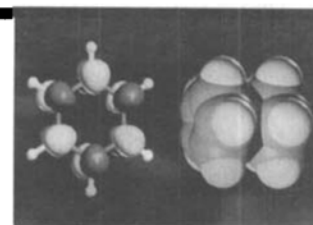# COMPUTATIONAL CHEMISTRY COLUMN

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Comment on the Relevance of Phosphorus and Sulfur 3d Orbitals

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Since the times of Valence Bond (VB) theory, which assigned a 2-electron orbital to each chemical bond, textbooks on phosphorus and sulfur [1] often emphasize the importance of the empty 3d orbitals on these elements, in an attempt to rationalize the differences between them and their corresponding first-row homologues. Noteworthy features, displayed by the second-row elements, include:

1) *Hypervalence* (*i.e.*, the easy formation of PR_5, PR_6, SR_5, and SR_6 compounds while the agreed 'maximal valence', according to the octet rule, would be four),

2) Softness of P- and S-ligands, compared to their N- and O-homologues: π-acidity, back-bonding, stabilization of carbanions at phosphorus or sulfur atoms (*Wittig* reagents).

In the framework of the VB formalism [2], both features are 'explained' with the help of spd-*hybrid* orbitals. Specifically, sp^3d hybrids are invoked for trigonal bipyramidal geometries at P, and sp^3d^2 hybrids for octahedral geometries at S [3]. The VB theory, which offered a theoretical justification for the organic chemist's intuitive and experimentally founded concept of valence [4], falls, however, short in explaining chemical bonding in a more general context. Phenomena like electron-deficient cluster bonds or solid-state metallic bonds are definitely out of its range;

they require a molecular orbital (MO) treatment. Even the organic chemist's familiar concepts of sp, sp^2, and sp^3-hybridized C-atoms cannot be maintained in the light of quantum physics: it is in fact possible to make four equal chemical bonds out of three p orbitals alone; the s orbital is not really needed! The only requirement is, that the symmetry of the coordination geometry (tetrahedral in this case) coincides with the symmetry of the electron cloud, as a corollary of the *Jahn-Teller* theorem. The experimental fact that ESCA spectroscopy yields **two** valence-shell ionization peaks at two different energies for 'sp^3' methane (corresponding to the carbon p- and s-shell ionizations, respectively) [5], can be viewed as a decisive **disproof** of the VB formalism, which, in turn, would predict only one such peak in this case. The localized sp^3-hybrid orbitals, although obtained by a unitarian transformation from the atomic (s,p) basis orbital set, are no longer stationary solutions of the molecular *Schrödinger* equation; to all evidence, these hybrid orbitals are coupled together by the electron-electron repulsion operator, and a rediagonalization splits them up again into s and p waves!

The substitution of the chemically founded, ambiguous concept of *valence* by the better defined concepts of *oxidation state* ('main valence') and *coordination number* ('secondary valence') was first effected by *A. Werner* in his 'Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie' [6], and has opened the way for a rapid rationalization of all aspects of inorganic chemistry after the advent of quantum mechanics. In the field of organic chemistry, however, the conventional valence concept kept much longer alive, as it apparently did a good job in almost all of the known cases [7].

The VB formalism in organic chemistry got furthermore an unexpected boost by the popularization of *R. Hoffmann*'s extended *Hückel* method [8], where additional d functions in the basis orbital sets of the elements Si, P, S, and Cl turned out to improve the results substantially [9]. Had not MO theory finally joined the chemist's intuitional view, that elements which show more than four conventional valencies must also have more than four available 2-electron orbitals?

The answer to this question is given by a series of *Herman-Skillman* atomic struc-

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Table 1. *Conventional ICON Parametertrization for Si, P, S, and Cl* [14]

	$\zeta s,\zeta p$	ζd	Es [eV]	Ep [eV]	Ed [eV]
Si	1.383	1.383	–17.3	– 9.2	–6.0
P	1.600	1.400	–18.6	–14.0	–7.0
S	1.817	1.500	–20.0	–13.3	–8.0
Cl	2.033	2.033	–30.0	–15.0	–9.0

ture calculations [10] for the elements Si to Ti, including the 8 orbitals 1s, 2s, 2p, 3s, 3p, 3d, 4s, and 4p (*Table 1*). These calculations represent spherically and spin averaged values for the indicated (n,l) electronic configurations, and may be taken as a picture of the atom's situation in a closed-shell molecular environment [11].

The results of these calculations show that the 3d orbitals are throughout energetically high-lying ($E = -1.5$ eV) and diffuse (*Slater*-zeta = 0.35) orbitals for the elements Si to Ar. Their contribution to bonding is thus small [12]. It is noteworthy that the energies of the 4s and 4p orbitals lie throughout below the energies of the 3d shell (–2.9 to –3.7 eV and –2.0 to –2.5 eV, respectively) and that the 4s and 4p orbitals are much less diffuse (*Slater*-zetas = 0.61–0.75 and 0.47–0.58, respectively) than the 3d orbitals. If higher-lying atomic orbitals were to play a role in the chemistry of Si, P, S, and Cl, one had thus first to look about the 4s and 4p orbitals!

Potassium is the very first element, where the 3d orbitals may play a chemical role. In the K^+ ion, the 3d orbitals lie merely 2.3 eV above the 4s orbital and have very similar *Slater*-zeta values. For calcium, the empty 3d orbitals fall already below the 4s orbital. The fact that calcium still shows an $(Ar)s^2$-ground-state configuration is due to the higher interelectronic repulsion exerted by the atomic field on an electron in a 3d orbital, compared with that exerted on an electron in a 4s orbital. The (Ar)sd state has thus a higher overall energy than the $(Ar)s^2$ state. The 3d orbitals play also a role in the Ca^{2+} ion, where they lie below the 4s orbitals by 2.2 eV. The marked particularities in catalytic behavior of potassium and calcium compounds, compared to their earlier homologues of sodium and magnesium, may thus well be explained on such grounds. The elements following calcium, *i.e.*, scandium and titanium, have already an occupied 3d shell in their atomic ground state.

The chemical irrelevance of the 3d orbitals for elements with atomic numbers lower than or equal to 18 (Ar) is also emphasized by the results of scattering theory. *S.T. Manson* [13] of the American National Bureau of Standards calculated the electron scattering phase shifts as a function of electron energy and atomic number. He found that no appreciable phase shift is exerted on electronic d waves of low energy by the field of atoms with ordinal numbers lower or equal 18. This means that bonding interaction with 3d orbitals is energetically irrelevant for the elements preceding potassium! In a similar way, *Manson* shows that 4f orbitals

Table 2. *Results of* Herman-Skillman *Calculations for the Elements Si to Ti.* Orbital type (n,l), electronic occupation, orbital energy (*E*), and *Slater* exponent (ζ) are given for the indicated elements and configurations.

SILICON (NE)S2P2

	E		ζ
1S (2):	–1829.6986	eV;	13.14787
2S (2):	–153.5876	eV;	4.44696
2P (6):	–110.3906	eV;	4.26630
3S (2):	–13.9981	eV;	1.58398
3P (2):	–6.7996	eV;	1.14839
3D (0):	–1.5643	eV;	0.35099
4S (0):	–2.9156	eV;	0.61077
4P (0):	–2.0351	eV;	0.47362

PHOSPHORUS (NE)S2P3

	E		ζ
1S (2):	–2130.6160	eV;	14.12300
2S (2):	–189.0680	eV;	4.88310
2P (6):	–140.8466	eV;	4.71816
3S (2):	–17.7065	eV;	1.80186
3P (3):	–8.7309	eV;	1.34971
3D (0):	–1.5660	eV;	0.35163
4S (0):	–3.1457	eV;	0.65256
4P (0):	–2.1885	eV;	0.50852

SULPHUR (NE)S2P4

	E		ζ
1S (2):	–2454.6129	eV;	15.10126
2S (2):	–227.6379	eV;	5.32156
2P (6):	–174.3151	eV;	5.17984
3S (2):	–21.5408	eV;	2.01164
3P (4):	–10.7840	eV;	1.54182
3D (0):	–1.5619	eV;	0.35020
4S (0):	–3.3522	eV;	0.69091
4P (0):	–2.3117	eV;	0.53628

CHLORINE (NE)S2P5

	E		ζ
1S (2):	–2801.7225	eV;	16.08212
2S (2):	–269.3484	eV;	5.75724
2P (6):	–210.8436	eV;	5.64681
3S (2):	–25.5466	eV;	2.20396
3P (5):	–12.9392	eV;	1.72640
3D (0):	–1.5557	eV;	0.34805
4S (0):	–3.5403	eV;	0.72594
4P (0):	–2.4146	eV;	0.56026

ARGON (NE)S2P6

	E		ζ
1S (2):	–3171.9101	eV;	17.06495
2S (2):	–314.2198	eV;	6.19404
2P (6):	–250.3236	eV;	6.11972
3S (2):	–29.7151	eV;	2.39762
3P (6):	–15.2179	eV;	1.90309
3D (0):	–1.5490	eV;	0.34579
4S (0):	–3.7139	eV;	0.75820
4P (0):	–2.5026	eV;	0.58012

POTASSIUM (AR)S

	E		ζ
1S (2):	–3575.1107	eV;	18.03878
2S (2):	–371.7721	eV;	6.64158
2P (6):	–302.5628	eV;	6.59009
3S (2):	–41.5679	eV;	2.72247
3P (6):	–24.6200	eV;	2.31815
3D (0):	–1.9039	eV;	0.67591
4S (1):	–4.2750	eV;	0.85910
4P (0):	–2.7170	eV;	0.63338

POTASSIUM(+) (AR)

	E		ζ
1S (2):	–3582.2947	eV;	18.03898
2S (2):	–378.8434	eV;	6.64360
2P (6):	–309.6470	eV;	6.59224
3S (2):	–48.3346	eV;	2.70761
3P (6):	–31.4063	eV;	2.30264
3D (0):	–8.3695	eV;	1.18111
4S (0):	–10.6679	eV;	1.11838
4P (0):	–8.1313	eV;	0.93888

CALCIUM (AR)S2

	E		ζ
1S (2):	–4003.5631	eV;	19.01445
2S (2):	–434.0513	eV;	7.08816
2P (6):	–359.7445	eV;	7.07473
3S (2):	–54.4090	eV;	3.03051
3P (6):	–35.0633	eV;	2.64601
3D (0):	–6.2480	eV;	1.57392
4S (2):	–5.5170	eV;	1.03833
4P (0):	–3.1679	eV;	0.74193

CALCIUM (AR)SD

	E		ζ
1S (2):	–3999.0160	eV;	19.01595
2S (2):	–428.7723	eV;	7.08487
2P (6):	–354.5203	eV;	7.07217
3S (2):	–50.0699	eV;	2.96386
3P (6):	–30.9422	eV;	2.56040
3D (1):	–3.1873	eV;	1.15289
4S (1):	–4.7204	eV;	0.93586
4P (0):	–2.8644	eV;	0.67321

CALCIUM(++) (AR)

	E		ζ
1S (2):	–4020.4362	eV;	19.01485
2S (2):	–450.6956	eV;	7.09166
2P (6):	–376.4155	eV;	7.07839
3S (2):	–70.4652	eV;	3.03511
3P (6):	–51.0931	eV;	2.65853
3D (0):	–22.1434	eV;	1.84450
4S (0):	–19.8833	eV;	1.42228
4P (0):	–16.0600	eV;	1.24355

SCANDIUM (AR)S2D

	E		ζ
1S (2):	–4449.9547	eV;	19.99380
2S (2):	–493.2361	eV;	7.53014
2P (6):	–413.6082	eV;	7.53845
3S (2):	–62.0582	eV;	3.24176
3P (6):	–40.5854	eV;	2.83914
3D (1):	–7.7825	eV;	1.78524
4S (2):	–5.9299	eV;	1.09429
4P (0):	–3.2975	eV;	0.77562

TITANIUM (AR)S2D2

	E		ζ
1S (2):	–4919.1629	eV;	20.97415
2S (2):	–555.2506	eV;	7.97345
2P (6):	–470.2399	eV;	8.00330
3S (2):	–69.6622	eV;	3.44034
3P (6):	–46.0256	eV;	3.03220
3D (2):	–9.1674	eV;	1.96325
4S (2):	–6.2837	eV;	1.14393
4P (0):	–3.3967	eV;	0.80063

start to play a chemical role at earliest at atom number 55 (Cs) or 56 (Ba).

The '3d orbitals' used by *R. Hoffmann et al.* in their extended-*Hückel* calculations on Si, P, S, and Cl compounds can, therefore, by no means be real 3d orbitals. This is shown as well by the recommended parameter set for the **ICON** program (*Table 1*) [14], which deviates very much from what is obtained from atomic structure calculations (*Table 2*). The 'd orbitals' in *Table 1* merely play a role as polarization functions, enlarging the basis set of the variational calculus and enabeling the resulting wave-functions to get closer to the real molecular wave-functions. In this context, one could use, with equal success, double- or triple-zeta expansions for the second-row elements' s and p orbitals, because **every additional component** in the basis set, **of any imaginable type,** will enhance the accuracy of the variationally obtained molecular wave-functions. In a later paper, *R. Hoffmann* and coworkers explicitely discuss about the *deus ex machina* role that d functions were to play during some time in second-row elements' chemistry, concluding that such functions were at best useful as a calculation trick to enhance the precision of the EH energies [15].

But how to reply then to the more difficult arguments of *hypervalence* and *softness* of the second-row elements Si, P, S, and Cl?

1) Hypervalence is a concept formulated with respect to the VB formalism. It poses by no means a problem in the framework of quantum theory, in which the chemical bonding does not depend on the availability of a 2-electron orbital for every chemical bond of a molecule. The *pseudoproblem* of hypervalence can most easily be solved through a rigorous substitution of the somewhat ambiguous concept of 'valence' by the better defined concepts of 'oxidation state' and 'coordination number', along *A. Werner's* guidelines. The quantum-chemical requirement for a stable bonding situation is merely, that coordination geometry and electron configuration of a molecule are symmetry compatible.

2) Softness can be explained by the lower bond strengths of the bonds involving second-row elements, compared to bonds involving first-row elements. A low bond strength means, however, that the molecule has low-lying antibonding orbitals, or, in other words, remaining unsaturated valence! The bonds may easier be formed and broken in such a situation, and the atom

may also be involved into more bonds at a time. π-Acidity and backbonding in phosphines and thio-compounds are, therefore, rather tied to to the presence of low-lying antibonding (σ^*) orbitals than to the presence of empty 3d orbitals. The observation of, *e.g.* a **lengthening** of the P–C bonds in alkyl- or arylphosphine complexes, in which the P-atom acts as a π-acid, could be a proof of this statement [16]. Such a lengthening would, in contrast, not occur in the case where the acceptor orbitals were phosphorus 3d orbitals.

Prof. Dr. *Claude Daul*, of the University of Fribourg, is cordially acknowledged for a copy of the *Herman-Skillman* Program as well as for advice concerning the exchange functional.

[1] See, *e.g.* J.B. Hendrickson, D.J. Cram, G.S. Hammond, 'Organic Chemistry', 3rd edn., McGraw-Hill, New York, 1970, Chapt. 19: 'Sulphur and Phosphorus'; H. Kwart, K. King, 'd-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur', Series 'Reactivity and Structure Concepts in Organic Chemistry', Springer-Verlag, Berlin, 1977, Vol. 3.

[2] P.W. Atkins, 'Physical Chemistry', 5th edn., Oxford University Press, Oxford, 1994, Chapt. 14.

[3] L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, Ithaka, 1938.

[4] Remember that *atomism* was a working postulate of chemistry long before experimental proofs for the real existence of atoms were available: John Dalton, 'A New System of Chemical Philosophy', 1808; and that the concepts of *chemical valence* and *chemical bond* were forget long before any physical explanation of the nature of these phenomena could be given: E. Frankland, *J. Chem. Soc.* **1866**, *19*, 372. Modern MO theory as well as the application of other exact physical methods to chemistry must have been perceived (and are, maybe, still perceived) by certain chemists as an intrusion of physics into someone else's preserves.

[5] D.W. Turner, C. Baker, A.D. Baker, C.R. Brundle, 'Molecular Photoelectron Spectroscopy; A Handbook of He 584 Å Spectra', Wiley-Interscience, London, 1970.

[6] A. Werner, 'Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie', Friedr. Vieweg & Sohn, Braunschweig, editions 1905, 1908, 1913, 1919. See also the contributions in *Helv. Chim. Acta* **1967**, 'Fasciculus Extraordinarius *Alfred Werner*'.

[7] The need for revisions became only apparent at very recent times, when metalloorganic chemistry revealed the existence of such things as sandwich compounds, penta- and hexacoordinated carbon atoms in metal clusters and agostic interactions of protons, carbocations, and metal centers

with saturated C–H and C–C bonds.

[8] R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397.

[9] R. Hoffmann, J.M. Howell, E.L. Muetterties, *J. Am. Chem. Soc.* **1972**, *94*, 3047.

[10] F. Herman, S. Skillman, 'Atomic Structure Calculations', Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963. A modified version of the original program was used, which includes *J.P. Perdew's* empirical parameter free GGA91 exchange functional, combined with *R. Latter's* tail correction of the exchange potential. For the underlying theory see: J.P. Perdew, Wang Yue, *Phys. Rev., B* **1986**, *33*, 8800; and R. Latter, *Phys. Rev.* **1955**, *99*, 510. *Slater*-type orbitals were fitted to the outer parts of the obtained numerical wave-functions, and the corresponding zeta values (ζ) are reported together with the energies (E) of the orbitals.

[11] The disturbance of an atom due to its chemical environment is relatively small compared with the binding energies of the electrons in the atom itself; even in the case of the most affected valence electrons, the chemical effects amounts to only 10–20% of the electron's total binding energy.

[12] The stabilizing effect of an empty orbital onto energetically lower-lying electrons becomes negligible, when the energy level of the empty orbital approaches the vacuum level (zero).

[13] S.T. Manson, *Phys. Rev.* **1969**, *182*, 97.

[14] J. Howell, A. Rossi, D. Wallace, K. Haraki, R. Hoffmann, ICON8, Quantum Chemistry Program Performing extended *Hückel* Calculation; Quantum Chemical Program Exchange, QCPE No. 344, 1978.

[15] R.A. Wheeler, R. Hoffmann, J. Strähle, *J. Am. Chem. Soc.* **1986**, *108*, 5381.

[16] A.G. Orpen, N.G. Connelly, *J. Chem. Soc.*, *Chem. Commun.* **1985**, 1310.