The total energy of the ground state is

$$E_0 = 2\sum_k E_k^{\mathrm{N}} + \sum_k\sum_l (2J_{kl} - K_{kl}) \qquad (24)$$

When an electron is removed from the nth orbital, a doublet state results whose energy is

$$E_2 = 2\sum_k^{n-1} E_k^{\mathrm{N}} + E_n^{\mathrm{N}} + \sum_l^{n-1} (2J_{kn} - K_{kn}) + \sum_k^{n-1}\sum_l^{n-1} (2J_{kl} - K_{kl}) \qquad (25)$$

The ionization potential is taken to be the difference between E_0 and E_2, *i.e.*

$$E_2 - E_0 = -E_n^{\mathrm{N}} - \sum_k^{n-1} (2J_{kn} - K_{kn}) - J_{nn} = -e_n \qquad (26)$$

In general there is a satisfactory agreement between the magnitudes of the calculated and observed ionization potentials (Table IV). As exemplified by NF_3, the least satisfactory agreement was achieved with fluorinated species. The latter problem may result from our neglect of one-center exchange integrals. Preliminary calculations on NF_3 where such integrals are included led to a substantial increase in the calculated ionization potential.

(iii) **Equilibrium Structure Predictions.** The performance of the theory in relation to the calculation of rotational barriers can be seen in Table V. In each case the staggered conformer is the more stable and the barrier height is taken to be the difference in energy between the staggered and eclipsed forms. For ethane, we calculate a barrier of 3.17 kcal mole^{-1} which is in good agreement with the experimental value[21] of 3.0 kcal mole^{-1}. Our calculated barrier may also be compared with the range 2.52–3.54 kcal mole^{-1} which is obtained from more rigorous calculations on ethane.[22–25] The extended Hückel[4] and CNDO[5] methods yield values of 4.0 and 2.42 kcal mole^{-1}, respectively, for this barrier. The *ab initio* SCF–LCAO–MO calculated barriers for CH_3NH_2 are 2.02[25] and 2.42[26] kcal mole^{-1}.

(iv) **Comparison with Other Methods.** In Table VI the energies of the occupied molecular orbitals as calculated by the present procedure are compared with those calculated by nonempirical methods and by the semiempirical YYK method.[15] In general the agreement between the present calculations and more rigorous calculations appears to be satisfactory. However, it will be noted that our method changes the order of the b_{2u} and b_{3u} orbitals of B_2H_6.

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The Calculation of Nuclear Spin Coupling Constants. II. One- and Two-Bond Couplings

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Abstract: The parameterized LCAO–SCF molecular orbital theory which was described in the preceding paper is applied to the calculation of the signs and magnitudes of a variety of nuclear spin coupling constants on the basis of the Fermi contact contribution. The treatment considers one- and two-bond couplings involving the nuclei ^1H, ^{11}B, ^{13}C, ^{14}N, ^{19}F, ^{29}Si, and ^{31}P.

In the foregoing paper[2] we have discussed the form of a semiempirical LCAO–SCF molecular orbital theory which appears to be appropriate for calculation of the contact contribution to nuclear spin coupling constants. The purpose of the present paper is to illustrate the applicability of this method to the calculation of the signs and magnitudes of a variety of one- and two-bond couplings involving the nuclei ^1H, ^{11}B, ^{13}C, ^{14}N, ^{19}F, ^{29}Si, and ^{31}P. We have discussed some of these directly bonded coupling constants previously.[3] However, in the earlier work the relevant eigenvectors and eigenvalues were calculated by extended Hückel or CNDO–SCF methods.

The interactions which lead to a nuclear spin coupling in fluids were first formulated by Ramsey[4] in terms of a contact (Fermi) mechanism, a spin-orbital mechanism, and a spin-polarization mechanism. Both McConnell[5] and Pople and Santry[6] have described modifications of Ramsey's equations which are suitable for use with

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LCAO molecular orbitals. In the present paper we employ the Pople and Santry approach[6] because McConnell's use of the "mean excitation energy approximation" necessarily results in the same relative sign for all directly bonded coupling constants.

The molecular orbital expression for the contact contribution to the spin–spin coupling between directly bonded nuclei A and B is given by[6]

$$J_{\mathrm{AB}} = -(64/9)\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}h\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}({}^3\Delta E_{i\rightarrow j})^{-1} \times (\psi_i|\delta(r_{\mathrm{A}})|\psi_j)(\psi_j|\delta(r_{\mathrm{B}})|\psi_i) \quad (1)$$

where β is the Bohr magneton, γ is the magnetogyric ratio, and the terms in the summation relate to the interaction of the triplet excited states with the singlet ground state evaluated at the A and B nuclei. In the LCAO approximation eq 1 becomes

$$J_{\mathrm{AB}} = -(64/9)\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}h\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}({}^3\Delta E_{i\rightarrow j})^{-1} \times \sum_{\lambda\mu\nu\sigma} C_{i\lambda}C_{j\mu}C_{j\nu}C_{i\sigma}(\phi_\lambda|\delta(r_{\mathrm{A}})|\phi_\mu)(\phi_\nu|\delta(r_{\mathrm{B}})|\phi_\sigma) \quad (2)$$

If only one-center integrals involving valence s orbitals on atoms A and B are retained, *i.e.*, ϕ_λ and ϕ_μ are valence s orbitals on A (s_{A}) and ϕ_ν and ϕ_σ are valence s orbitals on B (s_{B}), then

$$J_{\mathrm{AB}} = -(64/9)\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}h(s_{\mathrm{A}}|\delta(r_{\mathrm{A}})|s_{\mathrm{A}})(s_{\mathrm{B}}|\delta(r_{\mathrm{B}})|s_{\mathrm{B}}) \times \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}({}^3\Delta E_{i\rightarrow j})^{-1}C_{is_{\mathrm{A}}}C_{js_{\mathrm{A}}}C_{js_{\mathrm{B}}}C_{is_{\mathrm{B}}} \quad (3)$$

In eq 3 the singlet–triplet excitation energy, ${}^3\Delta E_{i\rightarrow j}$, is given by[7]

$${}^3\Delta E_{i\rightarrow j} = e_j - e_i + (\psi_j{}^2|\frac{e^2}{r_{12}}|\psi_i{}^2) \quad (4)$$

where e_i and e_j are the Hartree–Fock orbital energies. The integral, $\psi_j{}^2|(e^2/r_{12})|\psi_i{}^2$, represents the Coulombic repulsion between molecular orbitals ψ_i and ψ_j. In the LCAO approximation, this integral (J_{ij}) becomes

$$J_{ij} = \sum_k\sum_l\sum_m\sum_n C_{ki}C_{li}C_{mj}C_{nj}(\phi_k\phi_l|\frac{e^2}{r_{12}}|\phi_m\phi_n) \quad (5)$$

where C_{ki}, C_{li}, C_{mj}, and C_{nj} represent the LCAO coefficients, and ϕ_k, ϕ_l, ϕ_m, and ϕ_n are the corresponding atomic orbitals. Of course in the extended Hückel method, J_{ij} is omitted because of the neglect of interelectronic repulsion, and hence the excitation energies are taken to be the differences of the one-electron energies.

Method of Calculation. The eigenvectors and eigenvalues which are necessary for the calculation of coupling constants according to eq 3 were obtained from SCF calculations in which overlap is included. This method, its attendant approximations, and empirical parameterization were discussed in the previous paper.[2] The atomic coordinate data were taken from the literature, and the sources of such data will be indicated in the appropriate tables. The necessary magnetogyric ratios and magnitudes of the valence s atomic orbitals at the respective nuclei are presented in Table I.

Table I. Magnetogyric Ratios and Magnitudes of the Valences Atomic Orbitals at the Nuclei

Nucleus	Magnetogyric ratio[a,b]	$(s\|\delta(r)\|s)$[c,d]
^{1}H	2.7927	0.55
^{11}B	2.6880	1.4080
^{13}C	0.7022	2.7670
^{14}N	0.4036	4.7700
^{19}F	2.6273	11.3900
^{27}Al	3.6385	2.3580
^{29}Si	−0.5548	3.8069
^{31}P	1.1305	5.6251
^{35}Cl	0.8209	10.6435

[a] In units of $eh/4\pi M_{\mathrm{p}}c = 5.0493 \times 10^{-24}$ erg/G. [b] Values taken from "High-Resolution Nuclear Magnetic Resonance," J. A. Pople, W. G. Schneider, and H. J. Bernstein, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 480. [c] In units of $a_0{}^{-3}$ where a_0 = 0.529 Å. [d] Values taken from J. R. Morton, J. R. Rowlands, and W. H. Whiffen, National Physical Laboratory Report, BPR 13, Teddington, England, 1962.

Table II. One-Bond Couplings (Hz) Involving Group III Elements

Compound[a]	Coupling	Calcd	Obsd[c]	Ref
B_2H_6	^{11}B–^{1}H (terminal)	+64.02	+137	*d*
	^{11}B–^{1}H (bridge)	+14.19	+48	*d*
BH_3	^{11}B–^{1}H	+117.47	...	
BF_3[b]	^{11}B–^{19}F	−14.39	−15	*e*
BF_4^-	^{11}B–^{19}F	+43.38	1–5	*f*
BF_2Cl	^{11}B–^{19}F	−43.42	−34	*e*
$BFCl_2$	^{11}B–^{19}F	−68.86	−74	*e*
CH_3BF_2	^{11}B–^{19}F	−46.10	−77	*g*

[a] Structural data assumed: BH_3 (B–H = 1.19 Å, D_{3h} symmetry); BF_2Cl and $BFCl_2$ (B–F = 1.29 Å, B–Cl = 1.74 Å, C_{2v} symmetry). Other data taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. [b] Compound used to evaluate boron atom β parameter. [c] The signs are based on relative sign determinations in other molecules; see Table V and text. [d] W. D. Phillips and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [e] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960). [f] Reference 9. [g] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

Results and Discussion

(a) Group III Directly Bonded Couplings. In all cases except the tetrafluoroborate anion the calculated signs of the coupling constants (Table II) are such that the ^{11}B–^{1}H and ^{11}B–^{19}F couplings are positive and negative, respectively. The experimental signs have not been related to the ^{13}C–^{1}H coupling. However, in the molecule BF_2H $J_{^{11}B-^{1}H}$ and $J_{^{11}B-^{19}F}$ were found to be of opposite sign.[8] The most reasonable interpretation is that $J_{^{11}B-^{19}F}$ is negative and thus in agreement with the signs of the coupling constants for other first-row elements directly bonded to fluorine. Experimentally the ^{11}B–^{19}F coupling constant of BF_4^- has been found to be very small[9] (1–5 Hz), and the relative sign appears to depend on the solvent.[9b] Our calculations indicate that the $J_{^{11}B-^{19}F}$ coupling constant is positive in BF_4^-,

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Table III. One-Bond Couplings Involving Group IV Elements

Compound[a]	Coupling	Calcd	Obsd[c]	Ref
CH_4	$^{13}C-^1H$	+100.50	+125	*d*
C_2H_6	$^{13}C-^1H$	+79.75	+126	*e*
C_2H_4	$^{13}C-^1H$	+126.04	+157	*e*
C_2H_2	$^{13}C-^1H$	+226.87	+249	*e*
HCN	$^{13}C-^1H$	+228.11	. . .	
CH_3NH_2	$^{13}C-^1H$	+69.63	+133	*f*
CH_3PH_2	$^{13}C-^1H$	+78.61	+128	*g*
CH_3SiH_3	$^{13}C-^1H$	+78.18	+122	*h*
CF_4[b]	$^{13}C-^{19}F$	−251.30	−259	*i*
CF_3PH_2	$^{13}C-^{19}F$	−295.13	−314	*j*
CH_3SiH_3	$^{13}C-^{29}Si$	+6.76	. . .	
CH_3SiHCl_2	$^{13}C-^{29}Si$	−7.77	−66	*k*
CH_3SiH_3	$^{29}Si-^1H$	−124.36	−194	*h*
SiH_4	$^{29}Si-^1H$	−162.89	−203	*l*
Si_2H_6	$^{29}Si-^1H$	−120.19	−196	*m*
	$^{29}Si-^{29}Si$	+10.32	. . .	
SiF_4[b]	$^{29}Si-^{19}F$	+179.79	+178	*n*

[a] All structural data except for CF_3PH_2 taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. The data for CF_3PH_2 are taken from I. Y. M. Wang, J. E. Boggs, A. H. Cowley, and C. O. Britt, *J. Chem. Phys.*, **48**, 812 (1968). [b] Carbon and silicon atom β parameters evaluated from CF_4 and SiF_4, respectively. [c] The signs are based on relative sign determinations in other molecules; see Table V and text. [d] Reference 10. [e] R. M. Lynden-Bell and N. Sheppard, *Proc. Royal Soc.* (London), **A268**, 385 (1962). [f] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959). [g] Reference 28. [h] E. A. V. Ebsworth, *Trans. Faraday Soc.*, **59**, 1518 (1963). [i] S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963). [j] S. L. Manatt, D. D. Elleman, and A. H. Cowley, submitted for publication. [k] Reference 13. [l] Reference 26. [m] C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1071 (1964). [n] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

Table IV. One-Bond Couplings Involving Group V Elements

Compound[a]	Coupling	Calcd	Obsd[c]	Ref
NH_3	$^{14}N-^1H$	+30.15	40	*d*
NH_4^+	$^{14}N-^1H$	+23.29	53.5	*e*
CH_3NH_2	$^{14}N-^1H$	+26.23	. . .	
N_2H_4 *gauche*	$^{14}N-^1H$	+27.92	. . .	
NF_3[b]	$^{14}N-^{19}F$	−153.56	−155	*f*
N_2F_2 *trans*	$^{14}N-^{19}F$	−203.83	−136	*f*
N_2F_2 *cis*	$^{14}N-^{19}F$	−185.98	−145	*f*
N_2F_4 *gauche*	$^{14}N-^{19}F$	−99.93	−117	*g*
PH_2^-	$^{31}P-^1H$	+130.56	139	*h*
PH_3	$^{31}P-^1H$	+146.32	+182.2	*i*
PH_4^+	$^{31}P-^1H$	+297.02	+547	*j*
P_2H_4 *gauche*	$^{31}P-^1H$	+168.99	+186.5	*i*
P_2H_4 *trans*	$^{31}P-^1H$	+160.00	. . .	
P_2H_4 *cis*	$^{31}P-^1H$	+167.61	. . .	
CH_3PH_2	$^{31}P-^1H$	+179.37	+186.83	*k*
$CH_3PH_3^+$	$^{31}P-^1H$	+246.30	. . .	
CF_3PH_2	$^{31}P-^1H$	+122.07	+199.9	*l*
PF_3[b]	$^{31}P-^{19}F$	−1407.30	−1441	*m*
P_2F_4 *gauche*	$^{31}P-^{19}F$	−1189.48	−1125	*n*
P_2F_4 *trans*	$^{31}P-^{19}F$	−1160.77	. . .	
P_2F_4 *cis*	$^{31}P-^{19}F$	−1250.73	. . .	
P_2F_4 *gauche*	$^{31}P-^{31}P$	+219.75	+227.4	*o*
P_2F_4 *trans*	$^{31}P-^{31}P$	+707.36	. . .	
P_2F_4 *cis*	$^{31}P-^{31}P$	+212.16	. . .	
P_2H_4 *gauche*	$^{31}P-^{31}P$	−53.50	−108.2	*i*
P_2H_4 *trans*	$^{31}P-^{31}P$	+169.03	. . .	
P_2H_4 *cis*	$^{31}P-^{31}P$	−84.63	. . .	
CH_3PH_2	$^{31}P-^{13}C$	−20.87	. . .	
CF_3PH_2	$^{31}P-^{13}C$	+42.37	. . .	
$CH_3PH_3^+$	$^{31}P-^{13}C$	+7.47	. . .	

[a] The following structural data were assumed: PH_2^- (P–H = 1.42 Å, ∠HPH = 125°); P_2H_4 (P–P = 2.21, P–H 1.42 Å, ∠PPH = 100°, ∠HPH = 92°); P_2F_4 (P–P = 2.21, P–F = 1.57 Å, ∠PPF = 110°, ∠FPF = 110°). The structural data for CF_3PH_2 are taken from I. Y. M. Wang, J. E. Boggs, A. H. Cowley, and C. Britt, *J. Chem. Phys.*, **48**, 812 (1968). The remaining data are taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. [b] Nitrogen and phosphorus atom β parameters evaluated from NF_3 and PF_3, respectively. [c] The signs are based on relative sign determinations in other molecules; see Table V and text. [d] J. V. Acrivos, *J. Chem. Phys.*, **36**, 1097 (1962). [e] G. Fraenkel, *et al.*, *ibid.*, **44**, 4647 (1966). [f] Reference 15. [g] R. Ettinger and C. B. Colburn, *Inorg. Chem.*, **2**, 1312 (1963). [h] G. M. Sheldrick, *Trans. Faraday Soc.*, **63**, 1071 (1967). [i] Reference 18. [j] G. M. Sheldrick, *Trans. Faraday Soc.*, **63**, 1077 (1967). [k] Reference 28. [l] S. L. Manatt, D. D. Elleman, and A. H. Cowley, submitted for publication. [m] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959). [n] Reference 22. [o] Reference 20.

but the generally small magnitude of the $^{11}B-^{19}F$ coupling renders unequivocal prediction impossible.

(b) Group IV Directly Bonded Couplings. The trend of calculated magnitudes of $J_{^{13}C-^1H}$ for the compounds CH_4, C_2H_4, C_2H_2, and HCN (Table III) gives a reasonable fit of coupling constant *vs.* per cent s character, thus reproducing the well-known experimental trend.[10] It should be pointed out that our calculations do not include π contributions for C_2H_2, C_2H_4, and HCN since eq 3 concerns the LCAO coefficients of valence s orbitals. The π contribution to the $^{13}C-^1H$ coupling has been estimated to be −2.16 Hz for C_2H_4.[11] Somewhat more negative values (but still small in magnitude) might be expected for C_2H_2 and HCN. We do not have an explanation for the low calculated value for the $^{13}C-^1H$ coupling in ethane, although a similar diminution appears to persist in the other CH_3X compounds (X = NH_2, PH_2, and SiH_3). Evaluation of the silicon atom β parameter using the $^{29}Si-^{19}F$ coupling of SiF_4 yields satisfactory calculated coupling constants involving ^{29}Si in SiH_4, Si_2H_6, and CH_3SiH_3. In considering couplings which involve the ^{29}Si nucleus, it should be recalled that the magnetogyric ratio of this nucleus is negative. In some respects it is preferable to employ a "reduced coupling constant," K_{AB}, defined by[6]

$$K_{AB} = (2\pi/\hbar\gamma_A\gamma_B)J_{AB} \qquad (6)$$

which is independent of the magnetogyric ratios. On the basis of "reduced coupling constants," all the relative signs in Table III pertaining to ^{29}Si would change except for the $^{29}Si-^{29}Si$ coupling. In the calculations performed thus far, $J_{^{29}Si-^1H}$ and $J_{^{29}Si-^{19}F}$ are consistently negative and positive, respectively, in accord with the experimental sign determinations in the molecules $(CH_3)_3SiH$,[12] CH_3SiHCl_2,[13] and $(CH_3)_3SiF$.[12] For CH_3SiH_3 and CH_3SiHCl_2 the coupling constants (*J*) for the $^{29}Si-^{13}C$ linkage are calculated to be positive and negative, respectively. Experimentally, negative signs have been found for this coupling in $(CH_3)_4Si$[14] and CH_3SiHCl_2.[13]

(c) Group V Directly Bonded Couplings. The

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Table V. Relative Sign Data for One-Bond Couplings

Coupling	Rel sign	Compd	Ref
$^{11}B-^{1}H$	+	BF_2H	*a*
$^{11}B-^{19}F$	−	BF_2H	*a*
$^{13}C-^{1}H$	+	*p*-$NO_2C_6H_4CH_3$	*b*
$^{13}C-^{19}F$	−	$CHCl_2F$	*c*
$^{29}Si-^{1}H$	−	$(CH_3)_3SiH$	*d*
		CH_3SiHCl_2	*e*
$^{29}Si-^{19}F$	+	$(CH_3)_3SiF$	*d*
$^{29}Si-^{13}C$	−	CH_3SiHCl_2	*e*
		$(CH_3)_4Si$	*f*
$^{14}N-^{19}F$	Probably −	N_2F_2	*g*
$^{31}P-^{1}H$	+	CF_3PH_2	*h*
		P_2H_4	*i*
		$(CH_3O)_2P(O)H$	*j*
$^{31}P-^{19}F$	−	CF_3PF_2	*h*
$^{31}P-^{13}C$	±	+ in $(CH_3)_2C_6H_5P^+HBr^-$	
		− in $(CH_3)_2C_6H_5P$	*k*
$^{31}P-^{31}P$	±	+ in $(HP_2O_5)^{3-}$	*l*
		− in P_2H_4	*h, i, m*
		$(CH_3)_4P_2$, $(CH_3)_2P-P(CF_3)_2$, and $(CH_3)_3P^+-P^-CF_3$	

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Table VI. Two-Bond Couplings Involving Group IV and Group V Elements

Compound[a]	Coupling	Calcd	Obsd[b]	Ref
CH_4	$^{1}H-C-^{1}H$	−12.92 Hz	−12.4 Hz	*c*
C_2H_6	$^{1}H-C-^{1}H$	−7.82	−7.7	*d*
CH_3NH_2	$^{1}H-C-^{1}H$	−8.30	. . .	
CH_3PH_2	$^{1}H-C-^{1}H$	−7.68	. . .	
CH_3SiH_3	$^{1}H-C-^{1}H$	−6.44	. . .	
SiH_4	$^{1}H-Si-^{1}H$	−2.45	2.75	*d*
Si_2H_6	$^{1}H-Si-^{1}H$	+0.88	. . .	
CH_3SiH_3	$^{1}H-Si-^{1}H$	−3.27	. . .	
NH_3	$^{1}H-N-^{1}H$	−19.13	−10.35	*e*
CH_3NH_2	$^{1}H-N-^{1}H$	−13.23	. . .	
NH_4^+	$^{1}H-N-^{1}H$	−10.84	−11.67	*f*
N_2F_2 *cis*	$^{14}N-N-^{19}F$	+17.96	+37.0	*g*
N_2F_2 *trans*	$^{14}N-N-^{19}F$	+20.91	+73.0	*g*
PH_3	$^{1}H-P-^{1}H$	−18.75	−13.43	*h*
CH_3PH_2	$^{1}H-P-^{1}H$	−14.12	−12.46	*i*
CF_3PH_2	$^{1}H-P-^{1}H$	−4.02	−13.37	*i*
PHF_2	$^{1}H-P-^{19}F$	+34.41	+41.7	*j*
CF_3PH_2	$^{31}P-C-^{19}F$	+47.88	+48.83	*k*
CH_3PH_2	$^{31}P-C-^{1}H$	+2.95	+3.99	*l*
$CH_3P^+H_3$	$^{31}P-C-^{1}H$	−7.67	. . .	

[a] All structural data except for CF_3PH_2 and PHF_2 taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. The data for CF_3PH_2 are taken from I. Y. M. Wang, J. E. Boggs, A. H. Cowley, and C. O. Britt, *J. Chem. Phys.*, **48**, 812 (1968). The data for PHF_2 (P–F = 1.582 Å, P–H = 1.412 Å, ∠HPF = 96.3°, ∠FPF = 99°) are taken from R. L. Kuczkowski, *J. Am. Chem. Soc.*, **90**, 1705 (1968). [b] The signs are based on relative sign determinations in other molecules; see Table V and text. [c] M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **27**, 597 (1957). [d] N. Muller and D. E. Pritchard, *ibid.*, **31**, 1471 (1959). [e] R. A. Bernheinz, *ibid.*, **40**, 3446 (1964). [f] G. Fraenkel, *et al.*, *ibid.*, **44**, 4647 (1966). [g] Reference 15. [h] Reference 18. [i] S. L. Manatt and A. H. Cowley, submitted for publication. [j] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965). [k] S. L. Manatt, *et al.*, submitted for publication. [l] Reference 28.

results obtained with a variety of group V compounds are shown in Table IV. The compounds NF_3 and PF_3 were used to evaluate the atom β parameters for nitrogen and phosphorus. The $^{14}N-^{1}H$ and $^{14}N-^{19}F$ couplings are calculated to be positive and negative, respectively. There appear to be no data pertaining to the sign of the $^{14}N-^{1}H$ coupling. Noggle and Baldeschweiler[15] have found that the NF and NNF couplings are opposite in sign but neither of these have been related to $J_{^{13}C-^{1}H}$. It might also be pointed out that the $^{14}N-^{1}H$ coupling constant can be converted into the corresponding $^{15}N-^{1}H$ coupling by multiplying $J_{^{14}N-^{1}H}$ by −1.403.

The $^{31}P-^{1}H$ coupling has been shown to be positive in CF_3PH_2,[16] $(CH_3O)_2P(O)H$,[17] and probably P_2H_4.[18] Our calculations are consonant with these findings. A satisfactory agreement between the calculated and observed magnitudes is also apparent. However, to some extent the theoretical approach was frustrated by lack of structural data, notably on P_2H_4 and PH_2^-. Thus, we were obliged to perform computations on *cis*, *trans*, and *gauche* P_2H_4 models, and to employ a variety of HPH bond angles (90–160°) in the PH_2^- model. The results conformed to expectation, namely that the $^{31}P-^{1}H$ coupling in P_2H_4 is relatively insensitive to rotation about the P–P bond, while the same coupling in the phosphide anion displayed a marked angular dependence, varying from −9.0 Hz at 90° to +700 Hz at 160°. The best agreement with the observed magnitude occurred with an HPH angle of 125°. It is of interest to note that the bond angle of the NH_2^- ion has been estimated[19] to be in the range of 103–109°.

Very recently Finer and Harris[20] have shown that the sign of the P–P coupling constant is dependent upon the valence state of phosphorus and probably also upon the substituent electronegativity and bulk. Of immediate concern to the present paper was the suggestion[20] that the $^{31}P-^{31}P$ coupling in P_2F_4 is positive while that in P_2H_4 is negative. Our calculations support this conclusion, but with the restriction that the *trans* conformation of P_2H_4 is excluded. As expected rotation around the P–P linkage causes profound changes in the bonding. Reasonable agreement between the calculated and observed magnitudes of $J_{^{31}P-^{31}P}$ occurs if either the *cis* or *gauche* conformers of P_2H_4 and P_2F_4 are adopted. Unfortunately precise structural data are not available for either of these molecules, although the nmr data of P_2H_4[18] and P_2F_4[21] have been interpreted as favoring the *trans* conformation or rapid rotation in each case. Vibrational spectroscopic studies favor the *trans* conformation for P_2F_4[22] and the *gauche* conformation for P_2H_4.[23]

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Similar changes of sign are apparent in the $^{31}P-^{13}C$ coupling constant. Thus, McFarlane[24] has observed that the $^{31}P-^{13}C$ (methyl) coupling is negative in dimethylphenylphosphine and positive in the dimethylphenylphosphonium cation. Our calculations on CH_3PH_2 and $CH_3PH_3^+$ reproduce this trend since $J_{^{31}P-^{13}C}$ is computed to be -20.87 Hz in the phosphine and $+7.47$ Hz in the phosphonium cation. In addition our results suggest that the P–C coupling in primary phosphines is dependent upon the substituent since the calculated values of $J_{^{31}P-^{13}C}$ for CH_3PH_2 and CF_3PH_2 are -20.87 and $+42.37$ Hz, respectively. We are currently seeking experimental confirmation of this suggestion.

Two-Bond Couplings. In Table VI we present the results of the application of the SCF theory to the calculation of a variety of two-bond couplings. It is clear that more experimental data would be very desirable in this area. However, comparison with the available experimental data reveals a satisfactory correlation with the computed values.

A great deal of effort has been expended in attempting to understand the variation of the sign and magnitude of the geminal proton–proton coupling. It has been found[25] that this coupling constant increases from -12.0 to $+2.0$ Hz as the HCH angle opens out from tetrahedral to 120°. The calculated negative sign for all the $^{1}H-C-^{1}H$ couplings shown in Table VI would, therefore, appear to be reasonable since, as shown by the similar $^{13}C-^{1}H$ directly bonded coupling in these compounds (Table III) the carbon atom hybridization remains effectively constant.

The calculated magnitudes for $J_{^{1}H-Si-^{1}H}$ in the three silicon compounds considered in Table VI are small; hence both positive and negative signs are predicted for this coupling. Very recently it has been shown[26] that the geminal H–H coupling constant is positive in a variety of Si, Ge, and Sn hydrides. There appear to be no experimental sign data for the geminal proton–proton coupling constant in nitrogen compounds. However, in view of the established[27] negative sign for the $^{1}H-P-^{1}H$ coupling in primary phosphines the calculated negative sign for the $^{1}H-N-^{1}H$ coupling appears to be reasonable. The $^{14}N-N^{19}F$ couplings in both *cis*- and *trans*-N_2F_2 are calculated to be positive, and thus opposite in sign to $J_{^{14}N-^{19}F}$ in accord with the experimental results.[15]

There is now a considerable body of evidence that $J_{^{31}P-C-^{1}H}$ changes from positive to negative when a phosphine is quaternized[24,28] or enters into adduct formation.[29] The calculated change of sign of the $^{31}P-C-^{1}H$ coupling in going from methylphosphine to the methylphosphonium cation is consistent with these experimental findings.

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