rather than by electronic details. Transitions to the energetically closest neutral vibrational level were generally found to be larger than those to other levels.

Our work aimed at understanding the multiple-photon ICR experiments is continuing. The computational data on LiH^- and OH^- provide us with a range of rates within which we expect most v–e ejection rates to fall. They also give some insight into how the electronic and vibrational factors affect the v–e rates and branching ratios. We are presently in the process of performing an ab initio simulation of the v–e ejection rate of the enolate H_2C^-COH, in which the torsion and "puckering" of the H_2C group is treated as the single active vibration.

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Registry No. LiH^-, 7580-67-8; OH^-, 14280-30-9.

Importance of Multicenter Integrals in Semiempirical Calculations of Nuclear Spin–Spin Coupling Constants. 1. Isotropic Coupling

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Abstract: A study of Fermi contact, orbital, and spin-dipolar contributions to isotropic nuclear spin–spin coupling constants is presented in terms of a semiempirical (INDO) molecular orbital (MO) approach that extends existing theory to include all integrals for the three types of terms over Slater-type orbitals (STO's). All contributions are evaluated by the first-order polarization propagator approach (FOPPA), which is equivalent to the coupled Hartree–Fock (CHF) theory. Calculated coupling constant results for representative molecules are compared with experimental data, and reasonable correspondence is noted between these noncontact contributions and ab initio results with large Gaussian basis sets. Detailed comparisons are also made with semiempirical SCPT-MO results in the one-center integral approximation. Since the latter procedure leads to identically zero orbital and dipolar contributions if either one of the coupled nuclei is a proton, this extension of the theory is applicable to many very important types of coupling. For example, the calculated geminal and vicinal ^1H–^{19}F coupling constants, for which the OB and SD contributions are important, are in better conformity with the experimental data. It is now clear that the scaling of the one-center integrals for carbon far above the atomic Hartree–Fock values may be a consequence of the neglect of the multicenter integrals. The introduction of multicenter integrals into semiempirical methods greatly extends the number and the complexity of molecules for which contributions of all mechanisms can be investigated.

Theoretical studies of nuclear spin–spin coupling constants are extensive and have been the subject of several recent reviews.[2] Within the usual Ramsey perturbation formulation[3] the isotropic nuclear spin–spin coupling constant between nuclei N and N′ is written as the sum of four terms

$$J_{NN'} = J_{NN'}^{(1a)} + J_{NN'}^{(1b)} + J_{NN'}^{(2)} + J_{NN'}^{(3)} \qquad (1)$$

where $J_{NN'}^{(1a)}$ and $J_{NN'}^{(1b)}$ are the one- and two-electron orbital (OB) contributions, respectively,[4] $J_{NN'}^{(2)}$ is the spin-dipolar (SD) contribution, and $J_{NN'}^{(3)}$ denotes the Fermi contact (FC) contribution.[2,3] By far the largest number of calculations have been based on the finite perturbation theory (FPT) formulation in the intermediate neglect of differential overlap (INDO)[5] approximation of semiempirical MO theory. Only the Fermi contact (FC) term in eq 1 is included and, as usually carried out, the INDO-FPT method retains only the one-center integrals

$$\langle ns_N|\delta(r_N)|ns_N\rangle \equiv s_N^2(0) \qquad (2)$$

where ns_N denotes an s-type orbital at nucleus N. The empirical determination of $s_N^2(0)$ in a least-squares sense[5] from the experimental data compensates for a number of severe approximations.

Multicenter integrals (MCI) of the types $\langle\phi_B|\delta(r_A)|\phi_B\rangle$, $\langle\phi_A|\delta(r_A)|\phi_B\rangle$ and $\langle\phi_B|\delta(r_A)|\phi_C\rangle$, which are not included in the usual semiempirical calculations, have been discussed by several authors.[6-8] An important anomaly arises in zero differential overlap (ZDO) schemes, which use Slater-type orbitals (STO's) and neglect inner shell orbitals. Since electron densities $s_N^2(0)$ in eq 2 vanish identically for $n \geq 2$, only interproton coupling contributions to the Fermi contact term are rigorously nonvanishing (vide infra).

The next largest number of computations of nuclear spin–spin coupling constants is based on the self-consistent perturbation theory (SCPT) formulation,[9] which is an alternative coupled Hartree–Fock (CHF) scheme. This approach uses semiempirical MO theory but also includes algorithms for calculating the orbital (OB, $J_{NN'}^{(1b)}$ in eq 1) and spin-dipolar (SD, $J_{NN'}^{(2)}$ in eq 1) contributions. The one-center integral approximation is adopted with integrals of the type

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$$\langle 2p_{\mathrm{N}}|r_{\mathrm{N}}^{-3}|2p_{\mathrm{N}}\rangle = \langle r^{-3}\rangle_{\mathrm{N}} \tag{3}$$

which occur in the expressions for both $J_{\mathrm{NN'}}^{(1b)}$ and $J_{\mathrm{NN'}}^{(2)}$. In this formulation $s_{\mathrm{N}}^2(0)$ and $\langle r^{-3}\rangle_{\mathrm{N}}$ are treated as empirical parameters, and the coupling constants are calculated from an equation of the type[2]

$$J_{\mathrm{NN'}} = a_{\mathrm{NN'}}j_{\mathrm{NN'}}^{(3)} + b_{\mathrm{NN'}}[j_{\mathrm{NN'}}^{(1b)} + j_{\mathrm{NN'}}^{(2)}] \tag{4}$$

where the $j_{\mathrm{NN'}}$ denote the parts of the coupling exclusive of $a_{\mathrm{NN'}}$, and $b_{\mathrm{NN'}}$, and

$$a_{\mathrm{NN'}} = s_{\mathrm{N}}^2(0)s_{\mathrm{N'}}^2(0) \tag{5a}$$

$$b_{\mathrm{NN'}} = \langle r^{-3}\rangle_{\mathrm{N}}\langle r^{-3}\rangle_{\mathrm{N'}} \tag{5b}$$

Unfortunately, for some nuclei it is necessary to scale $\langle r^{-3}\rangle_{\mathrm{N}}$ to values that are far above the Hartree–Fock values. Undoubtedly, this compensates for a number of inadequacies of the method including the neglect of multicenter integrals and leads to erroneous conclusions about the relative importance of contact vs. noncontact terms. This difficulty with the method has been noted by others.[2,10,11] Moreover, the one-center or monocentric integral approximation causes $b_{\mathrm{NN'}}$ and, therefore, values of both the orbital and dipolar terms to vanish identically if either N or N′ is a hydrogen atom. For example, the poor correspondence between the SCPT-MO results and experimental data for H–F coupling constants is indicative of this inadequacy. In a recent attempt[12] to overcome this difficulty, polarization functions (2p atomic orbitals on hydrogen) were introduced, but the results are in poor conformity with those based on nonempirical calculations with large basis sets.[13]

Many fewer calculations of coupling constants have been based on ab initio methods. Furthermore, these have been limited to molecules with a few second-row atoms. As a consequence, the number of reliable calculations of noncontact contributions is severely limited. Therefore, presented here are semiempirical INDO-MO calculations which are obtained at the coupled Hartree–Fock level, but with the inclusion of all integrals entering the FC, OB, and SD operators. The results provide a substantial improvement for a number of types of ^{1}H–^{1}H, ^{13}C–^{13}H, ^{1}H–^{19}F, and ^{13}C–^{13}C coupling constants. However, the results for ^{13}C–^{19}F and ^{19}F–^{19}F will require additional study to explain certain disparities between the several theoretical methods.

Theoretical Section

The polarization propagator, which describes the propagation of a density disturbance through the interacting system, has been shown to be useful for calculations of a variety of excitation properties of molecular systems.[14-16] The mathematical description of this approach, which is cast in Green's function and second quantization formalisms, are described in almost all standard works on many body theory[14] and would be cumbersome to reproduce here. The polarization propagator can be written as the sum of an infinite number of terms in the Dyson series, but only the first-order term, i.e., the first-order polarization propagagor (FOPPA), is used in this study.[14-16] This corresponds to the coupled Hartree–Fock or FPT level of accuracy in the calculation of the coupling constants. Molecular wave functions are based on the INDO (intermediate neglect of differential overlap approximation).[5]

In the polarization propagator approach, the second-order contributions to the energy, i.e., the coupling constants, arising from the different indirect isotropic interactions between nuclear spins, can be obtained in a straightforward way using existing formulas.[15,16] In this formalism the second-order contributions to the isotropic coupling constants between nuclei N and N′ due the orbital, $J_{\mathrm{NN'}}^{(1b)}$, dipolar, $J_{\mathrm{NN'}}^{(2)}$, and Fermi contact, $J_{\mathrm{NN'}}^{(3)}$, interactions become

$$J_{\mathrm{NN'}}^{(1b)} = -(16\beta^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}\hbar/3\pi)\sum_{ia,jb} P^*_{ia,jb} \sum_{\alpha=x,y,z} \langle i|r_{\mathrm{N}}^{-3}L_{\alpha\mathrm{N}}|a\rangle\langle j|r_{\mathrm{N'}}^{-3}L_{\alpha\mathrm{N'}}|b\rangle \tag{6}$$

$$J_{\mathrm{NN'}}^{(2)} = -(4\beta^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}\hbar/3\pi)\sum_{ia,jb} P_{ia,jb} \times \Big[\sum_{\alpha=x,y,z} \langle i|r_{\mathrm{N}}^{-5}(\alpha_{\mathrm{N}}^2 - r_{\mathrm{N}}^2)|a\rangle\langle j|r_{\mathrm{N'}}^{-5}(\alpha_{\mathrm{N'}}^2 - r_{\mathrm{N'}}^2)|b\rangle + \sum_{\substack{\alpha,\beta=x,y,z\\ \alpha\neq\beta}} \langle i|r_{\mathrm{N}}^{-5}\alpha_{\mathrm{N}}\beta_{\mathrm{N}}|a\rangle\langle j|r_{\mathrm{N'}}^{-5}\alpha_{\mathrm{N'}}\beta_{\mathrm{N'}}|b\rangle\Big] \tag{7}$$

$$J_{\mathrm{NN'}}^{(3)} = -(256\beta^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}\hbar/9)\sum_{ia,jb} P_{ia,jb}\langle i|\delta(r_{\mathrm{N}})|a\rangle\langle j|\delta(r_{\mathrm{N'}})|b\rangle \tag{8}$$

where the equations are written in the MO basis set with the usual notation for the interaction operators; $|i\rangle$ and $|j\rangle$ denote MO's which are occupied in the ground-state configuration and $|a\rangle$ and $|b\rangle$ are vacant. The polarization propagators P and P^*, which correspond to triplet and imaginary singlet excitations, respectively, can be obtained as the inverses of the matrices[15,16]

$$(P^{-1})_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} - \langle ij|ab\rangle - \langle ib|ja\rangle \tag{9}$$

$$(P^{*-1})_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} - \langle ij|ab\rangle + \langle ib|ja\rangle \tag{10}$$

where ϵ_i and ϵ_a are the orbital energies of the *i*th-occupied and *a*th-vacant molecular orbitals. The Mulliken notation is used for the Coulomb and exchange integrals, i.e.,

$$\langle ij|ab\rangle \equiv \int \mathrm{d}\tau_1\mathrm{d}\tau_2 i(1)j(1)r_{12}^{-1}a(2)b(2) \tag{11}$$

In the calculations reported in this paper P^{-1} and P^{*-1} matrices were calculated at the INDO level of accuracy, using the CNINDO.3.3.3 program[17] to evaluate the wave functions and some subroutines developed previously[18] to evaluate the Coulomb and exchange integrals and the P^{-1} and P^{*-1} matrices. The inversion of these matrices were performed by using the subroutine MINV.[19]

The evaluation of the integrals $\langle i|\mathrm{H}_{\mathrm{op}}|a\rangle$ over the MO basis set was performed for the orbital and dipolar operators using a computer program developed by Tokuhiro et al.[20] to calculate the integrals over Slater atomic orbital. The calculation of the integrals over the atomic orbital basis set was performed numerically by the Gaussian transform method in the molecular frame, and all one-, two-, and three-centered integrals are included. By means of the deorthogonalization procedure[21-24] described below, they were transformed to the MO basis set using the coefficients obtained in the calculation of the wave functions.

The calculations of the Fermi contact integrals are simple because of the form of the operator. However, the most important

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Table I. Calculated ^{13}C–H and ^{1}H–^{1}H Coupling Constants in Methane Obtained with and without the Deorthogonalization Procedure[a,b,c]

	without deorthogonalization			with deorthogonalization		
N–N′	$J_{NN'}^{(3)}$	$J_{NN'}^{(1b)}$	$J_{NN'}^{(2)}$	$J_{NN'}^{(3)}$	$J_{NN'}^{(1b)}$	$J_{NN'}^{(2)}$
$C-H_1$	88.84	−0.26	−0.64	227.47	−0.44	0.13
$C-H_2$	88.84	−0.26	0.17	227.47	−0.44	0.13
H_1-H_2	−1.55	0.36	0.22	0.77	0.90	0.38
H_2-H_3	−1.55	0.36	0.14	0.77	0.90	0.38

[a] All values in Hz. [b] The $C-H_1$ bond is taken along the z axis. [c] Values without scaling of the contact term.

contributions occur for the one-center integrals. Since these vanish identically for 2s Slater-type orbitals, this inconsistency is removed by the form

$$2s_N'(r) = s_N^2(0)\delta(r_N) + 2s_N(r) \qquad (12)$$

where $s_N^2(0)$ is the density at the nuclei. These parameters were taken from the atomic Hartree–Fock calculations.[25] Integrals were transformed from the atomic to the molecular basis set without deorthogonalization (vide infra).

All calculations were performed on a Control Data Corp. CYBER 175 computer. Extensive use of mass storage was required because of the large matrices which occur in the FOPPA method. By far the largest amount of computer time is associated with the numerical evaluation of the dipolar and orbital integrals. Molecular geometries were based on a standard geometrical model.[26]

Orthogonal basis sets are implicit in MO methods such as INDO, which invoke the zero differential overlap approximation. Within the usual Hartree–Fock method an orthogonal basis set can be formally interpreted as arising from a transformation from the nonorthogonal atomic orbital (ao) functions.[21-24] However, the calculations of molecular properties with multicenter integrals require the transformation of these integrals, evaluated in the ao basis set, to the orthogonal basis set. This procedure has been called "deorthogonalization".[27]

Matrix elements of some operator q in the orthogonal basis set Q' are related to those in the nonorthogonal one Q by

$$Q' = \mathbf{S}^{-1/2}Q\mathbf{S}^{-1/2} \qquad (13)$$

where

$$\mathbf{S}^{-1/2} = \mathbf{O}d^{-1/2}\mathbf{O}^{\dagger} \qquad (14)$$

in which $\mathbf{O}$ denotes the matrix of eigenvectors of the overlap matrix $\mathbf{S}$ and $d^{-1/2}$ is the diagonal array of the reciprocals of the square roots of the eigenvalues of $\mathbf{S}$.[21]

Calculations for a number of representative molecules were performed by means of the deorthogonalization procedure applied to the FC, OB, and SD terms. For example, calculated results for the methane molecule, which were obtained with and without deorthogonalization, are entered in Table I. Calculated results for the SD term indicate a dependence on the orientations of the C–H bonds or H–H internuclear axes if the deorthogonalization procedure is not used. The very large changes in the magnitudes of the FC term are symptomatic of the inadequacies that arise on combining the deorthogonalization procedure with the introduction of the δ function term in eq 12. On the basis of a number of calculations, of which the results in Table I are typical, the FC terms do not present problems of rotational invariance. For this reason as well as the extreme sensitivity of the FC terms, the deorthogonalization procedure was used only for the OB and SD calculations. The representative results in Table I clearly show that the procedure eliminates the orientational dependence of the calculated coupling constants.

Table II. Atomic Orbital Densities in Several Computational Schemes

	$s_N^2(0)$				
N	INDO-FPT[a]	INDO-SCPT[b]	SCF[c]	HF[d]	this work[e]
H	0.3724	0.3724	0.550[f]		0.3930
C	4.0318	3.7387	2.767	3.358	4.0957
N	6.9265	3.5727[g]	4.770	5.599	5.599
O	12.0658		7.638	8.669	8.669
F	21.3126	16.3668	11.966	12.53	8.6557

[a] From ref 5. Calculations included only the FC term. [b] From ref 9. In this scheme, due to the monocentric approximation the noncontact terms vanish for couplings involving protons. [c] SCF calculations using Slater atomic orbitals [Morton, T. R.; Rowlands, T. P.; Whiffen, D. F. National Physical Laboratory Report BPR 13, 1962], cited by: Murrell, J. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1970**, *6*, 1. [d] Extrapolated values of the numerical Hartree–Fock wave function [Herman, F.; Skillman, S. "Atomic Structure Calculations"; Prentice Hall: Englewood Cliffs, NJ, 1963] given in ref 25. [e] See the discussion in the text. [f] This value was based on an effective nuclear charge of 1.2. [g] Estimated from calculations in C–N coupling constants.[2]

For reasons that are not yet clear, the inclusion of multicenter integrals in the FC calculations with Hartree–Fock values for the atomic densities $s_N^2(0)$ leads to values that are in poor conformity with nonempirical values and with experimental results. Entered in Table II are the empirical values of the atomic densities $s_N^2(0)$, which were used in INDO calculations. The SCF and HF values are included for comparison. In the present study a second approximation to the atomic orbital densities, in H, C, and F, was obtained by scaling the Fermi contact with the experimental values after subtracting the OB and SD contributions. The necessity for this procedure is due in large part to the inconsistencies of the method; inclusion of only the valence basis set and neglect of the inner shell 1s orbitals, which are not orthogonal to the 2s orbitals, lead to a poor representation of the nodal properties of the wave function and the atomic densities. The resulting values of $s_N^2(0)$, which are also entered in Table II, were then used to recalculate the Fermi contact contributions. The procedure could be carried out in an iterative fashion; this was not done because it would have the major effect of improving some calculated values at the expense of others. It is important to note in Table II that the atomic densities for carbon and fluorine are much closer to the SCF values than the empirical values which were used in the INDO-FPT calculations. Furthermore, the atomic densities in Table II are the *only* parameters introduced in all of the calculations reported herein.

Results and Discussion

Calculated semiempirical MO results for representative molecules, which are based on the FOPPA-INDO method with multicenter integrals (MCI), are entered in Table III along with results of ab initio calculations obtained with large Gaussian basis sets at the CHF level of approximation. With a few exceptions the results obtained here for the OB and SD contributions show good conformity with the ab initio results. It is most important to note that the major inadequacy of these and other semiempirical CHF results is the Fermi contact contributions rather than the orbital and dipolar terms. As both the SD and FC contributions are obtained with the same polarization propagator it seems likely that the difficulties are related to the use of only the valence basis set of atomic orbitals and the neglect of electron correlation effects.[2] For coupling constants involving at least one proton it is most important to recognize that all existing calculations, which are based on the monocentric integral approximation, lead to identically zero values for OB and SD contributions. For most types of coupling, which are reported in Table III, this severe approximation cannot be justified.

In Table IV are tabulated the calculated FOPPA INDO/MCI results for the geminal and vicinal H–H coupling constants in a series of representative compounds, the INDO-FPT results (which

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Table III. Comparison of the Semiempirical FOPPA-INDO/MCI MO Results for Spin-Spin Coupling Constants with Those Based on ab Initio CHF Calculations[a]

	FOPPA-INDO/MCI				ab initio[b]				
	FC	OB	SD	total	FC	OB	SD	total	exptl[c]
H-D, $^1J_{HD}$	62.64	0.0	0.59	63.23	51.0[d]	0.78[d]	0.48[e]	52.26	42.9
H-F, $^1K_{HF}$	-3.62	19.44	-2.84	12.98	42.3	17.4	-0.9	58.8	46.9
H_2O, $^2J_{HH}$	-7.36	8.18	1.22	2.04	-23.8	7.1	1.4	-15.3	-7.2
H_2O, $^1K_{OH}$	12.03	5.41	-1.04	16.40	48.8	7.5	-0.4	55.8	48.0
NH_3, $^2J_{HH}$	-3.53	3.42	0.80	0.69	-24.3	4.7	0.8	-18.8	-10.35
NH_3, $^1K_{NH}$	32.37	0.02	-0.20	32.19	57.5	2.4	-0.2	59.7	50.0
CH_4, $^2J_{HH}$	-3.09	0.90	0.38	-1.81	-25.4	2.7	0.4	-22.3	-12.4
CH_4, $^1K_{CH}$	44.00	-0.15	0.05	43.90	48.2	0.5	-0.1	48.6	41.3
CH_3F, $^2J_{HF}$	40.71	21.34	-3.61	58.44	58.5[f]	12.3[f]	-4.2[f]	66.6[f]	46.3[f]
CH_3F, $^1J_{CF}$	-93.27	2.39	7.65	-83.23	149.5[f]	32.4[f]	19.6[f]	-97.5[f]	-161.9[f]

[a] All coupling constants (J) are in Hz. The reduced coupling constants (K) are in 10^{19} m^{-2} Kg s^{-2} A^{-2}. [b] All values taken from ref 13, except those of the HD and CH_3F. [c] Taken from ref 2. [d] Schulman, J. M.; Lee, W. S. *J. Chem. Phys.* **1979**, *71*, 922. [e] Schulman, J. M.; Lee, W. S. *Ibid.* **1980**, *73*, 1350. [f] Ditchfield, R.; Snyder, L. C. *Ibid.* **1972**, *56*, 5823.

Table IV. Calculated Geminal and Vicinal $^1H-^1H$ Coupling Constants Based on the FOPPA-INDO/MCI Method and Compared with Previously Obtained Semiempirical MO Results and the Experimental Data[a]

		FOPPA-MCI				
compound	FPT-INDO[b]	FC	OB	SD	total	exptl
geminal						
CH_4	-6.13	-3.09	0.90	0.38	-1.81	-12.4[c]
C_2H_6	-5.22	-2.50	0.83	0.36	-1.31	
CH_3F	-1.85	1.90	0.61	0.38	2.89	-9.6[d]
CH_3CN	-7.73	-5.34	0.91	0.33	-4.10	-16.9[e]
$H_2C{=}CH_2$	3.24	7.89	0.95	0.24	9.08	2.5[f]
$H_2C{=}CHF$	-0.18	4.50	1.04	0.24	5.78	-3.06
$H_2C{=}O$	31.82	38.16	0.44	0.24	38.84	40.2[h]
NH_3	-6.37	-3.53	3.42	0.80	0.69	-10.35[i]
H_2O	-8.07	-7.36	8.18	1.22	2.04	-7.2[j]
vicinal						
C_2H_6, trans	18.63	16.85	0.79	0.10	17.74	18.0[k]
gauche	3.25	2.93	0.13	0.09	3.15	3.2[k]
$H_2C{=}CH_2$, cis	9.31	7.81	-0.56	0.05	7.30	11.7[f]
trans	25.15	23.48	0.06	0.40	23.94	19.1[f]
$H_2C{=}CHF$, cis	4.74	3.88	-0.53	0.05	3.40	4.70[g]
trans	20.73	19.76	0.09	0.40	20.25	12.68[g]
$HFC{=}CHF$, cis	2.87	2.52	-0.50	0.05	2.07	-2.07[l]
trans	19.41	18.77	0.06	0.44	19.27	9.53[l]
$HC{\equiv}CH$	10.99	14.33	0.71	0.39	15.43	9.5[f]

[a] All values are in hertz. [b] Values based on the INDO-FPT method[5] are taken from ref 2, 12, and 24. The OB and SD contributions vanish at this level of approximation. [c] Karplus, M.; Anderson, D. H.; Farrar, T. C.; Gutowsky, H. S. *J. Chem. Phys.* **1957**, *27*, 597. [d] Bernstein, H. J.; Sheppard, N. *Ibid.* **1962**, *37*, 3012. [e] Barfield, M.; Grant, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 4726. [f] Lynden-Bell, R. M.; Sheppard, N. *Proc. R. Soc. London, Ser. A*, **1962**, *269*, 385. [g] Smith, S. L.; Ihrig, A. M. *J. Chem. Phys.* **1967**, *46*, 1181. [h] Shapiro, B. L.; Kopchik, R. M.; Ebersole, S. J. *Ibid.* **1963**, *39*, 3154. [i] Bernheim, R. A.; Batiz-Hernandez, H. *J. Phys. Chem.* **1964**, *40*, 3446. [j] Holmes, J. R.; Kivelson, D.; Drinkard, W. C. *J. Chem. Phys.* **1962**, *37*, 150. [k] Values estimated by Lynden-Bell and Sheppard, footnote *f*. [l] Measured in cyclohexane by: Ihrig, A. M.; Smith, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 34.

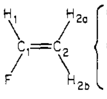
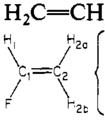
are equivalent to the SCPT-INDO results), and the experimental data. The multicenter integrals lead to substantially different results for the FC term than those based on the fictitious s-orbital densities at the nuclei. For protons bonded to carbon the sums of the OB and SD terms do not exceed 1.3 Hz, i.e., CH_4, but increase to 4.2 Hz in NH_3 and 9.4 Hz in H_2O. As a consequence, the "agreement" between the calculated and experimental values for H_2O in the monocentric approximation is fortuitous. Except in cases in which substituent effects dominate, i.e., H_2CO, the calculated geminal coupling constants at this level of approximation are invariably bad.

In the several examples of vicinal H-H coupling constants in Table IV the sum of the OB and SD terms is less than 1.1 Hz. Reasonable conformity between calculated and experimental results is found even if the multicenter integrals are neglected. The INDO-FPT method has been reasonably successful for vicinal and long-range H-H coupling.

In those cases in which one of the coupled nuclei corresponds to an atom in the first row, it is necessary to consider the additional complexity associated with the STO's by introducing eq 12. Calculated values for directly bonded and geminal $^{13}C-^1H$ coupling constants are entered in Table V along with the INDO-FPT results for the FC contributions and available experimental data. Again, the OB and SD contributions vanish in the monocentric approximation. The magnitudes of the OB and SD terms for the first 13 entries in Table V do not exceed 0.5 Hz and assume the greatest importance for $^2J_{CH}$ in acetylene ($^2J_{CH}{}^{(1b)} + {}^2J_{CH}{}^{(2)} =$ 2.8 Hz). This still does not account for the disparity between the calculated and experimental values. In general, substantial improvement in the quality of the FC contributions is required before more effort need be spent on the OB and SD terms.

Examples of coupling constants involving protons are geminal and vicinal $^1H-^{19}F$ coupling for which the calculated and experimental data are given in Table VI. These results clearly show the importance of including the multicenter integrals in calculations of nuclear spin-spin coupling. With the exception of the $^2J_{HF}$ in CF_3H the calculated results in Table VI are in good agreement with the experimental data. This is in marked contrast to the INDO-FPT results, which are uniformly unsatisfactory. The orbital contributions for $^3J_{HF}$ are 1 to 2 orders of magnitude smaller than those for $^2J_{HF}$. However, a major factor in the improved results is due to the FC terms which are generally greater

Table V. Calculated Directly Bonded and Geminal $^{13}C-^{1}H$ Coupling Constants, Which Were Based on the FOPPA INDO/MCI Method, Compared with Previous Semiempirical MO Results and Experimental Data[a]

		FOPPA-MCI				
compound	FPT-INDO[b]	FC	OB	SD	total	exptl
directly bonded						
CH_4	122.91	132.90	−0.44	0.14	132.60	125.45[c]
C_2H_6	122.12	129.42	−0.37	0.05	129.10	124.9[d]
CH_3F	140.08	148.90	−0.57	0.10	148.43	148.8[e]
CF_3H	271.65[f]	218.16	−0.18	0.05	218.03	238.1[g]
CH_3CN	122.50	131.48	−0.21	0.07	131.34	135.66[h]
$H_2C{=}CH_2$	156.70	163.47	−0.38	0.00	163.09	156.4[d]
 H_1-C_1	183.11	187.72	−0.42	−0.02	187.28	200.18[i]
H_{2a}-C_2	162.35	173.07	−0.29	0.03	172.81	162.16[i]
H_{2b}-C_2	153.26	165.12	−0.23	−0.01	164.88	159.18[i]
HFC=CHF cis	187.04	192.18	−0.39	0.01	191.80	
trans	179.51	187.37	−0.36	−0.01	187.00	
$H_2C{=}O$	180.51	188.43	−1.23	−0.10	187.10	172.0[j]
$HC{\equiv}CH$	232.65	237.73	0.04	−0.05	237.72	248.7[d]
HCN	232.68	248.99	−1.14	−0.08	247.77	269.0[k]
geminal						
C_2H_6	−7.20	−6.67	0.00	0.06	−6.61	−4.5[d]
CH_3CN		−9.26	−0.18	0.15	−9.29	(−)9.87[l]
$H_2C{=}CH_2$	−11.57	−10.26	−1.86	−0.25	−12.37	−2.4[d]
 H_1-C_2	−4.23	−2.53	−1.82	−0.23	−4.58	
H_{2a}-C.	−3.63	2.29	−1.62	−0.28	0.39	
H_{2b}-C_1	−13.77	−7.17	−1.72	−0.27	−9.16	
HFC=CHF cis	4.15	7.52	−1.61	−0.27	5.64	
trans	−6.98	−5.14	−1.81	−0.26	−7.21	
$HC{\equiv}CH$	2.52	8.45	2.51	0.29	11.25	49.3[d]

[a] All values are in hertz. [b] Values taken from ref 2, 12, and 24 are those obtained by the INDO-FPT method.[5] The OB and SD contributions vanish identically in the monocentric approximation. [c] Jameson, A. K., private communication, 1972. [d] Lynden-Bell, R. M.; Sheppard, N. *Proc. R. Soc. London, Ser. A* **1962**, *A269*, 385. [e] Krugh, T. A.; Bernheim, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 2385. [f] Johnston, M. D.; Jr.; Barfield, M. *J. Chem. Phys.* **1971**, *54*, 3083. [g] Cox, R. H.; Smith, S. L. *J. Magn. Reson.* **1969**, *1*, 432, in CCl_4. [h] Measured in CCl_4 by Watts, V. S.; Goldstein, J. H. *J. Phys. Chem.* **1966**, *20*, 3887. [i] Mayo, R. E.; Goldstein, J. H. *J. Mol. Spectrosc.* **1964**, *14*, 173. [j] Malinowski, E. R.; Pollara, L. Z.; Larmann, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 2649. [k] Olah, G. A.; Kiovsky, T. E. *Ibid.* **1968**, *90*, 4666. [l] Gray, G. A.; Maciel, G. E.; Ellis, P. D. *J. Magn. Reson.* **1969**, *1*, 407.

Table VI. Calculated Geminal and Vicinal $^{1}H-^{19}F$ Coupling Constants, Which Were Obtained by the FOPPA INDO/MCI Method, Compared with Previous Semiempirical MO Results and Experimental Data[a]

		FOPPA-MCI				
compound	FPT-INDO[b]	FC	OB	SD	total	exptl
geminal						
CH_3F	4.68	40.71	21.34	−3.61	58.44	46.36[d]
CF_3H	32.34	14.16	10.88	−4.19	20.85	79.25[e]
$HFC{=}CH_2$	16.61	88.62	19.52	−2.90	105.24	84.67[f]
cis-HFC=CHF	8.06	74.70	22.06	−2.59	94.17	71.84[g]
trans-HFC=CHF	14.83	77.69	22.24	−2.56	97.37	75.10[g]
vicinal						
$F_2C{=}CH_2$ cis	11.80	2.35	−1.46	−1.15	−0.26	0.64[g]
trans	57.41	43.57	−0.22	−0.49	42.86	33.90[g]
$HFC{=}CH_2$ cis	26.7	12.42	−0.81	−0.97	10.64	19.63[f]
trans	66.20	50.83	−0.05	−0.86	49.92	51.81[f]
trans-HFC=CHF cis	11.91	5.54	1.75	−0.87	6.42	2.80[g]
cis-HFC=CHF trans	40.34	19.82	0.27	−0.72	19.37	19.77[g]

[a] All values in hertz. [b] Values taken from ref 2, 12, and 24 are based on the monocentric integral approximation for the FC term. The OB and SD terms vanish in this approximation. [c] Measured in cyclohexane solvent unless noted otherwise. All signs are taken to be positive in accordance of the work of: Flynn, G. W.; Matsushima, M.; Baldeschwieler, J. D.; Craig, N. C. *J. Chem. Phys.* **1963**, *38*, 2295, and Barfield, M.; Baldeschwieler, J. D. *J. Mol. Spectrosc.* **1964**, *12*, 23. [d] Frankiss, S. G. *J. Phys. Chem.* **1963**, *67*, 756. [e] Cox, R. H.; Smith, S. L. *J. Magn. Reson.* **1969**, *1*, 432, in CCl_4. [f] Smith, S. L.; Ihrig, A. M. *J. Chem. Phys.* **1967**, *46*, 1181. [g] Ihrig, A. M.; Smith, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 35.

for $^{2}J_{HF}$ and invariably smaller for $^{3}J_{HF}$. The monocentric FC (FPT) results for geminal and vicinal $^{1}H-^{19}F$ coupling are uniformly smaller and larger, respectively, in magnitude than the experimental data.

In Table VII are tabulated the results for directly bonded $^{13}C-^{13}C$ coupling constants in the selected group of compounds used in this study. Also included in the table are the INDO-FPT results for the FC contributions and the SCPT-INDO results for $^{1}J_{CC'}{}^{(1b)}$ and $^{1}J_{CC'}{}^{(2)}$. The FC contributions to $^{1}J_{CC'}$ in Table VII do not differ significantly from those obtained by the FPT method in the monocentric approximation. This conclusion is consistent with the results of Archirel et al.[8] In order to make a meaningful comparison of the OB and SD contributions obtained via the INDO-MCI method with those based on SCPT-INDO results in the monocentric approximation, the latter[9] were rescaled to the STO values of $\langle r^{-3}\rangle_C$ for the one-center integrals. In Table VII

Table VII. Calculated Directly Bonded ^{13}C–^{13}C Coupling Constants, Which Were Obtained by the FOPPA INDO/MCI Method, Compared with Previous Semiempirical MO Results and Experimental Data[a]

	FC		OB		SD		total		
compound	MCI	FPT[b]	MCI	SCPT[c]	MCI	SCPT[c]	MCI	SCPT[d]	exptl
C_2H_6	43.24	41.43	−1.45	−0.72	0.59	0.36	42.38	33.45	34.6[e]
CH_3CN	78.83	76.20	−1.54	−0.63	0.43	0.28	77.72	63.97	57.48[f]
$H_2C{=}CH_2$	84.22	82.11	−6.96	−4.59	2.09	1.94	79.35	55.95	67.2[e]
$HFC{=}CH_2$	96.53		−6.41		2.31		92.43		
$H_2C{=}CF_2$	119.53		−5.55		2.40		116.38		
cis-$HFC{=}CHF$	112.98		−5.91		2.77		109.84		
trans-$HFC{=}CHF$	124.81		−6.22		2.73		121.32		
$HC{\equiv}CH$	164.49	163.70	1.09	5.82	3.79	4.10	169.37	173.66	170.6[e]

[a] All values are in hertz. [b] Results from ref 24 are based on the monocentric approximation for integrals; the OB and SD contributions were not included in the calculations. [c] Values based on the SCPT-INDO calculations of Blizzard and Santry, but they were multiplied by the ratio of $\langle r^{-3}\rangle_C$ for an STO to the empirical $\langle r^{-3}\rangle_C$ from ref 9 in order to see the importance of the multicenter integrals. As noted in an erratum[9] the SD results were multiplied by a factor of 2. [d] Values based on the SCPT-INDO monocentric approximation in which $s^2_N(0)$ for the FC term and $\langle r^{-3}\rangle_N$ for the OB and SD term have been adjusted to fit the experimental data.[9] [e] Graham, D. M.; Holloway, C. E. *Can. J. Chem.* **1963**, *41*, 2114. [f] Gray, G. A.; Maciel, G. E.; Ellis, P. D. *J. Magn. Reson.* **1969**, *1*, 407.

Table VIII. Calculated Directly Bonded and Geminal ^{13}C–^{19}F Coupling Constants, Which Were Obtained by the FOPPA INDO/MCI Method, Compared with Previous Semiempirical MO Results and the Available Experimental Data[a]

	FC		OB		SD		total		
compound	MCI	FPT[b]	MCI	SCPT[c]	MCI	SCPT[c]	MCI	SCPT[d]	exptl
directly bonded									
CH_3F	−93.27	−236.85	3.39	−8.38	7.65	7.99	−83.23	−202.68	−162.1[e]
CF_3H	−115.06	−214.23	−11.59	−19.29	4.35	4.40	−122.30	−285.16	−274.3[f]
$HFC{=}CH_2$	−100.27		0.55		1.36		−98.36		
$F_2C{=}CH_2$	−85.11	−218.96	−5.65	−17.23	0.43	1.23	−90.33	−284.87	−287[g]
$FC{\equiv}CF$	−24.51		2.35		−3.39		−25.55		
geminal									
$HFC{=}CH_2$	3.21		−13.24		3.85		−6.18		
$F_2C{=}CH_2$	32.61		−13.58		3.35		22.38		
$FC{\equiv}CF$	94.22		−6.53		5.65		93.34		

[a] All values are in hertz. [b] Values based on the monocentric approximation of FPT-INDO theory and are taken from ref 24. [c] Values from ref 9 but are scaled to the STO one-center integral by multiplying by 0.5278 to compare with the results of this study. [d] Values taken from ref 9; as a consequence the FC, OB, and SD terms in columns three, five, and seven must be scaled drastically to obtain these results. [e] Krugh, T. R.; Bernheim, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 2385. [f] Frankiss, S. G. *J. Phys. Chem.* **1963**, *67*, 752. [g] Muller, N.; Carr, D. T. *Ibid.* **1963**, *67*, 112.

Table IX. Calculated Values of Geminal and Vicinal ^{19}F–^{19}F Coupling Constants by FOPPA INDO/MCI Compared with Semiempirical MO Results and Available Experimental Data[a]

	FC		OB		SD		total		
compound	MCI	FPT[b]	MCI	SCPT[c]	MCI	SCPT[c]	MCI	SCPT[d]	exptl
geminal									
CF_3H	8.18	30.06	104.94	45.85	70.47	39.01	183.59	103.68	
NF_3	9.72		246.78		132.99		389.49		
$F_2C{=}CH_2$	184.36	−13.27	111.89	39.18	64.77	36.12	361.02	42.95	36.4[e]
vicinal									
trans-$HFC{=}CFH$	12.97	−38.99	−111.43	65.42	14.75	11.58	−83.71	−100.47	−124.8[e]
$FC{\equiv}CF$	−25.97		−172.75		−19.57		−218.29		

[a] All values in hertz. [b] Values taken from ref 24 correspond to the INDO-FPT semiempirical results. [c] Values obtained from the SCPT-INDO[9] results in the one-center integral approximation. These values were scaled to the one-center STO values of $\langle r^{-3}\rangle_F$ by multiplication by the factor 0.9698. [d] SCPT-INDO results from ref 9. [e] Flynn, G. W.; Matsushima, M.; Baldeschwieler, J. D.; Craig, N. C. *J. Chem. Phys.* **1963**, *38*, 2295.

these contributions are only about 25% of the values based on the Blizzard and Santry empirical value for $b_{CC'}$. In all cases the magnitudes of the contributions based on the one-center integral approximations are smaller. However, this is not so important for $^1J_{CC'}$ because the sum of the OB and SD contributions is less than 6% of the FC contribution. It is interesting to note that the inadequacies of the INDO-FPT method applied to ^{13}C–^{13}C coupling are sometimes attributed to the neglect of the OB and SD terms.

The total SCPT values[9] in Table VII are smaller in magnitude than the sums of the FC, OB, and SD SCPT contributions because of the scaling of both $a_{CC'}$ and $b_{CC'}$ in eq 4. The agreement between the calculated results and experimental data for $^1J_{CC'}$ is comparable in the two methods, but the inclusion of the MCI's avoids the problem of having to scale the $\langle r^{-3}\rangle_C$ integrals far beyond the atomic Hartree–Fock values.

Calculated results for directly bonded and geminal ^{13}C–^{19}F and geminal and vicinal ^{19}F–^{19}F in the representative molecules of this study are entered in Tables VIII and IX, respectively, along with the INDO-FPT results and the SCPT-INDO results for the OB and SD contribution which have been scaled to the STO values of the product of $\langle r^{-3}\rangle_C$ and $\langle r^{-3}\rangle_F$. This procedure reduces the values of these terms to the same order of magnitude as those obtained with the STO's and inclusion of the multicenter integrals. However, the latter procedure leads to drastic changes in the calculated values of the FC term. Factors other than multicenter integrals will be required for satisfactory descriptions of these types of coupling.

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Conclusion

For most types of nuclear spin-spin coupling, the inclusion of multicenter integrals in the semiempirical MO description leads to values of FC, OB, and SD contributions which are in reasonable accord with the ab initio results. Of particular importance is the extension of semiempirical methods to include the OB and SD contributions for coupling constants involving at least one proton. These are found to be substantial in magnitude for certain directly bonded and geminal coupling constants. Moreover, disparities between experimental values and those based on semiempirical FC terms, which are often ascribed to neglect of the OB and SD, are probably not justified. This conclusion is also supported by the insensitivity of the OB and SD contributions to substituent effects. In the tables included herein it is observed that the noncontact contributions are mainly determined by the hybridization of the atoms involved in the coupling and not by the substituent effects. For many types of spin-spin coupling the contributions of the multicenter integrals to the FC terms can be substantial, but they are not fully understood. This introduction of a reliable semiempirical method to estimate the OB and SD terms will provide the basis for further investigations of the electronic factors which determine the FC contributions.

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Ab Initio Calculations of Rotational Barriers for the Diselenide Bridge in Dimethyl Diselenide[1a]

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Abstract: Ab initio calculations of the rotational barrier for the diselenide bridge, Se-Se, in dimethyl diselenide, $H_3CSeSeCH_3$, have been performed by using STO-3G and Dunning-Hay basis sets for C and H atoms and a modified Lehn-Wipff-Demuynck basis set for the Se atom consisting of a primitive [12s,8p,2d] set contracted into a [6s,4p,2d] set. Total energies as a function of $|\theta|$, the torsion angle about the Se-Se bond, and cis and trans torsional barriers are discussed in light of available experimental data.

Dimethyl diselenide ($H_3CSeSeCH_3$) is the simplest model compound containing the four consecutive atoms CSeSeC. The rotational or torsional barrier about the bond between two chalcogen atoms such as S or Se is known to be 2-fold in nature on the basis of general theoretical considerations[2] and more detailed molecular orbital (MO[3]) calculations (for specific references, see our previous papers[4,5]): the most stable conformation corresponds to a torsion angle θ[6] in the neighborhood of ±90°, and the cis barrier ($\theta = 0°$) is always calculated to be greater than the trans barrier ($\theta = 180°$).

We recently reported the results of a semiempirical CNDO/2 MO study of these barriers in dimethyl diselenide and noted that their heights were higher than the similarly calculated heights of the corresponding barriers about the S-S bond of the isologue dimethyl disulfide (H_3CSSCH_3).[4] The general shape of torsional barriers can be often be calculated, but the heights of the barriers are, in some cases, either unrealistically high or low.[7] For example, the CNDO/2 method does not adequately account for nonbonded interactions,[8] and deficiencies such as this may be, in part, responsible for the unreliable values of the calculated barrier heights. Realistic values of these heights, however, can be calculated by ab initio MO methods, provided that suitable basis sets for the MO's are chosen.[9]

Here we report an ab initio MO study of the torsional barrier about the Se-Se bond of dimethyl diselenide as part of our continuing theoretical investigation[4,5] of simple dichalcogen compounds that we are performing to learn more about the relative conformational flexibility of torsional movement about S-S, S-Se, and Se-Se bonds in cystine-containing molecules and their selenium isologues. Estimated barrier heights obtained from MO studies of these model compounds should be quite useful as input parameters in classical potential energy studies of these larger molecules—i.e., peptides. To our knowledge, this is the first report of an ab initio MO calculation of the cis and trans torsional barriers about the Se-Se bond.

Method

We performed ab initio MO calculations at two levels of refinement: at a lower level, which utilized an augmented minimal basis (AMB) set,

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(1) (a) This paper is dedicated to the memory of Professor Roderich Walter. (b) Deceased, Sept 19, 1979.

(2) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1949**, *35*, 495-499.

(3) Abbreviations: AEB, augmented extended basis; AMB, augmented minimal basis; *b*, bond length; CNDO/2, complete neglect of differential overlap, version 2; DH, Dunning-Hay; *E*, total energy; E_0, minimum total energy; MLWD, modified Lehn-Wipf-Demuynck; MO, molecular orbital; STO , Slater-type orbital; ΔE_{cis}, $E(0°) - E_0$, height of cis barrier; $\Delta E_{\mathrm{trans}}$, $E(180°) - E_0$, height of trans barrier; ζ, orbital exponent; θ, torsion angle about S-S or Se-Se; θ_0, torsion angle corresponding to E_0; τ, bond angle.

(4) Renugopalakrishnan, V.; Wyssbrod, H. R.; Walter, R.; Druyan, M. E. *J. Chem. Phys.* **1982**, 77, 1362-1367.

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(6) Throughout this paper θ refers to the particular torsion angle defined by the four consecutive atoms A-B-B-A, where B is either S or Se. θ corresponds to the torsion angle χ^3 in the disulfide bridge region of the amino acid cystine or in the dichalcogen bridge region of selenocystine. The eclipsed cis conformation is defined as 0°, and the trans conformation as ±180°. Positive and negative torsion angles correspond to right-handed (*P*) and left-handed (*M*) screw senses, respectively. These algebraic signs are in accordance with the recommendations of the IUPAC Commission on Nomenclature of Organic Chemistry ("Nomenclature of Organic Chemistry"; Pergamon Press: Oxford, U.K., 1979; p 483).

(7) E.g., see (a) Herndon, W. C.; Feuer, J.; Hall, L. H. *Tetrahedron Lett.* **1968**, 2625-2628. (b) Gordon, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3122-3130.

(8) Gregory, A. R.; Padden-Row, M. N. *J. Am. Chem. Soc.* **1976**, *98*, 7521-7523.

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