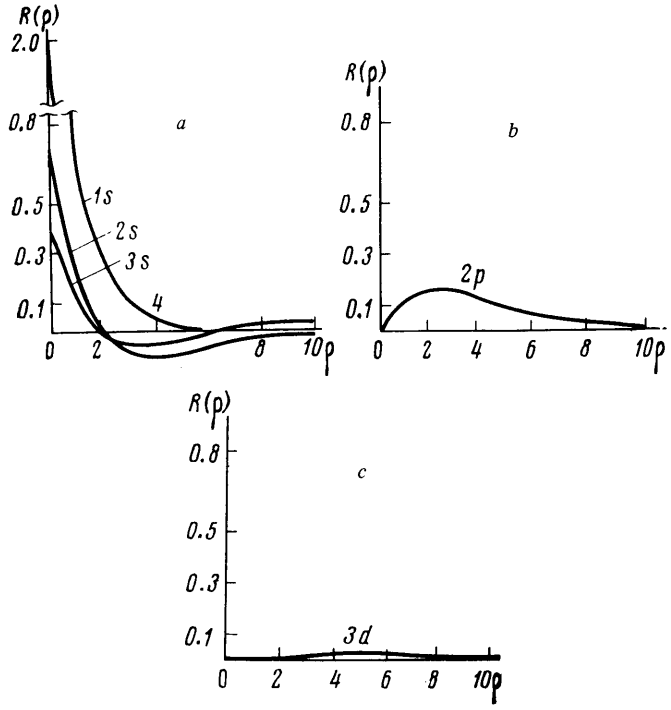


Figure 3. The radial wave functions $R(\rho)$ of the hydrogen atom (ρ is the distance from the nucleus in atomic units).

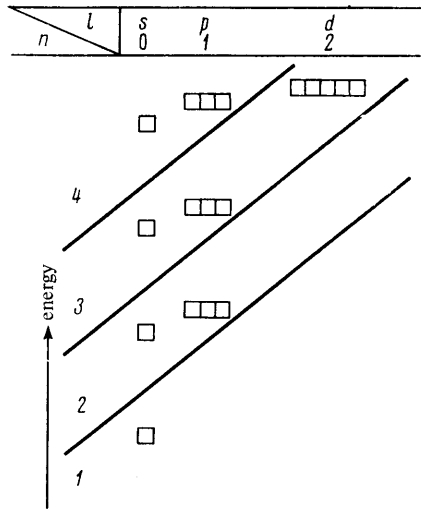


Figure 4. Schematic illustration of the arrangement of atomic orbitals in terms of energies in a multielectron atom.

The same qualitative pattern holds for the Third Period: the ionisation potential of phosphorus is greater than those of silicon and sulphur:

	Si	P	S
I, eV	8.15	10.48	10.36

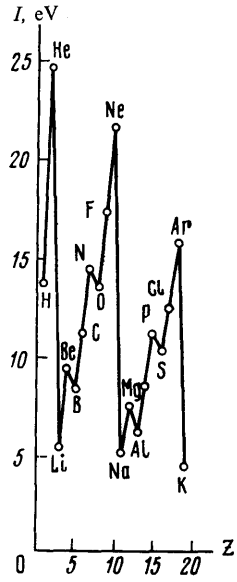


Figure 5. Ionisation potentials of atoms.

However, despite the complete repetition of qualitative features, there is a considerable quantitative difference between nitrogen and phosphorus. The valence electrons of the phosphorus atom are at a much greater distance from the nucleus than in nitrogen, so that, despite the higher effective nuclear charge, the ionisation potential of phosphorus is approximately 4 eV smaller than that of nitrogen.

Another atomic property very important for chemistry is electron affinity. In the carbon atom, the nucleus is incompletely shielded by valence electrons, there is a vacant *p* orbital, and the atom exhibits an appreciable electron affinity. In the nitrogen atom, the additional electron must enter a *p* orbital which is already occupied and the interelectronic repulsion is so great that the electron affinity is negligible. In the oxygen atom, the increased nuclear charge partly compensates this effect and the electron affinity increases:

	C	N	O
E, eV	2.1	0.05	1.47

The same qualitative pattern is repeated for the atoms of the Third Period: the electron affinity of phosphorus is smaller than that of its neighbours—silicon and sulphur:

	Si	P	S
E, eV	1.46	0.77	2.07

On the other hand, the mutual repulsion of the electrons located in the same orbital in the phosphorus atom with its larger valence orbitals is less marked than in nitrogen. As a result, the electron affinity of phosphorus is greater than that of nitrogen. The more ready deformation of the electron cloud of phosphorus under the influence of external fields, i.e. the greater polarisability of the phosphorus atom compared with the nitrogen atom, is associated with the greater size of the valence orbitals of the phosphorus atom and the greater diffuseness of its electron cloud. Consequently, owing to the greater size of phosphorus orbitals compared with nitrogen orbitals, the ionisation potential of phosphorus is much smaller, its electron affinity is much greater, and its polarisability is greater.

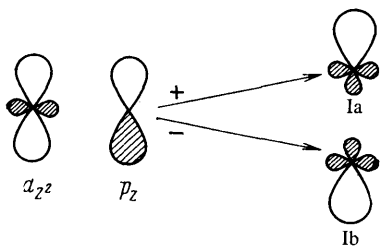
We shall consider yet another difference between phosphorus and nitrogen. The valence shell of the phosphorus atom contains *d* orbitals and the question of their properties arises. The states of hydrogen are arranged in Fig. 1 in terms of energies on a uniform scale. A similar arrangement of the electrons in phosphorus is impossible (the ionisation potential of the valence electron of the phosphorus atom is of the order of 10 eV, while the ionisation potential of the 1*s* electrons of phosphorus is of the order of thousands of electron-volts). Fig. 4 merely shows qualitatively that the energy of the vacant *d* orbitals is higher than that of the *s* and *p* orbitals of the next shell. It is seen from the atomic spectra of phosphorus[2] that the first transitions are $3p \rightarrow 4s$ (7–8 eV), are followed next by $3p \rightarrow 4p$ transitions (8–8.5 eV), and only then by transitions to 3*d* orbitals (about 9 eV). Consequently, despite the fact that the *d* orbitals of the phosphorus atom are located in the valence shell, they are less favourable than the 4*s* and 4*p* orbitals in the next shell. As already mentioned, this is because the shielding of the *d* orbitals from the nucleus by other electrons is particularly effective. The weak attraction of *d* electrons to the nucleus leads to the expansion of their orbitals. As a result of the diffuseness of the *d* orbitals of phosphorus, their overlapping with the valence orbitals of neighbouring atoms is negligible. With this statement, we complete the consideration of the properties of isolated phosphorus and nitrogen atoms and proceed now to an examination of their valence states.

Phosphorus and nitrogen atoms each have three unpaired electrons located in *p* orbitals. The p^3 state may be regarded as their ground valence state, despite the fact that the bonding orbitals acquire some *s* character and the lone electron pair occupies an orbital with an admixture of *p* character and not a pure *s* orbital[3].

The lone electron pair can form a bond with a proton, with an alkyl cation, with BF_3, and in general with Lewis acids. This results in the formation of ammonium and phosphonium compounds in which tetravalent nitrogen and phosphorus cations are in a tetrahedral sp^3-hybrid valence state. If the substituents are not the same, the tetrahedron is distorted, the distortion being particularly pronounced in compounds such as phosphine and amine oxides; nevertheless, the valence states in these compounds can be regarded as largely sp^3 states. Compounds of the type NR_5 are known, but their discoverer (Schlenck) already showed that the bonds in such compounds are non-equivalent[4]. They are salt-like and contain the tetravalent ammonium cation NR_4^+ and the carbanion R^-.

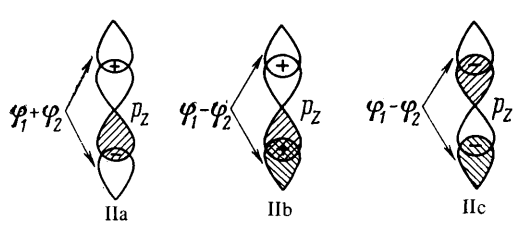
On the other hand, penta- and hexa-coordinate compounds with more or less equivalent bonds are known for phosphorus. Pentacoordinate phosphorus compounds, for example PF_5, have a trigonal bipyramidal structure. It has come to be assumed that the valence shell of phosphorus is expanded in these compounds owing to the vacant *d* orbital. Bonds with three equatorial ligands are formed by the trigonal sp^2-hybrid phosphorus orbitals, while the

remaining p_z orbital is hybridised with the d_{z^2} orbital in order to form bonds with the axial ligands. The hybrid *dp* orbital (Ia) obtained when the above orbitals are combined is involved in the formation of a bond with the upper ligand and the residual hybrid *dp* orbital (Ib) forms a bond with the ligand located at the lower vertex of the bipyramid.



It is therefore usually assumed[5] that phosphorus exists in the dsp^3 valence state.

Nevertheless the involvement of *d* orbitals is by no means necessary for the description of the bonding in pentacoordinate phosphorus compounds. This is easily shown using the molecular orbital method[6]†. The linkages with the three ligands in the equatorial plane are again regarded as two-centre bonds formed by the trigonal sp^2-hybrid orbitals of phosphorus. In order to describe the bonds with the axial ligands, we construct molecular orbitals from the p_z orbital of phosphorus and the atomic orbitals of the ligands. The overlap integral for the symmetrical combination of the ligand orbitals $\varphi_1 + \varphi_2$ with the p_z orbital of phosphorus is zero‡ [the positive overlap with the upper lobe of the p_z orbital is compensated by the negative overlap with the lower lobe of this orbital (IIa)]. The interaction is therefore impossible and this combination constitutes the non-bonding orbital ψ_2, the energy of which is equal to the energy of the atomic orbitals of the ligands (Fig. 6).



On the other hand, the antisymmetric combination of the ligand orbitals $\varphi_1 - \varphi_2$ forms with the p_z orbital of phosphorus the energetically extremely favourable and highly bonding three-centre molecular orbital ψ_1 (Fig. 6) [the positive overlap of the ligand orbitals with the upper lobe of the p_z orbital of the phosphorus atom $\Theta\cdot\Theta$ is supplemented by the positive $\Theta\cdot\Theta$ overlap with the lower lobe (IIb)] and the three-centre antibonding molecular orbital ψ_3 [the negative overlap $\Theta\cdot\Theta$ with the upper lobe of the p_z orbital is added to the negative $\Theta\cdot\Theta$ overlap with the lower lobe (IIc)].

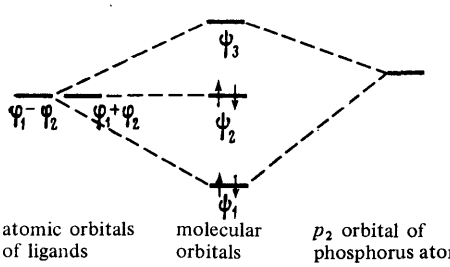


Figure 6. Correlation diagram for a three-centre bond.

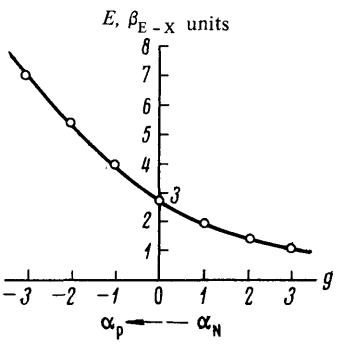


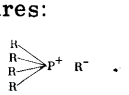
Figure 7. Dependence of the energy *E* of the three-centre bond X–E–X on the Coulombic integral of the central atom $\alpha_E = \alpha_X + g\beta(E - X)$ (the Hückel approximation). The arrows show the direction of the change in α_E from N to P in parallel with the change in the ionisation potential.

In the resulting molecular orbitals—the bonding orbital ψ_1, the non-bonding orbital ψ_2, and the antibonding orbital ψ_3—four-electrons should be located: the two electrons of the lone pair of phosphorus and one electron from each ligand. They occupy the bonding ψ_1 molecular orbital and the non-bonding ψ_2 orbital and, although the electrons in the non-bonding orbital give no energy gain, the bonding molecular orbital is energetically so favourable that the two electrons located in it are sufficient to ensure the formation of a linkage between the phosphorus atom and the ligands located at the upper and lower vertices of the bipyramid. The energy of the three-centre "four-electron" bond depends strongly on the energy of the lone pair electrons. This energy increases rapidly with decrease of the ionisation potential of the lone electron pair and the three-centre bond must therefore be much more favourable for phosphorus than for nitrogen (Fig. 7).

We shall consider now how the above description is altered when account is taken of the *d* orbital of the phosphorus atom. In contrast to the p_z orbital, the *d* orbital

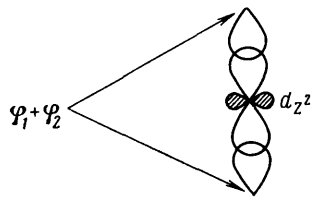
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†The description by the valence bond (VB) method without resorting to *d* orbitals corresponds to the resonance of five ionic structures:



‡The overlapping of the functions is described by the integral of the product of these functions (the overlap integral *S*): $S = \int \bar{\Phi}_1 \Phi_2 d\tau$ (integration over the entire space). The parts of the space where the two overlapping functions have the same sign make a positive contribution to the integral, while those regions where the signs of the functions are different make a negative contribution.

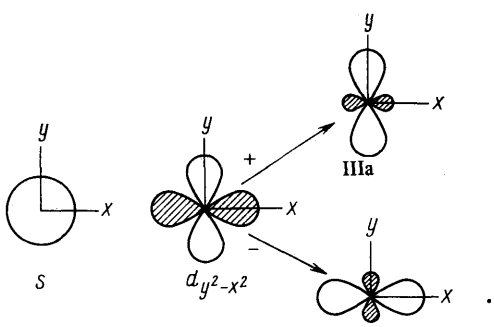
of phosphorus can interact with the symmetrical combination $\varphi_1 + \varphi_2$ of the ligand orbitals (IId):



IId

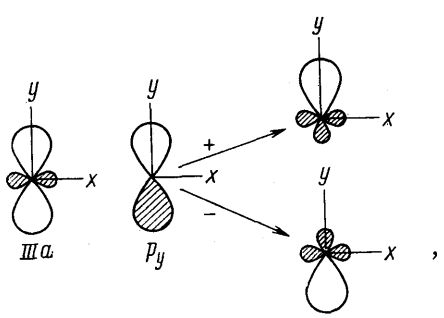
But, since the d orbital is energetically unfavourable and very diffuse, its interaction can only be very weak. Because of it, the non-bonding molecular orbital ψ_2 becomes slightly bonding. However, this weak interaction does not play a fundamental role.

In the traditional description of ions containing hexacoordinate phosphorus such as PF_6^-, one postulates an expansion of the valence shell of phosphorus by two d orbitals. One of these, the d_{z^2} orbital, is hybridised with the p_z orbital, forming hybrid dp orbitals directed to the upper and lower ligands. This description is exactly the same as that of the bonds with the axial ligands in PF_5. A second d orbital of phosphorus, namely the $d_{y^2-x^2}$ orbital, is invoked, in addition to the s, p_x, and p_y orbitals to describe the bonds with the four ligands in the equatorial plane. We shall describe the hybridisation in stages. On combining the $d_{y^2-x^2}$ orbital with the s orbital, we obtain orbitals extended along the y axis, ($s + d_{y^2-x^2}$, IIIa) and along the x axis ($s - d_{y^2-x^2}$, IIIb):



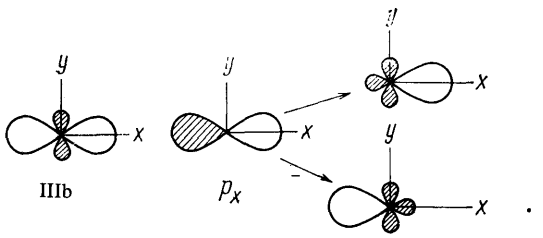
IIIa IIIb

The first of these forms with the p_y orbital two orbitals directed to the ligands located on the y axis:



IIIa ,

while the second forms with the p_x orbital two orbitals directed to the ligands located on the x axis:



Each of the six hybrid phosphorus orbitals obtained forms a two-centre bond with the atomic orbitals of the ligands. In this description, it is assumed that phosphorus is in the d^2sp^3 valence state.

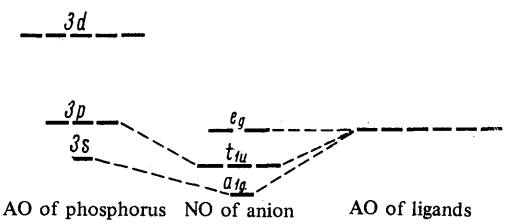


Figure 8. Correlation diagram for an octahedral anion.

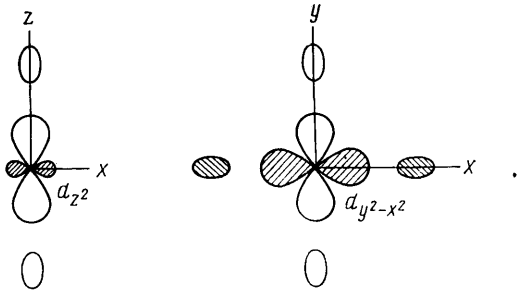
However, as for the pentacoordinate phosphorus compounds, it is found that the hypothesis of the expansion of the valence shell is not essential for a description of the bonds between phosphorus and the ligands in its hexacoordinate compounds. Indeed, the sum of the atomic orbitals of all the ligands is combined with the s orbital of phosphorus, forming an energetically very favourable bonding seven-centre molecular orbital (group designation a_{1g}, Fig. 8).

The antisymmetric combination of the ligand orbitals located on the z axis forms a strongly bonding three-centre molecular orbital with the p_z orbital of the phosphorus atom [similar to the three-centre linkage (IIb) between phosphorus and the axial ligands in PF_5]. Exactly the same three-centre molecular orbitals are obtained from the p_x (and p_y) orbitals of the phosphorus atom and the antisymmetric combination of the orbitals of the ligands located along the x (and y) axis. The energies of these three three-centre molecular orbitals are the same, i.e. they are degenerate (group designation t_{1u}, Fig. 8).

Eight electrons are located in the resulting orbitals—one seven-centre and three three-centre orbitals. The remaining four electrons (there are altogether twelve electrons: six from the ligands, five from the phosphorus atom, and one additional electron, since hexacoordinate phosphorus species exist in the form of anions) are distributed in two degenerate non-bonding molecular orbitals formed from the ligand orbitals alone (group designation e_g, Fig. 8). These two non-bonding molecular orbitals are shown in diagrams IVa and IVb. Although the last four electrons make no contribution to the bonding, the energy gain due to the eight electrons located in the strongly

bonding molecular orbitals is so great that it is quite sufficient to account for the bonding between phosphorus and the ligands in its octahedral anions (Fig. 8).

We shall now consider the changes in the above pattern when account is taken of the phosphorus *d* orbitals. The symmetry of two of the phosphorus *d* orbitals (the d_{z^2} and $d_{y^2-x^2}$ orbitals) is such that they can interact with the non-bonding molecular orbitals e_g.



(IVa) (IVb)

Next one can repeat what has already been said in the discussion of the pentacoordinate phosphorus compounds. Owing to the diffuseness and the energetically unfavourable nature of the phosphorus *d* orbitals, this interaction makes no significant contribution to the bonding: the non-bonding orbitals e_g become slightly bonding. It is clear from the foregoing that the concept of the expansion of the valence shell of phosphorus and of the existence of its dsp^3 and d^2sp^3 valence states is not essential for the description of the bonding in its pentacoordinate and hexacoordinate compounds.

III. NON-EMPIRICAL CALCULATIONS ON ANALOGOUS NITROGEN AND PHOSPHORUS COMPOUNDS

We shall now proceed to a comparison of the main classes of nitrogen and phosphorus compounds and shall attempt to find a fairly probable physical explanation of the differences between their properties. The traditional explanation of these properties is based on the concept of *d* orbitals. The concept of vacant *d* orbitals of silicon, phosphorus, and sulphur is widely used in the discussion of the properties of the compounds formed by these atoms[7-9]; *d* orbitals are invoked to account for the characteristics of the elements of the Third Period in relation to those of the Second Period.

The concept of *d* orbitals is based on the fact that the valence electrons of the elements of the Second Period are in the second shell, where there are no *d* orbitals, while the valence electrons of the elements in the Third Period are in the third shell. Apart from the *s* and *p* states, *d* states are possible in the third shell. Consequently, in contrast to the elements of the Second Period, those of the Third Period have vacant *d* orbitals in the valence shell. This led to the conclusion that the valence shell may be expanded and that additional bonds may be formed in pentacoordinate and hexacoordinate compounds via the *d* orbitals. The electron-accepting properties of the elements of the Third Period are accounted for by these orbitals and bonding with these elements and reactivity have been described with their aid, for example, by Ivanov and Zheltukhin[10]. This concept proved attractive and has been rapidly and extensively adopted[11]. This is, as it were, the chemical aspect of the problem of vacant *d* orbitals.

Qualitative considerations were followed by attempts to confirm them by calculations, which immediately encountered difficulties[12,13]. It was shown above that the *d* orbitals of the phosphorus atom are energetically very unfavourable and diffuse and are therefore incapable of effective interaction. This is also true of the *d* orbitals of the silicon and particularly sulphur atoms[2]. When atomic *d* orbitals are used in the calculation, as has been done for other valence orbitals, it is therefore immediately found that the *d* orbitals can play no role. It was then postulated that the atomic *d* orbitals in the molecule are altered (compressed), and modified *d* orbitals began to be used in calculations in place of the *d* orbitals of the free atoms. Since the contribution of these modified orbitals is found to be appreciable (see, for example, Refs. 14–17), it was concluded on this basis that the calculation confirms the *d* orbital concept.

Nevertheless the modified *d* orbitals have essentially no relevance to the vacant orbitals in the valence shell of the atom. They play the role of corrections in the calculation[18]. Thus a new aspect of the problem of *d* orbitals arose. In recent years there has been a vigorous growth of the number of quantum-chemical calculations, increasingly complex computational methods being devised and applied. For each new version of the calculation, the methodological problems have been solved, particularly the problem of the basis set—the set of initial functions from which the wave function of the molecule is constructed. The specific problem of the advantages of expansion of the basis set by additional functions of the *s* and *p* type or functions of the *d* type has been solved among others. This problem is associated with purely methodological difficulties and its chemical significance is almost or completely nil. The inadequate separation of these two aspects of the *d* orbital problem entails a multiplicity of misunderstandings. In the discussion of the concept of *d* orbitals, it is therefore useful to enumerate the possible situations in order to examine the available data and to attempt to discover which situation corresponds to reality.

1. Vacant atomic *d* orbitals of the valence shell of the elements of the Third Period influence directly the chemical properties of the latter, interacting effectively with the valence orbitals of the neighbouring atoms.

2. Orbitals of the *d* type have nothing in common with the atomic orbitals. They are introduced into the calculations in order to expand the basis set and play the role of corrections. Such corrections, which are in no way related to the presence or absence of *d* orbitals in the valence shell, can be introduced also into calculations on compounds of the elements of the Second Period. It may then be found that (a) the role of the *d*-type corrections in calculations on compounds of the elements of the Second and Third Periods is approximately the same or (b) the role of *d*-type corrections in calculations on compounds of the elements of the Third Period is much greater than in calculations on compounds of elements of the Second Period.

The considerations adduced in Section II are sufficient to rule out the first possibility. Orbitals whose energy exceeds that of the valence orbitals approximately by 10 eV (this is in fact the energy of the vacant *d* orbitals of the phosphorus atom) cannot have an appreciable influence on chemical properties and cannot effectively interact with the

valence orbitals of the neighbouring atoms. The chemistry of the elements of the Third Period also provides evidence against the first possibility. However great the differences between the chemical properties of the elements of the Third and Second Periods, they are in no way comparable to the truly radical changes which occur in the presence of "working" vacant orbitals. Indeed, the appearance of such *d* orbitals alters the initial form of Mendeleev's periodic table and leads to the appearance of a class of completely unusual elements—the transition metals [$(n-1)$ *d* orbitals]. The presence of "working" vacant orbitals in the second shell is responsible for the tervalence of boron and the quadrivalence of carbon, which determine the entire chemistry of these elements (*p* orbitals). The existence of five chemically significant vacant *d* orbitals should have converted phosphorus into an electron-deficient element, which is not the case. The differences between the properties of phosphorus and nitrogen are large, but, as we shall see below, can be fully accounted for by the differences between the properties of the *s* and *p* valence orbitals of these elements.

However, having recognised that the role of *d* orbitals reduces to that of computational corrections, one must nevertheless elucidate the comparative importance of these corrections in calculations on compounds of the elements of the Third and Second Periods[19]. It is quite likely that the *d*-type corrections for elements of the Third Period are much greater than for elements of the Second Period, since the electronic systems of the former are much more complex and their orbitals are larger and more diffuse. If the *d*-orbital type corrections were indeed larger for the elements of the Third Period, they might assume a new importance. Without being in any way a true physical cause of the differences between the properties of the elements of the Third and Second Periods, the *d* orbitals might be used as a convenient language for the description of these differences. The widespread occurrence of the *d*-orbital "explanations" in the chemical literature might then be in a sense justified (with the essential proviso that the language be used correctly). Clearly, in view of the approximately identical values of the *d*-orbital corrections in calculations on compounds of elements of the Third and Second Periods (situation 2*a*), *d* orbitals can be used neither for the explanation nor for the description of the differences between the properties of these compounds. Thus the special role of *d* orbitals in phosphorus might be considered only if it were found that the *d*-orbital corrections for the phosphorus atom are much greater than for the nitrogen atom. Since this formulation of the problem is as yet not altogether usual, the comparison will have to be made largely on the basis of studies of different workers carried out at different times for quite different purposes.

We shall begin the comparison with elemental phosphorus and nitrogen. In 1967 Boyd and Lipscomb[20] carried out a calculation on the P_2 molecule and reached the following conclusion: "This study establishes a quantitative evaluation of the large participation of 3*d* orbitals in molecular bonding of P, and hence qualitatively of second-row atoms.... The total energies ... are significantly improved, and the electron densities are significantly changed upon the inclusion of 3*d* orbitals". Indeed the application of *d*-orbital corrections led to an energy gain of 3.75 eV. However, in their conclusion the authors failed to take into account the studies of Nesbet[21], who introduced orbitals of the *d* type into a calculation on the N_2 molecule and obtained as a result an energy gain of 3.25 eV, i.e. almost the same as above. In 1971 Mulliken and Liu[22] compared in the same calculation and by the same method the role of *d* corrections for N_2 and P_2. In particular, the energy gain for N_2 (2.58 eV) actually proved to be greater than for P_2 (2.53 eV).

It is clear from these investigations that the differences between the properties of elemental nitrogen and phosphorus are not associated with the contribution of *d* orbitals. Nevertheless the differences between N_2, an inert gas, which condenses at −196°C, and P_4, which is an extremely reactive crystalline substance, are very great. They can be accounted for in the following way. In the N_2 molecule, the σ bond is formed from compact orbitals and the optimum distance for their overlap is small. At this distance, the p_x orbitals overlap very markedly forming a strong π bond. A similar strong π bond is also formed by p_y orbitals. This results in a very stable N_2 molecule, in which the nitrogen atoms are linked by a strong triple bond. In phosphorus, the orbitals are much larger and much more diffuse than in nitrogen. The optimum distance for the formation of the σ bond is so great that π overlapping at this distance is very slight and π bonds are energetically unfavourable; this is why multiple bonds are altogether uncharacteristic of the elements of the Third Period. In the case of phosphorus, the formation of three single bonds with three adjacent atoms at the vertices of the tetrahedron is energetically more favourable than the formation of a triple bond in the P_2 molecule§. Admittedly, all these bonds are of the "banana" type, since the orbitals deviate from the bond axes. However, for large diffuse orbitals, this does not unduly impair the conditions for overlap.

Thus the differences between the properties of elemental nitrogen and phosphorus are due to the differences between the sizes of the orbitals.

We shall now consider tricoordinate compounds. We shall begin with the simplest examples: phosphine (PH_3) and ammonia (NH_3). Boyd and Lipscomb[20] carried out a calculation on the PH_3 molecule and found that the contribution of *d* orbitals is very significant. The importance of *d* orbitals for ammonia was established by Clementi and coworkers[23].

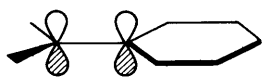
The values of the *d*-orbital corrections depend very strongly on the quality of the calculation. Thus in the calculation of Hillier and Saunders[24] the population of the *d*-type orbitals of phosphorus in PH_3 was 0.26*e*. On the other hand Rothenberg et al.[25] obtained 0.08*e* for this population in a more accurate calculation, which led them to the conclusion that the role of *d*-type orbitals is great in those cases where they compensate the defects of an inadequate *s*,*p*-basis set. Finally a comparison of PH_3 and NH_3 in a single calculation was carried out by Petke and Whitten[26], who found that the *d* corrections for ammonia are no less important than for phosphine and for this reason the *d* orbitals do not play a special role in PH_3. However, it may be that in phosphine *d* orbitals do not play a special role simply because of the lack of π-donor ligands. It is therefore necessary to examine calculations on molecules with such ligands. There are literature data for PF_3. Hillier and Saunders[27] obtained 0.71*e* for the population of the *d*-type orbitals in PF_3 and concluded that the population of the *d* orbitals of phosphorus increases with increase of the π-donor capacity of the ligands. However, calculation on this molecule using a much better approximation[28] yielded no population for *d* orbitals. Thus one may assume that in tricoordinate compounds the

§These molecules exist only in the vapour phase.

role of *d*-type corrections for phosphorus and nitrogen is the same.

The different properties of these compounds are also caused by the sizes of the orbitals. Owing to the larger size of the valence orbitals of the phosphorus atom, its bonds are longer, which is very important for molecular geometry. A calculation was carried out in 1973 on ammonia[29], in which the N–H bond length has varied. For smaller bond lengths than the experimental value, the molecule was found to be planar; with increase of bond length, it became non-planar and the angle of the pyramid decreased. The angle reached the experimental value when the N–H bond length became equal to the experimental bond length. On further increase of bond length, the pyramid became increasingly sharp, the angle reaching 90° ultimately. In phosphine, the bonds are so long that the angle is almost 90°.

We shall now consider how the difference between the angles of the pyramid affects the properties of aromatic compounds, for example, aniline and phenylphosphine. The pyramid is flattened at the nitrogen atom and the lone electron pair has a greater amount of *p* character, i.e. it is virtually located in a *p* orbital. The N–C bond length is such that π overlapping is effective,



and there is conjugation between the electron pair and the ring, so that the nitrogen atom in aniline is a stronger donor. On the other hand, the N–H bonds are located in the plane of the ring and their orbitals cannot overlap with the p_Z orbitals of the carbon atom. Consequently, they hardly interact with the π-electron system of the benzene ring. In phenylphosphine, the valence angle is close to 90° and the orbital of the lone electron pair has almost pure *s* character. It cannot therefore interact with the antisymmetric p_Z orbitals of the carbon atom and there is no conjugation with the ring and no electron transfer to the latter:



However, one of the P–H bonds is formed by the p_Z orbital of the phosphorus atom, which may interact with the p_Z orbital of the carbon atom. Thus, in contrast to aniline, in phenylphosphine the bonds (and not the lone electron pair) interact with the benzene ring.

The concept of σ, π conjugation (hyperconjugation) is widely used in chemistry[30,31]. Hyperconjugation is understood as symmetry-allowed interaction of σ bonds with π-electron systems. The direction of the hyperconjugation effect depends on the polarisation of the σ bonds. The hyperconjugation effect of methyl groups is believed to be of the donor type and is represented by arrows

$$H_3\overset{\frown}{C}-CH=CH_2$$

or by resonance structures of the type

$$H^+\begin{matrix}H\\H\end{matrix}\!\!>C=CH-\bar{C}H_2 \quad .$$

The hyperconjugation effect of trifluoromethyl groups is believed to be of the acceptor type and is represented by arrows

$$F_3\overset{\frown}{C}-\overset{\frown}{C}H=CH_2$$

or by resonance of structures of the type[32]

$$F^-\begin{matrix}F\\F\end{matrix}\!\!>C=CH-\overset{+}{C}H_2.$$

The electronegativity of the phosphorus atom is less than that of the carbon atom and even less than that of oxygen, the halogens, etc. As a result the σ bonds of phosphorus with the substituents are polarised in the direction $P^{\delta+}-X^{\delta-}$. The σ,π conjugation with the σ bonds of phosphorus, can therefore be of the acceptor type. The reality of the hyperconjugation effects of both methyl[33] and trifluoromethyl[34–36] groups has been questioned in recent years. Indeed, the interaction of the very strong and compact C–H bonds and even more so the C–F bonds with π-electron systems should be so slight that it can hardly be a real cause of the phenomena for the explanation of which the hyperconjugation effect is invoked. For elements of the Third Period, the situation is different. The bonds of silicon, phosphorus, and sulphur are formed by the much more diffuse valence orbitals of these elements. For this reason, the strength of these bonds, their polarisability, and their mobility are comparable to the corresponding characteristics of π orbitals. This is why the effects of σ,π conjugation with the σ bonds of the elements of the Third Period should be observed.

Thus the acceptor properties of tricoordinate phosphorus can be explained by the size and diffuseness of its *s* and *p* orbitals and not by the presence of *d* orbitals in its valence shell. The change in the size of the valence orbitals led to a change in geometry, i.e. a change in conjugation conditions (conjugation with σ bonds and not with a lone electron pair), and to an increase in the extent of σ,π conjugation[37–39].

Using tetracoordinate phosphorus and nitrogen compounds as examples, one can conveniently explain what is understood by *d* corrections. In amine oxides the bond is believed to be semipolar and its formation is represented as follows. An electron passes from the nitrogen atom to oxygen. One unpaired electron, which remains in O^-, forms a σ bond with the quadrivalent ammonium nitrogen atom and the six other electrons (five from O and one from N) form lone pairs. Two of these are located in the p_X and p_Y orbitals, i.e. have π character. This description conveys only very approximately the real form of the electron cloud, since the form of the p_π orbitals of the oxygen atom in this cloud remains the same as in the isolated oxygen atom:

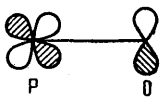


Furthermore, the molecule of the oxide contains the positively charged N^+ atom next to O^-. Under the influence of the positive charge, the electron cloud should be deformed and drawn into the region of the bond:

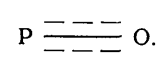


The traditional description of amine oxides does not reflect this deformation. Here the attraction of the electron cloud to the region of the bond is represented with the aid of the *d* orbitals of the phosphorus atom. For example, it is assumed that the p_X orbital of the oxygen

atom interacts with the d_{xz} orbital of the phosphorus atom and forms a π bond:



A similar bond is formed by the p_y orbital of the oxygen atom with the d_{yz} orbital of the phosphorus atom. Thus in phosphine oxides the linkage is partly of the triple bond type:



The attraction of the electron cloud into the region of the bond in amine oxides might be described in exactly the same way with the aid of fictitious *d* orbitals of nitrogen, since in the case of phosphorus one employs fictitious and not atomic *d* orbitals. However, this attraction in both phosphine and amine oxides can be represented in a different way. It is required that the form of the orbitals of the oxygen atom should be modified so that they become extended into the region between the atoms:



This can be achieved with the aid of the *d* orbitals of the oxygen atom. We combine the p_x orbital with an orbital of the d_{xz} type:



Naturally, the latter orbital has nothing in common with the atomic *d* orbitals: this is the so called polarisation correction and the admixture of the *d*-type orbital is postulated only in order to account for the change in the shape of the electron cloud. The particular atom in the molecule to which the polarisation correction is applied has no fundamental importance, since it is a purely formal procedure—it can be applied to phosphorus, nitrogen, and oxygen. Such calculations have not been made for oxides, but one cannot rule out the possibility that *d* orbitals in oxygen would give a good description of the change in the shape of the electron cloud. On the other hand, it is known that the *d*-orbital corrections for silicon hardly affect the results of calculations on silylamine, while the *d*-orbital corrections for nitrogen greatly improve the result.[40]

There are very few quantitative data for amine and phosphine oxides. Nevertheless Hillier[41] has carried out a calculation on the F_3PO molecule and obtained a high population of the phosphorus *d* orbitals (0.5*e*) in the PO bond. Choplin and Kaufmann[42] performed a calculation on the same molecule and on the oxide F_3NO without taking into account the *d* orbitals for the nitrogen atom. We mention this study, because its authors understood the necessity of including also the *d* orbitals for the nitrogen atom, although they were unable to do this for technical reasons. Frost et al.[43] carried out a calculation on the PO and NO linkages in the F_3PO and F_3NO molecules taking into account the *d* orbitals and obtained approximately equal contributions of the *d* orbitals for nitrogen and phosphorus atoms; however, they performed only a model calculation by the valence bond method. Unfortunately comparable non-empirical calculations on amine and phosphine oxides have not so far been made.

It must be emphasised that the differences in the chemistry of nitrogen and phosphorus compounds are to a large extent determined by the ease of formation of the phosphoryl linkage, i.e. its greater strength. The illusory nature of the traditional explanation of the comparative strength of the PO linkage and its triple bond character was demonstrated above. It is reasonable to suppose that the increased tendency of the lone electron pair of the phosphorus atom towards oxidation is determined mainly by the properties of the initial lone pair and not of the oxide linkage formed. The electrons of the compact lone pair of the nitrogen atom are comparatively more strongly attracted to the nucleus, which increases the energy expenditure on the removal of the electron and makes the formation of the *N*-oxide linkage less favourable compared with the phosphoryl linkage and makes it weaker.

These considerations can be confirmed by a comparison, using a fairly clear-cut example, of the ionisation potentials of the lone pairs with the strengths of the oxide linkages formed in analogous phosphorus and nitrogen compounds. It is difficult to compare the hydrides owing to the large differences between the geometries and the associated differences between the hybridisations of the lone pairs. Comparison of alkyl and particularly aryl derivatives is hindered by the appreciable delocalisation of the lone pair of the nitrogen atom in these compounds. Fluorides are the most suitable for the comparison, since the differences between their geometrical structures and hence between the hybridisations of the lone pairs are slight ($\angle FPF \simeq 98°$, $\angle FNF \simeq 102°$) and the changes in geometry on oxidation are also small ($\Delta\angle FPF \simeq +3.5°$, $\Delta\angle FNF \simeq -1.2°$).[142] Owing to the exceptionally high electronegativity of fluorine, the ionisation potential in this instance can be attributed to the lone pair with a greater degree of justification than for any other substituents. The ionisation potential of NF_3 does indeed exceed that of PF_3 by 80 kcal mole^{-1}. It is not therefore surprising that the PO linkage in F_3PO is much stronger than the NO linkage in F_3NO (by more than 30 kcal mole^{-1}). Thus in this case too the differences between the properties are ultimately determined by the differences between the sizes of the valence orbitals of the nitrogen and phosphorus atoms.

We shall now turn to penta- and hexa-coordinate compounds. Santry and Segal[15] carried out a calculation on the PF_5 molecule and obtained a population of the *d* orbitals of the phosphorus atom equal to 1.6*e*. Later Brown and Peel[44], made a similar calculation, obtained a population of the phosphorus *d* orbitals of 0.3*e*, and concluded that there is no reason for invoking *d* orbitals in order to describe the electronic structure of this molecule. Highly accurate non-empirical calculation on the PH_3F_2 molecule and the hypothetical PH_5 and NH_3F_2 molecules have been published recently[45]. The authors concluded that the stability of the PH_3F_2 and PF_5 molecules can be accounted for without invoking *d* orbitals and that the decisive factor responsible for the stability of the PH_3F_2 molecule, on the one hand, and the instability of NH_3F_2, on the other, is the difference between the ionisation potentials of the planar PH_3 (7.8 eV) and NH_3 (10.3 eV) species. On the other hand, the authors[45] note that the energy gain following the expansion of the basis set by including *d*-type orbitals and the population of these orbitals are greater for PH_3F_2 than for NH_3F_2. However, it must be emphasised that the roles of the *d*-orbital corrections were compared for a configuration which is stable in one of the molecules (PH_3F_2) and unstable in the other (NH_3F_2). Indeed, when

the basis set was expanded by including *d*-type orbitals in the nitrogen atom, it was found that the stable configuration of NH_3F_2 is of the C_{3v} type, corresponding to the tetrahedral ammonium cation NH_3F^+ and the F^- anion associated with it by purely electrostatic forces, and not a trigonal bipyramid (D_{3h}) as in the PH_3F_2 molecule. The latter result suggests in addition that the differences between PH_3F_2 and NH_3F_2 are associated with steric hindrance (see below).

A calculation has been performed on the PF_6^- anion[46], which yielded an appreciable population of the *d* orbitals (1.2*e*). However, exactly the same calculation on SF_6 yielded a charge of $-0.3e$ on the sulphur atom. It is unlikely that the sulphur atom surrounded by fluorine atoms should have a negative and not a positive charge. Thus, from the chemical standpoint alone, the *d*-orbital population in this calculation is much too high. On the other hand, theoretical analysis demonstrates the necessity for a high population of the *d* orbitals of the central atom in octahedral molecules[47]. One must therefore expect that, in the calculation by the same method on the octahedral NF_6^- anion, a high population of the *d* orbitals would also have been obtained for the nitrogen atom. Unfortunately a calculation on this hypothetical anion has not been made.

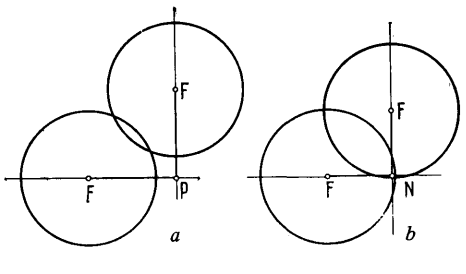


Figure 9. Comparison of the P–F (*a*) and N–F (*b*) bond lengths with the van der Waals radius of the fluorine atom.

We shall now consider why the anion does not exist. Fig. 9*a* illustrates the P–F bond length and the van der Waals radius of the fluorine atom. Evidently fluorine atoms hardly overlap and only a slight increase in bond length is required for the disappearance of steric hindrance to the formation of the molecule; at the same time, the diffuse phosphorus orbitals are relatively insensitive to a slight increase in bond length. Fig. 9*o* illustrates the same situation for the nitrogen atom. Evidently fluorine atoms overlap very strongly. In order to eliminate steric hindrance, it is necessary to extend the N–F bond to such an extent that it is ruptured. In other words, penta- and hexa-coordinate compounds of nitrogen cannot exist owing to considerable steric hindrance. Consequently penta- and hexa-coordinate compounds of phosphorus exist simply because its atom is sufficiently large to accommodate five (or six) ligands around it and not because it has a *d* orbital available for the formation of additional linkages. Therefore, bonding in these compounds can be accounted for, as shown above, without invoking *d* orbitals.

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Thus the differences between the properties of phosphorus and nitrogen compounds can be explained by a very simple but very important factor: the difference between the effective sizes of the *s* and *p* orbitals of the nitrogen and phosphorus atoms.

The presence of vacant *d* orbitals in the valence shell of the phosphorus atom can in no way influence the properties of phosphorus compounds, since these orbitals are so unfavourable energetically and so diffuse that they are incapable of any appreciable interaction with other valence orbitals.

d Orbitals can play the role of polarisation corrections, which is important from the standpoint of the method of calculation but has almost no chemical importance or no chemical importance whatsoever. As far as one can judge, from the available data, the roles of these corrections for nitrogen and phosphorus are approximately the same.

In view of the identical orders of magnitude of the *d*-orbital corrections in the case of nitrogen and phosphorus, the concept of *d* orbitals cannot be used correctly as a language suitable for the description of the differences between the properties of compounds of these elements.

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