Nuclear Spin–spin Coupling between Directly Bound Elements

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1 Introduction

The nuclei of many isotopic species possess inherent angular momentum or spin. This is quantized and is measured in half integral multiples of the modified Planck constant $\hbar$ ($h/2\pi$). If a pair of such nuclei are placed in proximity their spins may be coupled, that is they may interact so that different combinations of the allowed spin states differ in total energy. There are several mechanisms by which nuclear spins may be coupled, and those which arise when the nuclei are connected by a sequence of chemical bonds are of greatest interest to chemists. The degree of coupling is measured by the coupling constant J (in Hertz) which may be used to study the behaviour of the bonding electrons. This review deals only with the spin coupling of nuclei of elements which are connected by a direct bond.

The energy involved in nuclear spin–spin coupling is relatively small—at most a few erg/mole, and often much less, and at present the only method of measuring coupling constants in bulk matter is by nuclear magnetic resonance (n.m.r.) spectroscopy.[1] The nuclear spins are polarised by placing the sample in a magnetic field, and the frequencies at which radio frequency radiation is absorbed give information about the environment of the nuclei, and about the coupling constants. If solid materials are examined much of the information about coupling constants within particular molecules is lost, because of direct interaction between nuclear spins in neighbouring molecules, and we shall be concerned primarily with measurements of fluid samples (generally liquids) by high resolution techniques. In these circumstances the direct dipole–dipole coupling between the nuclear spins is averaged to zero by the motion of the molecules, and the observed coupling constants arise solely from electronic interaction.[2]

This interaction between a pair of coupled nuclei may be positive or negative, that is the state of lower energy may be that with the spins anti-parallel or it may be that with the spins parallel. This determines the sign of the coupling constant. Clearly any theoretical treatment must predict the signs as well as the magnitudes of coupling constants; indeed, at present a correct prediction of the sign alone is regarded as valuable.[3]

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[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance', McGraw Hill, 1959; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon, 1965.

[2] A. Abragam, 'The Principles of Nuclear Magnetism', Oxford, 1960.

[3] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

The study of spin–spin coupling between the nuclei of directly bound elements is important because it provides a way of checking quantitative theories of chemical bonding at a fairly fundamental level.[3] At a lower level of sophistication correlations have been established between coupling constants and such parameters as atomic hybridization[4–6] and effective nuclear charge.[7] Finally, measurements of these coupling constants can sometimes be used to establish chemical structures, or distinguish pairs of isomers.[8]

2 Experimental Aspects

It is not proposed to treat experimental methods in detail, but some points must be dealt with to allow a proper consideration of the results. Unfortunately from our viewpoint, many interesting nuclei have spin quantum number $I > \frac{1}{2}$ which generally leads to quadrupole broadening in their n.m.r. spectra, and in the spectra of other nuclei associated with them. In certain rather rare situations (usually highly symmetrical) this may not occur, but usually coupling constant information will be difficult to obtain for such nuclei, and most high resolution work is done on nuclei with $I = \frac{1}{2}$, *e.g.* ^{1}H, ^{19}F, and ^{31}P.

A. Single-resonance Methods.—These are the easiest to apply, and most of the older data were obtained in this way. Unless the spin system exhibits appropriate second-order features at the measuring field strength (and this will be uncommon with the heteronuclear systems that interest us) no information about the signs of the coupling constants will be obtained from single-resonance experiments. The magnitude of the coupling constant between a pair of nuclei of different species can be found from the resonance of either, and normally the one with the highest inherent sensitivity to n.m.r. detection will be chosen. This sensitivity factor depends on the magnetic moment of the nucleus, and is relatively high for the proton and fluorine, but low or very low for other nuclei. Thus data are plentiful for couplings which involve hydrogen or fluorine, but rather sparse for other elements. A further difficulty is that many important nuclei are of low natural abundance—*e.g.* ^{13}C 1%, ^{15}N 0·35%, ^{119}Sn 8·6%. This can be circumvented by using isotopically enriched samples, but synthesis of the appropriate compounds may not be easy, and the expense is considerable. However, coupling constants between ^{13}C and a variety of other nuclei have now been measured in this way in simple compounds.[9,10] Instrumental improvements have also helped here, and the use of large spinning sample tubes, and spectral accumulation enable fair signal-to-noise ratios to be attained for many nuclei.[11]

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[4] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 768.
[5] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2198.
[6] J. N. Shoolery, *J. Chem. Phys.*, 1959, **31**, 1427.
[7] D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, 1965, **87**, 3994.
[8] A. Pidcock, R. E. Richards, and L. M. Venanzi, *Proc. Chem. Soc.*, 1962, 184.
[9] F. J. Weigert, M. Winoker, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 1566.
[10] G. Mavel and M. J. Green, *Chem. Comm.*, 1968, 742.
[11] G. E. Hall, *Adv. N.M.R. Spectroscopy*, 1968, **1**, 227.

B. Double-resonance Methods.—In these the sample is exposed to two radio frequency fields simultaneously, at the Larmor frequencies of two different nuclei in the system.[12] If these nuclei are of different species the term heteronuclear is used.[13] Normally only one detection system is employed (but see reference 14), and if this operates at the frequency of the more sensitive nucleus the sensitivity will be correspondingly high. The n.m.r. parameters of the nucleus for which the resonance is not observed directly can still be determined with high precision, and an adapted proton (or ^{19}F) spectrometer can thus be used to study other nuclei in compounds in which they are coupled to protons (or ^{19}F nuclei). Furthermore, coupling constants can be measured between pairs of nuclei, neither of which is observed directly, as was demonstrated by McLauchlan, Whiffen, and Reeves for $^1J(^{13}C\text{–}Hg)$* in mercury dimethyl.[15] The fundamental advantage of the double resonance approach is that it gives the relative signs of coupling constants. In a spin system AMX, if A is the directly observed nucleus, and X is irradiated (this can be denoted[12] by A–{X}), then the signs of J_{AM} and J_{MX} relative to one another will be found. The inverse X–{A} experiment will give the same information, and in general two distinct (*i.e.* not mutually inverse) double resonance experiments must be performed to find all three relative signs in this system. The technique is equally applicable to more complex systems, and the favourable sensitivity feature has significantly reduced the need to use isotopically enriched samples. At present the detection record seems to be for proton observation of doubly substituted species in organo–silicon compounds containing ^{13}C and ^{29}Si, both in natural abundance.[16,17] (1% and 4·6% respectively.) An obvious disadvantage of the method is that it cannot be used for compounds that have neither protons nor ^{19}F nuclei coupled to the other nuclei of interest, but in practice this is not often a serious limitation.

C. Absolute Signs.—The results of a double resonance experiment are invariant with respect to a reversal of the signs of all the coupling constants, so some way is needed to put the relative signs determined by the methods of the preceding section (or otherwise) onto an absolute basis. This can be done if the rotational motion of the molecules can be sufficiently restricted for there to be incomplete averaging of the direct dipole–dipole coupling.[18] At the same time the overall molecular movement must not be seriously hindered or line-widths will be excessive, and small coupling constants will not be observed. These apparently incompatible conditions can be fulfilled by molecules which have been partially

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* The symbol ^nJ indicates that the coupled nuclei are separated by $n-1$ atoms.

[12] J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, 1963, **63**, 81; R. A. Hoffman and S. Forsen, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 15.

[13] W. McFarlane, *Adv. N.M.R. Spectroscopy*, 1968, **1**, 131.

[14] D. D. Elleman, S. I. Manatt, A. J. R. Bourn, and A. H. Cowley, *J. Amer. Chem. Soc.*, 1967, **89**, 4545.

[15] K. A. McLauchlan, D. H. Whiffen, and L. W. Reeves, *Mol. Phys.*, 1966, **10**, 131.

[16] K. A. McLauchlan, *Mol. Phys.*, 1966, **11**, 303; R. R. Dean and W. McFarlane, *ibid.*, 1967, **12**, 289.

[17] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1275.

[18] A. D. Buckingham and E. G. Lovering, *Trans. Faraday Soc.*, 1962, **58**, 2077.

oriented by dissolution in a liquid crystal,[19] by occlusion in a cavity in a crystal lattice, or by the application of a strong (*ca.* 20 kv/cm.) electric field.[20] The *inter*-molecular dipole–dipole coupling is then still averaged to zero, but the *intra*-molecular coupling is not and contributes to the observed coupling constant. Comparison with the value found in a fluid medium then gives the sign of the indirect spin–spin coupling constant relative to the direct dipole–dipole coupling, which can be taken as positive. This subject has been reviewed.[21] The dipole–dipole interaction also affects relaxation processes, and studies of these can also give absolute signs of coupling constants.[22] In general the methods of this section are best used to determine the absolute signs of certain key[23] coupling constants [*e.g.* $^1J(^{13}C-^1H)$] which can then be related to others by double resonance experiments, etc. The spin–spin coupling constants will in general be anisotropic, but in fluid media only averages will be observed, and this aspect will not be pursued here.

D. Other Methods for Obtaining Signs.—The observed magnitudes of coupling constants sometimes change in response to variations in some property (*e.g.* dielectric constant) of the solvent. Often this change will be in a particular absolute direction, so the measured coupling may be seen to increase or decrease, according to its sign.[24] Unfortunately solvent effects are not well understood, and only when the behaviour in similar circumstances of related coupling constants of known sign has been examined, can valid predictions be made. The sign of $^1J(^{19}F-^{119}Sn)$ has been predicted correctly in this way.[25] No doubt other circumstantial methods will be developed, but they must be scrutinised carefully before their conclusions are accepted.

3 Theoretical Considerations

A. Fundamentals.—An idea of how the bonding electrons can contribute to nuclear spin–spin coupling may be gained as follows.[26] Consider the molecule HD. (^1H has spin $\frac{1}{2}$, ^2D has spin 1.) In either of the isolated atoms the single electron would tend to align itself with its magnetic moment anti-parallel to the nuclear moment. In the molecule however, the electron spins will be paired, that is the electron magnetic moments will be aligned anti-parallel. Hence the two nuclear spins will be aligned anti-parallel in HD. Whilst this explanation is adequate to explain the ability of the spin orientation of one nucleus to influence the other, it cannot account satisfactorily for the existence of more than one energy level. This requires that account be taken of all nucleus–electron and

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[19] A. Saupe and G. Englert, *Phys. Rev. Letters*, 1963, **11**, 462.

[20] A. D. Buckingham and K. A. McLauchlan, *Proc. Chem. Soc.*, 1963, 144.

[21] A. D. Buckingham and K. A. McLauchlan, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 63.

[22] E. L. Mackor and C. McLean, *J. Chem. Phys.*, 1966, **44**, 64.

[23] M. Karplus, *J. Amer. Chem. Soc.*, 1962, **84**, 2458.

[24] C. L. Bell and S. S. Danyluk, *J. Amer. Chem. Soc.*, 1966, **88**, 2344; S. L. Smith and R. H. Cox, *J. Chem. Phys.*, 1966, **45**, 2848.

[25] P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1968, 698.

[26] N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, 1952, **85**, 143.

electron–electron interactions, and a suitable theory has been developed by Ramsey.[27]

In this theory the indirect coupling between two nuclei, N and N′ is written as the sum of three terms.

$$J_{NN'} = J_{NN'}(1) + J_{NN'}(2) + J_{NN'}(3) \tag{1}$$

$J_{NN'}(1)$ arises from the interaction of the orbital electronic currents with the nuclear magnetic moments. Each nuclear magnetic moment induces currents in the molecule which then set up secondary magnetic fields which are experienced by the other nuclei. Detailed quantum-mechanical treatment shows that there are actually two contributions $J_{NN'}(1a)$ and $J_{NN'}(1b)$ to $J_{NN'}(1)$, and that both are proportional to $\gamma_N\gamma_{N'}$, the product of the magnetogyric ratios* of the two nuclei. $J_{NN'}(2)$ is due to dipole–dipole interaction between the nuclear magnetic moments and the electronic magnetic moments. It too is proportional to $\gamma_N\gamma_{N'}$. Often $J_{NN'}(1)$ and $J_{NN'}(2)$ are relatively small, and the major contribution arises from $J_{NN'}(3)$. This is very similar to a term introduced by Fermi[28] in 1930 to account for the hyperfine structure in atomic spectra, and since it depends on the properties of electrons at the nucleus it is called the Fermi contact interaction. More effort has been applied to the calculation of $J_{NN'}(3)$ than the other terms, and it also is proportional to $\gamma_N\gamma_{N'}$. The relative importance of the various terms in the case of the molecule HD can be judged from a calculation done by Ishiguro.[29] He allowed for the effect of molecular vibration and found:

$$\begin{aligned} J_{HD}(1a) &= -\,0{\cdot}254\text{ Hz};\ J_{HD}(1b) = +\,0{\cdot}354\text{ Hz};\\ J_{HD}(2) &= +\,0{\cdot}202\text{ Hz};\ J_{HD}(3) = +\,36{\cdot}837\text{ Hz}.\\ &\textit{i.e. } J_{HD} = +\,37{\cdot}139\text{ Hz}. \end{aligned}$$

This compares with an experimental value of ± 43·0 Hz,[30] so the agreement is reasonable. Further calculations of this type will be considered later.

An important feature of the above breakdown of indirect nuclear spin–spin coupling constants is that all the terms are proportional to $\gamma_N\gamma_{N'}$. This gives a simple relation between coupling constants involving different nuclear species. Thus the effect of replacing ^{1}H by ^{2}D is to multiply coupling constants involving the replaced nucleus by γ_D/γ_H. In order to use coupling constants as a measure of electronic interaction it is therefore convenient to divide the measured values by $\gamma_N\gamma_{N'}$. Different versions of this process have been proposed by various workers,[31] and we shall adopt Pople and Santry's[3] reduced coupling constant K, which is defined as

$$K_{NN'} = J_{NN'}\,.\,2\pi/\hbar\,(\gamma_N\gamma_{N'}) \tag{2}$$

Its units are cm.$^{-3}$, and typical values of K for directly bound nuclei lie between

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* The magnetogyric ratio is the magnetic moment of the nucleus divided by its angular momentum, and is a constant for a particular nuclear species. It determines the resonant frequency of the nucleus in a given magnetic field.

[27] N. F. Ramsey, *Phys. Rev.*, 1953, **91**, 303.

[28] E. Fermi, *Z. Physik*, 1930, **60**, 320.

[29] E. Ishiguro, *Phys. Rev.*, 1958, **111**, 203.

[30] H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 1952, **88**, 415.

[31] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, 1962, *A*, **269**, 385.

10^{21} and 10^{24} cm.$^{-3}$. Some nuclei have a negative magnetogyric ratio, and if this is the case for *one* of a pair of coupled nuclei, K and J will be of opposite sign. Thus $\gamma(^{14}\text{N})$ is positive and $\gamma(^{15}\text{N})$ is negative, so $^{1}J(^{14}\text{N–H})$ is positive while $^{1}J(^{15}\text{N–H})$ is negative, these signs being respectively the same as, and opposite to that of $^{1}K(\text{N–H})$.

B. *A priori* Calculation.—Most calculations of spin–spin coupling constants in 'large' molecules have adopted the step taken by McConnell[32] and simplified the theory by using the mean excitation-energy approximation. In this, the several ground-state-to-excited-state electronic excitation energies that appear in most of the terms listed in the preceding section are replaced by a single average excitation energy ΔE. One of the most thorough investigations was by Pople and Santry[3] who used the LCAO approximation of Molecular Orbital theory to examine coupling between the nuclei of elements in the first row of the periodic table, and to determine the limitations of the mean excitation-energy approximation in the case of $K(3)$.

They show that for the orbital contribution, K(1a) vanishes if the approximation is made of retaining only one-centre integrals, and that

$$K_{\mathrm{NN}'}(1\mathrm{b}) = \frac{8}{3} \, . \, \beta^2 \, \langle r^{-3}\rangle_{\mathrm{N}} \, . \, \langle r^{-3}\rangle_{\mathrm{N}'} \, (^{1}\Delta E)^{-1} \, P^{(1)} \qquad (3)$$

where β is the Bohr magneton, $^{1}\Delta E$ is a mean singlet excitation energy, obtained by taking an average value (normally this will be an estimate) of the various individual ground-state-to-singlet-state electronic excitation energies. $\langle r^{-3}\rangle_{\mathrm{N}}$ is the mean value of the inverse cube of the radial distance between the nucleus and an electron in a $2p$ orbital of atom N. The symbol $P^{(1)}$ represents a simple combination of the orders of the bonds which involve $2p$ atomic orbitals and is zero for directly bound atoms unless there is π bonding between N and N′. Even when there is a double bond between the coupled nuclei the contribution of $K(1)$ to the total is rather small. *E.g.* for C=C, $K(1) = -12{\cdot}5 \times 10^{20}$cm.$^{-3}$, which may be compared with an observed value for this reduced coupling constant in ethylene[32] of $+\ 89{\cdot}0 \times 10^{20}$cm.$^{-3}$. The calculation has not been extended to the heavier elements, and here the d orbitals would have to be considered.

If similar assumptions are made in the calculation of the electron dipole–nuclear dipole interaction we find

$$K_{\mathrm{NN}'}(2) = \frac{4}{25} \, \beta^2 \, \langle r^{-3}\rangle_{\mathrm{N}} \, \langle r^{-3}\rangle_{\mathrm{N}'} \, (^{3}\Delta E)^{-1} \, P^{(2)} \qquad (4)$$

$^{3}\Delta E$ is a mean ground-to-triplet-state excitation energy, and $P^{(2)}$ is another simple combination of $2p$ bond orders. In this case, for a single bond between a pair of sp^3 hybridised atoms $P^{(2)}$ is 9/8, and is about four times as great for a triple bond between sp hybridised atoms. However, calculations of $K(2)$ still lead to small values because of the factor 4/25. *E.g.* for C–C we obtain $+\ 1\ \times$

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[32] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 460.

10^{20}cm.$^{-3}$. An exception occurs with fluorine, for here $\langle r^{-3}\rangle_F$ is large. Thus the calculated value of $K_{FF}(2)$ in F_2 is $+ 44 \times 10^{20}$cm.$^{-3}$. Calculations have not been done for the heavier elements, but $K(2)$ may be fairly large because of the greater values[33] of $\langle r^{-3}\rangle_{np}$. However, as the next section shows, the contribution from $K(3)$ is also much larger for these elements, and $K(2)$ remains relatively unimportant.

In calculating the contact contribution $K(3)$ Pople and Santry were able to make the mean excitation energy approximation at a very late stage, and thus assess its importance. When only one-centre integrals are retained they find

$$\mathrm{K}_{NN'}(3) = \frac{64\pi^2}{9}\, \beta^2 [s_N\, |\delta(r_N)|\, s_N][s_N'\, |\delta(r_N')|\, s_N']\, \pi_{NN'} \tag{5}$$

The term $[s_N\,|\delta(r_N)|\,s_N]$ represents the magnitude of the valance atomic s orbital at nucleus N, and is positive. Accordingly the sign of $K(3)$ resides in $\pi_{NN'}$, the mutual polarisability of the valence s-orbitals of N and N′. This is the ability of changes in electron density in s_N to affect s_N' or vice versa, and depends on the sum of appropriate electronic excitations. For a molecule like CH_4, in which the $2s$ and $2p$ orbitals of carbon are of comparable energy, it is permissible to make the mean excitation energy approximation, and replace $\pi_{NN'}$ by $P_s{}^2/{}^3\Delta E$, where P_s is the N–N′ s-bond order. This result was also obtained[32] by McConnell by making the approximation at an earlier stage. Reasonable estimates of the other parameters then lead[3] to $+ 44 \times 10^{20}$cm.$^{-3}$ for $K(3)$ in methane, which may be compared with the experimental value for K of $+ 41{\cdot}8 \times 10^{20}$. Fair agreement with experiment is also obtained when similar calculations are done for the isoelectronic and isostructural species NH_4^+ and BH_4^-.

In a molecule like hydrogen fluoride, the fluorine $2s$ electrons are very tightly bound, and therefore of much lower energy than the hydrogen $1s$ or the fluorine $2p$ electrons. In this case the mean excitation energy approximation is not valid, and we must use the full version of equation (5). The sign of π_{FH} actually depends on a delicate balance between contributions of opposite sign from two different excitations. The negative one is from a molecular orbital of low s-character to a vacant anti-bonding orbital, and will dominate if β_{FH}, the overlap integral between the fluorine and hydrogen s-orbitals, is small enough, and/or the energy of the fluorine $2s$ orbital is sufficiently low. β_{FH} depends on $\epsilon_{F(2s)}$, the energy of the fluorine $2s$ electrons. The detailed calculations yield $- 87 \times 10^{-20}$cm.$^{-3}$ for $K(3)$ in HF. The observed magnitude is 54×10^{-20}, but unfortunately the sign is not known. Rather poor agreement between theory and experiment is found for NH_3 and H_2O, but it is difficult to obtain accurate values of the excitation energies and suitable atomic wave functions.

The theory as it stands can be applied to coupling between other elements in the first row of the periodic table, and should be qualitatively correct for heavier elements. Thus when the mean excitation energy approximation is made we may write[34]

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[33] R. G. Barnes and W. V. Smith, *Phys. Rev.*, 1954, **93**, 95.

[34] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1707.

$$K_{NN'}(3) \propto (\Delta E)^{-1}\, \alpha_N^2\, \alpha_{N'}^2\, |\psi_{N(ns)}(0)|^2\, |\psi_{N'(ns)}(0)|^2 \qquad (6)$$

where $|\psi_{N(ns)}(0)|^2$ is the electron density of the orbital at the parent nucleus and α_N^2 is the *s*- character of the hybrid orbital used by N for the N–N′ bond. We thus predict positive signs for reduced coupling constants between nuclei of directly bound elements, unless one with tightly bound valence *s* electrons is involved. In this case an equation like (5) must be used, and with fluorine ϵ_{2s} is so low that negative coupling constants will almost always result. With nuclei of rather less electronegative elements ϵ_{ns} will generally not be quite so low, and β will be more important. Thus the sign of the coupling constant may depend on the substituents attached to the atom.

Table 1 lists experimental signs for reduced coupling constants between a selection of pairs of nuclei, and it will be noticed that the above conclusions are borne out. An important feature of equations (5) and (6) is the dependence on the valence densities at the nuclei. These are largest for heavy elements, and within a given group of the periodic table the coupling constants do increase as the atomic number becomes larger. Pople and Santry predicted[3] that couplings involving carbon should exhibit parallel behaviour to those involving hydrogen, and several entries in Table 1 appear to contradict this. However, these arise when carbon is bound to a Group V or VI element, and the negative values will be due to these elements having valence *s* electrons of low energy. Furthermore, in these cases the coupling constants are often of relatively small magnitude. It is of interest to notice that all experimental signs involving H are positive, while all involving F are negative.

Table 1 *Signs of reduced coupling constants between directly bound nuclei*

	H	B	C	N	F	Si	P	Se	Sn	Te	Pt	Hg	Pb
H		$+^f$	$+^g$	$+^h$		$+^i$	$+^j$	$+^k$	$+^l$		$+^m$		$+^l$
C	$+^g$		$+^n$	$+^o$	$-^p$	$+^q$	$\pm^b$	$-^r$	$+^s$	$-^p$		$+^t$	$+^u$
P	$+^j$		$\pm^b$		$-^v$		$\pm^b$		$-^c$		$+^d$		
Se	$+^k$		$-^r$		(−)			small^w	$-^x$		$+^e$		
F		$-^a$	$-^f$	(−)		$-^y$	$-^v$	(−)	$-^z$	$-^\phi$			

Parentheses indicate that the sign is not finally established, but that empirical trends make it extremely probable.

[a] In trigonal boron compounds, in BF_4^- *K* can become positive, Refs. 59 and 62; [b] Depends on valence of P. Refs. 52 and 69; [c] P^{III} compound. M. F. Lappert, W. McFarlane, and J. Poland, unpublished observation; [d] P^V compounds. W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1922; [e] Tricoordinate Se. W. McFarlane, *Chem. Comm.*, 1968, 775; [f] Ref. 59; [g] Ref. 22; [h] W. McFarlane and R. R. Dean, *J. Chem. Soc.*, 1968, 1535; [i] Ref. 17; [j] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1148; [k] W. McFarlane, *Chem. Comm.*, 1968, 963; [l] H. Dreeskamp, *Z. Naturforsch.*, 1964, **19a**, 139; [m] W. McFarlane, *Chem. Comm.*, 1967, 772; [n] K. A. McLauchlan, *Chem. Comm.*, 1965, 105; [o] W. McFarlane, *Mol. Phys.*, 1966, **10**, 603; [p] Ref. 43; [q] Ref. 16; [r] Ref. 55; [s] Ref. 46; [t] Ref. 15; [u] Ref. 48; [v] Ref. 58; [w] W. McFarlane, *J. Chem. Soc.* (*A*), 1969, 670; [x] W. McFarlane, unpublished work; [y] Ref. 57; [z] Ref. 60; [ϕ] Ref. 61

4 Semi-empirical Correlations

In this section we consider some of the more important correlations that have been established, and their theoretical background.

A. ^{13}C—H Coupling Constants.—These are relatively easy to measure, and more data are available than for other coupling constants. Observed magnitudes all lie within the range 118—250 Hz,[1] and as regular changes occur when substituents are varied it is clear that all are of the same sign. This is positive.[19,20,22] A selection of values is presented in Table 2, and those for CH_4, C_2H_4, and C_2H_2 obey the relation[4]

$$J(^{13}C\text{–}H) = 500\,\alpha_C^2 \qquad (7)$$

where α_C^2 is the *s*-character of the C–H hybrid orbital. This dependence on the hybridization of carbon follows directly from equation (6), and was also derived more simply by Muller and Pritchard[4] using molecular orbital theory, and by Gutowsky and Juan[5] from valence bond theory. Equation (7) can be used to calculate values of α_C^2 in the other compounds, and the results are presented in column three of Table 2. Whilst the values obtained appear reasonable for methane and the unsaturated hydrocarbons, they imply rather unusual inter-bond angles in some of the halogenated derivatives, *e.g.* $CHCl_3$. This discrepancy can be accounted for[35] by the concept of bent bonds; that is, the inter-orbital angles (which reflect the true state of hybridization of an atom) may not be the same as the observed interbond angles. It has been pointed out[5] that there is

Table 2 *Selected values of* $^1J(^{13}C\text{–}H)$ *and related parameters*

Compound	$^1J(^{13}C\text{–}H)$ (Hz) [a]	α_C^2	$(Z_K/Z_{CH_4})^3$ [b]	*r*(C–H) (Å)
CH_4	125	0·250	—	—
C_2H_6	126	0·252	—	1·105[c]
C_2H_4	157	0·333	—	1·086[c]
C_2H_2	249	0·500	—	1·059[c]
C_6H_6	159	0·336	—	1·084[c]
MeCN	136	0·272	—	1·102[d]
MeOH	141	0·282	—	—
MeF	149	0·298	1·213	1·097[d]
MeCl	150	0·300	1·181	1·096[d]
MeBr	152	0·304	1·166	1·095[d]
MeI	151	0·302	1·141	1·096[d]
CH_2Cl_2	178	0·356	1·383	1·082[d]
$CHCl_3$	209	0·418	1·607	1·073[d]
CHF_3	238	0·476	1·725	—

[a] Reference 5; [b] Reference 7; [c] Reference 54; [d] Reference 35.

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[35] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 1471.

no combination of atomic *s* and *p* orbitals which can account for the measured interbond angles in methylene dichloride.

If the ^{13}C–H coupling constant does depend solely on the state of hybridization of the carbon atom then it should be simply related to the C–H length.[36] For substituted methanes the empirical equation

$$r(\text{C–H}) = 1{\cdot}1597 - 0{\cdot}000417 \times J(^{13}\text{C–H}) \tag{8}$$

where r(C–H) is the bond length in Angstrom units, has been found.[35] Some observed values of r(C–H) are included in Table 2, and in general agreement is good unless the carbon atom has very electronegative substituents. A correction for this has been proposed.

All of the above discussion is based on the assumption that bond polarities have little effect upon the coupling constants. Muller and Pritchard[35] claim that this is indeed so, and point to the similarities of the values of $J(^{13}$C–H) in the methyl halides, where the C–X bond polarities vary considerably, as evidence. It is clear from equation (6) however, that any factor which influences $|\psi_{\text{C}(2s)}(0)|^2$ (or $|\psi_{\text{H}(1s)}(0)|^2$, but this will normally be a second-order effect) will affect $J(^{13}$C–H). This point was noted by Shoolery,[6] and Grant and Litchman[7] show that the expression for the coupling constant can be written as

$$J_{\text{K}} = \left(\frac{\Delta E_{\text{CH}_4}}{\Delta E_{\text{K}}}\right)\left(\frac{N_{\text{K}}}{N_{\text{CH}_4}}\right)^2\left(\frac{\alpha_{\text{K}}}{\alpha_{\text{CH}_4}}\right)^2\left(\frac{Z_{\text{K}}}{Z_{\text{CH}_4}}\right)^3 \times 125 \text{ Hz.} \tag{9}$$

where J_{K} is $J(^{13}$C–H) in compound K, ΔE_{K} is the mean excitation energy for the C–H bonds, N_{K} is a bond normalization constant that differs little from unity, and Z_{K} is the effective nuclear charge of the carbon atom. Z_{K} can be estimated by considering the degree of charge transfer between carbon and its substituents. Electronegative groups will increase $(Z_{\text{K}}/Z_{\text{CH}_4})^3$ and some calculated values are given in Table 2; these are adequate to explain the gross trends observed in $J(^{13}$C–H), and it is claimed that variations of α_{C}^2 are relatively unimportant. Some experimental support for this view is provided by an observed correlation[37] between C–H stretching force constants and $J(^{13}$C–H). It can be shown theoretically that the force constant should depend on C–H bond polarity (which will in turn depend on the electronegativity of the other groups attached to carbon) but not directly on the carbon atom hybridization. Huheey[38] finds extremely good correlation between $J(^{13}$C–H) in halogenated methanes and the electronegativity of the substituents when orbital electronegativities[39] are used. That is, the effect of varying orbital occupancy upon different orbitals of the same atom is taken into account. Douglas[40] has pointed out that there is correlation between $J(^{13}$C–H) in CH$_3$X and the electronegativity of X within a particular period of the periodic table, but that the linear plots so obtained are of different slopes. He concludes that while factors

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[36] N. Muller, *J. Chem. Phys.*, 1962, **36**, 359.

[37] T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, 1966, **44**, 2238.

[38] J. E. Huheey, *J. Chem. Phys.*, 1966, **45**, 405.

[39] J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

[40] A. W. Douglas, *J. Chem. Phys.*, 1966, **45**, 3465.

other than C–H bond *s*-character can affect C–H coupling constants, consideration of changes of hybridization cannot be neglected.

The present position is that variations of $J(^{13}C–H)$ can be accounted for by changes in *s*-character if the electronegativity of the substituents varies little (*e.g.* amongst different saturated and unsaturated hydrocarbons), and by changes in electronegativity if the bulk of the substituents is roughly constant. The two factors are actually related, and if both vary significantly then both must be considered. This has been done seldom.

On a purely empirical level Malinowsky[41] has observed that for molecules of the type CHXYZ, the C–H coupling constants are given by the additivity relationship

$$J(^{13}\mathrm{C{-}H}) = \zeta_X + \zeta_Y + \zeta_Z \qquad (10)$$

The Malinowsky parameter ζ_K is the contribution to the coupling constant from substituent K, and can be found readily from the corresponding methyl derivative CH_3K, since

$$\zeta_K = J(^{13}\mathrm{C{-}H})_K - 2\zeta_H \qquad (11)$$

where $\zeta_H = 41{\cdot}7$ Hz. Agreement between predicted and observed values is generally good, unless highly electronegative groups are present.[42]

B. $^{13}C—^{19}F$ Coupling Constants.—As with C–H couplings the range[1] of these is such as to suggest that all are of the same sign, and in several cases this has been shown to be negative,[43] as Pople and Santry predict.[3] Some values are given in Table 3, together with the magnitudes of the corresponding $^{13}C–^{12}C$ isotopic shifts[44] of the ^{19}F resonance frequency. The two parameters are related by equation (12) for the saturated compounds, and

$$\Delta\phi(^{13}\mathrm{C}–^{12}\mathrm{C}) = +\,0{\cdot}007 + 4{\cdot}36 \times 10^{-4} J_{CF}\ \text{p.p.m.} \qquad (12)$$

there is a similar relation for unsaturated compounds. The significance of these is not fully understood, but they may depend on the changes in vibrational amplitudes brought about by isotopic substitution. The changes in $J(^{13}C–^{19}F)$ caused by variations of the substituents attached to carbon are similar to those found for $^{13}C–H$ couplings. Since the two types of coupling constant are of opposite sign this indicates that they must arise from variations of α_C^2 or $|\psi_{C(2s)}(0)|^2$ (changes in the corresponding quantities for H or F should be an order of magnitude less), and not of π_{CF}. This in turn suggests that ϵ_{2s} for fluorine must be sufficiently low for it, rather than β_{CF}, to be the dominating factor in π_{CF}. On the other hand, changes in solvent parameters have been observed[24] to have opposite effects upon the magnitudes of $J(^{13}C–^{19}F)$ and

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[41] E. R. Malinowsky, *J. Amer. Chem. Soc.*, 1961, **83,** 4479.

[42] N. Muller and P. I. Rose, *J. Amer. Chem. Soc.*, 1962, **84,** 3973.

[43] G. V. D. Tiers, *J. Phys. Chem.*, 1963, **67,** 1373.

[44] S. G. Frankiss, *J. Phys. Chem.*, 1963, **67,** 752.

Table 3 *Selected values of* $^1J(^{13}C–^{19}F)$ *and the isotopic* $^{13}C–^{12}C$ *fluorine chemical shift*[a]

Compound	$^1J(^{13}C–^{19}F)$ (Hz)	ϕ ($^{13}C–^{12}C$) (p.p.m.)
CH_3F	158	0·067
CH_2F_2	232	0·143
C_6H_5F	244	—
CF_4	257	0·105
$(CF_3)_2O$	265	0·116
CF_3H	272	0·133
CF_3Cl	299	0·152
$CFCl = CCl_2$	303	0·112
CF_3Br	324	0·152
CF_2Cl_2	325	0·164
$CFCl_3$	337	0·192
CF_3I	344	0·132
CF_2Br_2	358	0·168

[a] Reference 1.

$J(^{13}C–H)$ in the same compound. An alteration in π_{CF} must be dominant here, and this seems reasonable as this parameter should be sensitive to changes in electric field strength near the fluorine atom. Attempts[45] to predict $^{13}C–^{19}F$ coupling constants by using Malinowski parameters have been reasonably successful, although the appropriate ζ values are larger than the corresponding ones for $^{13}C–H$ coupling constants. This again indicates that variations of $\alpha_C{}^2$ and/or $\psi_{C}{}^{2}{}_{(2s)}$ are the main factor.

C. Coupling between ^{13}C and Other Elements.—Most studies[15,16,46,47] of this type of coupling have used double resonance techniques, but a few results have been obtained from single ^{13}C resonance with enriched samples.[9,10,31] Values of the reduced coupling constants C–X in compounds for different X are given in Table 4. For the Group IV elements it is probably reasonable to use equation (6) and we see that K will depend on the hybridization of both C and X. The values of $J(^{13}C–H)$ in the tetramethyl compounds Me_4X indicate that $\alpha_C{}^2$ changes as we descend the group,[48] and this can be allowed for by using equation (7). The *s*-character of the carbon hybrid orbital used for the C–X bond can thus be estimated, and K can then be corrected to give K^*, the reduced coupling constant between sp^3 hybridized C and X. The values of K^* so obtained are found to be linearly related to the atomic number of X; this is reasonable since values of $|\psi_{X(ns)}(0)|^2$ do increase with increasing atomic number. According to

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[45] R. K. Harris, *J. Phys. Chem.*, 1962, **66**, 768.
[46] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 528.
[47] H. Dreeskamp, *Proc.* 13*th Colloque Ampere*, Leuven, 1964, 400.
[48] W. McFarlane, *Mol. Phys.*, 1967, **13**, 587.

Table 4 *Coupling constants involving carbon*

Compound	X	$^1J(^{13}C–X)$ (Hz)	$^1K(C–X) \times 10^{-20}$ (cm.$^{-3}$)	*Ref.*
CH_4	^1H	+125	+42	30
C_2H_6	^{13}C	+35	+46	31
MeCN	^{15}N	−17·5	+57	Table 1 (*o*)
CF_4	^{19}F	−257	−91	43
Me_4Si	^{29}Si	−52	+87	16
Me_4Sn	^{119}Sn	−330	+302	46
Me_4Pb	^{207}Pb	+250	+395	48
Me_3P	^{31}P	−14	−11·5	52
Me_4P^+	^{31}P	+55·5	+45	52
Me_2Se	^{77}Se	−62	−108	55
Me_2Te	^{125}Te	+162	−170	55
Me_2Cd	^{113}Cd	−536	+803	51
Me_2Hg	^{199}Hg	+687	+1,280	15

Reeves[49] the correlation should be between K (or possibly K^*) and $Z_X{}^2$, because the latter can be related to $|\psi_{X(ns)}(0)|^2$ in certain cases. The main objections to the correction procedure outlined above are that it ignores the effects of changing the effective nuclear charges of C and X, and no account is taken of unequal sharing of electron density by the different orbitals of the same atom. Dreeskamp and Stegmeier[50] note linear relations between log K, log Z_X and log $\psi_{X(ns)}{}^2$ for the Group IV elements, and conclude the coupling is dominated by the contact interaction. Most of the other couplings involving the less electronegative elements support the idea of dominance by the Fermi contact interaction, although they fall less readily into groups which are convenient for comparison purposes.[51]

The sign of K(P–C) depends on the valence of phosphorus,[52] and changes in it are accompanied by changes in ^2K(P . . . H) in the opposite direction.[53] In this case it is probably true that the coupling constant can be used to assess the hybridization of phosphorus, because the sign reversal must arise from a variation of π_{PC}, and this will be governed by β_{PC} which depends on the *s*-character of the P–C bond. The situation is not however analogous to that for C–H coupling constants. Furthermore, changes in the valence of phosphorus are known to be accompanied by alterations in the interbond angles.[54] In P^{III} compounds these are rather small (low *s*-character, negative coupling constants) while in P^V compounds they are close to tetrahedral (large *s*-character, positive coupling constants).

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[49] L. W. Reeves, *J. Chem. Phys.*, 1964, **40**, 2132.

[50] H. Dreeskamp and G. Stegmeier, *Z. Naturforsch.*, 1967, **22a**, 1458.

[51] H. Dreeskamp and K. Hildebrand, *Z. Naturforsch.*, 1968, **23a**, 940.

[52] W. McFarlane, *Chem. Comm.*, 1957, 58; *Proc. Roy. Soc.*, 1968, *A.*, **306**, 185.

[53] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Comm.*, 1966, 89.

[54] A. F. Wells, 'Structural Inorganic Chemistry', Oxford Univ. Press, 1962, p. 642.

K(Se–C) is negative,[55,56] relatively small (Se is a third-row element, so $|\psi_{Se(4s)}(0)|^2$ is correspondingly large) and apparently insensitive[55] to changes in valence. However this last feature may be because little rehybridization accompanies the formation of Me_3Se^+ from Me_2Se, as the ion still has a lone pair of electrons which could occupy an orbital of high *s*-character. In this connexion the change of effective nuclear charge of the selenium atom seems to be unimportant.

D. Couplings Involving ^{19}F.—Numerical values are in Table 5, and in all cases for which the sign determination has been made *K* is negative,[43,57–61] although in BF_4^- a zero coupling constant has been observed.[62] The most extensive

Table 5 *Coupling constants involving* ^{19}F *in symmetrical species*

Compound	X	$^1J(^{19}F–X)$ (Hz)	$^1K(F–X) \times 10^{-20}$ (cm.$^{-3}$)
HF	^{1}H	615	54·5
BF_3	^{10}B	−10	−2·8
NF_3	^{14}N	160	195
PF_3	^{31}P	−1,441	−314
PF_5	^{31}P	−916	−200
BeF_4^{2-}	^{9}Be	40	25
BF_4^-	^{10}B	*ca.* 0	0
CF_4	^{13}C	−257	−91
NF_4^+	^{14}N	234	285
SiF_4	^{29}Si	+178	−79
GeF_4	^{73}Ge	179	455
SiF_6^{2-}	^{29}Si	+110	−49
SnF_6^{2-}	^{119}Sn	+1,555	−368
SbF_6^-	^{121}Sb	1,843	687
TeF_6	^{125}Te	+3,688	−1,030
SeF_6	^{77}Se	1,400	645
AsF_6^-	^{75}As	930	438
PF_6^-	^{31}P	−710	−154
MoF_6	^{95}Mo	44	59
WF_6	^{183}W	48	103

Signs are quoted only when established experimentally.

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[55] W. McFarlane, *Mol. Phys.*, 1967, **12,** 243.

[56] H. Dreeskamp and G. Pfisterer, *Mol. Phys.*, 1968, **14,** 295.

[57] S. L. Danyluk, *J. Amer. Chem. Soc.*, 1965, **87,** 2300.

[58] R. R. Dean and W. McFarlane, *Chem. Comm.*, 1967, 840; S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Amer. Chem. Soc.*, 1967, 4544.

[59] E. B. Whipple, T. H. Brown, T. C. Farrar, and T. D. Coyle, *J. Chem. Phys.*, 1965, **42,** 1841.

[60] W. McFarlane and R. J. Wood, *Chem. Comm.*, 1969, 000.

[61] G. W. Fraser, R. D. Peacock, and W. McFarlane, to be published.

[62] R. J. Gillespie and J. S. Hartman, *J. Chem. Phys.*, 1966, **45,** 2712; R. J. Gillespie, J. S. Hartman and M. Parekh., *Canad. Journ. Chem.*, 1968, **46,** 1601.

correlations are those found by Reeves and co-workers.[63,64] In series of isostructural and isoelectronic molecules or ions, such as SnF_6^{2-}, SbF_6^-, TeF_6, or SF_6, SeF_6, TeF_6, they find linear relationships between K_{FX} and Z_X^2. These are paralleled by similar relationships between $|\psi_{X(ns)}(0)|^2$ and Z_X^2, so the variations appear to be due to differences in valence *s*-electron density at the nucleus X. In particular the rather small values found for K_{FX} when X is a transition element are ascribed to small values of $|\psi_{X(ns)}(0)|^2$ in these cases. The straight lines obtained do not pass through the origin, so for low atomic number the variation of π_{FX} begins to dominate. This introduces the possibility of a change in the sign of *K* in a given series, but only for NF_4^+, CF_4, BF_4^-, BeF_4^{2-} does this seem likely. As mentioned earlier, K_{FB} in BF_4^- can be zero under the appropriate conditions,[62] so K_{FBe} is probably of opposite (*i.e.* positive) sign to K_{FC} and K_{FN} in these tetrahedral species. Similar reasoning was used to predict that K_{FTe} and K_{FSn} are of like sign, and this has been demonstrated to be so.[61]

The numerical values of $J(^{19}F-^{129}Xe)$ in XeF_2, XeF_4, $XeOF_4$ are 5690, 3864, and 1163 Hz respectively.[65] According to one theory[66] of the bonding in these compounds the hybridizations of xenon should be *ps*, p^2ds, and p^3d^2s, corresponding to *s*-characters 1/2, 1/4 and 1/6 respectively.[67] The trend in the coupling constants agrees with this, although the numerical fit is rather poor. The signs of these couplings are unknown and variations of π_{FXe} may account for some of the discrepancy.

E. Couplings involving ^{31}P.— P–P Coupling constants in compounds with a direct bond between two phosphorus atoms are very interesting because the 3*s* electrons of phosphorus are of such an energy that $\pi_{PP'}$ is dominated by $\beta_{PP'}$, and alteration of the substituents can change the sign of the coupling constant. Some values of $J(^{31}P-^{31}P)$ in different compounds are given in Table 6. Only in a few cases[68,69] are experimental signs known, but it has been shown that rationality may be achieved if the signs in parentheses are used.[69] A plot of the coupling constant against $\beta_{PP'}$ (estimated on intuitive grounds from the electronegativities of the substituents) is a smooth curve, with maximum gradient near $J(^{31}P-^{31}P) = 0$. The positive couplings occur for large $\beta_{PP'}$, *i.e.* high *s*-character for the P–P bond.

Coupling between phosphorus and transition metals has received considerable attention because of the light that might be thrown on π-bonding. $J(^{31}P-^{195}Pt)$ is about +3500 Hz in *cis*-$(R_3P)_2PtCl_2$ (R = Alkyl) and + 2500 Hz in the *trans*-

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[63] L. W. Reeves, *J. Chem. Phys.*, 1964, **40**, 2423; P. T. Inglefield and L. W. Reeves, *ibid.*, 1964, **40**, 2425.

[64] J. Feeney, R. Haque, L. W. Reeves, and C. P. Yue, *Canad. J. Chem.*, 1968, **46**, 1389.

[65] T. H. Brown, E. B. Whipple, and R. H. Verdier, *Science*, 1963, **140**, 178; *J. Chem. Phys.*, 1963, **38**, 3029; A. C. Rutenberg, *Science*, 1963, **140**, 993.

[66] L. C. Allen, *Science*, 1962, **138**, 892; *J. Amer. Chem. Soc.*, 1962, **84**, 4344.

[67] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 2285.

[68] R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282; R. K. Harris and E. G. Finer, *Mol. Phys.*, 1967, **13**, 65; R. M. Lynden-Bell, *Trans. Faraday Soc.*, 1961, **57**, 888.

[69] R. K. Harris and E. G. Finer, *Chem. Comm.*, 1968, 110.

Table 6 *Coupling constants between phosphorus atoms connected by a direct bond*[a]

Compound	$^1J(^{31}P-^{31}P)$ (Hz.)[b]
LiEtP–PPhEt	(−) 396
$Et_2P-P(CycloC_6H_{11})_2$	(−) 282
$Ph_2P-P(CycloC_6H_{11})_2$	(−) 224
$Me_2P(S)-PMe_2$	− 220
Me_2P-PMe_2	− 180
H_2P-PH_2	(−) 108
$Me_2P(S)-P(S)Me_2$	± 19
$Et_2P(S)-P(S)(CycloC_6H_{11})_2$	± 69
F_2P-PF_2	+ 227
$[O_3P-P(H)O_2]^{3-}$	+ 465·5
$(EtO)_2P(S)-P(O)(OEt)_2$	(+) 583

[a] Reference 69.
[b] Signs placed in parentheses are regarded as probable for the reasons given in the text; the others have been established experimentally.

isomer, and this was originally interpreted as showing that $d_\pi-p_\pi$ bonding between Pt and P contributes to the coupling mechanism. Similarly, the much larger values of the coupling constant found in phosphite complexes (phosphites are normally regarded as being especially good π-bonding ligands) were attributed to greater π-bonding. However, comparable differences between *cis*- and *trans*-isomers are observed in Pt^{IV} complexes in which π-bonding is supposed to be much less important, and the original workers now believe[34] that a mechanism involving only the σ-bonds is responsible for the difference in coupling constants. Indeed, the existence of any π-bonding in these complexes has been questioned,[70] and the *trans*-effect, for example, is claimed to arise from a re-hybridization of the platinum σ-orbitals in response to a change in the σ-orbitals of the ligand.

There is a reasonable correlation[71] between $J(^{31}P-^{183}W)$ and the C–O stretching frequencies in $R_3PW(CO)_5$ (R = alkyl, aryl, alkoxy, *etc.*) which is in the direction (if the coupling constant is positive) to be expected if the conrolling factor is π-bonding. However, it has been shown[72] that changes in C–O frequencies in compounds of this type can be explained solely by variations in the σ-donor ability of the ligand. Furthermore, the approach of Grant and Litchman[7] (equation 9) can presumably be applied to these couplings, and the changes of $J(^{31}P-^{183}W)$ when R_3P is replaced by $(RO)_3P$ are of about the size to be expected if a variation in the effective nuclear charge of phosphorus is the main factor. This is equivalent to saying that the σ-donor ability of the ligand is dominant. It is clear that more work must be done on these systems.

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[70] L. M. Venanzi, *Chemistry in Britain*, 1968, 162.
[71] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 1967, **89**, 5573; S. O. Grim, P. A. McAllister, and R. M. Singer, *Chem. Comm.*, 1969, 38.
[72] R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 1968, **7**, 959.

5 Conclusion

Recent experimental advances, notably in double resonance techniques,[13] are making data on coupling between the nuclei of directly bound elements readily available. The results can be understood qualitatively in terms of domination by the Fermi contact interaction, and in simple cases reasonable quantitative agreement with MO theory is obtained.[3] Three situations can be distinguished: (i) Neither atom has valence *s*-electrons of low energy. Equation (6) will then hold; the reduced coupling constant will be positive, and will depend on the effective nuclear charge of each atom and the *s*-character of the orbitals used to form the bond. (ii) One atom has valence *s*-electrons of low energy. Equation (5) must be used; the coupling constant will be negative, and its magnitude will be related to *s*-character and effective nuclear charge as under (i). (iii) The valence *s*-electrons are of moderately low energy. Equation (5) must again be used; but the sign of the coupling constant will depend on π, which in turn will be dominated by β, the resonance integral between the valence *s*-orbitals of each atom. Thus the sign will be very sensitive to changes in the substituents on the two atoms.[69]

Measurements of coupling constants can therefore be used to estimate hybridization and/or effective nuclear charge, and so assess theories of chemical bonding. They also have diagnostic value. For example, *cis*- and *trans*-isomers of platinum complexes may be readily distinguished,[34,73] and the magnitude of $J(^{13}C-^{19}F)$ in CF_3SNCO strongly indicates a direct CF_3–S bond.[45]

I wish to thank Professor D. H. Whiffen, F.R.S., for discussions, and suggestions.

[72] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.