6

THEORETICAL CONSIDERATIONS: SPIN–SPIN COUPLING

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6.1 The Spin–Spin Coupling Tensor

The indirect electron-coupled spin-spin interaction between two nuclei can be written as an interaction energy:

$$E_{NN'} = h\mathbf{I}_N \cdot \underline{\mathbf{J}} \cdot \mathbf{I}_{N'} \tag{6-1}$$

in which J coupling is described by a tensor that is anisotropic. Only the isotropic average is observed in liquids and gases. In oriented molecules, such as small molecules dissolved in liquid crystals, in powders, or in single crystals, splittings are observed that depend on the components of the sum of the dipolar and indirect coupling tensors (see Chapter 4). In molecules in which the interspin axis coincides with a high-symmetry axis of the molecule, the coupling tensor is strictly axially symmetric and the two independent components may be taken as $\underline{\mathbf{J}}_{\parallel}$ and $\underline{\mathbf{J}}_{\perp}$. The relative anisotropy in $\underline{\mathbf{J}}$ is $(\underline{\mathbf{J}}_{\parallel} - \underline{\mathbf{J}}_{\perp})/J_{\text{iso}}$. If the coupling is dominated by the electrons that directly take part in a σ bond between the coupled nuclei, the $\underline{\mathbf{J}}$ tensor should be nearly axially symmetric. Appreciable $\underline{\mathbf{J}}$ anisotropy has been observed, especially for nuclear pairs with high atomic numbers. For example, ^1J(PP) in tetraethyldiphosphine (in which the isotropic coupling constant has an absolute value of 30 Hz), one possible assignment yields nearly axial symmetry with an anisotropy of +2980 Hz[1]; ie, the electron-coupled interaction favors antiparallel spins when the external magnetic field is along the bond. In $Ag_4P_2O_6$, $J_{\parallel} - J_{\perp} \simeq 800 \pm 80$ Hz, while the isotropic coupling constant ^1J(PP) = 500 Hz.[2] In $Me_3P{=}Se$, ^1J(PSe) = −700 Hz, $J_{\parallel} - J_{\perp} = -680 \pm 180$ Hz.[3] The relative anisotropy of J increases with an increase in atomic number, enhanced by relativistic effects.[4]

When comparing magnitudes and signs of coupling between various nuclei, it is convenient to write the interaction energy in terms of the nuclear magnetic moments:

$$E_{NN'} = K\mu_N\mu_{N'} = hJI_NI_{N'} \tag{6-2}$$

so that the reduced coupling constant, $K(NN')$ is related to the measured coupling constant by:

$$K(NN') = \frac{4\pi^2 J(NN')}{h\gamma_N\gamma_{N'}} \tag{6-3}$$

where K is of the order of $1 \times 10^{19}\ \mathrm{m^{-2}\cdot kg\ s^{-2}\ A^{-2}}$.

6.2 Mechanisms of Spin–Spin Coupling

6.2.1 Theoretical Formulation

Ramsey described the electron-coupled interactions between nuclear spins in terms of the nonrelativistic hyperfine Hamiltonian[5]:

$$\mathscr{H} = \mathscr{H}_{1a} + \mathscr{H}_{1b} + \mathscr{H}_2 + \mathscr{H}_3 \tag{6-4}$$

The terms that describe the interaction between the nuclear magnetic moments and the orbital motion of the electrons are:

$$\mathscr{H}_{1a} = e\hbar\mu_B\left(\frac{\mu_0}{4\pi}\right)^2 \sum_{NN'}\gamma_N\gamma_{N'}\sum_k r_{kN}^{-3}r_{kN'}^{-3} \times [(\mathbf{I}_N\cdot\mathbf{I}_{N'})(\mathbf{r}_{kN}\cdot\mathbf{r}_{kN'}) - (\mathbf{I}_N\cdot\mathbf{r}_{kN'})(\mathbf{I}_{N'}\cdot\mathbf{r}_{kN})] \tag{6-5}$$

$$\mathscr{H}_{1b} = \frac{2\mu_B\hbar}{i}\frac{\mu_0}{4\pi}\sum_N\gamma_N\mathbf{I}_N\cdot\sum_k r_{kN}^{-3}(\mathbf{r}_{kN}\times\nabla_k) \tag{6-6}$$

where μ_B is the Bohr magneton, $\mathbf{r}_{kN}$ is the radius vector from electron k to nucleus N, and the other symbols conform to standard usage. The term that describes the dipole-dipole interaction between the nuclear and electron spins is:

$$\mathscr{H}_2 = 2\mu_B\hbar\frac{\mu_0}{4\pi}\sum_N\gamma_N\sum_k[3(\mathbf{S}_k\cdot\mathbf{r}_{kN})(\mathbf{I}_N\cdot\mathbf{r}_{kN})r_{kN}^{-5} - (\mathbf{S}_k\cdot\mathbf{I}_N)r_{kN}^{-3}] \tag{6-7}$$

The Fermi contact interaction involving the Dirac delta function $\delta(\mathbf{r}_{kN})$ describes the interaction between nuclear and electron spins due to the finite density of the electron at the nucleus.

$$\mathscr{H}_3 = \frac{16\pi\mu_B\hbar}{3}\frac{\mu_0}{4\pi}\sum_N\gamma_N\sum_k\delta(\mathbf{r}_{kN})\mathbf{S}_k\cdot\mathbf{I}_N \tag{6-8}$$

All the interactions in the Hamiltonian given above are small compared with the electrostatic terms in the molecular Hamiltonian. Therefore, perturbation theory may be applied. The terms that are bilinear in the coupled nuclear spins can be selected from the perturbation energy and equated to $h\mathbf{I}_N\cdot\underline{\mathbf{J}}_{NN'}\cdot\mathbf{I}_{N'}$. The term $\mathscr{H}_{1a}$ is already a sum of terms of the form $h\mathbf{I}_N\cdot\underline{\mathbf{J}}_{NN'}^{(1a)}\cdot\mathbf{I}_{N'}$. The other terms are linear in the nuclear angular momentum, so that they contribute to the electron-coupled nuclear spin–nuclear spin interaction in second-order perturbation theory. The sum of all the terms gives the total coupling constant tensor:

$$\underline{\mathbf{J}} = \underline{\mathbf{J}}^{(1a)} + \underline{\mathbf{J}}^{(1b)} + \underline{\mathbf{J}}^{(2)} + \underline{\mathbf{J}}^{(3)} + \underline{\mathbf{J}}^{(4)} \tag{6-9}$$

where $\underline{\mathbf{J}}^{(1a)}$ is called the diamagnetic orbital contribution to the coupling and depends only on the unperturbed ground state of the molecule:

$$\underline{\mathbf{J}}^{(1a)} = \frac{4}{h}e\hbar\mu_B\left(\frac{\mu_0}{4\pi}\right)^2\gamma_N\gamma_{N'}\left\langle 0\left|\sum_k(\mathbf{r}_{kN}\cdot\mathbf{r}_{kN'})r_{kN}^{-3}r_{kN'}^{-3}\right|0\right\rangle \tag{6-10}$$

The term $\underline{\mathbf{J}}^{(1b)}$ is called the (paramagnetic) orbital contribution (OB) and corresponds to second-order energy correction due to $\mathscr{H}_{1b}$:

$$\underline{\mathbf{J}}^{(1b)} = \left(\frac{-2}{h}\right)(2\mu_B\hbar)^2\left(\frac{\mu_0}{4\pi}\right)^2\gamma_N\gamma_{N'}\sum_n({}^1E_n - E_0)^{-1} \times\left\langle 0\left|\sum r_{kN}^{-3}\nabla_k\right|n\right\rangle\left\langle n\left|\sum_j r_{jN'}^{-3}(\mathbf{r}_{jN'}\times\nabla_j)\right|0\right\rangle \tag{6-11}$$

$\underline{\mathbf{J}}^{(2)}$ is called the spin-dipolar (SD) term coming from $\mathscr{H}_2$:

$$\underline{\mathbf{J}}^{(2)} = \left(\frac{-2}{h}\right)(2\mu_B\hbar)^2\left(\frac{\mu_0}{4\pi}\right)^2\gamma_N\gamma_{N'}\sum_n({}^3E_n - E_0)^{-1} \times\left\langle 0\left|\sum_k 3r_{kN}^{-3}(\mathbf{S}_k\cdot\mathbf{r}_{kN})\mathbf{r}_{kN} - r_{kN}^{-3}\mathbf{S}_k\right|n\right\rangle \times\left\langle n\left|\sum_j 3r_{jN'}^{-3}(\mathbf{S}_j\cdot\mathbf{r}_{jN'})\mathbf{r}_{jN'} - r_{jN'}^{-3}\mathbf{S}_j\right|0\right\rangle \tag{6-12}$$

and $\underline{\mathbf{J}}^{(3)}$ is the Fermi contact term:

$$\underline{\mathbf{J}}^{(3)} = \left(\frac{-2}{h}\right)\left(\frac{16\pi\mu_B\hbar}{3}\right)^2\left(\frac{\mu_0}{4\pi}\right)^2\gamma_N\gamma_{N'}\sum_n({}^3E_n - E_0)^{-1} \times\left\langle 0\left|\sum_k\delta(r_{kN})\mathbf{S}_k\right|n\right\rangle\left\langle n\left|\sum_j\delta(r_{jN'})\mathbf{S}_j\right|0\right\rangle \tag{6-13}$$

Finally, $\underline{\mathbf{J}}^{(4)}$ is a cross-term between the spin-dipolar and contact Hamiltonians, which together with $\underline{\mathbf{J}}^{(1b)}$ and $\underline{\mathbf{J}}^{(2)}$ contributes to the anisotropy of the coupling tensor. The cross-term $\underline{\mathbf{J}}^{(4)}$ has a zero isotropic average, $\underline{\mathbf{J}}^{(3)}$ is purely isotropic, and all the other terms have isotropic and anisotropic parts.

The form of the magnetic dipole hyperfine Hamiltonian given in eqs. (6-5) to (6-8) is correct for a point nucleus at the nonrelativistic limit. Relativistic effects are important to consider in spin–spin coupling, which depends on electronic wave functions near nuclei where the electrons move rapidly. Relativistic effects on the electronic structure of atoms and molecules consist of a contraction of s and p shells, the spin–orbit splitting of the non-s shells, and the relativistic self-consistent field expansion of d and f shells.[6] The contraction of s and p shells leads to larger hyperfine interactions for atoms and molecules than are given by eq. (6-8). In addition the spin–orbit splitting of the non-s shells in relativistic atoms means that Russell–Saunders coupling, which is assumed in Ramsey's formulation of the theory, no longer holds for such systems. Pyykkö has derived a relativistic analogue to Ramsey's theory, using a relativistic hyperfine Hamiltonian and j–j or intermediate coupling. Equations (6-6) to (6-8) are replaced by a single hyperfine Hamiltonian, and (6-5) in relativistic theory is replaced by a second-order contribution. The relativistic non-s electron terms in the coupling constant goes to the sum of $\underline{J}^{(1b)} + \underline{J}^{(2)}$ or (OB + SD) in the nonrelativistic limit. The relativistic s-orbital contribution is equivalent to the $\underline{J}^{(3)}$ (FC) term.

The relativistic spin densities for the heavy atoms are much larger than those calculated in eq. (6-8), since the corrections due to the s and p contraction can be large for heavy atoms. A correction of eq. (6-8) by a multiplicative factor $B(n, Z)$ depending on the principal quantum number n and the nuclear charge Z was suggested by Breit.[7] For example, for the 6s shell of lead, $B(6, 82)$ is 2.592; for the 5s shell of tin, $B(5, 50) = 1.348$.[8] This factor is roughly proportional to Z^2. For couplings involving the heavier nuclei, the relativistic effects can be very important. Since the ratio of Pb/C atomic s densities from the nonrelativistic values is 7.4, use of an uncorrected equation (eq. 6-8) would yield roughly this ratio of $^1K(\mathrm{PbH})/^1K(\mathrm{CH})$. Thus, the 23-fold change in $^1K(\mathrm{XH})$ in the XH_4 molecules in going from X = C to Pb can be reproduced only by including relativistic correction factors.[9]

6.2.2 Computation Schemes

The second-order perturbation equations, 6-10 to 6-13 as given by Ramsey, require knowledge of all the excited states of the molecule, including the continuum. Various approaches have been developed using truncated sets of excited state wave functions of varying degrees of sophistication. If we write the coupling constant as $J = (\mu_0/3\pi)^2\mu_B^2 h\gamma_N\gamma_{N'}K'$, or the reduced coupling as $K = (\frac{4}{9})\mu_0^2\mu_B^2K'$, the working equations for the different methods may be compared directly. In the following, K' for the Fermi contact term is given; the other terms can be written in analogous form.

The simplest MO theory of spin–spin couplings is that of McConnell[10]:

$$K' = s_N^2(0)s_{N'}^2(0)P_{s_Ns_{N'}}^2({}^3\Delta E)^{-1} \tag{6-14}$$

where the bond order is given by

$$P_{s_Ns_{N'}} = 2\sum_i^{\mathrm{occ}} c_{iN}c_{iN'},$$

$$s_N^2(0) = \langle s_N|\delta(r_{kN})|s_N\rangle$$

c_{iN} is the coefficient of the valence s orbital centered on N in the ith occupied orbital, and $^3\Delta E$ is some average ground state to triplet state excitation energy, chosen ad hoc. Pople and Santry used a sum-over-states (SOS) method[11]:

$$K' = s_N^2(0)s_{N'}^2(0)\pi_{NN'} \tag{6-15}$$

where the mutual polarizability of the orbitals on N and N' is given by

$$\pi_{NN'} = -4\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{unocc}} \frac{c_{iN}c_{aN}c_{iN'}c_{aN'}}{\varepsilon_a - \varepsilon_i},$$

where ε_i and ε_a are orbital energies of the occupied and the virtual molecular orbitals, respectively. This is the form most commonly used with semiempirical MO theories such as complete or incomplete neglect of differential overlap (CNDO or INDO), involving only valence atomic orbitals. This is a simplified version of the following equation[12]:

$$K' = -4\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{unocc}} ({}^3\Delta E_{i\to a})^{-1}\langle i|\delta(r_{kN})|a\rangle\langle a|\delta(r_{kN'})|i\rangle \tag{6-16}$$

where $^3\Delta E_{i\to a}$ is the excitation energy corresponding to the excitation of an electron from the orbital i to virtual orbital a, the resulting electron configuration being a triplet. Within the "uncoupled" framework, various degrees of configuration interaction (CI) in the zero-order wave function may be used. For example, Ditchfield and Murrell[13] used:

$$K' = -4\sum_n ({}^3\Delta E_n)^{-1}\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{unocc}}\sum_j^{\mathrm{occ}}\sum_b^{\mathrm{unocc}} d_{i\to a}^n d_{j\to b}^n\langle i|\delta(r_{kN})|a\rangle\langle b|\delta(r_{kN'})|j\rangle \tag{6-17}$$

where $d_{i\to a}^n$ is the coefficient of the singly excited ($i \to a$) configuration in the nth triplet state wave function, obtained by diagonalizing the Hamiltonian matrix in the basis of configurations, and $^3\Delta E_n$ is the nth eigenvalue.

In the coupled Hartree–Fock (CHF) and in the finite perturbation (FPT) methods, the Hartree–Fock equation for the molecular orbitals is solved in the presence of a perturbation, so that the first-order correction to the wave function is obtained directly[14]:

$$K' = s_N^2(0)s_{N'}^2(0)2P_{s_Ns_{N'}}^{(1)} \tag{6-18}$$

where the first-order density matrix is given by

$$P_{\lambda\nu}^{(1)} = \sum_{i}^{occ} (c_{i\lambda}^{(0)} c_{i\nu}^{(1)} + c_{i\lambda}^{(1)} c_{i\nu}^{(0)})$$

Here $c_{i\lambda}^{(0)}$ is the coefficient of the λth atomic orbital in the ith molecular orbital obtained by an SCF calculation. The term $c_{i\nu}^{(1)}$ is the first-order coefficient, which is determined by (a) evaluating matrix elements of $\mathscr{H}_3$ over the zero order molecular orbitals and solving the simultaneous equations that are coupled together (hence the name) by the electron repulsion terms (CHF), or by (b) computing SCF wave functions for finite values of nuclear magnetic moments and evaluating their derivatives in the limit of vanishing magnetic moments (FPT).

Inclusion of electron correlation by configuration interaction in both the zero-order and the first-order wave functions involves substantial computational effort. If the first-order correction to the wave function is expanded in an arbitrary set of triplet configurations $|\mu\rangle$, the coupling is then written as[15]:

$$K' = 8 \sum_{\mu} c_{\mu N}^{(1)} \left\langle \mu \left| \sum_{k} \delta(r_{kN'}) S_{zk} \right| 0 \right\rangle \tag{6-19}$$

where $c_{\mu N}^{(1)}$ is the coefficient of the excited triplet configuration μ in the first-order correction to the wave function due to the Fermi contact interaction at nucleus N. The sum is over all the singly and doubly excited triplet configurations that can be constructed from the SCF MOs, and $|0\rangle$ is the singlet wave function obtained by configuration interaction.

Valence bond methods have also been used[16]:

$$K' = \phi_N^2(0)\phi_{N'}^2(0) 2P_{NN'}^{PD} ({}^3\Delta E)^{-1} \tag{6-20}$$

where $\phi_N(0)$ is the electron density at nucleus N, and $P_{NN'}^{PD}$ is the Penney-Dirac bond order between atoms N and N', which is obtained by summing over valence bond structures.

The working equations shown above for the Fermi contact contribution are elegantly simple, and the orbital and spin-dipolar terms have analogous forms. The computational effort is determined largely by the size of the set of basis functions used to describe the unperturbed wave function. Excellent reviews of the methods of calculations of coupling constants, as well as results for specific systems published in the period 1969-1981 have been given by Kowalewski.[17]

6.2.3 *Relative Magnitudes of Orbital, Spin–Dipolar, Contact, and Correlation Contributions*

Although all terms of Ramsey's nonrelativistic theory are combined into only one equation in the relativistic theory of coupling constants, it is nevertheless possible to separate a "Fermi contact" part as the contribution involving the s atomic orbitals on both nuclei. In this, the relativistic ns spin densities $|\psi(0)|^2$ may be calculated from radial hyperfine integrals.[18] These relativistic s densities are shown in Figure 6-1 for selected nuclei. Calculations show that the terms involving these s densities almost invariably dominate one-bond couplings. The only exceptions found are the couplings between group VI atoms or between group VII atoms, such as Se—Se or I—I.[18]

The distinction between the (noncontact) OB and SD terms is relevant only for light atoms in which nonrelativistic theory is adequate. These terms involve r_N^{-3} integrals, which are expected to be small when hydrogen is involved. The SD term is usually small. The OB term is important for one-bond coupling across a multiple bond. For example, the calculated (nonempirical CHF) OB contributions to ^1J(CC) in C_2H_6, C_2H_4, and C_2H_2 are 0.2, −9.7, and 15.3 Hz,

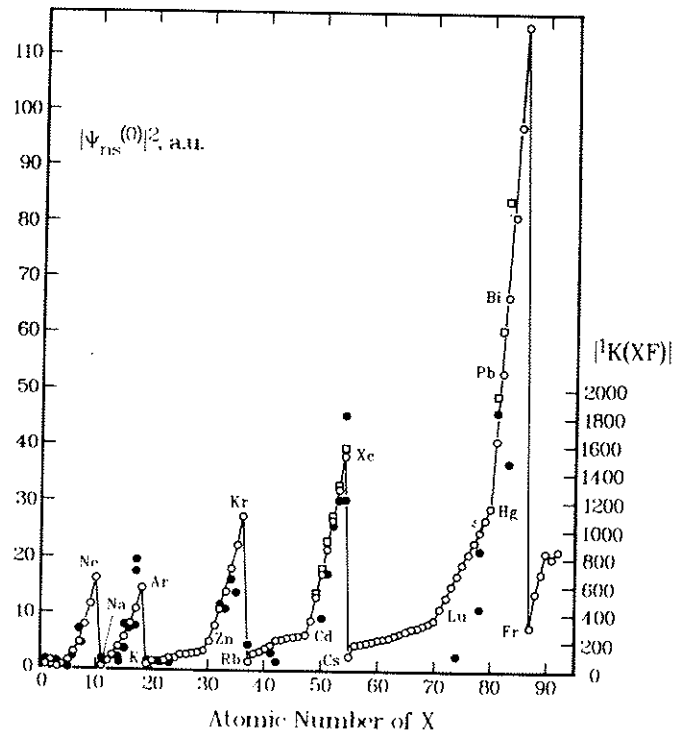

Figure 6-1 Electron densities at the X nucleus (left scale) for ground state atoms, corrected for relativistic effects using the Breit factors from ref. 8. More accurate relativistic values of densities are also shown for the heavier nuclei (open squares) where they differ significantly from the latter. Absolute values of ^1K(XF) observed in binary fluorides (right scale) show the same periodic behavior with atomic number of X.

TABLE 6-1. CALCULATED CONTRIBUTIONS TO THE ONE-BOND REDUCED COUPLING CONSTANT IN THE FIRST- AND SECOND-ROW HYDRIDES ($10^{19} M^{-2} \cdot KG\ S^{-2}\ A^{-2}$)

Compound	OB[a,b]	SD[a,b]	FC[c,d]	Correlation	Total	Experimental
CH_4	0.5	−0.1	49.0	−11.3	38.1	41.3
NH_3	2.4	−0.2	56.2	−12.3	46.1	50.0
OH_2	7.5	−0.4	51.3	−11.1	48.1	48.0
FH	17.4	−0.9	41.9	−11.2	47.2	46.9
AlH_3	−0.5	0.0	96.6[b]			
SiH_4	−0.2	−0.1	98.7	−18.3	79.7	84.9
PH_3	0.9	−0.4	45.7	−11.6	34.6	37.8
SH_2	4.5	−0.3	33.0	−5.3	31.7	
ClH	12.0	0.0	7.4	5.0	23.1	32.0

[a] Guest, M. F.; Saunders, V. R.; Overill, R. E. *Mol. Phys.* **1978**, *35*, 427.
[b] Guest, M. F.; Overill, R. E. *Chem. Phys. Lett.* **1980**, *73*, 612.
[c] Kowalewski, J.; Laaksonen, A.; Roos, B.; Siegbahn, P. *J. Chem. Phys.* **1979**, *71*, 2896.
[d] Kowalewski, J.; Laaksonen, A.; Saunders, V. R. *J. Chem. Phys.* **1981**, *74*, 2412.
[e] The correlation contribution is the difference between the Fermi contact term calculated at the CHF level and the calculation including configuration interaction.

respectively.[19] At the average energy approximation level both $J^{(1b)}$ and $J^{(2)}$ are nonvanishing for one-bond couplings only if a multiple bond exists between the coupled nuclei. Estimates of the dipolar and orbital contributions to ^1K(PSn) and ^1K(PPb) for certain formal hybridizations on P, Sn, and Pb show that these estimated noncontact terms are under 10% of typical experimental ^1K(PSn) and ^1K(PPb) values.[20] In transition metal complexes, which could have substantial π back-bonding between the coupled metal and ligand atoms, the dipolar and orbital contributions may have to be considered. Upper limits for the spin-dipolar term for one-bond couplings ^1K(XC) and ^1K(XF) in the absence of multiple bonds have been calculated for elements X = Li to Bi and displayed in periodic table form.[21]

The one-bond coupling in the first- and second-row hydrides (CH_4, NH_3, H_2O, HF, AlH_3, SiH_4, PH_3, H_2S, HCl) have been computed using nonempirical CHF and finite perturbation-configuration interaction methods, giving results that are in good agreement with experiment (see Table 6-1). The paramagnetic orbital term in ^1K(HX) increases rapidly when X moves to the right in the periodic table, whereas the diamagnetic orbital term and the SD term are always small. The sum of the Fermi contact term and the correlation contributions remains nearly the same for CH_4 to HF. Thus, the total ^1K(HX) remains nearly constant across the first row of X. For the second-row hydrides, on the other hand, the FC term decreases strongly in AlH_3 to HCl and the correlation term increases algebraically as X moves across the second row, negative for AlH_3 becoming positive for HCl. Relativistic calculations yield the same trends in ^1K(HX) for X in these two rows.[18] In addition, they reveal the trends in ^1K(HX) for the heavier X nuclei shown in Figure 6-2*a*.

^1K(HX)

H +42.9	B +20.8	C +41.3	N +50.3	O +48.5	F +46.9
	Al (+96.1)	Si +84.9	P +37.8	S (+28.5)	Cl +32
		Ge +232	As ±45 (+36)	Se +28.4	Br ±19 (−69)
		Sn +430	Sb (+5)	Te ±15.5 (−98)	I −33 (−223)
		Pb +938	Bi (−572)		

Figure 6-2*a*

^1K(CX)

H +41.3	B +4.85	C +49	N +14.7	O	F −57
Li +12.8		Si +83.3	P −11	S (+26)	Cl ±78.5
		Ge	As	Se −107	Br ±55
		Sn +300	Sb ±622	Te −169	I <96
	Tl +1096	Pb +396	Bi		

Figure 6-2*b*

$^1K(P^{III}X)/^1K(P^{IV,V,VI}X)$

H +37.8 / +112	B +28.5 / +84.2	C −11 / +76	N −120 / +54.8	O −23.2 / +182	F −314 / −154
		Si −43.7	P see Fig. 4	S / (+4)	Cl ∓252
		Ge	As	Se −221 / −752	Br ∓288
		Sn −460 / −119	Sb	Te / −1113	I
		Pb −131.5	Bi		

Figure 6-2*c*

$^1K(FX)$

H +46.9	B −23.1	C −91	N ∓195	O ∓196	F (+200)
Li +48		Si −79	P −314 −154	S ∓289	Cl +970 ±304
Na		Ge ∓455	As ∓438	Se ∓645	Br ±558
K ±60	In −865	Sn −546	Sb ∓687	Te −1030	I ±930 ±1210
Rb +210	Tl −2040	Pb	Bi ∓1485		
Cs +400					

Figure 6-2*d*

6.3 General Observations on the Signs and Magnitudes of *J*, and Their Theoretical Basis

It is generally observed that for a given pair of nuclei $^1K(XY) \gg {}^3K(XY) > {}^2K(XY) > {}^4K(XY)$ and that longer range couplings are two or more orders of magnitude smaller than one-bond couplings. These constants do not have mutually exclusive ranges. Nevertheless, this inequality is sufficiently widespread in a large variety of nuclei to be useful in making spectral assignments. It is also generally found that long-range couplings ^nJ decrease overall with increasing n, although the magnitudes for odd and even n may be reversed, ie, $^nJ > {}^{n-1}J$, due to structural factors.[22]

In cyclic and polycyclic systems there are multiple bond paths connecting a pair of nuclei. It is commonly assumed, and data appear to support the contention, that the net coupling constant that is observed is an algebraic sum of the couplings through alternative bond paths. For example, P—P couplings in derivatives of $P(NMeNMe)_3P$ are large, 32–132 Hz.[23] Couplings $^2J(PP)$ in polycyclic trivalent phosphorus systems and trialkyl phosphites are known to be larger than in their open-chain analogues.[24]

Multiple paths are introduced in metal complexes when bidentate ligands are involved. What would normally be a two-bond coupling involving the metal nucleus becomes a combination of $(^2J + {}^3J)$ when a five-membered ring is formed. Since ^2J and ^3J are commonly opposite in sign, the observed "two-bond" coupling with the metal nucleus may be quite small compared to that involving open-chain ligands. For example, the PP couplings can be attributed to the PMP (where M is the metal) and PCCP or PCCCP paths in $Pt^{(II)}$ chelates with ligands containing a $P(CH_2)_nP$ ($n = 2$, 3) moiety.[25] Not surprisingly, compared to the PP coupling in the free ligand, a decrease in magnitude is observed upon formation of a five-membered chelate ring (opposite sign $^2J + {}^3J$) and an increase upon formation of a six-membered ring (same sign $^2J + {}^4J$).

Pi-system contributions usually lead to unexpectedly large long-range J values; for example, $^nJ(PP)$ for $n = 5$–9 via an aromatic system, and $^nJ(PC)$ up to $n = 7$, with strict alternation of signs; + for ^1J, − for ^2J, + for ^3J, etc, has

Figure 6-2 Observed values of (*a*) $^1K(HX)$, (*b*) $^1K(CX)$, (*c*) $^1K(PX)$, and (*d*) $^1K(FX)$ displayed according to the position of X in the periodic table. Calculated values from ref. 18 are shown in parentheses. Units are $10^{19}\,m^{-2}\cdot kg\,s^{-2}\,A^{-2}$. (*a*) Data for H_2, BH_4^-, CH_4, NH_3, OH_2, FH, AlH_3, SiH_4, PH_3, SH_2, ClH, GeH_4, AsH_3, SeH_2, BrH, SnH_4, SbH_3, TeH_2, IH, TlH, $PbHMe_3$, and BiH_3. (*b*) Data for CH_4, BMe_3, CMe_4, $MeNH_2$, MeOH, MeF, $(MeLi)_4$, $SiMe_4$, PMe_3, MeSH, $CHCl_3$, Me_2Se, CD_3Br, $SnMe_4$, Ph_3Sb, Me_2Te, CH_3I, $TlMe_3$, and $PbMe_4$. (*c*) Data for PH_3/PH_4^+, $Me_2PBX_2/(MeO)_3PBH_3$, $Me_3P/Me_3P{=}O$, $(Me_2N)_3P/(Me_2N)_3P{=}O$, $(MeO)_3P{=}O/Me_3P{=}O$, PF_3/PF_6^-, R_3PAlX_3, $P(SiH_3)_3$, $Me_3P{=}S$, PCl_3, $Me_2PSeMe/Me_3P{=}Se$, PBr_3, $(Me_3Sn)_3P/(Me_3Sn)_3PM(CO)_5$, $Me_3P{=}Te$ and Me_3PbPH_2. (*d*) Data for HF, HBF_2, CF_4, NF_3, OF_2, F_2, LiF, SiF_4, PF_3, and PF_6^-; SF_6, ClF, and ClF_6^+; GeF_4, AsF_6^-, SeF_6, BrF_6^+, KF, InF, R_3SnF, SbF_6^-, TeF_6^-, IF_7, and IF_6^+; and RbF, TlF, BiF_6^-, and CsF.

been observed.[26] Calculated π-electron contributions to ^nJ(CC), ^nJ(CH), and ^nJ(HH) for $n = 1$–9 show the well-known characteristics: sign alternations of J^n depending on the number of bonds separating the coupled nuclei, and no dependence of J^n magnitudes either on the zig-zag path or on the number of bonds.[27]

6.3.1 Z Dependence

The magnitudes of one-bond coupling constants between a pair of nuclei are dependent on structural factors, but underlying these are influences that become apparent upon comparison of analogous compounds. For example, $^1K(\mathrm{SiX})/^1K(\mathrm{CX}) \simeq 1.9$ for X = H, B, C, Si, Sn,[28] and $^1K(\mathrm{SnX})/^1K(\mathrm{SiX}) \simeq 4.2$ for analogous compounds. This seems to indicate that outside of structural effects, some factor in $^1K(\mathrm{XY})$ is intrinsic to the identity of X and Y. All the mechanisms contributing to the coupling constant depend on the electronic distribution at the coupled nuclei or in their immediate vicinity: the densities $|\psi_{ns}(0)|^2$ and the averages $\langle r^{-3}\rangle$. In the comparison of Si—X and C—X couplings in analogous compounds the Si-to-C ratio of 1.9 may be compared with the s-electron densities at the nuclei for ground state atoms: Si/C = 1.41. The ratio 4.2 of SnX-to-SiX coupling may be compared with the ratio of s-electron densities, 4.61. For analogous hydrides (XH_4^-) of group III, the ratios of $^1K(\mathrm{XH})$ are 3.28 for Ga/Al and 2.61 for Al/B.[29] These can be compared with the ratios of s-electron densities: 3.29 and 1.72, respectively.

The widest variety of one-bond, spin-spin coupling to other nuclei is exhibited by ^{19}F. Underlying the variations in magnitude and sign due to structural factors is a periodicity in magnitudes of $^1K(\mathrm{XF})$, which mimics the variation of electron spin densities at the nuclei of the ground state X atoms, as shown in Figure 6-1. The atomic averages $\langle r^{-3}\rangle$ are known to vary with atomic number in a similar manner[30] so that the noncontact contributions also have the same underlying periodicity with increasing atomic number as in Figure 6-1.

6.3.2 Lone Pair Effects

The presence of one or more lone pairs on one or both of the coupled nuclei seems to be associated with a negative one-bond coupling constant except in coupling to H. Thus, we find that excepting coupling to H, most constants $^1K(\mathrm{FX})$ are negative; $^1K(\mathrm{OX})$, $^1K(\mathrm{SeX})$, and $^1K(\mathrm{TeX})$ are negative except for TeSe in $CH_3TeSeCH_3$,[31] PtSe, and PtTe. However, one $^1K(\mathrm{PtSe})$ has been found to be negative.[32] The only negative $^1K(\mathrm{SnC})$ and $^1K(\mathrm{SnSn})$ values reported are those in which the Sn has a lone pair.[33] PP coupling between tricoordinate phosphorus atoms, which have lone pairs, is negative. PP couplings involving four- and five-coordinate phosphorus, which has no lone pair, are positive or at least considerably less negative than in tricoordinate P bound to tricoordinate P or higher coordinate P. $^1K(\mathrm{PC})$ is negative when the phosphorus has a lone pair and positive when this lone pair is used in bonding, as in transition metal complexes or in adducts such as $X_3B—PY_3$. $^1K(\mathrm{NP})$ is negative when both P and N have lone pairs, as in $Me_2N—PMe_2$, becoming positive for higher coordinate P, as in $H_2N—PF_3X$. $^1K(\mathrm{SeC})$ is negative in all cases in which Se has 0–3 lone pairs but substantially less so when Se has no lone pair.[34] Just as dramatic is the algebraic increase in $^1J(\mathrm{PH})$ upon removal of the lone pairs on phosphorus. Thus in going from PH_2^- to PH_3 to PH_4^+, $^1J(\mathrm{PH})$ changes from 138–140 to 182–195 to 545.7–548.3 Hz.[35] This trend is reproduced by theoretical calculations.[36] The removal of the lone pair by complexation results in an algebraic increase in the coupling. For example, $^1K(\mathrm{SeP})$ (which is negative) increases algebraically (ie, the magnitude is reduced from that in the free ligand) upon coordination of $R_3P{=}Se$ with SO_2, $Cd^{(II)}$, or HgX_2.[37] $^1K(\mathrm{PC})$ and $^1K(\mathrm{SnP})$, which are negative in the free phosphine ligands, increase algebraically upon complexation with a metal.[20,38] It has been shown that $^1K(\mathrm{PC})$ actually undergoes a change in sign (from − to +). These examples indicate that the presence of one or more lone pairs on one or both of the coupled nuclei is associated with a negative contribution to the one-bond coupling constant. Theoretical calculations bear this out.[18]

6.3.3 Absolute Signs of One-Bond Coupling

Table 6-2 shows the signs of one-bond couplings, ^1K, between pairs of nuclei of various groups in the periodic table. These signs are well established and are based on a large number of systems involving different members of the groups as well as different structural environments (except for VI—VI). Where both signs are observed, the change in sign usually occurs with a change in some structural aspect, such as presence of lone pairs, independent of position in the group. However, there are a few examples of a systematic sign change in descending a column in the periodic table, and there are predictions by theory of a general sign change for couplings involving certain groups of the periodic table.

TABLE 6-2. ABSOLUTE SIGNS OF ONE-BOND COUPLINGS ^1K

	I	II	M[a]	III	IV	V	VI	VII	0
I	+		+	+	+	+	+	+/−	
II								?	
M	+		+	?	+	+	+/−	+/−	
III	+			+	+	+		−	
IV	+		+	+	+/−	+/−	−	−	
V	+		+	+	+/−	+/−	+/−	−	
VI	+		+/−		−	−	+	−	?
VII	+/−	?	+/−	−	−	−	−	+/−	?
0							?	?	

[a] Elements in the transition series.

Experimentally, the known examples are for

1. IV—IV coupling. ^1K(CC) is positive.[39] ^1K(PbC) is generally positive but in at least one case is negative.[40]
2. IV—V couplings. ^1K(CN)[41] and ^1K(SiN)[42] are positive, ^1K(SnN) +/−,[43] and ^1K(PbN) negative.[44]
3. V—VI coupling. ^1K(P=O) is positive, ^1K(P=Se) and ^1K(P=Te) are negative.[45]
4. VII—VII coupling. ^1K(ClF) is positive,[46] ^1K(II) is negative.[47]

The systematic trends in signs and magnitudes of one-bond couplings across the rows and down the groups of the periodic table were predicted in the late 1960s, before the advent of multinuclear spectrometers, when only a limited number of absolute sign determinations were available.[21] With the recent availability of advanced theoretical computation schemes yielding quantitative agreement with experiment, and the increase in the number of absolute sign determinations, it is useful to examine the "state of the art" of periodic-table-wide systematic trends in one-bond, spin-spin couplings. Theoretical calculations indicate that there are systematic trends that can be expected in the signs and magnitudes of one-bond coupling constants (some of which have not been observed yet) as one of the nuclei goes from group IV to group VII along a row of the periodic table or down a column of a given group. These trends are illustrated for HX, CX, PX, and FX couplings in Figure 6-2.

In Figure 6-2*a*, ^1K(HX) decreases (algebraically) strongly when X goes from group IV to group VII in all rows of the periodic table except the first one, for reasons already discussed. For X in group IV, the HX coupling is predicted to increase as X goes down the column. On the other hand, for X in group V, VI, or VII the HX couplings decrease algebraically with increasing atomic number, making them large and negative for the heaviest nuclei of the group. An experimentally verified sign change occurs as Z increases in group VII. ^1K(HF) is positive while ^1K(HI) is negative. Theory predicts a general trend of sign changes as shown in Figures 6-2*a* for HX couplings and 6-2*b* for CX couplings. The dichotomy in behavior arises from the absence of lone pairs in the case of group IV hydrides and the presence of lone pairs in the hydrides of groups V, VI, and VII.

Use of just one or two virtual (ie, unoccupied) molecular orbitals in a simple model, such as that of Pople and Santry,[11] can lead to a meaningful analysis. In this model, the Fermi contact term in the reduced coupling $K_{NN'}$ = constants × $s_N^2(0)s_{N'}^2(0)\pi_{NN'}$. For each occupied MO ($i$) that includes s orbitals on both nuclei N and N', there will be a contribution to $\pi_{NN'}$ by each virtual MO (a), which also includes s orbitals on both nuclei: $\pi_{NN'} = -4c_{iN}c_{aN}c_{iN'}c_{aN'}/(\varepsilon_a - \varepsilon_i)$. For a system without lone pairs, and with high symmetry, say octahedral or tetrahedral, only the totally symmetric MOs contain s orbitals on both the (coupled) central and ligand atoms. Here the positive contact contribution to ^1K arises from a single $a_1 \rightarrow a_1^*$ excitation. The MO a_1 would be a bonding one involving

the coupled nuclei, which in the simplest case would be a combination such as $\phi_X + \lambda\phi_H$ including some s character on each of the coupled atoms X and H. On the other hand, the a_1^* virtual molecular orbital would be a combination such as $\phi_X - \lambda\phi_H$. If ϕ_X has 25% s character, as in CH_4, then π_{XH} is approximately $-4(1/\sqrt{4})(-\lambda/\sqrt{4})(\lambda)(1)/(\varepsilon_{a_1}^* - \varepsilon_{a_1}) > 0$. Thus, the contact contribution would be positive. For atoms with no lone pairs, all the s character is isolated in bonding MOs of the proper symmetry (a_1 usually). On the other hand, for systems with lone pairs, some of the s character is in the lone pair orbitals, eg, some s_X character can reside in the nonbonding MO in a pyramidal molecule $X(CH_3)_3$. If the nonbonding molecular orbital 2σ in a linear XH molecule is a lone pair, there can be s character on the atom X. Because the latter nonbonding MO is antibonding with respect to the coupled X—C or X—H nuclei, it will give a negative contribution to the ^1K coupling constant, as seen in Figure 6-3. The relative magnitudes of the two terms need not always be in the inverse order of the orbital energy separations, so positive reduced couplings for atoms having lone pairs can be observed. The trend with increasing atomic number of X down a group or across a row in the periodic table is for the 1σ MO to become more stabilized and the nonbonding 2σ (lone pair) MO destabilized, especially so when relativistic effects are included,[18] as shown on the right-hand side of

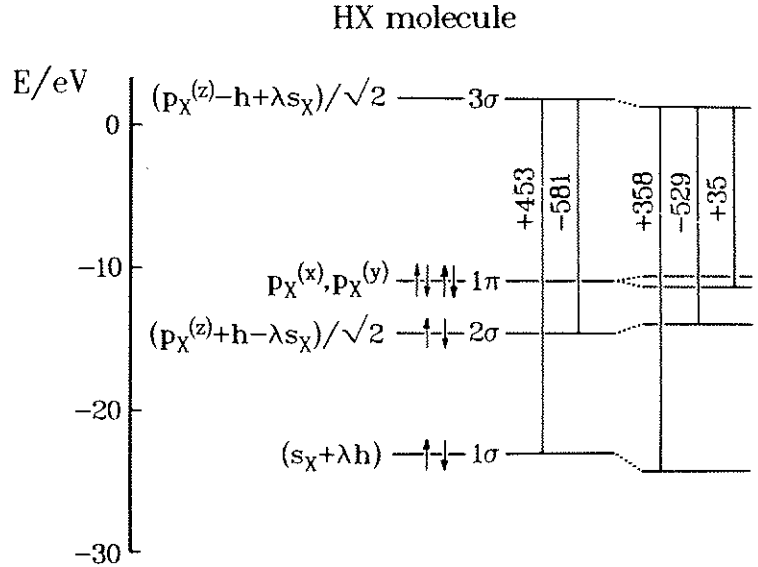

Figure 6-3 Molecular orbital energies for the HX molecule and the contributions to ^1K(HX) (numerical results for HI taken from ref. 18). Oversimplified molecular orbitals depict signs of the contributions of the atomic orbitals in each MO that can lead to a net negative ^1K when there is a lone pair on one of the coupled atoms. In this simplified picture the positive contribution to ^1K(HX) comes from $[4\lambda^2/(\varepsilon_{3\sigma} - \varepsilon_{1\sigma})]\phi_H(0)^2\phi_X(0)^2$ while the lone pair contribution comes from $[-4\lambda^2/(\varepsilon_{3\sigma} - \varepsilon_{2\sigma})]\phi_H(0)^2\phi_X(0)^2$.

Figure 6-3. Furthermore, with increasing atomic number the ns_x atomic orbital participation decreases in the bonding $1a_1$ or 1σ molecular orbital and increases in the nonbonding 2σ (or other) MO. The negative lone pair contribution then begins to dominate, since the orbital energy separation between the 2σ and the virtual MO is less than that between the 1σ or $1a_1$ MO and the virtual MO. Pyykkö and Wiesenfeld have shown that relativistic effects enhance these tendencies.[18]

The lone pair effect is clearly demonstrated in couplings involving phosphorus shown in Figure 6-2*c*. Three-coordinate P, which has a lone pair, shows negative couplings to all but H and B nuclei. On the other hand, four, five, and six-coordinate PX couplings are positive or of either sign for X in the first two rows of the periodic table. For $Me_3P{=}X$, relativistic calculations of $^1K(PX)$ reproduce the experimental trend of $^1K(PX)$ being large positive, changing to large negative for heavier X, as for X = O → Te.[18]

6.3.4 *Structural Factors Affecting Magnitudes of One-Bond Couplings*

6.3.4.1. Coordination Number, Oxidation State, and Formal Hybridization. The reduction of the magnitude of a coupling constant (in the free ligand) upon coordination is commonly used as a diagnostic tool for complexation. Although this is consistent with an algebraic increase in ^1K with apparent loss of a lone pair, a more general decrease in the magnitude of ^1K (positive or negative) upon increase in coordination is observed. For example, P=Se coupling constants (−724 to −1099 Hz) are much greater in magnitude than P—Se— couplings (−100 to −391 Hz).[48] $^1K(AgP)$ or $^1K(HgP)$ decreases with increasing n in phosphine complexes $[AgP_n]X$, $[HgP_n]X_2$ (n = 1-4). As n increases, the change in $^1J(AgP)$ follows the change in Ag hybridization from sp to sp^3.[49] $^1J(^{199}HgP)$ varies similarly but more dramatically with coordination number[50] (see Chapter 13).

An apparent exception to this general decrease in magnitude of ^1K with increasing coordination number is the increase in ^1K upon additional coordination with more electronegative atoms. There is a rather pronounced increase in coupling constant with increasing electronegativity of substituents at the coupled atoms which can dominate the coupling.

In summary, we note that an increase in coordination number of X (in going from linear to trigonal, tetrahedral, square planar, octahedral; or terminal to bridging; or free ligand to coordinated ligand) leads to a decrease in the magnitude of $^1K(XY)$ for the general reason that there is an increase in the number of bonds over which the s orbital is distributed. On the other hand, the removal of the lone pair of X accompanying an increase in coordination number of X causes an algebraic increase in $^1K(XY)$, since lone pairs are generally associated with a negative contribution to ^1K.

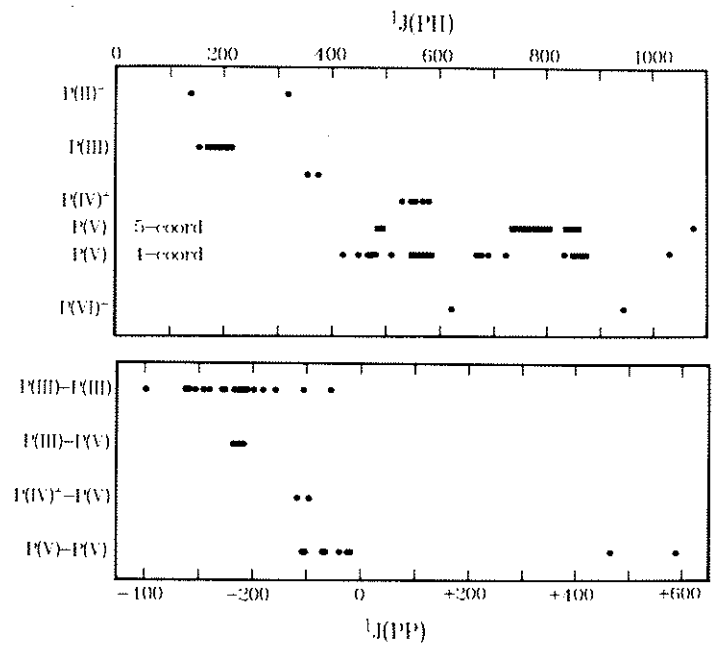

Figure 6-4 The dependence of $^1J(PH)$ and $^1J(PP)$ on oxidation state/coordination number of the phosphorus.

Figure 6-4 shows $^1J(PH)$ and $^1J(PP)$ for various oxidation states. Although the ranges of values overlap, there is a clear dependence of the coupling constant on the oxidation states of the coupled atoms. The oxidation state of the metal in phosphine complexes influences the magnitudes of the metal-phosphorus coupling constant. For example, $^1J(Rh^{(III)}P):{}^1J(Rh^{(I)}P) = 0.50\text{-}0.73:1$ in octahedral versus planar complexes.[51] It has also been noted that $^1J(Pt^{(IV)}P) \leq {}^1J(Pt^{(II)}P) \leq {}^1J(Pt^{(0)}P)$[20] (see Chapter 13).

The dependence of the one-bond coupling on the lone pair, coordination number, and oxidation state is often described in terms of the qualitatively useful construct hybridization. It is assumed that one can classify nuclear environments in terms of idealized equivalent hybrid orbital language (meaningful only when employing a minimum basis valence orbital description). Thus for the second row of the periodic table, we have sp^3 for tetrahedral or pyramidal coordination, sp^2 for trigonal, and sp for linear. While not quantitatively justifiable, this does provide a useful taxonomy. When the coordination number exceeds 4, d orbitals are generally included in the qualitative description, and classification by formal hybridization such as d^2sp^3 (octahedral), dsp^3 (trigonal bipyramidal), or dsp^2 (square planar) generally places $^1J(MP)$ into nonoverlapping ranges,[20,52] eg, $^1J(Rh^{(III)}, P)$ in octahedral complexes < $^1J(Rh^{(I)}, P)$ in planar complexes.

For positive $^1K(XY)$, when lone pairs are not involved, a mean energy approximation (as in eq. 6-14) works reasonably well, and it is actually possible to do comparative studies of coupling constants using only localized orbitals and formal hybridization.[53] In the simplest description using McConnell's equation,[10] the Fermi contact term is proportional to $(P_{sxsy})^2/^3\Delta E$. If we further simplify to localized bonds, the bond order $(P_{sxsy})^2$ will be proportional to the s characters of X and Y in the XY bond. For example, calculated values of $^1J(PC)$ are found to be linear with calculated s bond order for four- and five-coordinate phosphorus but not for phosphines.[54] General trends with respect to coordination number or oxidation state can be explained with this localized picture. The formal hybridizations inferred from linear, trigonal planar, and tetrahedral arrangements are sp, sp^2, sp^3, respectively, as in $Hg(PMe_3)_n^{2+}$ with $n = 2$, 3, and 4.[55] Here the ^{199}HgP couplings are 5505:3580:2255 Hz, respectively, which roughly equals $\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$. The observed ratios of corresponding couplings involving Rh^{III} and Rh^{I} with P, which should be 0.67:1 for hybridizations d^2sp^3 and dsp^2, respectively, are 0.59-0.73:1.[51] One cannot expect quantitative interpretations with such a simple description, but it does allow the dependence of the one-bond coupling on the coordination number of either coupled atom to be understood. This connection between the magnitude of the coupling constant and the so-called s character first came to investigators' attention in CH couplings.[53] At the next level of approximation (eq. 6-15) a correlation of the observed one-bond coupling constant with calculated mutual polarizability for the valence s orbitals of the coupled atoms can be expected. Indeed a fairly linear relationship was obtained between these two quantities for Pt—P coupling in compounds of the type $[Pt(RC{\equiv}CR')—(PPh_3)_2]$.[56]

6.3.4.2 Electronegativity of Substituents. The magnitude of ^1K increases with increasing electronegativity of substituents regardless of its sign. This was first observed in the case of $^1K(CH)$ in substituted methanes, but it has been found to be a very general phenomenon and is an important factor in any coupling. The magnitude of $^1K(XY)$ has been found to change by a factor of up to 2 or 3 with changes in substituents on X or Y; this is also the case for ^2K. Regardless of the choice of electronegativity measure (Allred-Rochow, Huggins, Sanderson, Pauling), a linear plot is generally found for ^1K versus electronegativity of substituents on one of the coupled nuclei. Linear relationships between ^1K and electronegativity have been found in many cases: eg, for WP,[57] SeP,[58] MoP,[59] and PP,[60] upon changing substituents on phosphorus. This is especially dramatic in $^1K(PP)$.[24,61] In the case of $^1K(MP)$, changing the electronegativity of other ligands on the metal appears to have less effect than changing the electronegativity of substituents on P.[20] These linear relations between the coupling constant and electronegativity are also described in terms of s character. The model of Walsh[62] (rediscovered by Bent[63]) states that "If group X attached to carbon is replaced by a more electronegative group Y then the carbon valency towards Y has more p character than it has towards X." Thus, a CH bond will have increasing s character in going from CH_4 to CH_3Y, CH_2Y_2, and CHY_3. This model was applied to the substituted methanes CHXYZ, to explain the nearly additive changes in $^1J(CH)$ with various substituents.[64] Theoretical calculations by Maciel and co-workers at the FPT INDO level, on a large number of compounds (methanes, ethylenes, acetylenes, substituted benzenes), do indeed show a systematic increase in the s bond order between C and H upon substitution at the carbon with a wide variety of electronegative substituents.[65] This explains why MP coupling constants tend to give linear plots against various electronegativity parameters for substituents at the phosphorus.

6.3.4.3 Stereospecificity of One-Bond Coupling. Sensitivity to Geometrical Arrangement of the Atoms Around the Coupled Nuclei

a. Axial Versus Equatorial. In a trigonal bipyramidal molecule, it is found that $|^1K(MX_{eq})| > |^1K(MX_{ax})|$. For example the ratio $^1J(PF)_{eq}/^1J(PF)_{ax}$ in the same five-coordinate phosphorus compound is 1.2[66] (see Chapter 7). PC couplings are more variable in magnitude: $^1J(PC_{eq})$ values are 169–448 Hz and $^1J(PC_{ax})$ are 0–115 Hz in an extensive series of phosphoranes.[67] A similar dependence of $^1J(RhP)$ and $^1J(PtP)$ has been observed in the trigonal bipyramidal complexes; for example, $^1J(RhP_{eq}) = 146$ Hz, $^1J(RhP_{ax}) = 116$ Hz in one case, and 206 and 143 Hz, respectively, in another case,[20] while $^1J(PtP_{eq})$ and $^1J(PtP_{ax})$ are 2730 and 2125 Hz, respectively.[68] The difference in equatorial/axial couplings in trigonal bipyramidal and square pyramidal molecules is only superficially a stereospecific effect, since it is commonly found that bond lengths for axial substituents differ significantly (are longer in trigonal bipyramidal and shorter in square pyramidal) from those for equatorial ones. The stereospecificity in the substituted octahedral case is clear: in Me_3NPF_5 values of $^1J(PF)$ are 848 (equatorial) and 747 (axial) respectively.[69] $^1J(HgP)$ values change with Hg—P bond lengths and P—Hg—P bond angles (3 kHz per 0.1 Å or 20° change) in $[HgX_2(PR_3)_2]$, and also decrease with XHgX angle. These observations are supported by calculations[70] (see also Chapter 13).

The concept of formal hybridization can be used to explain this general trend. In the equatorial bonds the central atom can be considered to have a formal hybridization of sp^2, as opposed to the axial bonds, which may be formally described with a dp hybrid orbital. This is consistent with the observation that equatorial bonds are generally shorter than axial ones in trigonal bipyramidal molecules.

b. Cis Versus Trans: The Trans Influence. The term "trans influence" is used to describe an indirect effect on a bond that a ligand trans to it exerts. It has been defined as the "tendency of a ligand to weaken the bond trans to itself."[71] This manifests itself as an alteration of the bond length and therefore has an effect on the magnitude of the one bond coupling.[72] The magnitude of $^1K(XY)$ is smaller if the XY bond is trans to a ligand that has a stronger trans influence. The empirical order of ligands according to their ability to affect the bond trans to

them is: $MePh_2Si > Ph > Me \gg R_3P > (PhO)_3P$, $CN > Et_3As > NO_2 >$ amine, NCO, NCS > Cl, Br, I > ONO_2 > F.[73] This order is not unique, since the trans influence will depend not only on the nature and properties of the ligand itself but on the metal, its oxidation state, and the degree of coordination. Thus, ^1K(MP) trans to Cl > ^1K(MP) trans to PR_3 with the ratio being 1.3–1.5:1; for ^1J(PtP) the range of values being 3200–3600 Hz vs 2200–2400 Hz, respectively.[20] One model is that a ligand with high trans influence weakens the bond trans to itself by causing rehybridization of the metal σ orbitals. This reduces the magnitude of the coupling constants involving the trans bond via the lower s character of the metal orbitals.

c. Dihedral Angle Dependence. A large temperature dependence of a coupling constant is observed when some internal rotation is taking place and there is a dihedral angle dependence of the coupling constant. In some systems, the coupling is observed in a more or less rigid configuration so that the dependence of the one-bond coupling on a dihedral angle can be ascertained by observing NMR spectra of the isomers.

In a fragment X—Y—Z the dihedral angle of interest is between the bond connecting the coupled nuclei XY and either a lone pair on Z or a bond to an electronegative substituent on Z. $|^1K(XY)|$ appears to be larger when a lone pair on Z has a large dihedral angle with the X—Y bond. The effect for a bond to an electronegative substituent such as O^- or OMe is opposite to that of the lone pair, that is, $|^1K(XY)|$ is larger when the Z—OMe bond is cis to the XY bond.

When the dihedral angle of interest is between lone pairs on the coupled nuclei, $|^1K(XY)|$ appears to be smaller when the lone pair on X and the lone pair on Y are trans to each other. ^1J(PP) for the *trans*-MePPMe moieties (in which the lone pairs are trans to each other) are smaller than in the *cis*-MePPMe moieties in alkyl-substituted cyclomonocarbaphosphines, eg, 219.8 (trans) versus 297.5 (cis) Hz.[74] Calculations of ^1J(PP) in the model system $H_2P—PH_2$ as a function of the dihedral angle (between the lone pairs) by various methods yield curves that are qualitatively similar.[18,75] The shapes of these curves seem to be consistent with the experimental data above, with small positive values for trans and large negative values for cis arrangements. A similar shape is obtained for ^1K(PN) in $H_2P—NH_2$, but with negative values for all dihedral angles in this case.[76]

d. Diastereotopic Nuclei. Geometric isomers have different one-bond coupling constants. For example, ^1J(PP) in the two diastereomers of 1,2-dimethyl-1,2-diphenylbiphosphine are -215 and -234 Hz.[77] In diastereomeric phosphorinanes one-bond couplings to the P nucleus are larger for the diastereomer with the coupled nucleus in the equatorial position, eg, $^1J(PN_{eq})$ and $^1J(PN_{ax})$ are 53 and 42, respectively.[78] $^1J(PC_{eq})$ and $^1J(PC_{ax})$ are 169–448 Hz and 0–115 Hz, respectively, in a series of phosphoranes.[67] The compound [Me-*t*-BuP(Se)]$_2$Se exists in diastereomeric forms and two values are observed for both the P—Se— and the P=Se coupling constants, respectively: -346.2 and -760.4 Hz for one form, and -390.6 and -751.1 Hz for the other.[48] Other examples are discussed in Chapter 13.

6.3.5 Structural Factors Affecting Signs and Magnitudes of Two- and Three-Bond Couplings

The magnitudes of ^2K are broadly related to atomic densities at the nuclei. For example, ^2K(XOP) increases in the order X = Al, Ga, In inanalogous complexes: 1.0, 1.42, and 2.87×10^{19} $m^{-2}kg\ s^{-2}A^{-2}$, respectively.[79] Both the sign and the magnitude of ^2K depend on oxidation state, coordination numbers, formal hybridization, and electronegativity of substituents on the coupled atoms, just as one-bond couplings do. Plots of one-bond and two-bond couplings in the same molecule indicate a very good correlation between ^1K and ^2K, for example, between PC and PCH couplings.[80] This correlation is so good that if one of these couplings changes sign in a series of compounds, but the other does not, it is possible to obtain the sign of the first from the plot if only the magnitudes of both ^1K and ^2K for the compound are known. The ratio ^2K(XCH)/^1K(XC) changes systematically with the position of X in the periodic table.[81]

The sign of ^1K(XY) relative to ^2K(XMY) is also dependent on the XMY bond angle, but it is usual for ^1K(XY) and ^2K(XMY) to be opposite in sign for most XMY bond angles.

The dependence of ^2K(XMY) on the oxidation states, coordination numbers, and formal hybridization of X and Y is basically the same as in ^1K(XY). While there is an algebraic increase in ^1K(PP) in going from tricoordinate to higher coordinate phosphorus, ^2K(PNP) has large positive values, is sensitive to relative orientation of lone pairs in three-coordinate phosphorus, and decreases greatly to a still positive value on increase of coordination numbers of the coupled P atoms.[60,82] This opposite algebraic behavior of the one- and two-bond coupling constants has to do with their opposite signs. Like ^1K, ^2K values also decreases when a coordination compound is formed, and this decrease can be used as a diagnostic tool for complexation studies.

Like $|^1K|$, $|^2K|$ increases with increasing electronegativity of substituents regardless of sign. ^2K(XMY) changes by as much as a factor of 2 or 3 upon substitution at either X or Y or both with electronegative groups or atoms. Many examples are available for ^2K(PMP),[57] as well as for other pairs of nuclei. ^2K(PMP) cis (which is negative) becomes more negative and ^2K(PMP) trans (which is positive) becomes more positive with increasing electronegativity of substituents.

The coordination number of M also determines the XMY bond angle, so these two factors are not always mutually exclusive. ^2K increases algebraically with decreasing coordination number of M. For example, in $R_2N—P(=NR)_2$ (R = $SiMe_3$), the coupling ^2J(PNSi) of the phosphorus to a silicon through the three-coordinate N is 1.2 Hz while through the two-coordinate N it is 16.7 Hz.[83]

When comparing analogous compounds, ^2K(XMY) increases algebraically as M descends a column of the periodic table. The values of ^2J(PXP) in $[(CF_3)_2P]_2X$ are 108.3 and 234.2 Hz for X = O, S, respectively.[84] ^2J(PMP) also increases algebraically as M descends in the triad Cr, Mo, W, for analogous cis-disubstituted complexes and for trans complexes.[20] Values of ^2J(PMC) for

M = Cr, Mo, W in analogous $(CO)_5MPR_3$ complexes show a similar algebraic increase in going from M = Cr to Mo, however Mo and W values are comparable, eg, −14.4, 10.0, 7.5 for $^2J(PMC)_{cis}$ and −8.5, 20.1, 18.6 Hz for $^2J(PMC)_{trans}$.[85]

The dependence of $^2K(XMY)$ on the XMY bond angle was predicted by theoretical calculations on the CH_2 fragment.[86] $^2J(HCH)$ increases algebraically with increasing HCH angle in both H_3C- and $H_2C=$ fragments, and calculations reproduce these trends.[87] Although extensive data on a variety of nuclei show that $^2K(XMY)$ depends on the XMY bond angle, they are not easily described by one simple formula (as the dihedral angle dependence in ^3K, eg) because other factors that influence $^2K(XMY)$, such as coordination number or formal hybridization of M, have consequences in the XMY bond angle. Comparison of different $^2K(XMY)$ involving the same intervening M atom in the same molecule minimizes such other factors. In the octahedral and square planar complex there are two angles to consider, 90° (cis) and 180° (trans) and in the trigonal bipyramidal complex there are 90° (axial-equatorial), 120° (equatorial-equatorial), and 180° (axial-axial) angles. The general rule that emerges from coupling data in these geometric types is that there are very pronounced differences in magnitudes, eg, |trans| > |cis|, and sometimes even in sign, so that, algebraically, $^2K(XMY)_{trans} > {}^2K(XMY)_{cis}$. This is so general that it serves as the basis for identification of octahedral and square planar isomers. The most extensive data are for $^2K(PMP)$[20]; however, the same general rule has been found to hold in PMC,[85,88] PMN,[89] PMSn,[90] PMH,[68,91] PMHg,[92] and PMF,[93] where M is any transition metal. A dramatic difference is observed for a ^{31}P nucleus trans and cis to the Pb atom in *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$ in which $^2J(PbP) = 3460$ Hz for the trans phosphorus and 260 Hz for the cis.[94] Care should be taken in applying this inequality to structural determination when only magnitudes of couplings are known; the relative signs of the cis and trans couplings may not be the same.

The three-bond coupling depends on some of the same factors as one and two-bond coupling: coordination number, formal hybridization, and electronegativity of substituents at the coupled atoms. With four atoms involved in the coupling path, it is not easy to isolate individual factors.

It is well known that the magnitudes and signs of the coupling constants $^2K(PX)$ and $^3K(PX)$ depend mainly on the orientation of the P lone pair. For example, both $^2K(PNC)$[95] and $^3K(PNCH)$[96] have large positive values when the dihedral angle ϕ (between the NC or the CH bond and the P lone pair direction) is small (cis or syn periplanar). As ϕ approaches 180° (trans or anti periplanar), these two couplings become small and may even become negative for $^3K(PNCH)$,[96] $^2K(PNC)$.[95] The dependence on the dihedral angle involving the lone pair and that involving a bond to an electronegative atom such as O or Cl is opposite. For example, values of $^2J(PCH)$ are larger for H gauche to the lone pair (than for trans) in phosphines, while they are larger for H trans to =O (than for gauche) in oxides.[97] For a series of $R_2P-N-PR_2$ compounds, $^2J(PNP)$ covers the range −35 to +665 Hz and the magnitudes are related to

the conformation adopted by the P—N bonds.[82,98] A parallel behavior of $R_2\underline{P}-N-\underline{C}$ and $R_2\underline{P}-N-\underline{P}R_2$ couplings is that both tend to be relatively small and negative when the nucleus coupling to P is trans to the phosphorus lone pair. On the other hand, $^2J(PNP)$ in compounds containing the $R_2P-NP(Z)R_2$ skeleton is positive in acyclic compounds (+55 to +121 Hz) in which the phosphorus and nitrogen lone pairs adopt an orthogonal relationship so that the $N-P(Z)R_2$ bond has a dihedral angle of about 0° with respect to the R_2P- lone pair. This coupling is negative in most cyclic or cage compounds (−6 to −35.6 Hz) in which this dihedral angle is close to 180°.[99]

The dependence of coupling constants on the dihedral angle has been found empirically in many cases to be of the form called the Karplus equation, named after the author of the original theoretical calculation of the dependence of $^3K(HH)$ on the geometry of the HCCH fragment[100]:

$$^3K = C\cos 2\phi + B\cos\phi + A \qquad (6\text{-}21)$$

This equation serves as a good qualitative guide, with a maximum at $\phi = 180°$ and a minimum close to 90°. However, since coupling constants depend on other factors, one can expect to use the equation to determine approximate conformations only if the examples on which the empirical values of *A*, *B*, and *C* have been based are similar to those to which the equation will be applied. It is especially important to take into account the electronegativity of substituents at the coupled nuclei, since this has a pronounced effect.[101] In addition, there may be other contributions, such as that of the π system, which may not be negligible especially when the dihedral dependence gives a low value ($\phi \sim 90°$), and that of "through-space" coupling when ϕ is close to zero. Although the Karplus equation was originally applied extensively to $^3K(HCCH)$, it is continuing to provide a way of categorizing the three-bond coupling ranges observed in a wide variety of coupling frameworks (PWNN, PCPSe, etc). Used with caution, the observed ^3J values and an empirical Karplus equation make a reasonable conformational probe.

Theoretical calculations at various levels of sophistication successfully reproduce the qualitative features of the dihedral angle dependence. A recent theoretical calculation of the dependence of the three-bond HH coupling on the dihedral angle in the HCCH fragment[102] compares very favorably with the empirical equation of the Karplus form that had been least-squares fitted to data from rigid systems of known geometry. In $^3J(HH) = A + B\cos\phi + C\cos 2\phi$, theory gives *A*, *B*, *C* = 6.9, −1.1, and 6.1 to be compared with the empirical values, *A*, *B*, *C* = 7, −1, and 5, respectively.[103] Theoretical calculations of $^2J(POC)$ and $^3J(POCH)$ as a function of dihedral angle in ethyl phosphate yield curves that resemble the empirical and theoretical Karplus-type shapes known for other ^3J couplings.[104] Similar qualitative behavior for $^3J(PH)$ and $^3J(PC)$ has been calculated by the FPT-CNDO/2 method.[105] The integrals describing the interaction of electrons in orbitals directed toward the coupled nuclei have a dihedral angle dependence and are responsible for this generally observed behavior of ^3J.

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