The Calculation of Nuclear Spin Coupling Constants.
I. Theoretical Considerations[1]

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Abstract: A parameterized LCAO–SCF molecular orbital theory which includes overlap is described. The principal difference between this and other theories concerns the expression for the off-diagonal core matrix elements, H_{ij}. The Coulomb integrals and core attraction integrals were evaluated by the semiempirical methods of Baird, Dewar, and Klopman. The theory is intended primarily for the calculation of the contact contribution to nuclear spin coupling constants (see following paper). In the present paper the usefulness of this theory is tested with respect to the calculation of dipole moments, ionization potentials, and rotational barriers.

In a previous publication[2] we described the calculation of the signs and magnitudes of a number of one-bond nuclear spin coupling constants involving phosphorus and silicon. These calculations were made by employing the Pople and Santry expression[3] for the contact term. The appropriate eigenvectors and eigenvalues were generated by both extended Hückel calculations[4] and by self-consistent field calculations in which differential overlap is neglected.[5] Generally, the most satisfactory calculation of coupling constant magnitudes was obtained by the extended Hückel method (which includes overlap, but excludes electron–electron interactions). However, both methods failed to reproduce the expected sign for the ^{29}Si–^{19}F coupling constant. Further, it was demonstrated that the difficulty with the calculated ^{29}Si–^{19}F coupling constant was not rectified by inclusion of the spin-orbital and spin-dipolar contributions to the coupling mechanism, although the net calculated value of these terms was in the correct direction.

Therefore, we were encouraged to see if the calculation of nuclear spin coupling constants could be improved by the development of a semiempirical LCAO–SCF molecular orbital method. The most successful type of calculation was found to be a parameterized SCF method which includes overlap in the diagonalization of the secular equation. This paper describes the essential features and approximations involved in the method, together with a discussion of the validity of the theory with respect to the calculation of dipole moments, ionization potentials, and rotational barriers. Finally comparisons are made between the present method and more rigorous methods in regard to calculated orbital energies.

Theoretical Approach

This method considers only valence-shell electrons. The inner-shell electrons are considered to constitute an unpolarizable core. The molecular orbitals, ψ_j, are assumed to be a linear combination of Slater-type atomic orbitals,[6] ϕ_i.

$$\psi_j = \sum_i C_{ij}\phi_i \qquad (1)$$

Unless otherwise indicated the AO basis sets comprised a 1s orbital for H; 2s and 2p orbitals for B, C, N, and F; and 3s and 3p orbitals for Si, P, and Cl.

For a closed-shell system, the LCAO–SCF method involves solving the Roothaan equations.[7]

$$\sum_j (F_{ij} - S_{ij}e_u)C_{ju} = 0 \qquad i = 1, 2, 3, \ldots, n \qquad (2)$$

Here, F_{ij} denotes the elements of the Hartree–Fock Hamiltonian matrix

$$F_{ij} = H_{ij} + \sum_k \sum_l P_{kl}[(ij,kl) - {}^1/_2(ik,jl)] \qquad (3)$$

where H_{ij} represents the matrix elements of the core interaction matrix of the one-electron Hamiltonian which includes kinetic energy and core attraction terms. The particular form of H_{ij} which is used in our approximation is discussed in detail later. P_{kl} corresponds to the matrix elements of the charge–bond order matrix and is obtained by summation of the LCAO coefficients over the occupied molecular orbitals, u.

$$P_{kl} = 2\sum_u^{\text{occ}} C_{ku}C_{lu} \qquad (4)$$

The symbols (ij,kl) and (ik,jl) are abbreviations for the multicenter Coulomb and exchange integrals, respectively, and are given by

$$(ij,kl) = \iint \phi_i(1)\phi_j(1)e^2/r_{12}\phi_k(2)\phi_l(2)\,d\tau(1)d\tau(2) \qquad (5)$$

and

$$(ik,jl) = \iint \phi_i(1)\phi_k(1)e^2/r_{12}\phi_j(2)\phi_l(2)\,d\tau(1)\,d\tau(2) \qquad (6)$$

for electrons 1 and 2.

S_{ij} denotes the elements of the overlap matrix

$$S_{ij} = \int \phi_i\phi_j\,d\tau \qquad (7)$$

and e_u and C_{ju} represent the eigenvalues and eigenvectors, respectively.

The next approximation involves replacement of the three- and four-center Coulomb integrals of (5) and the two-, three-, and four-center exchange integrals of (6) by two-center Coulomb integrals according to the method of Mulliken.[8]

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(1) Taken in part from the Ph.D. Dissertation of W. D. White, The University of Texas at Austin, 1968.

(2) A. H. Cowley, W. D. White, and S. L. Manatt, *J. Am. Chem. Soc.*, **89**, 6433 (1967).

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

(4) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963), and references therein.

(5) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

(6) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(7) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(8) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

Table I. Core Matrix Elements (U_i^A) and One-Center Integrals (γ_{AA})

Element	U(s), eV	U(p), eV	γ_{AA}, eV
Hydrogen	−13.595	. . .	12.845
Boron[a]	−33.6592	−29.383	9.59
Carbon	−49.884	−42.696	11.144
Nitrogen	−60.593	−58.669	11.975
Fluorine	−130.174	−109.284	15.996
Aluminum[a]	−22.44	−19.07	7.100
Silicon	−35.2	−28.862	7.335
Phosphorus	−50.759	−43.362	8.674
Chlorine	−85.592	−73.678	10.507

[a] Boron and aluminum values obtained from least-squares analysis of the remaining values in the table. The other values are taken from ref 12.

Table II. Values of β^0 for the LCAO–SCF Method

Atom	β^0	Atom	β^0
Hydrogen	1.1500	Aluminum	1.1110
Boron	1.1110	Silicon	1.0739
Carbon	1.07225	Phosphorus	1.1150
Nitrogen	1.1500	Chlorine	1.0600
Fluorine	1.0600		

$$(ij,kl) = \tfrac{1}{4}S_{ij}S_{kl}[(ii,kk) + (ii,ll) + (jj,kk) + (jj,ll)] \qquad (8)$$

One-center exchange integrals are neglected because of the orthogonality of two atomic orbitals on the same center. The two-center Coulomb integrals from eq 8 are further simplified by the assumption that all two-orbital, two-electron integrals between cores A and B are equal, and may be specified by

$$\gamma_{AB} = \left\langle \phi_s^A\phi_s^A \left| \frac{e^2}{r_{12}} \right| \phi_s^B\phi_s^B \right\rangle \qquad (9)$$

where ϕ_s^A and ϕ_s^B are valence s atomic orbitals on cores A and B, respectively. Pople and Segal[5] have described a procedure for evaluating γ_{AB} using Roothaan's tabulation of formulas for atomic integrals.[9] However, in the present work, we employed the semiempirical expression of Baird and Dewar.[10] The latter method has the advantage that it accounts for some electron correlation by assigning a smaller value to γ_{AB}. The equation for γ_{AB} is

$$\gamma_{AB} = e^2[R_{AB}^2 + (\rho_A + \rho_B)^2]^{-1/2} \qquad (10)$$

where R_{AB} is the internuclear distance between cores A and B in Å, and ρ_A and ρ_B are constants characteristic of the two atoms A and B with a boundary condition such that γ_{AB} approaches the one-center integral, γ_{AA}, as $R_{AB} \rightarrow 0$ (see Table I).

Next we consider the evaluation of the core matrix elements, H_{ij}. Following Pople, Santry, and Segal,[11] the diagonal matrix elements, H_{ii}, are expressed as follows.

$$H_{ii} = \left(\phi_i^A \left| -\tfrac{1}{2}\nabla^2 - \frac{Z_A}{r_{1A}} \right| \phi_i^A\right) - \sum_{B\neq A}\left(\phi_i^A \left| \frac{Z_B}{r_{1B}} \right| \phi_i^A\right)$$
$$= U_i^A - \sum_{B\neq A}(\phi_i^A|V_B|\phi_i^A) \qquad (11)$$

U_i^A is an atomic quantity which represents the kinetic energy of an electron in an orbital ϕ_i^A centered on core A together with the potential energy due to its attraction by core A. The U_i^A values used in the present work (Table I) are taken from Klopman's analysis of atomic spectroscopic data.[12] The second term in (11) concerns the interaction of an electron in ϕ_i (centered on A) with the remaining cores and is approximated as the core charge of atom B, Z_B, times the negative of the electron–electron repulsion between orbital ϕ_i and the valence-shell orbitals of B.[10,13]

$$(\phi_i^A|V|\phi_i^A) = -Z_B\gamma_{AB} = V_{AB} \qquad (12)$$

The most satisfactory expression for the off-diagonal core matrix elements (*i.e.*, the resonance integral) was found to be

$$H_{ij} = \tfrac{1}{2}\beta_{AB}S_{ij}\left[(U_i^A + U_j^B) - \left(\sum_{C\neq A} V_{AC} + \sum_{C\neq B} V_{BC}\right)\right] \qquad (13)$$

β_{AB} is a parameter which depends only upon the nature of the cores A and B and is given by the expression

$$\beta_{AB} = \tfrac{1}{2}(\beta_A^0 + \beta_B^0) \qquad (14)$$

The values of the empirical parameters, β^0, were chosen on the basis of the best agreement between calculated and observed directly bonded nuclear spin coupling constants for a few small molecules (Table II). This should not infer that this type of parameterization is suitable only for the nmr problem. Its application to dipole moment, ionization potential, and rotational barrier calculations will be discussed later in the present paper.

It will be noted that, unlike the CNDO–SCF method[5,11] (where $H_{ij} = \beta_{AB}S_{ij}$), our β^0 values do not show a regular trend with Z, the atomic number. This is because in the present theory it is the term

$$\tfrac{1}{2}\beta_{AB}\left[(U_i^A + U_j^B) - \left(\sum_{C\neq A} V_{AC} + \sum_{C\neq B} V_{BC}\right)\right]$$

which is characteristic of the cores A and B. This term, does, in fact, show the expected trend with respect to Z.

Although the general form of the expression for the H_{ij} elements (eq 13) bears a superficial resemblance to the widely used Wolfsberg–Helmholtz expression[14]

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (15)$$

it is perhaps important to point out the following differences.

(i) The Wolfsberg–Helmholtz expression relates to independent electron theory; *i.e.*, it does not involve electron–nucleus interaction terms directly such as V_{AC} in eq 13.

(ii) As pointed out by Pople, Santry, and Segal,[11] the two sides of eq 15 transform in different ways; *i.e.*, the eigenvectors and eigenvalues of this approximation will not be invariant to the hybridization of the atomic orbital basis set.

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[9] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[10] N. C. Baird and M. J. S. Dewar, *ibid.*, in press.

[11] J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

[12] G. Klopman, *J. Am. Chem. Soc.*, **86**, 1463 (1964).

[13] M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967).

[14] M. Wolfsberg and L. Helmholtz, *ibid.*, **20**, 837 (1952).

(iii) Relatively large values of K ($\sim$1.75) are required in eq 15. The theoretical value for this constant is unity. As can be seen from Table II, the empirical parameters employed in the present theory are much closer to unity. The off-diagonal core matrix element expression, eq 13, may be obtained from integration of the one-electron Hamiltonian over the orbitals ϕ_i^A and ϕ_j^B if the Mulliken approximation,[8] $\phi_i\phi_j = {}^1/_2S_{ij}(\phi_i^2 + \phi_j^2)$, is employed. Starting with the theoretical expression for H_{ij}

$$H_{ij} = (\phi_i^A|-{}^1/_2\nabla^2|\phi_j^B) - \sum_C(\phi_i^A|V_C|\phi_j^B) \qquad (16)$$

we have upon substitution for $\phi_i\phi_j$

$$H_{ij} = {}^1/_2S_{ij}\Big[(\phi_i^A|-{}^1/_2\nabla^2|\phi_i^A) + (\phi_j^B|-{}^1/_2\nabla^2|\phi_j^B) - \left(\phi_i^A\left|\sum_C V_C\right|\phi_i^A\right) - \left(\phi_j^B\left|\sum_C V_C\right|\phi_j^B\right)\Big] \qquad (17)$$

Further simplication results in the final expression, eq 19. Inserting the empirical parameter, β_{AB}, yields eq 13.

$$H_{ij} = {}^1/_2S_{ij}\Big[(\phi_i^A|-{}^1/_2\nabla^2 - V_A|\phi_i^A) + (\phi_j^B|-{}^1/_2\nabla^2 - V_B|\phi_j^B) - \left(\phi_i^A\left|\sum_{C\neq A} V_C\right|\phi_i^A\right) - \left(\phi_j^B\left|\sum_{C\neq B} V_C\right|\phi_j^B\right)\Big] \qquad (18)$$

$$= {}^1/_2S_{ij}\Big[(U_i^A + U_j^B) - \sum_{C\neq A}V_{AC} - \sum_{C\neq B}V_{BC}\Big] \qquad (19)$$

While the present work was in progress, a new semiempirical SCF–MO theory which included overlap was described by Yonezawa, Yamaguchi, and Kato (YYK).[15] However, the H_{ij} expression took the form of the Wolfsberg–Helmholtz approximation[14] (*vide supra*). Another significant difference lay in the method used for evaluating the various core and electron–electron interaction integrals. Generally the YYK method resulted in somewhat higher ionization potentials and rotational barriers than are calculated by the present method.

Finally, we note that the total energy of the molecule is the sum of the electronic energy and the core repulsion energy.

$$E_{\text{total}} = \sum_u^{\text{occ}} e_u + {}^1/_2\sum_i\sum_j P_{ij}H_{ij} + \sum\sum_{A<B} Z_AZ_B\gamma_{AB} \qquad (20)$$

Equation 20 differs from the corresponding Pople, Santry, and Segal expression[11] in the last term in that the core repulsion is $Z_AZ_B\gamma_{AB}$ rather than $Z_AZ_BR_{AB}^{-1}$. This change is necessitated by our earlier use of the Dewar–Klopman approximation[13] (eq 12).

Results and Discussion

As mentioned in the introductory section, the LCAO–SCF–MO method described in the present paper was designed primarily for calculation of the contact contribution to nuclear spin coupling constants. The results of such nmr calculations will be described in subsequent papers. However, we were also concerned with the applicability of the theory to other problems. Specifically, we consider dipole moment, ionization potential, and rotational barrier calculations.

Table III. Dipole Moment Data from the LCAO–SCF Method

Compound[a]	Dipole moment, D	Exptl, D[b]
BHF_2[c]	0.5705	0.971
CH_3BF_2	1.1007	1.63
CH_3SiH_3	0.5617	0.73
CH_3F	1.6279	1.79
CH_3NH_2	1.0651	1.29
CH_3CH_2Cl	1.8594	1.79
NH_3	1.1346	1.47
NF_3	0.2297	0.234
N_2H_4 *gauche*	1.7937	1.92
N_2F_4 *gauche*	0.3908	0.26
NCl_3	0.5267	0.60
PH_3	1.9319	0.55
CH_3PH_2	2.01	1.10
CF_3PH_2[c]	2.0787	1.92
PCl_3	0.7292	0.79
CH_3CH_2F	1.7048	1.92

[a] All structural data except for BHF_2 and 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. [b] All experimental dipole moment data except for BHF_2 and CF_3PH_2 taken from "Table of Experimental Dipole Moments," A. L. McClellan, Ed., W. A. Freeman and Co., San Francisco, Calif., 1963. [c] The structural and dipole moment data for BHF_2 and CF_3PH_2 are taken from T. Kasuga, W. J. Lafferty, and D. R. Lide, *J. Chem. Phys.*, **48**, 1 (1968), and I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, *ibid.*, **48**, 812 (1968), respectively.

(i) Calculation of Dipole Moments. Since overlap is included in the present theory, formulations of the type derived by Pople and Segal[5] are unsuitable for our dipole moment calculations. Furthermore, Mulliken[8] has indicated that calculated atomic charges *per se* are unsuitable for discussions of molecular dipole moments. In the present work, we employed the equation

$$\mu_z = 2.54\sum_A Q_Az_A - \sum_A P_{sp_z}{}^A\, K/Z'_s \qquad (21)$$

where Q_A = net atomic charge on atom A, z_A = z Cartesian coordinate (Å), $P_{sp_z}{}^A$ = s–p$_z$ bond order on core A, $Z'_s{}^A$ = Slater exponent of s-type atomic orbital centered on core A, K = empirical constant characteristic of the principal quantum, n, and μ_x and μ_y may be calculated analogously, and

$$\mu_{\text{total}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \qquad (22)$$

The first term of eq 21 represents the contribution to the dipole moment from the imbalance of atomic charges,[5] and the second term concerns the contributions from the lone pair(s). The lone-pair term in our treatment is parameterized because of the substantial number of contributions[16] which result from the inclusion of overlap. The value of the empirical parameter K which yielded the best agreement with experimental dipole moments was 3.5 au for second-row elements and 5.0 au for third-row elements.

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(15) T. Yonezawa, K. Yamaguchi, and H. Kato, *Bull. Chem. Soc. Japan*, **40**, 536 (1967).

(16) The additional contributions arise because the ZDO (zero differential overlap) approximation is no longer used. In our approach, we neglect all two-center terms and assume the lone-pair contribution to the dipole moment is proportional to $P_{sp_z}{}^A/Z'_s{}^A$.

Table IV. Ionization Potentials from the LCAO–SCF Method

Compound[a]	Ionization potentials, eV	Exptl, eV[b]
B_2H_6	13.33	12.1
CH_4	12.38	12.99
C_2H_2	9.34	11.4
C_2H_4	9.37	10.51
C_2H_6	10.28	11.65
CH_3CHCl_2	9.39	10.00
CH_3NH_2	9.38	9.41
CH_3CH_2Cl	9.32	10.97
SiH_4	11.37	12.2
NH_3	10.36	10.34
NF_3	9.59	13.2
N_2H_4 *gauche*	8.87	9.56
PH_3	10.06	10.0

[a] All structural data taken from "Table 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] All ionization potential data taken from "Bond Energies, Ionization Potentials, and Electron Affinities," V. I. Vedeneyev, *et al.*, Edward Arnold, London, 1966.

Table V. Rotational Barrier Data from the LCAO–SCF Method

Compound[a]	Calcd,[b] kcal/mole	Exptl, kcal/mole	Ref
C_2H_6	3.1655	3.0	*c*
CH_3CH_2F	2.8680	3.30	*g*
CH_3CH_2Cl	4.9113	3.56	*d*
CH_3BF_2	0.0100	0.014	*h*
CH_3SiH_3	1.783	1.70	*e*
CH_3NH_2	2.7625	1.94	*d*
CH_3PH_2	2.6373	1.958	*f*

[a] All structural 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] Energy difference between staggered and eclipsed forms. [c] Reference 21. [d] E. B. Wilson, *Advan. Chem. Phys.*, **2**, 367 (1959). [e] D. Kivelson, *J. Chem. Phys.*, **22**, 1733 (1954). [f] T. Kojima and E. Brieg, *ibid.*, **35**, 2139 (1961). [g] D. R. Herschbach, *ibid.*, **25**, 358 (1956). [h] R. E. Naylor and E. B. Wilson, *ibid.*, **26**, 1057 (1957).

In general the calculated trend of dipole moments (Table III) reproduces the experimental trend. The least satisfactory calculations concern PH_3 and CH_3PH_2. Other workers[17,18] have calculated correspondingly high values for the dipole moment of PH_3. However, in contrast to previous work, we were unable to effect an appreciable reduction of the calculated dipole moment of PH_3 by the inclusion of P(3d) orbitals. The problem with the calculated dipole moment of BHF_2 and CH_3BF_2 may relate to our method of evaluating the core integrals, U_i, and the one-center Coulomb integrals, γ_{AA}. Since there are insufficient spectroscopic states of elemental boron to afford an independent determination of these parameters, Klopman did not include this element in his tabulation. In the present work, we estimated U_i and γ_{AA} by a least-squares interpolation of Klopman's data for the second-row elements.[12]

(ii) Calculation of Ionization Potentials. The ionization potential of molecular orbital n can be approximated by the Hartree–Fock orbital energy of the nth orbital, e_n. This can be shown to be a special case of Koopmans' theorem.[19] The orbital energy of the nth orbital has been shown[20] to be

$$e_n = E_n^{\mathrm{N}} + \sum_l (2J_{nl} - K_{nl}) \tag{23}$$

where E_n^{N} is the expectation value of the one-electron Hamiltonian; J_{nl} and K_{nl} are the Coulomb and exchange integrals, respectively, and the sum is over the l molecular orbitals.

Table VI. Comparison of the Energies (eV) of the Occupied Molecular Orbitals for a Few Simple Molecules

(a) B_2H_6

	This work	Palke and Lipscomb[a]
b_{2g}	−13.34	−13.24
a_g	−13.77	−14.55
b_{2u}	−14.58	−15.68
b_{3u}	−15.05	−15.24
b_{1u}	−16.96	−17.85
a_g	−20.04	−24.48

(b) CH_4

	This work	Sinai[b]	Palke and Lipscomb[a]	YYK[c]	Exptl[d]
t_2	−12.38	−13.24	−14.74	−13.70	−13.16
a_1	−19.08	−25.04	−25.35	−21.50	−19.42

(c) C_2H_4

	This work	Moskowitz[e]	PL[a]	YYK[c]
b_{1u}	−9.37	−9.97	−10.09	−12.24
a_g	−10.84	−15.49	−13.76	−13.75
b_{1g}	−12.09	−13.88	−15.28	−13.98
b_{3u}	−14.15	−21.61	−17.61	−19.70
b_{2u}	−17.36	−17.62	−21.28	−15.65
a_g	−20.27	−28.31	−27.59	−24.09

(d) NH_3

	This work	Palke and Lipscomb[a]	Kaplan[f]	YYK[c]	Exptl[g]
a_1	−10.36	−9.96	−14.00	−12.21	−11.0
e	−13.32	−15.84	−19.31	−13.79	−17.0
a_1	−22.92	−29.96	−32.60	−24.95	...

(e) PH_3

	This work	Boyd and Lipscomb[h]	Exptl[i]
a_1	−10.06	−10.93	−10.2
e	−12.07	−14.72	...
a_1	−18.08	−22.65	...

(f) H_2O

	This work	Ellison and Shull[j]	YYK[c]	Exptl[k]
b_2	−10.40	−11.84	−12.88	−12.6
a_1	−11.24	−13.20	−13.48	−14.5
b_1	−12.29	−18.64	−14.66	−16.2
a_1	−26.41	−38.23	−32.50	...

[a] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966). [b] J. J. Sinai, *J. Chem. Phys.*, **39**, 1575 (1963). [c] Reference 15. [d] D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (London), **A241**, 194 (1957). [e] J. W. Moskowitz, *J. Chem. Phys.*, **43**, 60 (1965). [f] H. K. Kaplan, *ibid.*, **26**, 1704 (1957). [g] H. Sun and G. L. Weissler, *ibid.*, **23**, 1160 (1955). [h] D. B. Boyd and W. N. Lipscomb, *ibid.*, **46**, 910 (1967). [i] Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964). [j] F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955). [k] W. C. Price and T. M. Sugden, *Trans. Faraday Soc.*, **44**, 108 (1948).

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(17) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967).
(18) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).
(19) T. Koopmans, *Physica*, **1**, 104 (1933).
(20) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, New York, N. Y., 1959, pp 471–472.

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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