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Systematic Trends in the Coupling Constants of Directly Bonded Nuclei*

CYNTHIA J. JAMESON† AND H. S. GUTOWSKY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

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The indirect coupling constant J_{XN} has been observed for the magnetic nuclei in 50 different pairs of directly bonded X–N atoms. A synopsis is given of the reported values along with the corresponding reduced constant $K_{XN}=(2\pi/\hbar\gamma_X\gamma_N)J_{XN}$ which depends only on the molecular electronic structure. There are three nuclei, $N={}^1H$, ${}^{13}C$, and ${}^{19}F$ for which K_{XN} is now known for 15 or more different nuclei X, enough that trends are visible in the dependence of K_{XN} upon the position of X in the periodic table. The sign of K_{XN} (positive for H_2) changes across the table somewhat between Groups V and VI, the sense of the change for $N={}^{19}F$ being the reverse of that for $N={}^1H$ and ${}^{13}C$. Furthermore, there is a marked increase in the magnitude of K_{XN} with increasing nuclear charge of atom X in each Group, *for negative as well as positive coupling constants*. The significance of these observed trends is considered. The Ramsey theory for the electron coupling of the nuclear spins includes orbital, spin-dipolar, and contact contributions. For directly bonded atoms, the orbital contribution is zero unless there is multiple bonding, the tendency for which decreases with increasing Z in a given Group. The spin-dipolar contribution increases with increasing Z; however, it is positive, and the values calculated are an order of magnitude smaller than those found experimentally for K_{XN}. A model is presented attributing the observed trends to the contact contribution, which depends upon the nature of the bonding orbitals employed by each atom in the bond. If both atoms employ *ns* orbitals in the bond, the direct contact interaction term, which is positive, dominates. The bonding of Group VII and, to a lesser degree, Group VI atoms employs primarily *p* orbitals. In such atoms the contact interaction is indirect, involving polarization of the core *s* electrons and a change in sign of the term. The contact term with inclusion of such core polarization effects provides a model consistent with the data available. The model is used to predict the signs, in some cases also the magnitudes, of several coupling constants not yet observed. For example, in NF_3, OF_2, and F_2, we expect K_{NF} to be negative, K_{FF} to be positive, and K_{OF} probably to be positive. A number of features are discussed including the coupling in highly ionic bonds such as the Rb, Cs, and H fluorides, and the relationship of the model to nuclear hyperfine interactions in atoms and ions with unpaired spins and in organic free radicals.

I. INTRODUCTION

In nuclear magnetic resonance, experimental finesse has yielded a large number of precise values of chemical shifts and coupling constants which contain a wealth of information about molecular electronic structure, if they could be deciphered. However, the experimental determination of these observables has greatly outstripped developments in their theoretical interpretation. Calculations of coupling constants, in particular, have met with difficulties.[1] In a sense, the coupling constants are sensitive to so many aspects of molecular structure that the details have tended to obscure the general nature of the coupling mechanisms. Nonetheless, coupling constant data are now available for such a large number of nuclear species that it seems worthwhile to look for general trends and periodicities, and to consider their possible origins.

Such an approach to the chemical shifts revealed a periodic dependence of the range of chemical shifts on nuclear charge, which was attributed to the paramagnetic contribution $\sigma^{(2)}$ and its dependence on $\langle 1/r^3\rangle$ for the bonding electrons.[2] Similarly, it was noted that the M–H coupling constants J_{MH} of the Group IV hydrides increase with the nuclear charge Z_M, which is compatible with the coupling being dominated by the contact term.[2] The present paper reports the results of another, more general look at the coupling between directly bonded nuclei. This class of coupling constant is more amenable to theoretical treatment than the others, and data are on hand for over fifty different pairs of nuclei, enough to indicate some major trends over the periodic table, which we have sought to interpret.

Values of coupling constants were reported at first only as magnitudes. However, with the use of various methods of determining relative signs of coupling constants and with the absolute sign determination of a few coupling constants, absolute signs of coupling constants have bcome increasingly available. Relative signs have been determined by spectral analyses,[3] double resonance and heteronuclear multiple resonance,[4] double quantum transitions,[5] and nuclear Overhauser effects.[6] Absolute signs have been determined

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† Present address: Department of Chemistry, University of Illinois, Chicago Circle, Chicago, Ill.

[1] For a recent review of such difficulties, see M. Barfield and D. M. Grant, Advan. Mag. Resonance **1**, 149 (1965).

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from high-resolution NMR spectra in those cases in which cross terms between different relaxation mechanisms are important,[7] from spectra of partially oriented molecules obtained by application of a strong electric field to a sample of polar molecules[8] or by dissolving the molecule of interest in a liquid crystal matrix,[9] by a molecular beam technique,[10] and by line-shape analysis of broad-line spectra in the solid.[11]

From the few absolute signs measured, those of most other coupling constants in the same and related molecules have been determined via measurements of relative signs. All data available appear to be consistent with the ^{13}C–H directly bonded coupling being positive. For example, recent measurements of the relative signs of coupling constants in molecules with bonds such as Si–H, P–H, Si–F, and Te–C have led to absolute signs of these couplings, based on their signs relative to ^{13}C–H which is taken to be absolutely positive. Moreover, the sign of the ^{31}P–^{19}F coupling constant arrived at in this way is found in all cases which have come to our attention to be the same as that obtained by an absolute sign determination of the ^{31}P–^{19}F coupling constant in FPO_3^{2-}.[11] In Sec. II we review the various data at hand on the magnitudes and signs of the coupling constants and we consider the implications of the general trends which are discernible.

II. EXPERIMENTAL TRENDS IN K_{XN} AND THEIR SIGNIFICANCE

It has been pointed out[2,12] that the coupling constants for different pairs of nuclear species can be meaningfully compared only if the signs and magnitudes of the magnetogyric ratios of the nuclei are left out of the picture. Thus, we will discuss the reduced coupling constant K_{XN}, which is related to the observed coupling constants by the equation

$$K_{XN}=(2\pi/\hbar\gamma_X\gamma_N)J_{XN}. \qquad (1)$$

A summary is given in Appendix A of data presently available on coupling constants J_{XN} of directly bonded nuclei, along with the corresponding reduced values K_{XN}. The value of K_{XN} for a polyvalent atom X is of course sensitive to the bonding situation and to the nature of substituents other than N which are bonded to X. The resulting wide range of values for a particular K_{XN} is often larger than any differences due to X in the ranges for different pairs of nuclei, X_aN and X_bN. For example, K_{CH} has values from $+32$ to $+82$ in units of 10^{20} cm^{-3}, while K_{NH} has values from $+53$ to $+61$.

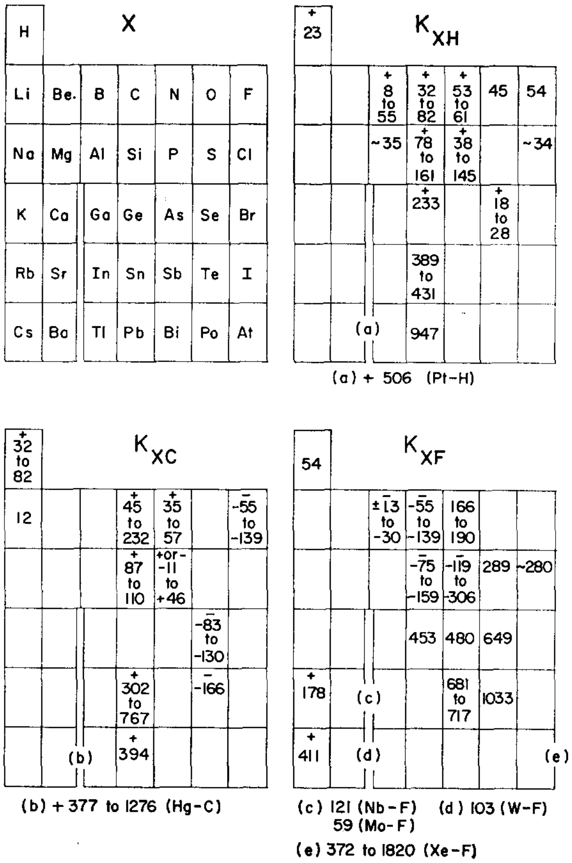

FIG. 1. The dependence of the reduced coupling constant K_{XN} upon the position in the periodic table of nucleus X, for N=H, C, and F. Numerical values are in units of 10^{20} cm^{-3}; sources of the data are given in Appendix A.

However, there are three nuclei, N=^{1}H, ^{13}C, and ^{19}F, for which the coupling constant K_{XN} has been measured for 15 or more different nuclei X, which are enough that trends are visible in the dependence of K_{XN} upon the position of nucleus X in the periodic table. In Fig. 1, separate charts are given for the XH, XC, and XF coupling constants as a function of the position of atom X in the periodic table. It is seen that there is a change in the sign of K_{XN} in going across the table, but apparently not in going from top to bottom. The changeover line appears to be somewhere between Groups V and VI. The sense of the sign change for N=F appears to be the reverse of that for N=H and C, except for RbF and CsF which probably are special cases. Furthermore, there is a marked increase in the magnitude of K_{XN} with increasing nuclear charge Z of atom X in each Group, for *both* positive and negative coupling constants. Also, for K_{XC} and K_{XF} there may be an increase in magnitude with increasing Z in each period.

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[8] A. D. Buckingham and E. G. Lovering, Trans. Faraday Soc. **58**, 2077 (1962). A. D. Buckingham and K. A. McLauchlan, Proc. Chem. Soc. **1963**, 144.

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[10] I. Ozier, P. Yi, and N. F. Ramsey, as cited by J. Schaefer and R. Yaris, Chem. Phys. Letters **1**, 173 (1967).

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

X	$K_{XC}^{(2)}$					
Li 0.04	Be 0.17	B 0.58	C 1.2	N 2.4	O 4.1	F 6.3
Na 0.24	Mg 0.74	Al 1.2	Si 2.2	P 3.4	S 4.8	Cl 6.9
K 0.4	Ca 1.1	Ga 3.4	Ge 5.5	As 7.2	Se 9.2	Br 13.0
Rb 0.8	Sr 1.9	In 5.5	Sn 8.3	Sb 11.4	Te 14.4	I 17.3
Cs 1.2	Ba 2.7	Tl 11.4	Pb 15.4	Bi 23.8	Po	At

X	$K_{XF}^{(2)}$					
0.2	0.9	3.1	6.3	12.6	22.1	33.7
1.2	4.0	6.6	11.9	17.9	25.8	36.7
2.5	5.8	18.0	29.5	38.5	49.4	69.5
4.4	10.3	29.3	44.4	60.5	77.0	92.3
6.6	14.6	60.5	82.1	126		

FIG. 2. Values of the spin-dipolar term $K_{XC}^{(2)}$ and $K_{XF}^{(2)}$ calculated as a function of atom X for the case $P_\sigma^2=1$, in units of 10^{20} cm^{-3}. These are to be compared with the observed values of K_{XC} and K_{XF} given in the bottom half of Fig. 1.

These trends reflect the periodic differences in atomic structure which affect each of the terms in the general expression for K_{XN}, namely[13]

$$K_{XN}=\underset{\text{(orbital)}}{K_{XN}^{(1)}}+\underset{\text{(spin-dipolar)}}{K_{XN}^{(2)}}+\underset{\text{(contact)}}{K_{XN}^{(3)}}\,. \quad (2)$$

The spin-dipolar and orbital terms both depend on the product $\langle r^{-3}\rangle_X\cdot\langle r^{-3}\rangle_N$.[13] The average atomic value of r^{-3} changes periodically[14] with Z. Moreover, $\langle(a_0/r)^3\rangle_{np}$ is relatively large (greater than 5.0) for F, Ne; Cl, Ar; Ge, As, Se, Br, Kr; In, Sn, Sb, Te, I, Xe; etc. In the coupling constants involving these nuclei, then the orbital and spin-dipolar terms could be important.

From calculations by Pople and Santry[12] of the spin-dipolar terms, it appears that they are always positive for directly bonded atoms. In order to assess the importance of the spin-dipolar contributions, values of $K_{XC}^{(2)}$ and $K_{XF}^{(2)}$ were calculated, using Pople and Santry's method,[12] for the hypothetical case $P_\sigma^2=1$, $P_\pi^2=P'^2_\pi=0$. This case corresponds to X using a pure np orbital and C and F using a pure $2p$ orbital in forming the X–C and X–F single bond. Any s participation makes $P_\sigma^2<1$ and makes the spin-dipolar term smaller.

These calculated values are given in Fig. 2. Their increase in magnitude with Z_X within each group and also within each period is consistent with the experimental trends shown in Fig. 1. But the calculated terms are an order of magnitude smaller than the observed coupling constants. More important, the positive sign of the calculated terms makes it impossible for them to account for either the large negative values observed for K_{SeC}, K_{TeC}, and K_{PF} or for the increase in magnitude of the negative values with Z_X.

Pople and Santry's calculations[12] also show that for directly bonded atoms, the orbital term is zero unless there is multiple bonding between X and N. However, for the heavier atoms in Period 4 and 5, for which $\langle a_0^3/r^3\rangle_{np}$ is large, multiple bonding is less likely than in the atoms of the first two rows. For example, it is well known that Si has far less tendency to form double and triple bonds than does C. Therefore, the orbital term $K_{XN}^{(1)}$ would tend to *decrease* with increasing Z_N within a given Group, which is the reverse of the experimental results. So it seems that the general trends exhibited by K_{XN} in Fig. 1 and Appendix A most likely are to be attributed to the contact term $K_{XN}^{(3)}$. In the next section we consider the nature of the contact interaction and how it may govern the values found for K_{XN}.

III. THE NATURE OF THE CONTACT INTERACTION

For directly bonded X and N nuclei the Fermi contact term in the coupling constant may be viewed as a correlation in the orientations of nucleus X and nucleus N. This correlation may be expressed as the net result of three interactions: (i) the Fermi contact interaction of nucleus X with electron 1 in the X–N bond; (ii) spin correlation of electron 1 with electron 2 in the bond; (iii) the Fermi contact interaction of electron 2 with nucleus N. Of these, (ii), the electron spin correlation in the bond, is relatively a very strong interaction so that the internuclear coupling is determined by the magnitudes and signs of the two nuclear spin–electron spin interactions, (i) and (iii). This leads to the three possibilities shown schematically in Fig. 3. The sign of $K_{XN}^{(3)}$ is negative only if just one of the nuclear spin–electron spin interactions is negative. A mathematical description of the model we use for $K_{XN}^{(3)}$ is given in Appendix B. In order to develop the model we need to consider the details of the contact hyperfine interaction, which we do first for atoms and ions and then for molecules.

Contact Hyperfine Interactions in Atoms or Ions with Unpaired Spins

The nature of the contact hyperfine interaction in atoms or ions with unpaired spins has been investigated rather thoroughly for the transition metal ions and to some degree for light atoms such as Li, N, and P. The interaction is commonly discussed in terms of spin densities in order to focus attention on the electronic part of the problem without being bothered by differences in sign and magnitude of magnetogyric ratios of the nuclei or in the number of unpaired spins. The Fermi contact Hamiltonian is

$$\mathcal{H}_3=(8\pi/3)g_e\beta_e\gamma_N\hbar\Sigma_k\delta(\mathbf{r}_{kN})\mathbf{S}_k\cdot\mathbf{I}_N. \quad (3)$$

The hyperfine constant is

$$a_N=(8\pi/3)g_e\beta_e\gamma_N\hbar\rho_s, \quad (4)$$

where the electron spin density ρ_s is

$$\rho_s=\langle\Sigma_{k\uparrow}\delta(\mathbf{r}_{kN})-\Sigma_{l\downarrow}\delta(\mathbf{r}_{lN})\rangle. \quad (5)$$

The spin density at the nucleus of an atom or ion may include contributions *from a ground-configuration open s shell, from accessible configurations with open s shells,* and *from core polarization.*

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[13] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

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

The first two contributions are positive, that is, the spin density at the nucleus is the same as that of the unpaired s electron. The contact term due to an unpaired s electron in the ground configuration can be obtained by a restricted Hartree–Fock calculation. For example, 627 MHz out of the 803-MHz hyperfine splitting observed for Li is accounted for by a restricted Hartree–Fock calculation for the $1s^2 2s$ configuration.[15] This approach yields zero contact spin densities for atomic configurations with no unpaired s electrons. However, it may be used to calculate the contributions from accessible configurations with open s shells, due to configuration interaction.[16] This involves a restricted Hartree–Fock function for each configuration, the weights of the configurations being determined by the variational method.

The contribution due to core polarization may be either positive or negative and therefore it is especially important in connection with the negative values found for K_{XN}. For configurations with no open s shells, this is the entire contribution to the spin density at the nucleus since p, d, and f orbitals have nodes at the origin. Calculations of spin density at the nucleus due to core polarization have been used to explain the internal magnetic fields experienced by nuclei in paramagnetic transition metal compounds and ferromagnetic substances. Exchange-polarized (spin-polarized) Hartree–Fock calculations such as those by Watson and Freeman[17] are unrestricted Hartree–Fock calculations in which the α and β electrons within an nl shell are allowed to have different radial wavefunctions, thereby responding to the fact that all α electrons have an exchange interaction with the electrons contributing to the net spin α, whereas those of spin β do not. The result of such calculations is a nonzero spin density in the closed s-electron shells of the atom,

$$\rho_s = \Sigma_{ns}\rho_{ns}, \tag{6}$$

where

$$\rho_{ns} = |\psi_{ns\uparrow}(r)|^2 - |\psi_{ns\downarrow}(r)|^2. \tag{7}$$

The spin density of the core s electrons varies with r, positive in some regions and negative in others. The *integrated* spin density of the core is, of course, zero.

The calculations show that the core s electrons with spin parallel to that of the net spin (the open d shell in the case of transition metal ions) are attracted into the $3d$ region, the regions outside then having spin antiparallel to that of the net spin. Contributions of inner shells ($1s$, $2s$) to the spin density at the nucleus are negative, becoming positive for outer shells ($3s$, $4s$), but the net spin density at the nucleus is negative. This led Watson and Freeman[17] to the statement that "the exchange-polarized spin density at an atomic nucleus of an open p, d, or f shell atom is therefore almost inevitably antiparallel that of the open shell." For $3d$ transition metal ions and atoms, exchanged-polarized Hartree–Fock calculations led to agreement with the experimental results in the negative sign of the interaction, in the trend of increasing, negative values with increasing Z, and also in the magnitudes.

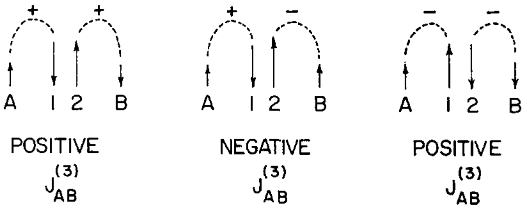

FIG. 3. A schematic representation of the manner in which the signs of the electron spin–nuclear spin interactions determine the sign of the contact contribution to J_{AB}. An interaction is defined as positive when it favors antiparallel correlation of the two spins involved.

When the unpaired electrons are of s type, *all* spin densities ρ_{ns} are found to be *positive*.[18] However, the reason why exchange polarization by s electrons is basically different from p or d electrons is not very well understood.

Contact Nuclear Spin–Electron Spin Interactions in Molecules

One may treat the nuclear spin–electron spin interactions in molecules in a fashion similar to that used for the nuclear spin–electron spin interactions in atoms or ions having unpaired spins. In the molecule, there is no unpaired electron, but the electron which we are concerned with, the electron in the atomic orbital of atom X participating in the bond with atom N, has an interaction with the nuclear spin. Just as in the case of the atomic hyperfine interactions, there are three contributions to the spin density at the nucleus of an electron in the atomic orbital involved in the bonding.

(1) If the ground configuration of the atom is an open s shell, such as hydrogen, the bonding orbital is an s orbital. The spin density of an electron in this orbital at the nucleus is simply $|\phi_{ns}(0)|^2$.

(2) If the atom has accessible[19] configurations with open s shells, mixing of these configurations with the ground configuration allows the other s orbitals to participate in the bonding. This could be the most important contribution if the ground configuration of the atom is not an open s shell but there are accessible configurations with open s shells, such that the valence state of the atom has an open s shell. An example is the $1s^2 2s^2 2p$ configuration of C, the bonding orbital of which has some s character, giving a positive contribution as in (1).

(3) Spin polarization of the core s shells by the electron in the bonding orbital leads to a finite spin density at the nucleus. This contribution could be the most

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[15] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).

[16] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961).

[17] A review of such calculations is given by R. E. Watson and A. J. Freeman in *Hyperfine Interactions*, A. J. Freeman and R. B. Frankel, Eds. (Academic Press Inc., New York, 1967).

[18] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[19] Here "accessible" is defined on the basis of promotional energy versus number of bonds formed and the bond energies.

important one if the ground configuration of an atom is not an open s shell and if there are no low-lying configurations with open s shells.

To illustrate these contributions, we consider three cases chosen such that each of the three contributions is dominant in one case:

Case A: Atom with open s-shell ground configuration.

Example: Li $1s^22s$

Bonding orbital: ϕ_{2s}

Contributions to spin density:

1. $|\phi_{2s}(0)|^2$ positive, dominant
2. Small
3. $[|\phi_{1s\uparrow,2s\uparrow}(0)|^2-|\phi_{1s\downarrow,2s\uparrow}(0)|^2]$ positive[18]

(The $1s$ spin density is due to polarization by the $2s$.)

Net effect: There is a positive spin density at the nucleus, leading to a positive electron spin–nuclear spin interaction.

Case B: Atom whose ground configuration is not an open s shell, but which has accessible configurations with open s shells, leading to a valence state with an open s shell.

Example: C $1s^22s^22p^2$ ground configuration
$1s^22s2p^2$ accessible configuration

Bonding orbital: $\alpha_s\phi_{2s}+\alpha_p\phi_{2p\sigma}$

Contributions to spin density:

1. None
2. $\alpha_s^2|\phi_{2s\uparrow}(0)|^2$ positive, dominant
3. $\alpha_s^2[|\phi_{1s\uparrow,2s\uparrow}(0)|^2-|\phi_{1s\downarrow,2s\uparrow}(0)|^2]$ positive[18] $+\alpha_p^2[|\phi_{1s\uparrow,2p\uparrow}(0)|^2-|\phi_{1s\downarrow,2p\uparrow}(0)^2]$ negative[20]

Net effect: There is a positive spin density at the nucleus, leading to a positive nuclear spin–electron spin interaction.

Case C: Atom whose ground configuration is not an open s shell, and which has no readily accessible configurations with open s shells; in other words, an atom, such as F $1s^22s^22p^5$, which has a valence state with a negligible admixture of an open s shell, like $1s^22s2p^6$.

Example: F $1s^22s^22p^5$

Bonding orbital: $\phi_{2p_z}+\lambda\phi_{2s}$ where $\lambda^2\ll 1$

Contributions to spin density:

1. None
2. $\lambda^2|\phi_{2s\uparrow}(0)|^2$ positive, small due to λ^2
3. $[|\phi_{2s\uparrow},2p_{\uparrow}(0)|^2-|\phi_{2s\downarrow,2p\uparrow}(0)|^2]$ possibly positive, small $+[|\phi_{1s\uparrow},2_{p\uparrow}(0)|^2-|\phi_{1s\downarrow,2p\uparrow}(0)|^2]$ negative, large

Net effect: There is a negative contact hyperfine interaction (see discussion below).

It should be borne in mind that core polarization by a valence electron in a molecule may differ significantly from that in the isolated atom because of the enhanced distribution of the valence electrons in the region between two covalently bonded atoms. For example, we might think of the electron in a covalently bonded F as being in an orbital which is more expanded in the region of the other atom than the $2p$ orbital is in an isolated F atom. Thus, the $2s$ orbital is more like an inner shell, making the spin-polarized core contribution more negative. This argument is based on the results of calculations by Goodings and Heine[21] of spin densities using $3d$ functions for metals which were artificially expanded (relative to the free-atom Hartree–Fock functions) at the maxima and over the tail regions. They found that "expanded" $3d$ functions make the $3s$ electrons behave more like an inner shell, with the net result that ρ_{3s} is less positive and the total spin density at the nucleus has a larger negative value. Such effects have not yet been studied in much detail.

The three cases which we have outlined serve to typify atoms in different parts of the periodic table. Case A includes H and the alkali atoms which have open s shells in the ground configuration. Case B includes Groups II (ns^2), III (ns^2np), and IV (ns^2np^2) which have configurations with open s shells which are fairly accessible, such that s hybridization is commonly invoked in describing their covalent compounds. On the other hand, Case C includes Group VII (ns^2np^5) and to some extent Group VI atoms, which commonly use primarily pure p orbitals in forming bonds. The s orbital is not used because of the prohibitive promotional energy, except for central atoms with three or more ligands, as in SF_6 and BrF_5. For these, hybridization such as d^2sp^3 and dsp^3 has been invoked.[22] The use of these hybridization schemes is justified by the argument that configurations above the ground configuration become more accessible when more bonds are formed or when bond energies are greater. An atom in a valence state corresponding to sp^3, d^2sp^3, dsp^2, dsp, or similar hybridization in which there is an open s shell, belongs to Case B.

Group V, having an ns^2np^3 configuration, could be considered a borderline case. In many Group V compounds, however, some s-orbital hybridization has been invoked in the interpretation of other observables.[22,23] In most cases then, Group V can be considered in Case B together with Groups II–IV.

IV. THE CONTACT CONTRIBUTION TO K_{XN}

Having considered the nature of the contact interaction, we turn now to the details of its contribution to K_{XN}. Of particular interest are the sign of $K_{XN}^{(3)}$ in

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[20] The exchange polarization of carbon $1s$ electrons by an unpaired electron in a $2p$ orbital has been calculated by M. Karplus and G. Fraenkel, J. Chem. Phys. **35**, 1312 (1961), and found to be -12.7 G.

[21] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[22] For example, D. P. Craig and E. A. Magnusson, J. Chem. Soc. **1956**, 4895.

[23] H. S. Gutowsky and J. Larmann, J. Am. Chem. Soc. **87**, 3815 (1965). R. Schmutzler, Angew. Chem. **77**, 530 (1965). G. Mavel, Progr. NMR Spectry. **1**, 251 (1966).

relation to the positions of atoms X and N in the periodic table, the dependence of $K_{XN}^{(3)}$ upon Z_X for various N's, and the dependence of $K_{XN}^{(3)}$ upon the character of the X–N bond.

The Sign of $K_{XN}^{(3)}$

As noted at the beginning of Sec. III and shown in Fig. 3, the sign of $K_{XN}^{(3)}$ is determined by the relative signs of the spin densities at nuclei X and N. Moreover, as given in Appendix B, the magnitude of $K_{XN}^{(3)}$ is determined by the product of the spin densities at the two nuclei. When both spin densities are of the same sign, that is, when both atoms belong to Case A or B, or both belong to Case C, $K_{XN}^{(3)}$ is positive. When they are of opposite sign, that is, when one atom belongs to Case A or B and the other atom belongs to Case C, $K_{XN}^{(3)}$ is negative. Using the preceding discussion of spin densities for atoms belonging to Cases A, B, and C, we would predict that the sign of the contact term $K_{XN}^{(3)}$ for a given N will change as X moves across the periodic table. $K_{XN}^{(3)}$ is predicted to be positive for X and N both in Groups I–IV, and negative for X in Groups I–IV and N in Groups VI–VII.[24] The model also predicts that $K_{XN}^{(3)}$ is positive for X and N both in Groups VI–VII, except for cases in which one is a central atom attached to three or more ligands. Thus, there would be a changeover in sign of $K_{XN}^{(3)}$ across the periodic table, for a given N. The changeover in sign is expected to occur somewhere between Group V and VI, $K_{XN}^{(3)}$ for atom N in Group V usually having the same sign as when N is in Groups I–IV. The sense of the sign changeover when N is a Class C atom is the reverse of that when N is a Class A or B atom.

Z Dependence of $K_{XN}^{(3)}$

In Cases A and B, for which the dominant contribution to the nuclear spin–electron spin interaction comes from an open *s* shell in the ground or some accessible configuration, the dependence of the interaction upon Z_X parallels that of the contact hyperfine interaction in atom X. The contact interaction is determined by $|\phi_s(0)|^2$, the spin density evaluated at the nucleus of the atom. Values of this function are summarized in Table I for Groups I–IV and V. It is seen that they increase with Z within each group, and also with Z within each period. This point was noted in our earlier discussion of K_{MH} in the Group IV hydrides.[2]

In those atoms in which an open *s* shell is not accessible and the nuclear spin–electron spin interaction is due almost entirely to core polarization, the magnitude of the interaction should also increase with Z down each group. This argument is based on the findings of Watson and Freeman[17] that in going from the $3d^m$ to the corresponding $4d^m$ transition metal ion the negative spin density due to core polarization, calculated by exchange-polarized Hartree–Fock method, increased threefold in magnitude. At the same time there was also an increase with Z along the third and fourth periods. They found that both the positive and negative contributions to the core spin density at the nucleus increased in magnitude, but in all cases the negative inner-shell contributions increased in magnitude to a greater extent than the positive outer-shell contributions, leading to a net increase in magnitude of spin density with Z.

TABLE I. Values of $|\phi_s(0)|^2$, in atomic units, calculated from the hyperfine splitting constants as given by Knight[a] for a number of atomic species.[b]

I	II	III	IV	VI
Li	Be			
0.21	0.714			
Na	Mg	Al	Si	
0.748	1.62	2.41	2.06	
K	Ca	Ga	Ge	Se
1.105	2.02	7.16	4.92	7.15
Rb	Sr		Sn	Te
2.33	3.77		8.16	11.0
Cs	Ba	Tl	Pb	
3.87	6.11	18.9	13.8	

[a] W. D. Knight, Solid State Phys. **2**, 120 (1956).

[b] Group I values were obtained from atomic-beam measurements and are the most accurate. Other values were obtained from atomic spectra, a correction being applied for each degree of ionization (+1 to +5 in Groups II to VI).

Thus, for a given N, and for X belonging to a given group in the periodic table, we expect an increase in the *magnitude* of $K_{XN}^{(3)}$ as Z_X increases down the group, regardless of the sign of $K_{XN}^{(3)}$. There will, of course, be variations in the magnitude of $K_{XN}^{(3)}$ with different bonding situations, particularly when atoms X and/or N belong to Case B with wide variations in α_s, as shown in the definition of Case B.

Dependence of $K_{XN}^{(3)}$ on the Bonding Situation

The bonding situation affects the sign of each of the nuclear spin–electron spin interactions. For example, consider an atom M belonging to Group V ($\cdots ns^2np^3$ ground configuration) and the MX_3 molecules. M could use three *np* orbitals for bonding in which case it would belong to Case C. However, it has been found[25] that interpretation of other observables (bond angles, chemical shifts, dipole moments) implies that sp^3 hybridization, with nonequivalent hybrid orbitals for M–X bonds and the lone pair, gives better agreement with experiment. This puts M in Case B, with α_s^2 varying with the kind of substituent X attached to M. As another example, consider sulfur ($\cdots 3s^2 3p_z^2 3p_x 3p_y$). When S is attached to only one atom (as in CS_2) or only two atoms (as in H_2S) it is likely that the bonding orbital used by sulfur is a $3p$ orbital, i.e., Case C.

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[24] See, however, the discussion of coupling in ionic structures.

[25] H. S. Gutowsky and J. Larmann, J. Am. Chem. Soc. **87**, 3815 (1965).

However, when S is attached to four or more atoms, as in SF_6, the bonding will probably involve use of sulfur d and s orbitals,[22] i.e., Case B.

In a formal sense α_s^2 varies with the number of bonds and hybridization used. For example, the value of α_s^2 for pure hybrids sp, sp^2, sp^3, dsp^2, dsp^3, and d^2sp^3 are, respectively, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{6}$. However, for real molecules, the treatment of $K_{XN}^{(3)}$ of course does not require that a hybridization model be used. α_s^2 is simply a quantitative measure of the s orbital participation in the bond. Whether the bonding situation is described adequately by the hybridization model or not is another matter.

The parameter α_s^2 varies with electronegativity. It has been frequently asserted that the s atomic orbital participation in a bond depends to some extent on the electronegativity of the other groups bonded to the atom.[26] The more electronegative a group such as X in CH_3X is, the more p orbital a C atom tends to use in bonding with the group X, presumably because a p orbital puts more electron density near the electronegative group. Thus, there is more s-orbital participation in the C–H bonds in CH_3X than in CH_4, and more p-orbital participation in the C–X bond in CH_3X than in CX_4.

The preceding discussions have focused mainly on the density at the nucleus of the bonding atomic orbital, say $\alpha_s\phi_{ns}+\alpha_p\phi_{np}$, centered on the same nucleus, as if such an orbital had a population of electrons equal to unity. However, in real molecules this is not usually the case. First, there are contributions to $K_{XN}^{(3)}$ from spin densities of orbitals not centered on X or N. These have not been considered in the foregoing discussions. However, they have been shown to contribute negligibly to directly bonded ^{13}C–H coupling constants,[2,27] and this probably holds in general. Second, if the two atoms are not identical, their orbital populations will not be equal. If the electron distribution were equivalent to a net transfer of fractional charge, i, from one atom to the other, both belonging to Case A or B, $K_{XN}^{(3)}$ would be approximately proportional to $(1+i)(1-i)$, the product of orbital populations. We see then that $K_{XN}^{(3)}$ decreases as i increases. This could be phrased as a dependence of $K_{XN}^{(3)}$ on the ionicity of the covalent bond.

Coupling in Ionic Structures

This brings us to the extreme case of an almost purely ionic structure M^+X^-. If there were no overlap or polarization of the X^- electron clouds by the positive ion, the electrons in the M atomic orbitals have negligible interaction with the electrons in the X atomic orbitals. Thus, we can no longer consider the M^+X^- coupling in the light of the model presented here for covalently bonded atoms. Also, since the X^- ion is spherically symmetric, the core polarization mechanism by an electron in a (quite) directional bonding orbital can no longer be invoked here.

Again, we look to hyperfine interactions in atoms or ions for a clue. It has been found that in paramagnetic fluoride (also chloride and bromide) complexes of $3d$ and $4d$ transition-metal ions, there are hyperfine interactions not only with the transition metal ion but also with the fluoride ions surrounding it. These "transferred hyperfine interactions" have been observed in many solids[28] as splittings whose number is appropriate to the number of nearest-neighbor X^- ions. The signs and magnitudes of the transferred hyperfine constants also have been determined by measuring the X contact shifts in NMR. They are *positive* in most cases. These transferred hyperfine interactions were interpreted quite successfully as due to small overlap and covalency effects. In other words, the filled ligand (X^-) s and p orbitals overlap with the metal-ion orbital which contains the unpaired d electron. This leads to a *positive* contribution to the spin density at the X nucleus. Also, any mixing (covalency) of the filled s and p ligand orbitals into the partially occupied $3d$ metal-ion orbital likewise leads to a *positive* spin density at the X nucleus.[17]

In an almost purely ionic bond, then, we would expect on the basis of the transferred hyperfine interaction in solids that the spin density at the X^- nucleus of an electron in the outer shell of the M atom is positive and relatively small. Such highly ionic bonds exist between the metals of Group I and the elements of Group VII. On the basis of the preceding discussion, we would expect *positive*, *relatively small* coupling constants between M and X in such structures.

V. DISCUSSION

Comparisons with Experimental Data for K_{XN}

As noted in Sec. II, the spin-dipolar and orbital contribution cannot account for the overall trends observed for K_{XN}. On the other hand, the contact term *with inclusion of core polarization effects* provides the model given in Sec. IV which is consistent with the data. This does not mean that the noncontact contributions are negligible. Instead, for example, in cases expected to have a small orbital term and a large spin-dipolar term with sign opposite to that observed, the contact term is large enough to offset the spin-dipolar term and to be the dominant contribution.

The core polarization aspect of the model, as discussed in Sec. IV, provides terms large enough[17] to explain the increase in magnitude of K_{XN} with Z_X, observed for both positive and negative values of K_{XN}. Furthermore, the model is in accord with the change in the signs of coupling constants observed across the periodic table. For example, in Fig. 1, the known signs of the reduced coupling constants of ^{1}H (Case A) with ^{2}D (Case A)

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[26] H. A. Bent, Can. J. Chem. **38**, 1235 (1960); Chem. Rev. **61**, 175 (1961); J. Inorg. Nucl. Chem. **19**, 43 (1961).

[27] D. Dugre, Ph.D. thesis, University of Illinois, 1967.

[28] For a review, see W. Low, Solid State Phys. Suppl. 2 (1960). J. H. E. Griffiths and J. Owen, Proc. Roy. Soc. (London) **A226**, 96 (1954). R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956); **108**, 1219 (1957); **109**, 1084 (1958).

and also with ^{11}B, ^{13}C, ^{29}Si, and ^{73}Ge (Case B) are positive as predicted by the model. The coupling of ^{13}C (Case B) with ^{1}H (Case A) and also with Group I–IV (Case B) is positive, becoming negative for atoms of Group VI–VII (Case C), as predicted by the model. The changeover in sign occurs, as predicted, somewhere between Groups V and VI. When bonded to ^{1}H and ^{13}C, Group V atoms are found to have positive coupling constants, which classifies them as Case B, with but one instance of a small negative coupling, that between ^{13}C and ^{31}P. However, Group VI atoms are found to have negative coupling constants, which categorize them with Case C, with the exception of some small positive couplings between ^{77}Se and ^{1}H. Experimental data would be of particular interest for K_{SH}, K_{OC}, and K_{SC}.

On the other hand, ^{19}F is a Case C atom and its coupling constants with Case B atoms such as ^{11}B, ^{13}C, ^{29}Si, and ^{31}P are negative, again as predicted by our model. Unfortunately, magnitude and/or sign data on K_{XF} are not yet available for NF_3 or OF_2, and that for F_2 is probably inaccessible. We expect K_{NF} to be negative, K_{FF} positive, and K_{OF} probably positive. Sign data for ClF, SF_4 and SF_6 would also be very interesting. In fact, the only values of K_{XF} observed to be positive thus far are those for the Group I atoms, Rb and Cs, which are Case A and for which covalent bonding would lead to a negative coupling. However, as pointed out at the close of Sec. IV, the highly ionic bonding in the alkali halides should give positive, relatively small coupling constants.

The signs and magnitudes of the internuclear coupling in $^{133}Cs^{19}F$ and in $^{85}Rb^{19}F$ and $^{87}Rb^{19}F$ were difficult to determine. So it seems relevant to point out that the data given for K_{CsF} and K_{RbF} in Fig. 1 and Appendix A were obtained from some recent, molecular beam electric resonance experiments performed by English and Zorn[29] on CsF, by Zorn *et al.*[30] on RbF and by Bonczyk and Hughes,[31] also on RbF. The results appear to be reliable, and their agreement with our model is encouraging. The Li–C bond should also be highly ionic and for it, the ^{7}Li–^{13}C coupling has been found to be fairly small in magnitude,[32] 12.4 compared to other coupling constants which range up to 1276 as listed in Fig. 1 for carbon. The sign of K_{LiC} is not yet known, but its magnitude is reasonable. The bonding in the hydrogen halides is considered to be fairly ionic so it would not be surprising if the H–Cl and H–F coupling constants in them also turn out to be positive.

For covalent compounds, the changeover in sign of the coupling constant appears to be rather sharp. There are large positive values right next to large negative values on the other side of the changeover line. One might expect a more gradual change from large positive to small positive and then small negative to large negative values. However, a closer look suggests that the sharpness of the change is a natural consequence of the core polarization effects. The core polarization, which becomes dominant and sign-determining at the right side of the periodic table, is present in all cases. However, polarization of inner closed *s* shells by the spin of an electron in a *p*, *d*, or *f* orbital leads to a *negative* spin density at the nucleus, whereas polarization by an electron in an *s* orbital leads to a *positive* spin density at the nucleus. Thus, in the Cases A and B where the positive open *s*-shell contribution dominates, the core polarization by the open *s* shell adds to it instead of subtracting.

With this as background we turn to the other cases in Fig. 1 and Appendix A for which the magnitude but not the absolute sign of K_{XN} has been measured. For hydrogen, our model predicts that K_{AlH}, K_{SnH} and K_{PbH} are positive; K_{OH} might be either positive or negative and we guess positive. For carbon, the prediction is that K_{LiC} is positive. For fluorine, the reduced coupling constants to Ge, As, Sb, and Te are probably all negative.

The fluorides of Group V and VIII elements are of interest in relation to the bonding state of the central atom. The S, Se, Te and Xe in SF_6, SeF_6, TeF_6, $XeOF_4$, XeF_4, and XeF_2 may be considered as Case B with valence states of the type d^2sp^3 and the like. If so, then the ^{33}S–F, ^{77}Se–F, ^{125}Te–F, and ^{129}Xe–F reduced coupling constants in the molecules are probably negative. There seems to be no consensus insofar as the bonding in these molecules is concerned. There are adherents to the view that only *np* orbitals of the central atom participate in the bonds.[33] There are also those who believe in some participation of $(n+1)s$ and *nd* orbitals.[34] The former type of bonding would place the central atom as well as F in Case C, leading to a positive reduced coupling constant, whereas the latter would place the central atom in Case B leading to a negative reduced coupling constant. If the model presented here is valid, then the sign and magnitude of the reduced coupling constant become an important and direct clue to the nature of the bonding in these and similar molecules.

A model proposed by Schaefer and Yaris[35] predicts that the sign of the coupling constants for directly bonded nuclei depends on the electronegativity difference between the atoms, being positive when this difference is less than 1.5 and negative when this difference is greater than 1.5. Inspection of Fig. 1 shows this does not hold for K_{SeC} and K_{TeC}. Both should be positive according to Schaefer and Yaris; in fact, they are both *negative and large.* Their prediction is likewise in error for Rb–F and Cs–F. Furthermore, because of the way in which electronegativity changes down the periodic table, their prediction would lead to the observation of crossover or borderline areas in which the coupling constant is small and changing sign. In

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[29] T. C. English and J. C. Zorn, J. Chem. Phys. **47**, 3896 (1967).
[30] J. C. Zorn, T. C. English, J. T. Dickinson, and D. A. Stephenson, J. Chem. Phys. **45**, 3731 (1966).
[31] P. A. Bonczyk and V. W. Hughes, Phys. Rev. **161**, 15 (1967).
[32] L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, J. Am. Chem. Soc. **90**, 3244 (1968).
[33] J. Jortner, S. A. Rice, and E. G. Wilson, J. Chem. Phys. **38**, 2302 (1963); J. Am. Chem. Soc. **85**, 815 (1963).
[34] See C. A. Coulson, J. Chem. Soc. **1964**, 1442, for a review.
[35] J. Schaefer and R. Yaris, Chem. Phys. Letters **1**, 173 (1967).

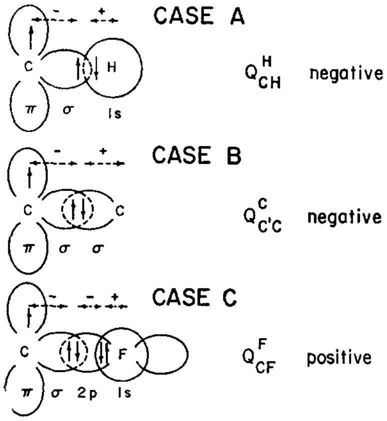

FIG. 4. Hyperfine interactions in organic free radicals from the point of view of the model presented here.

fact, these areas are not found where they are expected on the basis of the electronegativity differences.

According to Pople and Santry,[12] the coupling constant K_{HF} or K_{CF} can be negative if the fluorine $2s$ atomic energy level is sufficiently far below those for $2p_F$ and $1s_H$ or $2s_C$ and $2p_C$, in which case $2s_F$ mixes with $2p_F$ and $1s_H$ with a *negative* coefficient in the bonding molecular orbital. This appears to be equivalent to an exchange polarization of the $2s_F$ by the $2p_F$ and $1s_H$ orbitals. The model presented here for $K_{AB}{}^{(3)}$ agrees in part with Pople and Santry. If the fluorine $2s$ atomic energy level is sufficiently below that of $2p_F$, the F atom does not have accessible configurations with open s shells, thus classifying it into Case C. However, Pople and Santry's treatment would involve only the fluorine $2s$ orbitals, whereas our model involves polarization of the fluorine $1s$ core as well.

Signs of Hyperfine Coupling Constants

Although the model presented above is largely in terms of atomic hyperfine constants and hyperfine fields in $3d^m$ and $4d^m$ ions, in a sense it is an extension of theoretical treatments developed for hyperfine splittings in the ESR spectra of organic free radicals. Such splittings have been successfully interpreted in terms of sigma–pi exchange interaction in which an unpaired spin in a pi orbital polarizes the paired electrons in a sigma bond, leading to a negative spin density in the orbital of the atom sigma-bonded to the carbon with unpaired spin.[36] Examples which are most relevant to our discussion are the $\dot{C}$–H, $\dot{C}$–C′, and $\dot{C}$–F fragments, the interactions in which are shown schematically in Fig. 4.

In the $\dot{C}$–H fragment, a negative spin density in the $1s$ orbital of hydrogen is induced by sigma–pi interaction with the unpaired π electron. It gives a negative spin density at the hydrogen nucleus and a negative hyperfine splitting constant a_H. This relation is commonly written as

$$a_H = Q_{CH}{}^{H}\rho_C, \qquad (8)$$

where ρ_C is the spin density on the carbon π orbital and $Q_{CH}{}^{H}$ is about -23 G.[37] In the language of the model presented here, H belongs to Case A, and the σ–π interaction-induced negative spin density in its $1s$ atomic orbital leads to a spin density of the same (negative) sign at the H nucleus. Thus a_H is negative as shown in Fig. 4. Similarly, for the $\dot{C}'$–C fragment the coefficient of the spin density, $Q_{C'C}{}^{C}$ should also be negative, since carbon belongs to Case B.

But for the $\dot{C}$–F fragment, $Q_{CF}{}^{F}$ should be positive, opposite in sign to the previous two. As before, σ–π interaction with the unpaired electron on the carbon produces a negative spin density in the mainly $2p$ fluorine atomic orbital employed in bonding to the carbon. The chief effect of the negative spin density in the fluorine bonding orbital is to polarize the fluorine $1s$ and $2s$ core electrons in the sense negative to it, thereby giving a positive spin density at the F nucleus.

The observed values of a_H confirm the negative sign[37] of $Q_{CH}{}^{H}$. Also, the observed values of a_F (via contact shift measurements in aromatic ligands in which F is substituted for H) confirm that the sign of $Q_{CF}{}^{F}$ is opposite to that of $Q_{CH}{}^{H}$ in the same types of compounds.[38] The sign of $Q_{C'C}{}^{C}$ is not so directly confirmed, due to the fact that both C′ and C normally have some spin density. However, Karplus and Fraenkel[20] show that a_C values can be interpreted successfully in terms of the relation

$$a^C = S^C + \sum_{i=1}^{3} Q_{CX_i}{}^{C}\rho_C + \sum_{i=1}^{3} Q_{X_iC}{}^{C}\rho_{X_i}, \qquad (9)$$

where $Q_{X_iC}{}^{C}$ are negative for $X_i \equiv$ another carbon atom and $Q_{C'C}{}^{C} = -13.94$ G. The quantity S^C is the spin polarization of the $1s$ electrons of carbon by an unpaired electron in a π orbital of the same carbon atom; it is assumed by our model to be negative. It was calculated to be about -12.7 G by perturbation methods by Karplus and Fraenkel,[20] and also by Jemia and Lefebvre.[39]

Although our concern has centered on the coupling of directly bonded nuclei, similar arguments should hold with respect to the contact contribution to long-range coupling constants. When X and N are not directly bonded, the transfer of spin information from an electron i which has X nuclear spin information to an electron j which has N nuclear spin information, is an indirect one. Spins of i and j are no longer tightly coupled, the i to j transfer of spin information is less than 100% efficient, so that $J_{X\cdots N}{}^{(3)}$ is necessarily smaller than $J_{XN}{}^{(3)}$. The i–j interaction is measured by exchange integrals involving electrons i and j, and these are known to have signs and magnitudes which are sensitive to bond angles and distribution of electrons in the bonds.

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[37] H. M. McConnell, J. Chem. Phys. **24**, 632 (1956).

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APPENDIX A: SUMMARY OF EXPERIMENTAL DATA ON THE COUPLING CONSTANTS OF DIRECTLY BONDED NUCLEI

Nuclei (XN)	Range in J (Hz)	Compound(s)	Ref.	Sign of J	Ref.	K_{XN} (10^{20} cm^{-3})
Coupling Constants for ^1H						
^2DH	42.7	HD	(1)	+	(2)	+23.1
^{11}BH	29 to 211	$H_2B(H^*)BH_2(NMe_2)$, HBF_2	(3), (4)	+211 rel to J_{HBF}+in HBF_2	(4)	+7.5 to +54.7
^{13}CH	98 to 251	CH_3Li, ϕCC^*H	(5), (3)	+	(6)	+32.2 to 82.5
^{14}NH	46 to 53	NH3, NH_3D^+	(7)	+53 rel to J_{HND}−in NH_3D^+	(8)	+53 to 61
^{17}OH	73.5	H_2O	(9)			±45.1
^{19}FH	615	HF	(10)			±54.4
^{27}AlH	~110	$LiAlH_4$	(11)			±~35
^{29}SiH	187 to 383.9	ϕMe_2SiH, $HSiF_3$	(3)	−281.1 rel to J_{CH}+ in $MeSiHCl_2$; − rel to J_{HCSiH}+ in Me_2HSiCl	(12) (13)	+78.3 to +160.8
^{31}PH	186 to 707	P_2H_4, $HPO(OH)_2$	(3), (14)	+695.3 rel to J_{CH}+ in $(MeO)_2HP=0$; +186.5 rel to J_{HPPH}+in P_2H_4; +191 rel to J_{HPCH}+in Me_2PH	 (15) (16) (17)	+38.2 to 145.4
$^{35,37}ClH$	38	HCl	(18)			±~34
^{73}GeH	97.6	GeH_4	(19)			±~233
^{77}SeH	42.2, 44.7, 65.4	ϕCH_2SeH, MeSeH, HDSe	(20), (21)	+rel to J_{CH}+in CH_3SeH; +rel to J_{HCSeH}+	(21) (20)	+18.4 to +28.5
^{119}SnH	1744, 1931	Me_3SnH, SnH_4	(22)			±389.4, 431.2
^{195}PtH	1307	$(PEt_3)_2PtHCl$	(23)	+rel to J_{HCCH}+	(23)	+506
^{207}PbH	2379	Me_3PbH	(22)			±947.3
Coupling Constants for ^{13}C						
^7LiC	14.5		(24)			±12.4
^{13}CC	34 to 176	ϕCH_2CH_3, ϕCCH	(25)	+57.3 rel to J_{CH}+ in CH_3CN; +57.6 rel to J_{CH}+in CH_3COOH	(26) (27)	+44.8 to +231.7

Nuclei (XN)	Range in J (Hz)	Compound(s)	Ref.	Sign of J	Ref.	K_{XN} (10^{20} cm^{-3})
^{14}NC	7.6	^{13}CH$_3{}^{14}$NC	(28)	+rel to J_{CH}+	(28)	+34.8, +57.1
^{15}NC	17.5	CH$_3{}^{13}$C^{15}N	(29)	−rel to J_{CH}+	(29)	
^{29}SiC	52, 66	SiMe$_4$, MeSiHCl$_2$	(30), (12)	−52 rel to J_{CH}+in SiMe$_4$; −66 rel to J_{CH}+in MeSiHCl$_2$	(30) (12)	+86.6, +110
^{31}PC	14, 56	Me$_2\phi$P, Me$_2\phi$PHBr	(31)	−14 rel to J_{CH}+in Me$_2\phi$P; +56 rel to J_{CH}+in Me$_2\phi$PHBr	(31)	−11.4, +45.8
^{77}SeC	48 to 75	MeSeH, Me$_2$Se$_2$	(21), (32)	−48 rel to J_{CH}+in MeSeH; −50, −62, −75 rel to J_{CH}+in Me$_3$SeI, Me$_2$Se, Me$_2$Se$_2$	(21) (32)	−83.3 to −130.2
^{119}SnC	340, 864	SnMe$_4$, Me$_2$SnCl$_2$	(33), (34)	−rel to J_{CH}+in SnMe$_4$; −rel to J_{CH}+in Me$_2$SnCl$_2$	(33) (34)	+302 to +767.4
^{125}TeC	158.5	Me$_2$Te	(21), (32)	+rel to J_{CH}+in Me$_2$Te	(21), (32)	−166
^{199}HgC	203 to 687.4	Me$_2$C(OMe)CH$_2$HgCl, HgMe$_2$	(35)	+687.4 rel to J_{CH}+in HgMe$_2$	(36)	+376.9 to +1276.2
^{207}PbC	249	PbMe$_4$	(33)	+rel to J_{CH}+	(33)	+394
Coupling Constants for ^{17}O						
^{1}HO	73.5	H$_2$O	(9)			±45.1
^{129}XeO	692	XeOF$_4$	(37)			±1536
Coupling Constants for ^{19}F						
^{11}BF	4.8 to 108	BF$_4^-$, BFBr$_2$	(38), (39)	−84 rel to J_{HBF}+in HBF$_2$	(4)	±1.3 to −29.8
^{13}CF	157 to 395	CH$_3$F, CF$_3$SCF$_3$	(3)	−in CHFCl$_2$	(40), (11)	−55.2 to −139
^{14}NF	136, 145, 155	N$_2$F$_2$(t), N$_2$F$_2$(cis), NF$_3$	(42)			±166.5 to 189.8
^{29}SiF	169 to 356.6	SiF$_4$, SiF$_3{}^{29}$SiF$_2$SiF$_3$	(43), (44)	+267 2 rel to J_{CH}+in MeSiF$_3$; +275.1 rel to J_{SiH}−in HSiF$_3$	(45) (44)	−75.3 to −158.8
^{31}PF	545 to 1400	PMe$_3$F$_2$, PF$_3$	(3), (14)	−955 rel to J_{HCCH}+in (Me$_2$CHO)PFO; −1136.7 rel to J_{PH}+ in HPF$_2$; −rel to J_{PCF}+in CF$_3$PF$_2$ and (CF$_3$)$_2$PF	(46) (45) (47)	−119 to −306

Nuclei (XN)	Range in J (Hz)	Compound(s)	Ref.	Sign of J	Ref.	K_{XN} (10^{20} cm^{-3})
^{33}SF	251	SF_6	(48)			±289.4
^{35}ClF	∼310	$FClO_3$	(49)			±∼280
^{73}GeF	178.5	GeF_4	(48)			±452.7
^{75}AsF	930	AsF_6^-	(50)			±480.4
^{77}SeF	1400	SeF_6	(50)			±649
^{93}NbF	334	NbF_6^-	(51)			±120.9
^{95,97}MoF	44	MoF_6	(50)			±∼59
^{121}SbF	1843, 1940	SbF_6^-, $NaSbF_6$	(50), (52)			±681 to 717
^{125}TeF	3688	TeF_6	(50)			±1032.6
^{129}XeF	1163, 3864, 5690	$XeOF_4$, XeF_4, XeF_2	(53)			±371.9 to 1819.7
^{183}WF	48	WF_6	(50)			±103.1
^{205}TlF	12 000	TlF	(54)			±1840
Coupling Constants for ^{31}P						
^{11}BP	50	Me_2PHBH_3	(55)			±32
^{31}PP	108 to 583	P_2H_4, $(EtO)_2P(S)P(O)(OEt)_2$	(16), (56)	−108 rel to J_{HPPH}+in P_2H_4; −179.7 rel to J_{CH}+in Me_2PPMe_2; +465.5 rel to J_{PH}+ in $HP_2O_5^{3-}$	(16) (57) (56)	−54.8 to +296.1
^{63}CuP	1190, 1210	$Cu[P(OR)_3]_4^+ClO_4^-$	(58)			±923, 939
^{183}WP	265, 280	Octahedral W complexes	(59)			±1323, 1398
^{195}PtP	2435 to 5700	trans$(Et_3P)_2PtCl_2$; $[(Et_3O)_3P]_2PtCl_2$	(23), (60)	+rel to J_{HCCH}+	(23), (60)	+2330 to +5450
^{199}HgP	4216 to 4777	$Bu\phi_2PHgBr_2$, $(Bu_3P)_2HgBr_2$	(61)			±4862 to 5509
Coupling Constants for ^{203}Tl						
^{205}TlTl	2560	$(TlOEt)_4$	(62)			±646

List of References for Appendix A

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APPENDIX B: THE RELATION BETWEEN J_{XN} AND CONTACT HYPERFINE INTERACTIONS

The contact hyperfine constant for the free atom N is

$$a_N = \gamma_N (8\pi\hbar g_e\beta_e/3)[\rho_s(\mathrm{N})]_a, \qquad \text{(B1)}$$

where $[\rho_s(\mathrm{N})]_a$ is the spin density at the nucleus of the atom (a). By analogy, the reduced contact hyperfine constant for atom N in molecules containing the X–N bond may be written as

$$\mathcal{A}_N \equiv \gamma (8\pi g_e\beta_e/3)[\rho_s(\mathrm{N})]_m, \qquad \text{(B2)}$$

where the spin density is now that at nucleus N in the molecule (m). The expression for $J_{XN}^{(3)}$ in the context of the mean energy approximation is[13]

$$hJ_{XN}^{(3)} = \tfrac{1}{4}(\gamma_X\gamma_N/{}^3\Delta E)(8\pi\hbar g_e\beta_e/3)^2 P(s_Xs_N)^2 \times |s_X(0)|^2 |s_N(0)|^2, \qquad \text{(B3)}$$

where $P(s_Xs_X)^2$ is the s bond order of the X–N bond. In compounds for which X and N are Case A and/or Case B, we have

$$[\rho_s(X)]_m \times [\rho_s(N)]_m \simeq P(s_Xs_N)^2 |s_X(0)|^2 |s_N(0)|^2. \qquad \text{(B4)}$$

For these compounds, it is a good approximation to write

$$hJ_{XN}^{(3)} \simeq \tfrac{1}{4}\gamma_X\gamma_N\hbar^2\mathcal{A}_X\mathcal{A}_N/{}^3\Delta E, \qquad \text{(B5)}$$

or

$$K_{XN}^{(3)} \simeq \mathcal{A}_X\mathcal{A}_N/{}^3\Delta E.$$

The value for $\mathcal{A}_N$ in a molecule differs from that of a_N for the atom, so that the use of the latter in Eq. (B5) is at best a very rough approximation. The approximation of $\mathcal{A}_N$ by a_N is probably best in the H_2 molecule, which we use as an example. For H_2, by setting $\gamma_H\hbar\mathcal{A}_H \simeq$

$a_H = 1420$ MHz and with ${}^3\Delta E = 11.789$ eV,[40] one finds

$$\begin{aligned} J_{HH}{}^{(3)} &\simeq \tfrac{1}{4} a_H{}^2 / {}^3\Delta E \\ &= \tfrac{1}{4}(1420\ \text{MHz})^2 (4.136\times10^{-9}\ \text{eV/MHz}) \\ &\qquad \times (11.8\ \text{eV})^{-1} \\ &= 178\ \text{Hz}. \end{aligned} \tag{B6}$$

The measured HD coupling corresponds to a substantially larger value, $J_{HH} = 280$ Hz. We conclude that the use of atomic hyperfine constants in Eq. (B5) is semiquantitative at best, but it should give a reliable indication of the general trends which are the present concern.

Equations (B1)–(B6) can be extended to the core polarization effects, which are important for Case C atoms. In Eqs. (B1) and (B2) it is immaterial whether the spin densities are from "direct" *ns* contact interactions or from "indirect" core polarization effects. Adaptation of Eq. (B3) to describe the core polarization contribution to $J_{XN}{}^{(3)}$ requires that a detailed mechanism be introduced for the polarization, including the atomic orbitals and excited states involved. The details depend upon whether two class C atoms are involved or only one. It is apparent that nonetheless the general form of the contribution will be identical to Eq. (B5), but with $\mathcal{A}_N$ proportional to the spin density $[\rho_s(N)_{cp}]_m$ produced by core polarization. The magnitudes of such spin densities have been calculated for atoms[17] and determined for free radicals.[20] For class C atoms, the core polarization can readily be the dominant contribution to the contact term.

$\mathcal{A}_N$ may be expressed in terms of bond parameters like S (overlap integral), i (ionicity of the bond or fraction of charge transferred), α_s (s orbital participation), and α_p (p character of the bonding orbital). If the localized two-center molecular orbital for a single XN bond is written as

$$\begin{aligned} \psi = [2(1+(1-i^2)^{1/2}S)]^{-1/2}\{ & (1+i)^{1/2}[\alpha_s\phi_{ns}+\alpha_p\phi_{np}]_N \\ & +(1-i)^{1/2}[\alpha_s\phi_{ms}+\alpha_p\phi_{mp}]_X\}, \end{aligned} \tag{B7}$$

then

$$\begin{aligned} \mathcal{A}_N = {} & (8\pi g_e\beta_e/3)[2(1+(1-i^2)^{1/2}S)]^{-1}(1+i) \\ & \times[\alpha_s{}^2 \,|\, \phi_{ns}(0)\,|^2 + \alpha_s{}^2 \sum_{j=1}^{n-1} \\ & \times(|\,\phi_{js\uparrow,ns\uparrow}(0)\,|^2 - |\,\phi_{js\downarrow,ns\uparrow}(0)\,|^2) \\ & +\alpha_p{}^2 \sum_{j=1}^{n} (|\,\phi_{js\uparrow,np\uparrow}(0)\,|^2 - |\,\phi_{js\downarrow,np\uparrow}(0)\,|^2)]. \end{aligned} \tag{B8}$$

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