217. An Investigation of Charge Effects on NMR. Coupling Constants. The Charge Induced Variation of s-Densities at the Nucleus

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(6.VIII.80)

Summary

The dependence of the ns-density at the nucleus, $|\Psi_{ns}(0)|^2$, on atomic number and charge is examined for the elements helium to radon. The validity of the widely used assumption of a constant valence s-density at the nucleus, as well as the statement that metal-phosphorus NMR. coupling constants, $^1J(M,P)$, are strongly influenced by contraction of the phosphorus 3s orbital is critisized. A possible explanation by rehybridisation within an MO-framework is offered instead.

Introduction. - One bond metal to ligand atom coupling constants, $^1J(M,L)$ where M is ^{103}Rh, $^{107,109}Ag$, $^{111,113}Cd$, ^{183}W, ^{195}Pt, ^{199}Hg and L is ^1H, ^{13}C, ^{15}N, ^{31}P, are very often discussed in an empirical manner on the basis of the more theoretical formalism offered by *Pople & Santry* [1] as given by the expressions (1) or (2), under the assumption that the so-called *Fermi*-Contact term is dominant.

$$J(A,B)=\frac{-64\pi^2}{9h}(g\beta\hbar)^2\gamma_A\gamma_B\sum_i^{occ}\sum_j^{unocc}(\Delta E_{i\to j})^{-1}\sum_{p\in A}^{n}\sum_{q\in B}^{n^*}\Pi_{ijpq} \quad (1)$$

with $\Pi_{ijpq}=C^s_{ip}C^s_{iq}C^s_{jp}C^s_{jq}|\Psi_{sp}(0)|^2|\Psi_{sq}(0)|^2$

$$J(A,B)=\frac{16\pi^2}{9h}(g\beta\hbar)^2\gamma_A\gamma_B|\Psi_{ns,A}(0)|^2|\Psi_{ns,B}(0)|^2\cdot\Pi(A,B) \quad (2)$$

with $\Pi(A,B)=-4\sum_i^{occ}\sum_j^{unocc}\frac{C^s_{iA}C^s_{jA}C^s_{iB}C^s_{jB}}{\Delta E_{i\to j}}$

Therein is $g=2.0023$, γ is the nuclear gyromagnetic ratio, β is the *Bohr* magneton, $\Delta E_{i\to j}=\varepsilon_i-\varepsilon_j$ where ε is the energy of an occupied (ε_i) or an unoccupied (ε_j) molecular orbital, $C^s_{\lambda p}$ and $C^s_{\lambda q}$ are LCAO coefficients of s-type atomic orbitals

0018-019X/80/7/2054-17$01.00/0

centered on A(p∈A) and B(q∈B) and $|\Psi_{sp}(0)|^2$, $|\Psi_{sq}(0)|^2$ are the s-electron densities at the nucleus of A and B of the atomic orbitals p and q. The subscripts p and q run over all s-orbitals centered on A and B respectively and become constant in the case of equation (2) where only valence shell orbitals are included.

One of the most frequently discussed spin-spin coupling constants in transition metal chemistry is the one bond metal-phosphorus coupling constant, $^1J(M, ^{31}P)$. In such discussions the ns-density at the nucleus of M is often assumed constant [2]. On the other hand, a change of the corresponding value of phosphorus was introduced to account for changes in $^1J(M,PR_3)$ when R is substituted by Sn, C, N, O, I, Br, Cl and F [3]. It was argued that more electronegative substituents increase the charge on phosphorus, hence the phosphorus orbitals are contracted and $^1J(M,P)$ increases. The latter seems to be in contradiction with ESR. results that allow an explanation of the phosphine dependence of $^1J(M,P)$ on the basis of changing phosphorus s-character in the phosphorus metal bond [4]. To gain more insight into the mechanisms that determine $^1J(M,P)$, a systematic study of the effect of charge on the s-densities at the nucleus for the elements helium to radon was undertaken together with some calculations of the EHMO and *ab initio* type on the systems M-PR_3 and PR_3.

Experimental section. - *Calculations on atoms.* All non relativistic values of atoms were calculated from *Hartree-Fock* atomic orbitals of *Clementi & Roetti* [5] as long as not otherwise stated. These orbitals are of the p-zeta-*Slater* type (STO) as described by equation (3) with λ indicating the symmetry species, a accounts for the subspecies that transforms according to λ and i indicates the i^{th} orbital and p the p^{th} basis function of symmetry λ.

$$\Psi_{i\lambda a} = \sum_p \chi_{p\lambda a} C_{i\lambda p} \tag{3}$$

The basis functions $\chi_{p\lambda a}$ are STO's given by equation (4), wherein $R_{\lambda p}(r)$ are the radial parts and $Y_{\lambda a}(\Theta,\Phi)$ are spherical

$$\chi_{p\lambda a}(r,\Theta,\Phi) = R_{\lambda p}(r) \cdot Y_{\lambda a}(\Theta,\Phi) \tag{4}$$

harmonics. The calculation of the s-density in a p-zeta representation for the limiting case $r \rightarrow 0$ becomes extremely simple and is given by equation (5) where i refers to the main quantum number and ζ_{sp} is the orbital exponent of the 1s orbital.

$$|\Psi_{is}(0)|^2 = \left(\sum_p C_{isp}(\zeta_{sp}^3/\pi)^{1/2}\right)^2 \tag{5}$$

EHMO-calculations. The off diagonal elements, H_{ij}, of the hamiltonian matrix were calculated from the H_{ii}'s by a weighted *Wolfberg-Helmholtz* formula [6] with k = 1.75. The double zeta STO's of *Clementi & Roetti* [5] were taken as radial functions for phosphorus and chlorine atomic orbitals, hydrogen was represented by a single *Slater* function with exponent 1.3. The geometries used for PCl_3 and $HPCl_3^+$ were: Θ(Cl,P,Cl) = 98°, d(P,Cl) = 3.03 Å, d(P,H) = 1.42 Å.

Ab initio calculations. The GAUSSIAN 70 program was used [7a] with an internal STO-3G basis set [7b]. The geometries of compounds PR_3 and H_3B-PR_3 are given in *Table 1.*

Results and Discussion. - Our knowledge about calculated s-densities at the nucleus of atomic ground states or near ground state configurations is quite com-

Table 1. *Geometries used for the calculation of the compounds PR_3 and H_3B-PR_3*

R	d(P,R)[a])	d(P,B)[a])	d(B,H)[a])	Θ(R,P,R)[b])	Θ(H,B,H)[b])
Free phosphines					
H	1.4206	–	–	93.83	–
NH_2[d])	1.653	–	–	105.50	–
OH[e])	1.562	–	–	104.33	–
Cl	1.990	–	–	103.50	–
F	1.567	–	–	97.80	–
Borane complexes[c])					
H	1.399	1.937	1.212	101.13	114.65
CH_3[f])	1.819	1.901	1.212	105.00	113.50
NH_2[d])	1.653	1.887	1.150	105.50	115.09
OH[e])	1.562	1.879	1.200	104.33	115.00
Cl	1.990	1.870	1.200	105.00	115.00
F	1.538	1.836	1.207	99.88	115.02
PH_4^+	1.414	–	–	109.47	–
$F_3P=O$[g])	1.530	–	–	102.50	–

[a]) In Å; [b]) in degrees; [c]) all borane complexes had staggered conformation; [d]) d(N,H) = 0.90 Å, Θ(P,N,H) = 110.0°; [e]) d(O,H) = 1.05 Å, Θ(P,O,H) = 119.47°; [f]) d(C,H) = 1.08 Å, Θ(P,C,H) = 109.64°; [g]) d(P,O) = 1.44 Å.

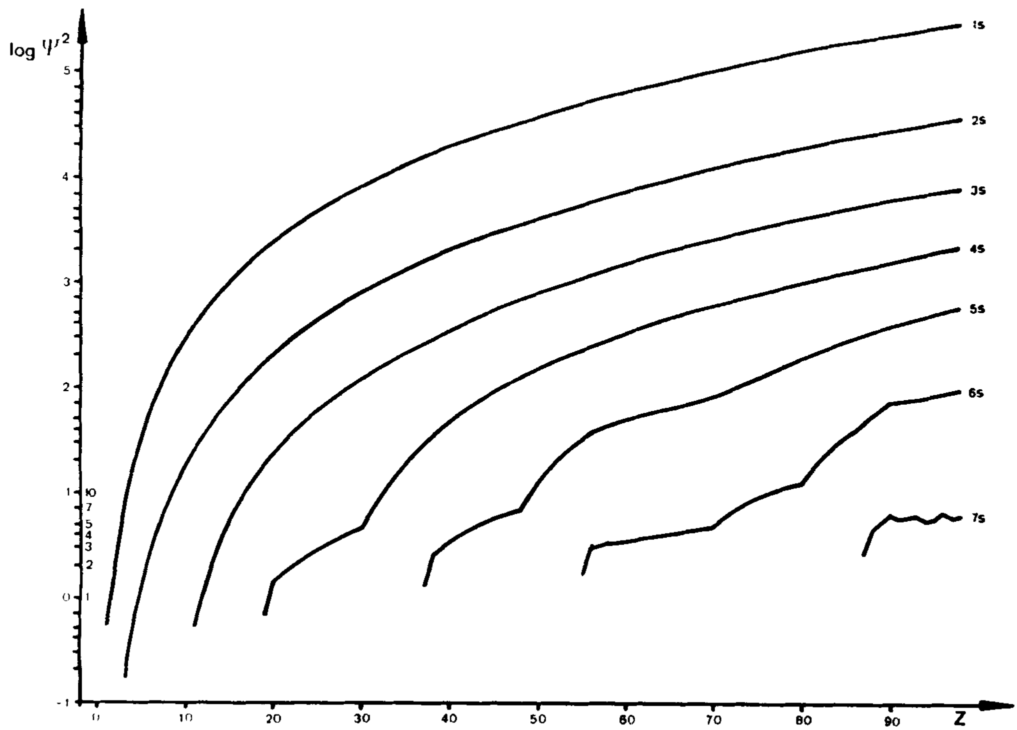

Fig. 1. *Logarithm of* $|\Psi_{ns}(0)|^2$ *for* $n = 1$-7 *as a function of atomic number Z.* Relativistic values calculated from wave functions of [8d]

plete throughout the periodic system [8]. From *Slater*'s rules [9], the density of an s-orbital with fixed main quantum number is expected to increase with increasing atomic number as a consequence of the raising effective nuclear charge felt by an electron in this orbital. This qualitative prediction is fully settled by both relativistic and nonrelativistic calculations [8].

The results for the ground states of the atoms hydrogen to berkelium are summarized in *Figure 1*. A comparison of s-densities at the nucleus calculated from relativistic atomic orbitals and from nonrelativistic *Hartree-Fock* atomic orbitals shows no significant differences for the ground states even for inner shells of heavier elements. Whereas the densities of the 1s, 2s and 3s atomic orbitals increase regularly, the corresponding values for the 4s, 5s and 6s orbitals show distinct regions of different slopes in the plot of the logarithm of $|\Psi_s(0)|^2$ *versus* atomic

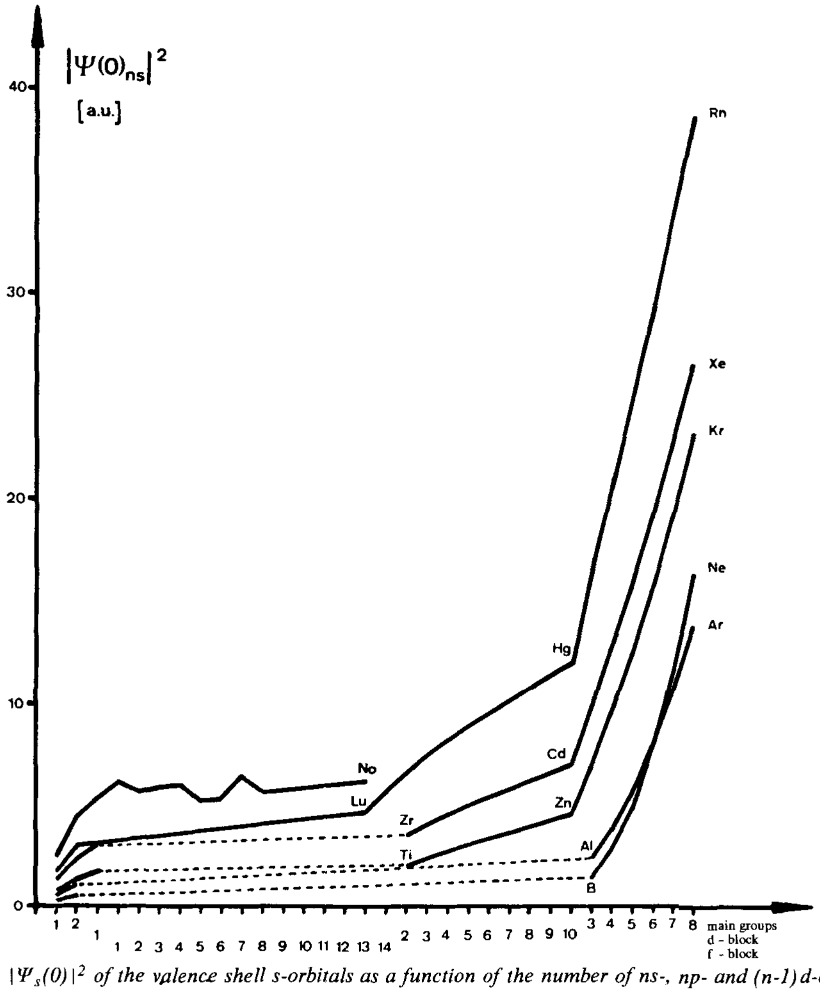

Fig. 2. $|\Psi_s(0)|^2$ *of the valence shell s-orbitals as a function of the number of ns-, np- and (n-1)d-electrons for the periods 2-7*

number, Z. These irregularities are exclusively observed for valence shell orbitals whereas the graph $|\Psi_s(0)|^2$ vs Z smoothens as soon as an orbital belongs to the 'core'.

The behaviour of the valence s-orbitals is once more pictured in *Figure 2*. Three distinct regions can be seen in this plot with approximately constant slope within each region. In this plot the periods two to seven are stacked such that the abscissa gives directly the number of ns, np, (n-1)d and (n-2)f electrons. It is obvious that the three regions correspond to the main group, d-block and f-block elements respectively. The main group elements show the steepest raise and the rare earths the flattest one. This behaviour can easily be understood through the concept of incomplete shielding which is described by *Slater*'s rule or by the more quantitative rules of *Clementi & Raimondi* [9] [10]. If the nuclear charge is increased by one charge unit and one more electron is added, the difference in nuclear charge effectively felt by a valence electron depends on the kind of the state of the added electron. The shielding of the additional nuclear charge is nearly complete if the additional electron is introduced into the n-2 shell, the shielding becomes less effective if it is introduced into the n-1 shell and becomes very incomplete in the valence shell. Obviously this concept reflects the behaviour of $|\Psi_s(0)|^2$ *versus* atomic number in *Figures 1* and *2*. Another feature of *Figure 2* is the crossover of the second and third period in the middle of p-block. This crossover is not due to errors of non-relativistic calculations as the comparison with relativistic values shows. Although this feature will not be discussed in detail it should be mentioned that the expectation values $\langle r^{-3} \rangle$ of the np orbitals of the noble gases also follow the sequence Ar < Ne < Kr and so do matrix induced shifts of spectra of species isolated in low temperature noble gas matrices [11].

To test the trends in the numerical values and the validity of equation (2), one may take the reduced one-bond coupling constant [1], $^1K(M,X)$, with a constant X-atom, say phosphorus, as a probe. If the density calculations and equation (2) are adequate, a linear dependence of $^1K(M,X)$ from $|\Psi_{M,ns}(0)|^2$ should be expected provided that the polarizability term $\Pi(A,B)$ does not alter significantly. *Figure 3* shows a plot of $|\Psi_{M,ns}(0)|^2$ *versus* $^1K(M,{}^{31}P)$. The length of the bars corresponds to the actual spread of the experimental coupling constants. Two different correlations seem to exist for main group elements and for transition metals. This can eventually be explained by differences in the polarizability term of equation (2)[1]. The variations of $^1J(M,P)$ for a given metal, or put in terms of *Figure 3*, the horizontal length of the bars, could result either from changes in the polarizability term or either of the $|\Psi_{ns}(0)|^2$ terms. There exist some hints to which is the leading term. On the basis of simple orbital contraction arguments one would expect larger values of $^1J(M,P)$ for the more positively charged octahedral Rh(III) and Pt(IV) phosphine complexes relative to the less positively

[1]) The phosphorus 3s-energy (~19 eV) corresponds roughly to the transition metal (n-1)d-levels (10-21 eV) whereas the 3p-energy (9.7 eV) is comparable to the ns-energies of transition metals (6-8 eV). If the transition metal is replaced by a main group element, the (n-1) orbitals drop to 32-87 eV and shrink considerably, and the ns- and np-orbitals are energetically placed (11-27 and 5-12 eV respectively) where formerly (n-1)d- and np-orbitals were located.

charged square planar Rh(I) and Pt(II) analogs, which is opposite to the observed trends. Indeed it is well known [3e] that for comparable ligands the sequence ^1J(Pt(IV),P) > ^1J(Pt(II),P) $\gtrsim$ ^1J(Pt(0),P) holds. This leads to the conclusion that the polarizability term is dominant.

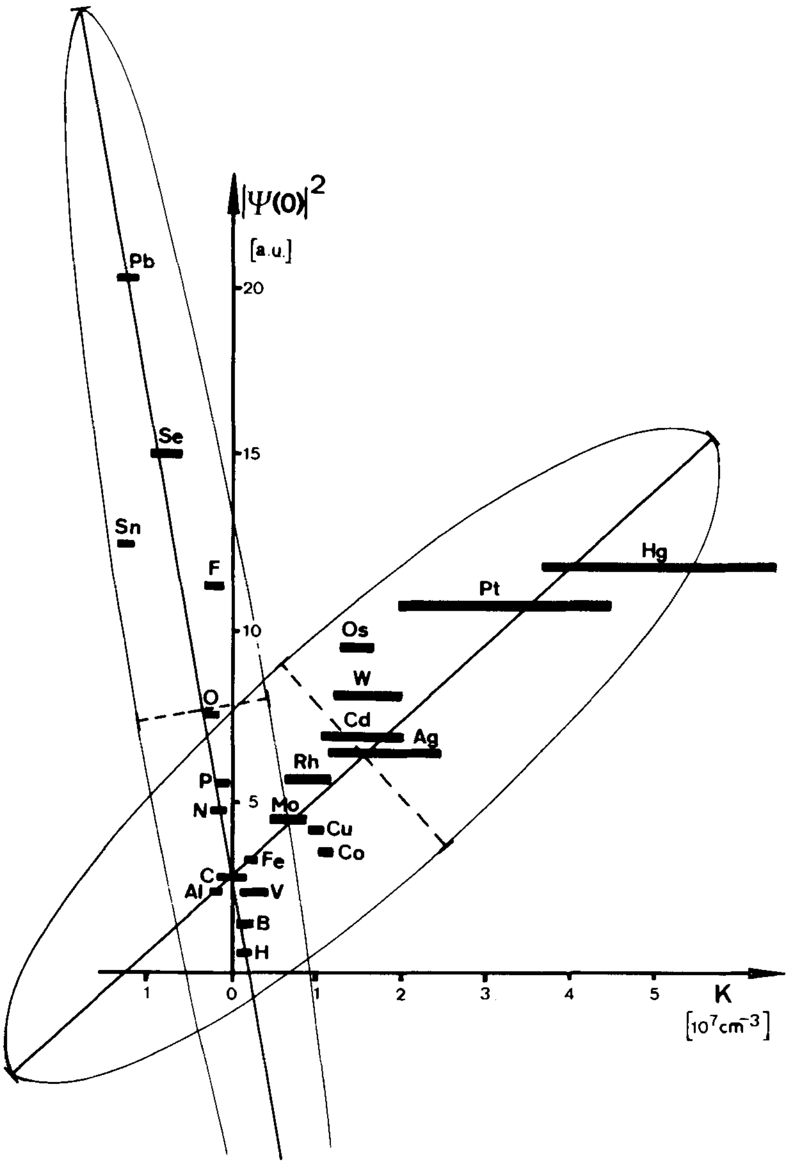

Fig. 3. $|\Psi_{ns}(0)|^2$ *versus the reduced coupling constant K(M,P).* The horizontal length of the bars corresponds to the actual spread of the observed coupling constants. Different correlations together with 95% confidence ellipsoids are shown for main group elements and transition metals.

Table 2. *Densities*[a]) *of the valence shell s-orbital at the nucleus for different configurations, spectroscopic terms and charges*

Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.	Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.
H			1		0	2S	0.5642	Al			2	2	−1	3P	2.1683
He			2		0	1S	1.4390							1D	2.2307
Li			2		−1	1S	0.0803							1S	2.3235
			1		0	2S	0.1671				2	1	0	2P	2.3554
Be			2		0	1S	0.5709				2		+1	1S	2.7449
			1		+1	2S	0.8130				1		+2	2S	3.4200
B			2	2	−1	3P	1.2678	Si			2	3	−1	4S	3.5075
						1D	1.3118							2D	3.5673
						1S	1.3433							2P	3.6146
			2	1	0	2P	1.4114				2	2	0	3P	3.8105
			2		+1	1S	1.7130							1D	3.8379
			1		+2	2S	2.1661							1S	3.8834
C			2	3	−1	4S	2.5073				2	1	+1	2P	4.2883
						2D	2.5773				2		+2	1S	4.8512
						2P	2.6168				1		+3	2S	5.7394
			2	2	0	3P	2.7715	P			2	4	−1	3P	5.3123
						1D	2.8013							1D	5.3555
						1S	2.8482							1S	5.4140
			2	1	+1	2P	3.2053				2	3	0	4S	5.6282
			2		+2	1S	3.7381							2D	5.6694
			1		+3	2S	4.4624							2P	5.6951
N			2	4	−1	3P	4.4817				2	2	+1	3P	6.2145
						1D	4.5263				2	1	+2	2P	6.8836
						1S	4.5903				2		+3	1S	7.6144
			2	3	0	4S	4.7745				1		+4	2S	8.7216
						2D	4.8226	S			2	5	−1	2P	7.4870
			2	2	+1	3P	5.3652				2	4	0	3P	7.9159
			2	1	+2	2P	6.0729							1D	7.9470
			2		+3	1S	6.8860							1S	7.9856
			1		+4	2S	7.9335				2	3	+1	4S	8.5656
O			2	5	−1	2P	7.2396				2	2	+2	1S	9.3543
			2	4	0	3P	7.6368							1D	9.3561
						1D	7.6717							3P	9.3281
						1S	7.7255				2	1	+3	2P	10.1911
			2	3	+1	4S	8.3010				2		+4	1S	11.0821
			2	2	+2	3P	9.2263				1		+5	2S	12.4335

O					1S	9.2884
					1D	9.2384
		2	1	+3	2P	10.2556
		2		+4	1S	11.3928
		1		+5	2S	12.8181
F		2	6	−1	1S	10.8440
		2	5	0	2P	11.4148
		2	4	+1	3P	12.2497
		2	3	+2	2P	13.3645
					2D	13.3343
					4S	13.2898
		2	2	+3	1S	14.6535
					1D	14.4980
					3P	14.5915
		2	1	+4	2P	15.9827
		2		+5	1S	17.4993
		1		+6	2S	19.3703
Ne		2	6	0	1S	16.2076
		2	5	+1	2P	17.2571
		2	4	+2	1S	18.6285
					1D	18.5732
					3P	18.5371
		2	3	+3	2P	20.0480
					2D	20.0383
					4S	19.9990
		2	2	+4	1S	21.7561
					1D	21.7231
					3P	21.6995
		2	1	+5	2P	23.5073
		2		+6	1S	25.4428
		1		+7	2S	27.8170
Na		2		−1	1S	0.2595
		1		0	2S	0.5288
Mg		2		0	1S	1.2138
		1		+1	2S	1.6997
Ti	4	1		−1	6D	0.9060
	3	2			4F	0.7725
	3	1		0	5F	1.6702
Cl		2	6	−1	1S	10.1237
		2	5	0	2P	10.6440
		2	4	+1	3P	11.3747
		2	3	+2	2D	12.2804
					4S	12.2590
		2	2	+3	1S	13.2327
					1D	13.2411
					3P	13.2217
		2	1	+4	2P	14.2775
		2		+5	1S	15.3474
		1		+6	2S	16.9428
Ar		2	6	0	1S	13.8764
		2	5	+1	2P	14.7385
		2	4	+2	1S	15.7331
					1D	15.6933
					3P	15.6866
		2	3	+3	2D	16.8013
					4S	16.7989
		2	2	+4	1S	17.9445
					1D	17.9664
					3P	17.9503
		2	1	+5	2P	19.1945
		2		+6	1S	20.4449
		1		+7	2S	22.3406
K		2		−1	1S	0.3409
		1		0	2S	0.6904
Ca		2		0	1S	1.3850
		1		+1	2S	1.9266
Sc	2	2		−1	3F	0.7084
	3	1			5F	1.0707
	2	1		0	4F	1.4082
	1	2			2D	1.6891
	1	1		+1	3D	2.3789
		2			1S	2.8462
Cu	10	2		−1	1S	1.6423
	10	1		0	2S	2.9611
	9	2			2D	4.1785
	8	2		+1	3F	6.7386

Table 2 (continued).

Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.
Ti		2	2			1G	2.0007
						3F	1.9532
						1D	1.9800
						3P	1.9833
						1S	2.0850
		2	1		+1	4F	2.8097
		1	2			2D	3.2614
V		4	2		−1	5D	0.8619
		5	1			7S	0.5784
		4	1		0	6D	1.9504
		3	2			2H	2.2673
						2G	2.2533
						4F	2.2218
						2F	2.3010
						2D	2.3070
						4P	2.2510
						2P	2.2673
		2	2		+1	3F	3.7019
		3	1			5F	3.2861
Cr		6	1		−1	6D	0.3170
		5	2			6S	0.9371
		5	1		0	7S	2.2162
		4	2			1I	2.5508
						3H	2.5293
						3G	2.5380
						1G	2.5806
						3F	2.5641
						1F	2.5784
						5D	2.4923
						3D	2.5531
						1D	2.6099
						3P	2.5641
						1S	2.6355
		4	1		+1	6D	3.7770
		3	2			4F	4.1301

Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.
Zn		10	2		0	1S	4.5407
		10	1		+1	2S	6.0233
			2	2	−1	1D	6.6213
			2	1	0	2P	6.9175
			2		+1	1S	7.8836
Ge			2	3	−1	4S	8.8164
						2D	8.9622
			2	2	0	3P	9.5433
						1D	9.6111
			2	1	+1	2P	10.6080
As			2	4	−1	3P	11.6970
						1D	11.7976
						1S	11.9420
			2	3	0	4S	12.4281
						2D	12.4971
						2P	12.5420
			2	2	+1	3P	13.5770
						1D	13.6261
						1S	13.6840
Se			2	5	−1	2P	14.9031
			2	4	0	3P	15.7229
						1D	15.8053
						1S	15.8608
			2	3	+1	4S	16.8971
						2D	16.9318
						2P	17.0018
Br			2	6	−1	1S	18.4194
			2	5	0	2P	19.3078
			2	4	+1	3P	20.6445
						1D	20.6939
						1S	20.7840
Kr			2	6	0	1S	23.3808
			2	5	+1	2P	24.7553
Rb			2		−1	1S	0.6668
			1		0	2S	1.2947

Mn	6	2		−1	5D	1.0961
	6	1		0	6D	2.4154
	5	2			2I	2.8413
					2H	2.8589
					4G	2.8184
					2G	2.8812
					4F	2.8537
					2F	2.8587
					4D	2.8266
					2D	2.9014
					4P	2.8231
					2P	2.9408
					6S	2.7674
					2S	2.8787
	5	1		+1	7S	4.2901
	4	2			5D	4.5986
Fe	7	2		−1	4F	1.2340
	7	1		0	5F	2.5733
					1I	3.1644
					3H	3.1510
					3G	3.1564
					1G	3.1895
					3F	3.1833
					1F	3.1869
					5D	3.1112
					3D	3.1672
					1D	3.2167
					3P	3.1833
					1S	3.2411
	6	1		+1	6D	4.6611
	5	2			6S	5.0640
Co	8	2		−1	3F	1.3742
	8	1		0	4F	2.7100
					2H	3.4848
					2G	3.7498
					4F	3.4527
					2F	3.5142
					2D	3.5226

Sr		2		+1	1S	2.3833
		1		+1	2S	3.3039
Y	3	1		−1	5F	1.7127
	2	2			3F	1.4724
	2	1		0	4F	2.6990
	1	2			2D	2.9848
		2		+1	1S	4.5970
Zr	4	1		−1	6D	1.7621
	3	2			4F	1.6320
	3	1		0	5F	3.1996
	2	2			3F	3.4589
	2	1		+1	4F	4.8270
	1	2			2D	5.2855
	1	1	1			10.443[b])
Nb	5	1		−1	7F	1.6502
	4	2			5D	1.7877
	4	1		0	6D	3.6383
	3	1		+1	5F	5.5473
	2	2			3F	5.9390
	2	1	1			11.740[b])
Mo	6	1		−1	6D	1.1068
	5	2			6S	1.9901
	4	2		0	5D	4.3186
	4	1		+1	6D	6.2682
	3	2			4F	6.5740
	3	1	1			12.110[b])
Tc	7	1		−1	5F	0.5244
	6	2			5D	2.1438
	6	1		0	6D	4.3739
	5	2			6S	4.6932
	5	1		+1	7S	6.9656
	4	2			5D	7.2082
	4	1	1			14.380[b])
Ru	6	2		0	5D	5.1517
	7	1			5F	4.5360
	6	1		+1	6D	7.4455
	5	2			6S	7.8032
	5	1	1			15.682[b])

Table 2 (continued).

Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.	Element	Configuration f	d	s	p	Charge	Term	$\|\Psi(0)\|^2_{ns}$ a.u.
Co						4P	3.4761	Rh		8	2		−1	3P	2.4495
						2P	3.4848			8	1		0	4F	4.6496
		6	2		+1	5D	5.6140			7	2			4F	5.6051
Ni		10	1		−1	2S	0.5195			7	1		+1	5F	7.8654
		9	2			2D	1.5195			6	2			5D	8.4977
		9	1		0	3D	2.8563			6	1	1			16.901[b])
		8	2			1G	3.8423	Pd		9	2		−1	2D	2.5981
						3F	3.8083			9	1		0	3D	4.7483
						1D	3.8232			8	2			3F	6.0270
						3P	3.8264			8	1		+1	4F	8.2097
						1S	3.8948			7	2			4F	9.1565
		7	2		+1	4F	6.1592			7	1	1			18.238[b])
Ag		10	2		−1	1S	2.7205	Tm	13		2		0		4.534
		10	1		0	2S	4.8022	Yb	14		2		0		4.661
		9	2			2D	6.4405	Lu	14	1	2		0		5.716
		9	1		+1	3D	8.6034	Hf	14	2	2		0		6.596
		8	2			3F	9.8207		14	1	1	1	+1		19.392[b])
		8	1	1			19.455[b])	Ta		3	2		0		7.393[c])
Cd		10	2							2	1	1	+1		21.821[b])
		10	1					W		4	2		0		8.137[c])
		9	2							3	1	1	+1		23.760[b])
In			2	2	−1	3P	8.8992	Re		5	2		0		8.839[c])
			2	1	0	2P	9.7362			4	1	1	+1		25.827[b])
			2		+1	1S	11.1402	Os		6	2		0		9.508[c])
Sn			2	3	−1	4S	11.6116			5	1	1	+1		27.664[b])
			2	2	0	3P	12.6795	Ir		7	2		0		10.151[c])
			2	1	+1	2P	14.1296			6	1	1	+1		29.581[b])
Sb			2	4	−1	3P	14.7701	Pt		9	1		0		10.769[c])
			2	3	0	4S	15.7732			7	1	1	+1		31.612[b])
			2	2	+1	3P	17.2812	Au		10	1		0		11.366[c])
Te			2	5	−1	2P	18.0550			8	1	1	+1		33.324[b])
			2	4	0	3P	19.1965								

			2	3	+1	4S	20.6504	Hg	10	2		0	11.946[c])
			2	6	−1	1S	21.4934		9	1	1	+1	35.064[b])
			2	5	0	2P	22.8239	Tl		2	1	0	16.2805[c])
			2	4	+1	3P	24.3637	Pb		2	2	0	20.5308[c])
Xe			2	6	0	1S	26.6880	Bi		2	3	0	24.8619[c])
			2	5	+1	2P	28.2829	Po		2	4	0	29.3335[c])
		1	1	1	+1		19.385[b])	At		2	5	0	33.9803[c])
Cs			1		0		1.669[c])	Rn		2	6	0	38.8213[c])
Ba			2		0		2.966[c])	Fr					2.544[d])
La		1	2		0		3.092[c])	Ra					4.396[d])
Ce	2		2		0		3.211[c])	Ac					5.322[d])
Pr	3		2		0		3.329[c])	Th					6.160[d])
Nd	4		2		0		3.446[c])	Pa					5.630[d])
Pm	5		2		0		3.563[c])	U					5.776[d])
Sm	6		2		0		3.680[c])						
Eu	7		2		0		3.799[c])						
Gd	7	1	2		0		3.918[c])						
Tb	9		2		0		4.039[c])						
Dy	10		2		0		4.161[c])						
Ho	11		2		0		4.284[c])						
Er	12		2		0		4.409[c])						

[a]) In atomic units, wave functions from ref. 5 where not otherwise stated. [b]) See [8a]. [c]) See [8d]. [d]) See [8b,c].

This conclusion is further confirmed by the following facts: (i) Isomeric compounds like the pairs *cis/trans*$[PtCl_2(PBu_3)_2]$, which should have comparable charges on platinum, show differences in their $^1J(Pt,P)$ values of 1128 Hz [12] comparable in magnitude to differences between Pt(IV) and Pt(II) complexes; (ii) In complexes of the type $[PtX(PR_3)_3]^+$ [13] the coupling constants ^1J(P-Pt-X) and ^1J(P-Pt-P) (that share the same $|\Psi_{6s,Pt}(0)|^2$ term) differ from each other by the same amount as $^1J(P,Pt)$ in the pairs *cis/trans* $PtX_2(PR_3)_2$. Moreover, in spite of the total positive charge the coupling constants are also comparable in magnitude to those of the uncharged species; (iii) The ^{31}P-NMR. spectrum of *cis*$[PtCl(CH_3)(PEt_3)_2]$ shows two resonances having coupling constants to platinum of 4179 and 1719 Hz [14]. Since these two coupling constants must share the same $|\Psi_{6s,Pt}(0)|^2$ term and presumably have nearly identical $|\Psi_{3s,P}(0)|^2$ values, this large difference must be entirely an effect of the polarizability term, $\Pi(Pt,P)$. Since these latter two values of $^1J(Pt,P)$ span approximately the whole range of platinum phosphine coupling constants it is proven that an explanation of that big a variation in $^1J(Pt,P)$ can be given solely on the basis of changes in the polarizability term. However, the importance of fluctuations of the $|\Psi_{ns}(0)|^2$ terms on $^1J(M,P)$ remains unclear. A systematic study of $|\Psi_{ns}(0)|^2$-values as a function of charge was therefore undertaken. The results of this study are presented in *Table 2* together with representative additional results in *Table 3* and shall now be discussed in some detail.

The s-densities depend within a formal charge upon the electron configuration and the spectroscopic term of a configuration. The influence of the term is small as can be seen from *Table 2*. The largest difference in $|\Psi_{ns}(0)|^2$ for the ground state configurations of Cr, Mn and Fe deviate 9%, 7% and 4% from the mean value. Higher multiplicities tend to have lower s-densities at the nucleus, whereas the dependence on the value of the total orbital angular momentum, L, seems irregular. The dependence of $|\Psi_{ns}(0)|^2$ on orbital occupation is much more pronounced as can be seen from *Table 2*. The excitation of an electron into a shell with increased main quantum number results after *Slater* [9] in a lesser shielding of the other electrons from the nuclear charge, which in turn increases the value of $|\Psi_{ns}(0)|^2$. If the electron in question is removed completely an even more pronounced raise in $|\Psi_{ns}(0)|^2$ is calculated.

The discussion of the dependence of $|\Psi_{ns}(0)|^2$ on formal charge can be done on the basis of two quantities, the s-density difference per charge unit or the slope of the s-density given by a second order polynoma in charge[2]). Both these quantities are larger for transition metals (mean difference 2.2 ± 0.8 atomic units between $Q=1$ and $Q=0$, mean slope 2.1 ± 0.7 atomic units per charge unit at zero charge)

[2]) The slope of the function $|\Psi_{ns}(0)|^2(Q) = a + bQ + cQ^2$, where Q is the charge, at zero charge is given by the value of b. The values of a, b and c can be analytically given if the points $Q = -1, 0, 1$ are used only.

$$a = |\Psi_{ns}(0)|^2(Q=0)$$
$$b = [|\Psi_{ns}(0)|^2(Q=1) - |\Psi_{ns}(0)|^2(Q=-1)]/2$$
$$c = [|\Psi_{ns}(0)|^2(Q=1) + |\Psi_{ns}(0)|^2(Q=-1) - 2|\Psi_{ns}(0)|^2(Q=0)]/2$$

Alternatively they could be optimized by a least squares treatment.

Table 3. *Dependence of* $|\Psi_s(0)|^2$ *of niobium and phosphorus on configuration and charge*

			$|\Psi_s(0)|^2$				
			5s	4s	3s	2s	1s
Nb^{-1}	d^5s	^7F	1.650	55.47	379.3	2166	21371
	d^4s^2	^5D	1.788	55.73	379.3	2166	21371
Nb^0	d^5	^6S	-	55.10	379.3	2166	21371
	d^4s^1	^6D	3.698	55.88	379.4	2167	21371
	d^3s^2	^4F	3.900	56.46	379.1	2164	21366
Nb^{+1}	d^4	^5D	-	55.45	379.4	2167	21371
	d^3s^1	^5F	5.547	56.52	379.2	2167	21371
	d^2s^2	^3F	5.939	57.62	379.6	2167	21370
P^{-1}	s^2p^4	^3P			5.312	74.74	1012
P^0	s^2p^3	^4S			5.628	74.62	1012
P^{+1}	s^2p^2	^3P			6.215	74.78	1013
P^{+2}	s^2p^1	^2P			6.884	74.88	1013
P^{+3}	s^2	^1S			7.614	75.16	1013
P^{+4}	s^1	^2S			7.722	75.17	1013

than for main group elements (mean difference 0.9 ± 0.4 atomic units between $Q=1$ and $Q=0$, mean slope 0.8 ± 0.4 atomic units per charge unit at zero charge). This is a consequence of the fact that changes in charge are due to changes in the number of (n-1) d electrons for the transition metals and to changes in the number of np electrons for the main group elements. Are changes even due to alteration in shells with larger main quantum number than of the s-orbital under consideration effects on the radial function of this orbital should merely exist. This expected behaviour is indeed observed for 'core' s-orbitals as shown in *Table 3*. Again the different shielding abilities of electrons in states with different main quantum numbers are demonstrated.

In the light of these results, the commonly used assumption of constant ns-densities at the nucleus in a series of compounds is justified for the main group elements but has to be used with caution in connection with transition metals. At the same time it seems unlikely that the raise in $^1J(M,P)$ by a factor of up to 6 when R in PR_3 is replaced by a more electronegative group R*[3]) (see also [15a–c]) can be explained by orbital contraction phenomena on phosphorus. As shown by *Table 4*, a total charge range on phosphorus in different environments of about one charge unit and a difference of about 0.7 charge units between phosphine and phosphite complexes seems possible. Only small changes in the phosphorus 2p binding energies occurred in ESCA. spectra which experimentally confirms minor alterations in charge [16]. One charge unit, on the other hand, is far less than what is needed to explain a factor of up to six in the observed

[3]) The coupling constant $^1J(W,P)$ in $W(CO)_5(PR_3)$ is for $P(SnMe_3)_3$ 143 Hz, PBu_3 227 Hz, PPh_3 280 Hz, $P(OEt)_3$ 391 Hz, $P(NMe_2)_3$ 297 Hz, $P(SCH_2)_3CC_5H_{11}$ 276 Hz, PI_3 334 Hz, PBr_3 398 Hz, PCl_3 426 Hz, PF_3 485 Hz. $^1J(W,P)$ is roughly following the electronegativity of the R group [3e]. $^1J(^{17}O,^{31}P)$ in $R_3P(O)$ are reported spanning the range from 90 to 205 Hz (factor of ~2.2) [15a]. $^1J(Se,^{31}P)$ in $R_3P(Se)$ has values from 936 to 699 Hz (factor of 1.3) [15b]. $^1J(V,^{31}P)$ in $[V(CO)_5(PR_3)]^-$ changes from 170 (PH_3) to 730 Hz (P-*i*-Bu_3) giving a factor of 4.3 and from 110 (Pcy_3) to 660 Hz (P-*i*-Bu_3) giving a factor of 6 [15c].

coupling constants solely by orbital contraction, since one charge unit results in only a 7% increase of the 3s-density on phosphorus. Even a range of five charge units could explain a factor of 1.45 only (see *Table 3*).

If orbital contraction on phosphorus can be excluded as a main source for the observed differences, the responsible term must be the mutual polarizability, Π(A, B), in equation (2) or put in terms of a valence bond description the s-character of the phosphorus lone pair. The influence of the electronegativity of R on the lone pair s-character in PR_3 and on ^1J(H, P) in HPR_3^+ was therefore studied by MO-calculations of the extended *Hückel* type. The R groups were single atoms with radial functions identical to those of chlorine. The different electronegativities were simulated by shifting the valence-state ionization potentials of the R atom from 5 and 10 eV for p and s orbitals respectively (roughly simulating R = alkyl) to 20 and 35 eV (corresponding to R = fluorine). As pictured in *Figure 4*, these

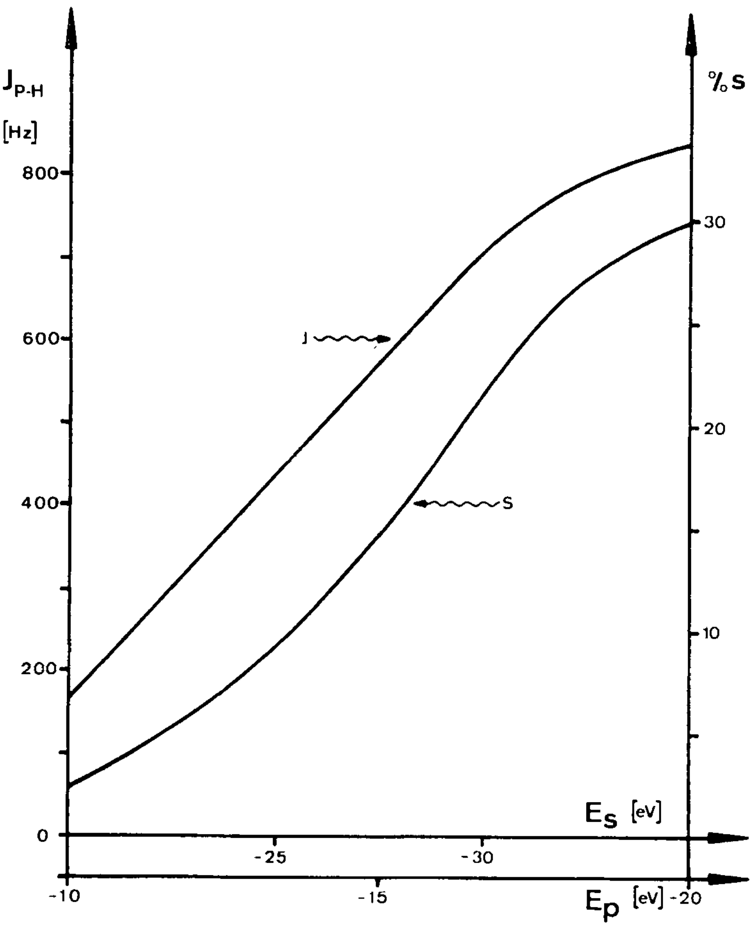

Fig. 4. *Percentage of s-character of the phosphorus lone pair in PX_3 and $^1J(P,H)$ in HPX_3^+* versus *VSIP of s- and p-orbitals of the x group as calculated by the EHMO method*

Table 4. *Calculated charges on phosphorus and boron of some compounds of the type PR_3 and H_3B-PR_3*

R	PR_3	H_3B-PR_3	
	Q(P)	Q(P)	Q(B)
H	+0.35	+0.57	−0.08
CH_3[a])	+0.35	+0.75	−0.12
NH_2	+0.86	+1.16	−0.18
OH	+1.01	+1.27	−0.13
Cl	+0.76	+0.90	−0.11
F	+0.95	+1.28	−0.17
PH_4^+	+0.66		
$F_3P=0$	+1.54		

[a]) See [18]

changes result in an increase of the s-character of the phosphorus lone pair from about 3% to 30%, whereas the p-character remains nearly constant between 44% and 48%. This is analogous to a possible explanation for the increase in inversion barrier along the series $NH_3 < PH_3 < AsH_3$ [17]. Furthermore, these results are in fair agreement with *ab initio* calculations that report the s-character of the lone pairs of PH_3, $P(CH_3)_3$ and PF_3 to be 17%, 14% and 35% respectively [18]. The same *Figure 4* shows the influence of the electronegativity of R on ^1J(H, P) in HPR_3^+. If R becomes more electronegative, the calculated coupling constant (constant s-densities were used) increases from about 180 to 820 Hz. These results too suggest that differences in $^1J(M, PR_3)$ as a function of the electronegativity of R are for the most part an effect of the polarizability term and to a minor extent of the s-density terms. These results are also in agreement with two ESR. studies [4] which report the phosphorus s-character in the Co-L bond in complexes of the type Co(TTP)L (TTP = tetraphenylporphyrin) for L = PF_3, $P(OMe)_3$, PMe_3, PMe_2Ph and PEt_3 to be 68%, 51%, 28% and 27%.

Conclusions. - The s-densities at the nucleus behave as qualitatively predicted by *Slater*'s rule. Fluctuations of $|\Psi_{ns}(0)|^2$ induced by alterations of charge may play a - although minor - role in determining the magnitude of the one bond coupling constant ^1J(M, X). The maximum charge range of an element in different chemical environments will probably be less than one charge unit and will become smaller the more covalent and extended the molecular framework in question is. Therefore, the $|\Psi_{ns,M}(0)|^2$ term of a transition metal will change by a factor of less than 1.8 if the alteration in charge is completely due to a change in d-orbital population. In typical organometallic compounds (meaning covalent extended molecules) changes will be less than one charge unit and only partially due to alterations in d-orbital occupancy and a factor of less than say 1.3 seems realistic and will be even nearer to unity for a series of compounds with merely changing proximity of the atom in question. If X is a main group element, its $|\Psi_{ns,X}(0)|^2$ will change by a factor of 1.1 for one charge unit and will practically not alter in a series of different environments. In summary, the s-densities at the nuclei can, as a first approximation, be assumed constant as long as differences in ^1J(M, X) of more than about 20% are discussed. Nevertheless, this assumption should be used with some care, especially if transition metals in changing proximities are involved.

Because of the characteristics summarized above, changes of the $|\Psi_{3s,P}(0)|^2$ term in expression (2), while changing the nature of R in PR_3, can be ruled out as a major effect on the magnitude of the coupling constant ^1J(M, P). An alternative explanation with the help of the mutual polarizability can be offered instead. The s-character of the phosphorus lone pair in PR_3 changes considerably with the electronegativity of R although the angle Θ (RPR) merely changes. This and the low values of the lone pair s-character in spite of Θ (RPR) being not far from 90° is in contradiction to simple rehybridization arguments which also seem to be in error if compared to *ab initio* results.

Acknowledgement is made to the *Swiss National Science Foundation*. Fruitful discussion with Dr. *P. S. Pregosin* is gratefully acknowledged.

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