An INDO Perturbation Theory of Magnetic Shielding Constants. Carbon-13 Chemical Shifts[1]

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Abstract: The SCF-MO theory of nuclear magnetic shielding constants is developed using gauge-invariant atomic orbitals. The resulting equations are applied to the INDO calculation of ^{13}C shieldings for a representative set of hydrocarbons, including carbonium ions. Two overlap approximations and reparameterization are explored. A modified set of INDO parameters together with the London overlap approximation lead to calculated chemical shifts that reproduce many of the important patterns in the corresponding experimental data.

The rapidly increasing interest and activity in ^{13}C magnetic resonance focuses attention on the need and desirability of a reliable theory of ^{13}C shielding. Such a theory would provide a framework for better understanding the nature of ^{13}C chemical shifts. It would also be directly useful in a variety of chemical applications, where comparisons between calculated and experimental results would make possible the identification of the structure or conformation of species in experimental samples, *e.g.*, carbonium ions. This latter function would place a requirement of computational practicability for a theoretical approach to realize maximum utility. In this regard, the computational simplicity of semiempirical approaches seems attractive.

Previously reported semiempirical approaches to the theory of ^{13}C chemical shifts have been based either upon Pople's molecular orbital theory of diamagnetism and shielding[3] or upon the simplified expression that comes from this theory or its equivalent, under the average-excitation-energy approximations,[4,5] or on an essentially equivalent valence-bond approach.[6] These applications have employed CNDO,[7] extended Hückel,[8] and other simple approaches to molecular wave functions and have been successful only to the extent of accounting for gross trends.[9-17] Indeed, in those cases where the average ΔE approximation is employed virtually any answer can be obtained depending upon one's choice of the parameter ΔE, and there is no *a priori* method for choosing its value.

The present study was undertaken to explore the applicability of INDO wave functions in a SCF perturbation theory of ^{13}C shielding. This particular method was chosen because of its computational simplicity and also because the INDO method has been reasonably successful in correlating experimental results for isotropic[18] and anisotropic[19] hyperfine coupling constants in radicals and isotropic nuclear spin coupling constants[20-22] for a large number of molecules. It is in this respect that the INDO method is attractive as a method of calculating magnetic shielding constants (chemical shifts), since the result would then be a relatively complete and unified approximate treatment of magnetic resonance parameters.

One of the goals in this work is to explore the alteration of the semiempirical INDO parameters as a step toward reparameterizing the INDO method with respect to certain readily accessible physical properties (*e.g.*, ^{13}C chemical shifts). For this reason, in order to minimize the number of parameters to be manipulated initially, we have limited our work at this stage to hydrocarbons.

Theory

A. Perturbed Hartree-Fock Theory with Gauge-Invariant Atomic Orbitals (GIAO). There have been several formal methods proposed for calculating magnetic susceptibilities and nuclear magnetic shielding constants. Of these, only the methods which utilize GIAO have been shown to be independent of the choice of origin of the coordinate system.[23] Indeed, the perturbed Hartree–Fock method which uses any finite basis set of ordinary atomic orbitals gives rise to magnetic shielding constants that vary linearly with the choice of origin.[24] Since the choice of origin is arbitrary and the relationship linear, the value of the shielding constant

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is arbitrary when obtained with this method. It is primarily for this reason that the method with GIAO is used in the present study.

The perturbed Hartree–Fock theory of magnetic susceptibility and nuclear magnetic shielding using GIAO has been previously developed by Hall and Hardisson.[25] These authors, however, were particularly interested in the "ring current" contributions to the magnetic susceptibility and shielding constants and, as a consequence, their development of the theory reflected the approximations of the π-electron method. It is thus desirable to redevelop the theory in a more generally applicable form.

The components of the magnetic shielding tensor $\boldsymbol{\sigma}$ are obtained from the second partial derivatives of the energy with respect to Cartesian components, α and β, of an external magnetic field **B** and a component of a nuclear magnetic moment $\boldsymbol{\mu}_{\mathrm{M}}$ of atom M.

$$\sigma_{\alpha\beta}{}^{(\mathrm{M})} = \left[\frac{\partial^2 E(\mathbf{B},\boldsymbol{\mu}_{\mathrm{M}})}{\partial \mathbf{B}_\alpha \partial \boldsymbol{\mu}_{\mathrm{M}_\beta}}\right]_{\mu_{\mathrm{M}}=\mathrm{B}=0} \tag{1}$$

In the Hartree–Fock method, the electronic energy of a molecule in the presence of the external field B and nuclear moment $\boldsymbol{\mu}_{\mathrm{M}}$ is given as the expectation value of the appropriate Hamiltonian operator using a single determinantal wave function. In terms of the doubly occupied molecular orbitals ϕ_i, this expression is

$$E(\mathbf{B},\boldsymbol{\mu}_{\mathrm{M}}) = \sum_{i=1}^{N/2} 2\langle\phi_i|h|\phi_i\rangle + \langle\phi_i|g|\phi_i\rangle \tag{2}$$

where

$$h = \frac{1}{2m}\left(-i\hbar\nabla + \frac{e}{c}\mathbf{A}\right)^2 - \sum_K^{\mathrm{atoms}} \frac{e^2 z_{\mathrm{K}}}{|\mathrm{r_K}|} \tag{3}$$

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathrm{r} + \boldsymbol{\mu}_{\mathrm{M}} \times \mathrm{r_M}/|\mathrm{r_M}|^3 \tag{4}$$

and

$$g = \sum_j^{N/2} \langle\phi_j(2)|\mathrm{r}_{12}{}^{-1}(2 - P_{12})|\phi_j(2)\rangle_2 \tag{5}$$

A is the vector potential due to the uniform external magnetic field **B** and the magnetic moment of nucleus M, $\boldsymbol{\mu}_{\mathrm{M}}$. The number of electrons is N, and z_{K} is the charge of the Kth nucleus. The vectors r and $\mathrm{r_K}$ are the distance vectors to the electron from the arbitrary origin of the coordinate system and nucleus K, respectively. The subscript 2 in eq 5 indicates integration over electron 2, while P_{12} is the permutation operator.

Gauge-invariant atomic orbitals are introduced into the calculation by expanding the molecular orbitals ϕ_i in the basis set χ

$$\phi_i = \sum_\nu^m \chi_\nu c_{\nu i} = \chi \mathbf{c}_i \tag{6}$$

where the basis functions are given as

$$\chi_\nu = f_\nu \chi_\nu{}^0 \tag{7}$$

$\chi_\nu{}^0$ represents the unperturbed basis function and the gauge factors f_ν are defined as

$$f_\nu = \exp\left(-\frac{ie}{\hbar c}\mathbf{A}_\nu \cdot \mathrm{r}\right)$$

or

$$f_\nu = \exp\left(-\frac{ie}{\hbar c}\mathbf{A}_\nu \cdot \mathrm{r}_\nu\right) \tag{8}$$

The vector potential is given as $\mathbf{A}_\nu = {}^1/_2\mathbf{B} \times \mathbf{R}_\nu$ where $\mathbf{R}_\nu$ represents the distance vector from the arbitrary origin of the molecular coordinate system to the atom on which the basis function χ_ν is centered. Both forms of eq 8 lead to the same results.

The expression for the energy in terms of the LCAO approximation is

$$E = \sum_i^{N/2} \mathbf{c}_i{}^\dagger[2\mathbf{H} + \mathbf{G}]\mathbf{c}_i \tag{9}$$

where elements of the matrices **H** and **G** are given by

$$H_{\mu\nu} = \langle\chi_\mu|h|\chi_\nu\rangle \tag{10}$$

$$G_{\mu\nu} = \sum_\eta^m\sum_\sigma^m R_{\eta\sigma}[2(\mu\nu|\eta\sigma) - (\mu\sigma|\eta\nu)] \tag{11}$$

where

$$(\mu\nu|\eta\sigma) = \iint \chi_\mu{}^*(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\eta{}^*(2)\chi_\sigma(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{12}$$

and **R** is the first-order density matrix, the elements of which are given by

$$R_{\eta\sigma} = \sum_i^{N/2} c_{\eta i}{}^* c_{\sigma i} \tag{13}$$

The operator h is defined in eq 3. Note that due to the nature of the perturbation and the gauge factors, both the integrals and LCAO expansion coefficients are complex. Since the basis functions do not depend on the nuclear magnetic moment, the Hellman–Feynmann theorem can be used to obtain the first derivative of eq 9 with respect to μ_{M_β}[26]

$$\frac{\partial E}{\partial \mu_{\mathrm{M}_\beta}} = 2\sum_i^{N/2} \mathbf{c}_i{}^\dagger \frac{\partial \mathbf{H}}{\partial \mu_{\mathrm{M}_\beta}}\mathbf{c}_i = 2\mathrm{Tr}\left[\mathbf{R}\cdot\frac{\partial \mathbf{H}}{\partial \mu_{\mathrm{M}_\beta}}\right] \tag{14}$$

so that a component of the shielding tensor of atom M becomes

$$\sigma_{\alpha\beta}(\mathrm{M}) = \left(\frac{\partial^2 E}{\partial B_\alpha \partial \mu_{\mathrm{M}_\beta}}\right)_{\mu_{\mathrm{M}}=\mathrm{B}=0} = \sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M}) + \sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M})$$

$$\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M}) = 2\mathrm{Tr}\left[\mathbf{R}(0)\left(\frac{\partial^2 H}{\partial B_\alpha \partial \mu_{\mathrm{M}_\beta}}\right)_0\right] \tag{15}$$

$$\sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M}) = 2\mathrm{Tr}\left[\left(\frac{\partial \mathbf{R}}{\partial B_\alpha}\right)_0\left(\frac{\partial \mathbf{H}}{\partial \mu_{\mathrm{M}_\beta}}\right)_0\right]$$

where **R**(0) refers to the density matrix obtained in the absence of the perturbation. The superscripts d and p refer to the diamagnetic and paramagnetic contributions, respectively. The LCAO expansion coefficients are obtained from the Roothaan equations[27]

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$$\begin{aligned} \mathbf{F}\mathbf{c}_i &= \mathbf{S}\mathbf{c}_i\epsilon_i \\ \mathbf{c}_i^{\dagger}\mathbf{S}\mathbf{c}_j &= \delta_{ij} \\ i, j &= 1, 2, \ldots, N/2 \end{aligned} \tag{16}$$

where $\mathbf{F} = \mathbf{H} + \mathbf{G}$. The derivatives of the expansion coefficients (and hence also the density matrix) with respect to a component of perturbing magnetic field are obtained by solving eq 16 in the presence of a small magnetic field and using a finite difference technique for the numerical differentiation.[26] Alternatively, eq 16 can be formally differentiated and then used to obtain these derivatives directly.[28]

B. INDO Approximations with GIAO. In the INDO method, the atomic orbital product $\chi_\mu^0\chi_\nu^0$ is selectively neglected; if χ_μ^0 and χ_ν^0 are centered on different atoms, their product is neglected everywhere except in the one electron energy matrix elements which are approximated as

$$H_{\mu\nu}^0 = \frac{1}{2}(\beta_\mu^0 + \beta_\nu^0)S_{\mu\nu}^0 \tag{17}$$

where the β_μ^0's are atomic parameters and $S_{\mu\nu}^0$ is the overlap integral. In the INDO theory with GIAO it is necessary that the neglect-of-differential-overlap-approximation be made in such a manner that the original INDO method, particularly eq 17, be recovered when the perturbing magnetic field is set equal to zero. For the two electron integrals there is no real problem. The product $\chi_\mu^*\chi_\nu$ (where the orbitals are GIAO) is simply neglected if χ_μ and χ_ν are centered on different atoms, and $\chi_\mu^*\chi_\nu = \chi_\mu^0\chi_\nu^0$ if they are on the same atom. However, certain ambiguities arise in the evaluation of the two-center one electron terms using GIAO. These can be written as

$$H_{\mu\nu} = \exp\left(\frac{ie}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_\mu \times \mathbf{R}_\nu\right)\int \exp\left(\frac{ie}{2\hbar c}\mathbf{B} \times \mathbf{R}_{\mu\nu}\cdot \mathrm{r}_\nu\right) \times \chi_\mu^0\left[\frac{1}{2m}\left(-i\hbar\nabla + \frac{e}{2c}\mathbf{B} \times \mathrm{r}_\nu + \frac{e}{c}\boldsymbol{\mu}_{\mathrm{M}} \times \mathrm{r}_{\mathrm{M}}/|\mathrm{r}_{\mathrm{M}}|^3\right)^2 - \sum_{K}^{\text{atoms}} e^2 z_K/|\mathrm{r}_K|\right]\chi_\nu^0 \, d\tau \tag{18}$$

where $\mathbf{R}_{\mu\nu} = \mathbf{R}_\nu - \mathbf{R}_\mu$ and the remaining quantities have been given earlier. The origin-dependent term has been factored outside the integral and the operation

$$\left[-i\hbar\nabla + \frac{e}{2c}\mathbf{B} \times \mathrm{r} + \frac{e}{c}\boldsymbol{\mu}_{\mathrm{M}} \times \mathrm{r}_{\mathrm{M}}/|\mathrm{r}_{\mathrm{M}}|^3\right]^2 f_\nu\chi_\nu^0 = f_\nu\left[-i\hbar\nabla + \frac{e}{2c}\mathbf{B} \times \mathrm{r}_\nu + \frac{e}{c}\boldsymbol{\mu}_{\mathrm{M}} \times \mathrm{r}_{\mathrm{M}}/|r_{\mathrm{M}}|^3\right]^2 \chi_\nu^0 \tag{19}$$

has been performed in deriving eq 18. The origin independence of the theory is maintained as long as approximations are made only to terms which appear inside the integral in eq 18. Care must also be taken to ensure that **H** remains Hermitian.

As a first step we invoke the usual London aproximation.[29] In the present case this is equivalent to expanding the exponential inside the integral and keeping only the leading (unity) term. Although this approximation preserves the origin independence, it is somewhat arbitrary in that it keeps some terms in **B** while neglecting others and it destroys the Hermitian property of **H** if no further approximations are made. Equation 18 can now be written as

$$H_{\mu\nu} = \exp\left(\frac{ie}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_\mu \times \mathbf{R}_\nu\right)\Big\{H_{\mu\nu}^0 + \sum_\alpha B_\alpha\langle\chi_\mu^0|h_\alpha^{01}|\chi_\nu^0\rangle + \sum_\alpha \mu_{\mathrm{M}\alpha}\langle\chi_\mu^0|h_\alpha^{10}(\mathrm{M})|\chi_\nu^0\rangle + \sum_\alpha\sum_\beta \mu_{\mathrm{M}\alpha}B_\beta\langle\chi_\mu^0|h_{\alpha\beta}^{11}(\mathrm{M})|\chi_\nu^0\rangle + \text{higher order terms}\Big\} \tag{20}$$

$$\alpha, \beta = x, y, z$$

where $H_{\mu\nu}^0$ is appropriate for the calculation in the absence of the perturbations and is given by eq 17 in the INDO method when χ_μ^0 and χ_ν^0 are on different atoms. The operators in the remaining integrals are defined as

$$h_\alpha^{01} = -\frac{e\hbar}{2mc}iL_{\nu\alpha} \tag{21}$$

$$h_\alpha^{10}(\mathrm{M}) = -\frac{e\hbar}{mc}i\frac{L_{\mathrm{M}\alpha}}{|\mathrm{r}_{\mathrm{M}}|^3} \tag{22}$$

$$h_{\alpha\beta}^{11}(\mathrm{M}) = \frac{e^2}{2mc^2}(\mathrm{r}_\nu\mathrm{r}_{\mathrm{M}}\delta_{\alpha\beta} - \mathrm{r}_{\nu\alpha}\mathrm{r}_{\mathrm{M}\beta})/|\mathrm{r}_{\mathrm{M}}|^3 \tag{23}$$

with

$$L_{\nu\alpha} = (\mathrm{r}_\nu \times \nabla)_\alpha \tag{24}$$

The higher order terms in eq 20 are not relevant in chemical shift calculations. Next, we assume that, with the exception of $H_{\mu\nu}^0$, all of the integrals in eq 20 are zero if χ_μ^0 and χ_ν^0 are centered on different atoms. Although this approximation is somewhat drastic, it is consistent with all previous applications of the INDO method to the calculation of molecular properties, including dipole moments[30] and esr and nmr spin coupling constants.[18-22] In the present case, this approximation also restores the Hermitian property of **H**. Recently, Amos and Roberts have studied various other approximations to some of these terms in the π-electron theory of proton chemical shifts.[31] Although we have not considered the inclusion of these two- and three-center integrals, we have performed calculations, reported here, in which the exponential appearing in front of the integral in eq 20 is also set equal to one. This we call the zero-order overlap approximation.

Within the framework of the above approximations, the expression (eq 15) for a component of the shielding tensor can be partitioned into mono- and diatomic contributions as follows

$$\sigma_{\alpha\beta}(\mathrm{M}) = \sigma_{\alpha\beta}^{\mathrm{d}}(\mathrm{M,M}) + \sigma_{\alpha\beta}^{\mathrm{p}}(\mathrm{M,M}) + \sum_{\mathrm{K}\neq\mathrm{M}}^{\text{atoms}}[\sigma_{\alpha\beta}^{\mathrm{d}}(\mathrm{M,K}) + \sigma_{\alpha\beta}^{\mathrm{p}}(\mathrm{M,K})] \tag{25}$$

$$\sigma_{\alpha\beta}^{\mathrm{d}}(\mathrm{M,K}) = 2\sum_\mu^{\mathrm{K}}\sum_\nu^{\mathrm{K}} R_{\mu\nu}(0)\langle\chi_\mu^0|h_{\alpha\beta}^{11}(\mathrm{M})|\chi_\nu^0\rangle \tag{26}$$

$$\alpha_{\alpha\beta}^{\mathrm{p}}(\mathrm{M,K}) = 2\sum_\mu^{\mathrm{K}}\sum_\nu^{\mathrm{K}}\left(\frac{\partial R_{\mu\nu}}{\partial B_\alpha}\right)_0\langle\chi_\mu^0|h_\beta^{10}(\mathrm{M})|\chi_\nu^0\rangle \tag{27}$$

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where the summations in eq 26 and 27 only include basis functions centered on atom K. For ^{13}C chemical shifts the dominant contributions will be due to the one-center terms, $\sigma_{\alpha\beta}{}^{d}(M,M)$ and $\sigma_{\alpha\beta}{}^{p}(M,M)$ of eq 25. From eq 26 and 27 and the definition of the operators $h_{\alpha\beta}{}^{11}(M)$ and $h_{\beta}{}^{10}(M)$ given in eq 22 and 23, these terms are proportional to the $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ integrals, respectively. For Slater-type orbitals these one-center integrals will in turn be proportional to ξ and ξ^3, respectively, where ξ is the orbital exponent of the Slater orbital in question. In the INDO method the exponents depend only on the type of atom on which the basis function is centered and not on the molecular environment of that atom. Karplus and Pople[5] noted that the integrals of the type $\langle r^{-3}\rangle$ in the paramagnetic contribution to the ^{13}C shielding constant were sensitive to the choice of ξ and proposed modifying these exponents by Slater's screening rules[32] in order to account for the different molecular environments of nonequivalent atoms. In the INDO method, this modification is given as

$$\xi_M = [3.25 - 0.35(p_{MM} - 4)]/2 \qquad (28)$$

where p_{MM} refers to the total valence-shell electron density on atom M. In the calculations reported herein, eq 28 was used in the evaluation of the $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ type integrals appearing in $\sigma_{\alpha\beta}{}^{d}(M,M)$ and $\sigma_{\alpha\beta}{}^{p}(M,M)$.

The integrals in the two-center terms $\sigma_{\alpha\beta}{}^{d}(M,K)$ and $\sigma_{\alpha\beta}{}^{p}(M,K)$ were evaluated using the long-range approximation given by McConnell[33] and Pople.[3] It is worth pointing out that these two-center terms, and the manner in which they are approximated, while relatively unimportant for ^{13}C chemical shifts, will be dominant for proton shifts. This is primarily due to the fact that the one-center term $\sigma_{\alpha\beta}{}^{p}(M,M)$ is zero for protons, so that the small values of their shifts will be due almost entirely to the two-center terms in the INDO method. Amos and Roberts, however, have shown[31] that proton shifts (in the π-electron theory) are also sensitive to integrals of the type $\langle\chi_\mu{}^0|h_{\alpha\beta}{}^{01}(M)|\chi_\nu{}^0\rangle$, where $\chi_\mu{}^0$ and $\chi_\nu{}^0$ are centered on different carbon atoms. Since we have neglected integrals of this type in the present treatment, we feel that a method as crude as INDO will not be applicable to proton shifts without a serious reconsideration of the approximations involved.

It remains only to specify how the derivative of the perturbed denisty matrix is calculated in the INDO theory. For this the finite perturbation method[26] was used in the present calculations. In this scheme, a small finite value of B_α is chosen (10^{-3} atomic unit was found to be optimal) and the elements of **F** constructed using the INDO approximations described earlier. The relevant SCF equations

$$\mathbf{F}\mathbf{c}_j = \mathbf{c}_j\epsilon_j \qquad (29)$$

are then solved iteratively. As mentioned earlier, the terms in eq 29 are necessarily complex, so that the iterative solution of eq 29 requires the diagonalization of a complex Hermitian matrix **F**. A computer program based on the Jacobi method was written for this purpose. The necessary modifications of the **F** matrix elements for the complex case in the INDO theory are given in the Appendix. The perturbed density matrix **R** is constructed as

$$\mathbf{R} = \sum_j^{N/2}\mathbf{c}_j{}^*\mathbf{c}_j{}^+ = \sum_j^{N/2}(\mathbf{c}_j{}^r\mathbf{c}_j{}^{r+} + \mathbf{c}_j{}^i\mathbf{c}_j{}^{i+}) + i\sum_j^{N/2}(\mathbf{c}_j{}^r\mathbf{c}_j{}^{i+} - \mathbf{c}_j{}^i\mathbf{c}_j{}^{r+}) = \mathbf{R}^r + i\mathbf{R}^i \qquad (30)$$

where the superscripts r and i refer to the real and imaginary components of $\mathbf{C}_j$ and **R**. In order to attain sufficient accuracy in the perturbed density matrix, it was found necessary to require that the rms difference between two successive density matrices be less than 10^{-7} for the convergence of the SCF procedure. The derivative of **R** with respect to a component of **B** was obtained numerically by a single difference

$$\left(\frac{\partial\mathbf{R}}{\partial B_\alpha}\right)_0 \approx i\mathbf{R}^i/B_\alpha \qquad (31)$$

where the fact that only the imaginary component of **R** will contribute to the derivative has been used.

Results and Discussions

Overlap Approximations and Sensitivity to Parameter Alteration. The effects of altering the diagonal and off-diagonal matrix elements of the core Hamiltonian were explored for both the zero-order and London overlap approximations. The off-diagonal elements, which in the CNDO and INDO approximate MO schemes are given by eq 17, were altered by varying the values of the β^0's. For evaluating the effects of these alterations, we chose for reference compounds a small set of hydrocarbons that represent a wide range of ^{13}C chemical shifts. Experimental data for the compounds, methane, ethane, acetylene, and ethylene, were compared with the results of two sets of calculations, *i.e.*, obtained either with or without application of the "corrections" of the pertinent integrals according to eq 28.

Using the standard INDO parameters[34] calculations with either overlap approximation and either with or without correcting according to eq 28 gave results that bear no obvious relationship to the experimental data. The sensitivity of calculated shifts to parameter variation was found to be relatively small when the zero-order overlap approximation was employed. In contrast to this, a substantial sensitivity of calculated results to parameter variation was found under the London overlap approximation. Several sets of parameters were explored.

Table I gives the results of employing the zero-order overlap approximation with standard INDO parameters and the results obtained using the London approximation with a specific set of altered parameters. The shielding values reported are the isotropic values (one-third the trace of the tensor) that correspond to systems undergoing rapid tumbling. Table I shows that the latter case provides a reasonable qualitative level of agreement with the experimental numbers that are presented for comparison. This set of parameters does not represent the only set that could give the same qualitative level of agreement that is noted in Table I and should not be considered a "best" or "final" set.

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Table I. Calculated ^{13}C Shieldings Using Standard and "New" INDO Parameters[a]

Standard INDO Parameters	New INDO Parameters
Hydrogen: $(1/2)(I + A) = 7.176$ eV,	Hydrogen: $(1/2)(I + A) = 7.176$ eV,
$\beta_0 = -9.0$	$\beta_0 = -12.0$
Carbon: $(1/2)(I + A)_s = 14.051$,	Carbon: $(1/2)(I + A)_s = 17.051$,
$(1/2)(I + A)_p = 5.572$,	$(1/2)(I + A)_p = 8.572$,
$\beta^0 = -21.0$	$\beta^0 = -17.0$

	Zero-order approximation				Experimental		London approximation			
	P_C	$\sigma^d(M)$[b]	$\sigma^p(M)$[c]	δ[d]	δ	Ref	P_C[e]	$\sigma^d(M)$	$\sigma^p(M)$	δ
CH_4	3.96	57.2	−120.4	−1.2	8	*f*	4.48	64.6	−64.7	0.3
CH_3CH_3	3.95	56.9	−119.0	0.0	0	*g*	4.17	61.6	−62.1	0.0
$CH{\equiv}CH$	4.05	58.4	−108.6	11.8	−68	*g*	4.15	59.9	−140.0	−79.7
$CH_2{=}CH_2$	4.00	57.7	−161.0	−41.3	−117.4	*h*	4.21	60.6	−179.9	−118.8

[a] Values given in ppm. No $\langle r^{-3}\rangle$ or $\langle r^{-1}\rangle$ corrections applied. [b] $\sigma^d(M)$ is the sum of $\sigma^d(M,M)$ and the $\sigma^p(M,K)$ terms. [c] $\sigma^p(M)$ is the sum of $\sigma^p(M,M)$ and the $\sigma^p(M,K)$ terms. [d] Chemical shifts with respect to ethane. [e] The computed total carbon valence-shell electron density. [f] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961). [g] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). [h] H. Spiesecke, private communication.

Table II. Calculated ^{13}C Shielding Using London Overlap Approximation with "New" INDO Parameters[a]

Compd	$\sigma^d(M,M)$	$\sum_{K\neq M}\sigma^d(M,K)$	$\sigma^p(M,M)$	$\sum_{K\neq M}\sigma^p(M,K)$	δ[b]	Experimental δ	Experimental Ref
CH_4	61.26	0.00	−55.20	0.00	3.00	8	*d*
	(64.59)[c]	(0.00)	(−64.69)	(0.00)	(0.34)		
CH_3CH_3	59.82	−0.03	−56.80	0.08	0.00	0	*d*
	(61.63)	(−0.03)	(−62.12)	(0.08)	(0.00)		
$HC{\equiv}CH$	58.90	−0.03	−129.29	−4.07	−77.55	−68	*d*
	(59.89)	(−0.03)	(−135.87)	(−4.07)	(−79.64)		
$H_2C{=}CH_2$	59.31	0.01	−167.76	−0.52	−112.04	−117.4	*d*
	(60.35)	(0.01)	(−179.40)	(−0.52)	(−119.12)		

[a] Values given in ppm. [b] Chemical shifts with respect to ethane. [c] Values in parentheses have been obtained *without* the $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ corrections embodied in eq 28. [d] See Table I.

Nevertheless, it demonstrates that a theory at this level can lead to satisfactory agreement if reparameterization is introduced. All further results discussed in this paper are based upon the particular set of INDO parameters indicated in Table I.

It should be noted that the altered INDO calculation differs from the standard procedure in one additional manner: the F^2 and G^1 integrals of ref 34 are calculated directly from the Slater orbitals, using equations given by Miller, Gerhauser, and Matsen.[35] In standard INDO, the F^2 and G^1 values were chosen empirically as the Slater-Condon atomic parameters.[34] This difference was not found to influence the results substantially.

Also presented in Table I are the atomic electron densities of carbon that were computed in the two schemes. Appreciable differences are exhibited, especially for methane. The atomic electron densities for carbon are larger with the new parameters. It may be noteworthy that the electron densities computed by INDO with the "new" parameters provide trends that in some cases are closer to those that have been obtained by *ab initio* calculation[36-38] than what are obtained with standard INDO.

Presented in Table II are additional details of the calculations represented in Table I. In Table II the calculated shieldings are broken down into one- and two-center contributions to both the diamagnetic and paramagnetic terms. Note that variations in the one-center paramagnetic term make the dominant contributions to variations in the overall calculated results. This is consistent with previous chemical shift theories, which have concluded that the local paramagnetic contribution, $\sigma^p(M,M)$, is largely responsible for the observed range of ^{13}C chemical shifts.[5,39] Accordingly, the computed local diamagnetic contributions, $\sigma^d(M,M)$, fall within a range of about 5 ppm of each other.

The two-center contributions, $\Sigma\sigma(M,K)$, are negligible for methane, ethane, and ethylene. For acetylene they are −4.1 ppm and are dominated by the paramagnetic contribution. The relatively minor role of these neighboring atom contributions displayed in Table II corroborates previous suggestions[6,11] that such contributions are usually not of major importance to ^{13}C chemical shifts. The patterns given in Table II are seen not to depend strongly upon the inclusion or exlcusion of the $\langle r^{-3}\rangle$ and $\langle r^{-1}\rangle$ corrections.

Table III gives the results of ^{13}C shielding calculations for a wider variety of hydrocarbons, including two carbonium ions. These cationic species were included so that the effects of strong electronic polarizations could be represented without introducing the uncertainties that would be associated with the introduction of heteroatoms and their corresponding INDO parameters.

Some of the features mentioned above are also apparent in Table III. For example, the general experimental pattern that alkyl carbons are more shielded

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(37) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

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Table III. Calculated ^{13}C Chemical Shifts Using the "New" INDO Parameters[a]

	Compound	$\sigma^d(M)$	$\sigma^p(M)$	$\sigma(M)$	δ^b	δ^c	Experimental δ	 Ref
1.	CH_4	61.26	−55.20	6.06	120.62	(118.50)	130.8	*f*
2.	$c\text{-}C_3H_6$[d]	58.90	−65.21	−6.31	108.25	(109.72)	130.7	*g*
3.	C_2H_6	59.78	−56.72	3.06	117.62	(118.16)	122.8	*h*
4.	$C^*H_3CH_2CH_3$	60.05	−60.47	−0.42	114.14	(113.79)	113.1	*i*
5.	$CH_3C^*H_2CH_3$	58.35	−55.04	3.31	117.87	(120.88)	112.6	*i*
6.	$C^*H_3C_6H_5$	60.33	−60.74	−0.41	114.15	(112.93)	107.2	*i*
7.	$C^*H_3CH{=}CH_2$	60.12	−60.07	0.06	114.50	(114.01)	108.2	*j*
8.	$c\text{-}C_6H_{12}$	58.78	−62.41	−3.62	110.94	(112.94)	100.9	*g*
9.	$C^*H_3C{\equiv}CH$	59.95	−58.53	1.42	115.98	(116.29)		
10.	$CH_3C^+(C^*H_3)_2$	60.80	−82.47	−21.67	92.89	(81.45)	81.3	*k*
11.	$HC^+(C^*H_3)_2$	60.63	−88.71	−28.09	86.47	(87.95)	67.8	*k*
12.	$CH_3C{\equiv}C^*H$	59.88	−132.44	−72.56	42.00	(35.16)	58.7	*l*
13.	C_2H_2	98.87	−133.36	−74.49	40.07	(38.51)	54.8	*h*
14.	$C^*H_2{=}C{=}CH_2$[e]	60.44	−143.08	−82.64	31.92	(20.78)	54.0	*m*
15.	$CH_3C^*{\equiv}CH$	57.11	−143.43	−86.32	28.24	(34.34)	43.0	*j*
16.	$CH_3CH{=}C^*H_2$	59.96	−166.01	−106.05	8.51	(−2.14)	12.2	*n*
17.	C_2H_4	59.30	−168.29	−108.98	5.58	(−0.68)	5.4	*m*
18.	$CH_3C_6H_5\text{-}4\text{-}C^*$	58.49	−172.71	−114.21	0.25	(−0.86)	4.0	*i*
19.	$CH_3C_6H_5\text{-}2\text{-}C^*$	58.79	−173.47	−114.68	−0.12	(−3.29)	0.3	*i*
20.	C_6H_6	58.31	−172.87	−114.56	0.0	(0.0)	0.0	*i*
21.	$CH_3C_6H_5\text{-}3\text{-}C^*$	58.14	−174.47	−116.32	−1.76	(−0.90)	1.1	*i*
22.	$CH_3C^*H{=}CH_2$	57.67	−177.83	−120.16	−5.60	(−1.84)	−7.1	*n*
23.	$CH_3C_6H_5\text{-}1\text{-}C^*$	56.74	−180.39	−123.66	−9.10	(0.43)	−8.2	*i*
24.	$CH_3C^{*+}(CH_3)_2$	53.68	−261.26	−207.58	−93.02	(−58.68)	−70.4	*k*
25.	$HC^{*+}(CH_3)_2$	54.72	−283.34	−228.61	−114.05	(−84.56)	−60.0	*k*
26.	$CH_2{=}C^*{=}CH_2$	56.26	−232.82	−176.56	−62.07	(−48.7)	−84.0	*m*

[a] Values given in ppm. Corrections of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ embodied in eq 28 have been included. [b] Calculated chemical shifts with respect to benzene. [c] Calculated chemical shift values with respect to benzene when no $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ corrections are made. [d] Geometry taken from ref 21. [e] Geometry taken from J. Overend and B. Crawford, Jr., *J. Chem. Phys.*, **29**, 1002 (1958). [f] See ref *f*, Table I. [g] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964). [h] See ref *g*, Table I. [i] G. E. Maciel, unpublished results. [j] V. J. Bartuska and G. E. Maciel, unpublished work. [k] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 580 (1969). [l] Values of the chemical shift were taken for $C_4H_9C{\equiv}CH$: D. D. Traficante and G. E. Maciel, *J. Phys. Chem.*, **69**, 1348 (1965). [m] See ref *h*, Table I. [n] G. B. Savitsky, P. D. Ellis, K. Namikawa, and G. E. Maciel, *J. Chem. Phys.*, **49**, 2395 (1968).

than acetylenic carbons, which in turn are more shielded than olefinic or aromatic carbons, is accounted for in the calculations. Comparison between calculated and experimental results exhibits a relatively good, nearly monotonic relationship. While some reversals occur, they are generally associated with small calculated differences and/or small experimental differences. It appears that the overall pattern of calculated *vs.* experimental agreement is improved by the inclusion of the $\langle r^{-3}\rangle$ correction, except for the case of the carbonium ions, where the correction causes a substantial "overshoot" in the calculated deshielding effect. However, it must be realized that the divergence between experimental systems and the structure of species employed in calculations may be largest for the carbonium ions, in which solvation interactions may be especially strong. The correction according to eq 28 seems especially helpful in accounting for the effect of the methyl group as a substituent, a topic discussed in more detail below. Thus, while a correction of $\langle r^{-3}\rangle_{2p}$ of the general sort represented by eq 28 seems to be desirable, it is by no means clear that this particular expression would result from research aimed at this specific consideration.

Entries 1, 3, 4, 6, 7, 9, 10, and 11 in Table III constitute a set of cases that can be viewed as substituted methanes. A nearly perfect monotonic relationship is seen between experimental data and calculated results.

Table IV. Calculated Effect of Methyl Substitution on Shielding Using "New" INDO Parameters[a]

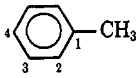
Compound	$\sigma^d(M)$	$\sigma^p(M)$	δ^b	Exptl[b,c] δ
$H\text{-}C^*H_3$	61.3	−55.2	120.6	130.8
$CH_3\text{-}C^*H_3$	59.8	−56.7	117.6	122.8
$H\text{-}C^*H_2CH_3$	59.8	−56.7	117.6	122.8
$CH_3\text{-}C^*H_2CH_3$	58.4	−55.0	117.9	112.6
$H\text{-}CH_2C^*H_3$	59.8	−56.7	117.6	122.8
$CH_3\text{-}CH_2C^*H_3$	60.1	−60.5	114.1	113.1
$H\text{-}C^*H{=}CH_2$	59.3	−168.3	5.6	5.4
$CH_3\text{-}C^*H{=}CH_2$	57.7	−177.8	−5.6	−7.1
$H\text{-}CH{=}C^*H_2$	59.3	−168.3	5.6	5.4
$CH_3\text{-}CH{=}C^*H_2$	60.0	−166.0	8.5	12.2
$H\text{-}C^*{\equiv}CH$	58.9	−133.4	40.1	54.8
$CH_3\text{-}C^*{\equiv}CH$	57.1	−143.4	28.2	43.0
$H\text{-}C{\equiv}C^*H$	58.9	−133.4	40.1	54.8
$CH_3\text{-}C{\equiv}C^*H$	59.9	−132.4	42.0	58.7
$H\text{-}C^{*+}(CH_3)_2$	54.7	−283.3	−114.0	−60.0
$CH_3\text{-}C^{*+}(CH_3)_2$	53.7	−261.3	−93.0	−70.4
$H\text{-}C^+(C^*H_3)_2$	60.6	−88.7	86.5	67.8
$CH_3\text{-}C^+(C^*H_3)_2$	60.8	−82.4	93.0	81.3

[a] Values given in ppm. Corrections of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ embodied in eq 28 have been included. [b] Chemical shifts with respect to benzene at zero. [c] For references see Table III.

Table IV, which is constructed from results given in Table III, focuses on the methyl group as a *substituent*. The results are grouped in pairs that can be viewed either as C*–H and $C^*\text{–}CH_3$ (α methyl effect) or as C*–C–H and $C^*\text{–}C\text{–}CH_3$ (β methyl effect). The correct sign of the methyl substituent effect is obtained in all cases except for the central carbon of propane or the central carbon of the *tert*-butyl carbonium ion. These cases are the only ones studied in which a methyl substituent effect is tested at a carbon atom to which a methyl group is already attached in the C*–H or C*–C–H case (*i.e.*, in ethane or in $CH_3C^*H^+CH_3$). This may represent a pattern of deficiency in the set of INDO parameters used here or in the basic approach employed. It is of interest that the effect of a methyl group compared to hydrogen has proven to be a difficulty in INDO calculations of spin–spin coupling constants[20] and in *ab initio* calculations of ^{13}C chemical shifts.[40]

A specific case of interest regarding the substituent effect of a methyl group is given in Table V, which provides a comparison of the calculated and experimental results for toluene. It is seen that the larger effects are given in the correct experimental order, while the small shifts among the ortho and meta carbons and benzene itself are not properly reproduced. However, these three experimental shifts are sufficiently small that they may be within the range of medium effects.[41] Also given in Table V are the computed total and π-electron densities, P and P_π, respectively. It can be seen that there is no simple correlation between either P or P_π and either the calculated or experimental chemical shifts.

Table V. Chemical Shift Calculations on Toluene Using "New" INDO Parameters[a]

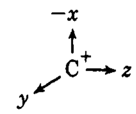
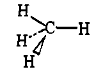
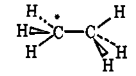
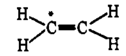
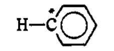
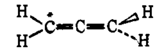
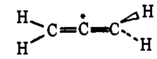


Carbon	$\sigma^d(M)$	$\sigma^p(M)$	δ	Exptl[b] δ	P_π[c]	P[d]
CH_3	60.3	−60.7	114.2	108.2		4.3478
4	58.5	−172.7	0.3	4.0	1.0272	4.1019
2	58.8	−173.5	−0.1	0.3	1.0413	4.1381
3	58.1	−174.5	−1.8	1.1	0.9845	4.0616
1	56.7	−180.4	−9.1	−8.2	0.9434	3.8937

[a] Values given in ppm. Corrections of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ embodied in eq 28 have been included. [b] Chemical shifts with respect to benzene. [c] Value of $P_{2p_y2p_y}$ where benzene ring is in xz plane, *i.e.*, atomic π-electron density. [d] Value of $P_{2s2s} + P_{2p_x2p_x} + P_{2p_y2p_y} + P_{2p_z2p_z}$, *i.e.*, total atomic electron density.

As the complete shielding tensor is obtained in these calculations, it is of interest to take note of the calculated shielding anisotropies, *i.e.*, the differences among the principal shielding tensor elements. Table VI summarizes results on seven representative compounds. Except for methane, substantial anisotropies are obtained, especially when π systems are present. While there are no experimental data now available to test these values, current advances in experimental techniques[42,43] should make some values accessible in the future. From the variations noted in Table VI, it would appear that such data will provide even more critical tests of shielding theories than do the isotropic average shielding values.

Table VI. Principle ^{13}C Shielding Tensor Elements Using "New" INDO Parameters[a]

	σ_{xx}	σ_{yy}	σ_{zz}
	6.06	6.06	6.06
	7.80	7.80	−6.40
	−251.90	17.40	−92.46
$H-\dot{C}\equiv C-H$	−130.00	−130.00	36.53
	−134.68	21.56	−230.58
	−198.94	6.26	−55.23
	−209.81	−209.81	−110.06

[a] Values given in ppm. Corrections of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ embodied in eq 28 have been included.

Summary and Conclusions

With an altered set of parameters, the INDO framework provides a scheme capable of accounting for many of the patterns of experimental chemical shifts for hydrocarbons. The most serious discrepancy occurs in representing the effect of methyl substitution on a carbon already attached to a methyl group. Although the calculated chemical shifts are by no means in general quantitative agreement with experiment, the results represent a considerable improvement over previous semiempirical calculations and lend encouragement for the further development of this method.

The correction of the $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ integrals according to Slater's rules seems moderately helpful, especially in handling the effect of methyl substitution, but the main features of calculated structural effects do not depend upon this correction.

Chemical shift anisotropies may provide the most critical tests of shielding theories, as the individual calculated shielding tensor elements show a great sensitivity to structural details.

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Appendix

F Matrix Elements in the INDO Approximations with GIAO. For a molecule in the presence of an external magnetic field **B**, the INDO method utilizing GIAO must be extended to accommodate the complex terms introduced by the perturbations. Thus, Fock matrix **F** will have both real and imaginary terms

$$\mathbf{F} = \mathbf{H} + \mathbf{G} = (\mathbf{H}^r + \mathbf{G}^r) + i(\mathbf{H}^i + \mathbf{G}^i) \qquad (A.1)$$

In the notation of ref 34

$$\begin{aligned} H_{pp}{}^r &= U_{pp} - \sum_{B(\neq A)}^{\text{atoms}} Z_B\gamma_{AB} + \\ &\qquad \text{INDO “core” corrections} \\ H_{pp}{}^i &= 0 \end{aligned} \qquad (A.2)$$

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(40) R. Ditchfield, D. P. Miller, and J. A. Pople, *J. Chem. Phys.*, **54**, 4861 (1970).

(41) M. R. Bacon and G. E. Maciel, to be published.

(42) G. P. Ceasar, C. S. Yannoni, and B. P. Dailey, *J. Chem. Phys.*, **50**, 373 (1969).

(43) W. Huttner, P. D. Foster, and H. G. Flygare, *ibid.*, **50**, 1710 (1969).

where basis function p is taken to be centered on atom A and U_{pp} and γ_{AB} are the diagonal atomic "core" matrix element and the two-center Coulomb integral defined in ref 34. The other elements are given as

$$H_{pq}{}^{r} = 0$$

$$H_{rq}{}^{i} = -\frac{eh}{2mc}\beta\cdot\int \chi_{p}{}^{0}(r_{q} \times \nabla)\chi_{q}{}^{0}\,d\tau \tag{A.3}$$

where p ≠ q, but both are centered on the same atom, and

$$\begin{aligned} H_{pq}{}^{r} &= \cos\left(\frac{e}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_{q} \times \mathbf{R}_{p}\right)\frac{1}{2}(\beta_{p}{}^{0} + \beta_{q}{}^{0})S_{pq}{}^{0} \\ H_{pq}{}^{i} &= \sin\left(\frac{e}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_{q} \times \mathbf{R}_{p}\right)\frac{1}{2}(\beta_{p}{}^{0} + \beta_{q}{}^{0})S_{pq}{}^{0} \end{aligned} \tag{A.4}$$

in the London approximation for the case where p and q refer to different atoms. In eq A.2–A.4 it has been assumed that a valence basis set of s and p Slater-type atomic orbitals is used. The elements of **G** become

$$\begin{aligned} G_{pp}{}^{r} &= \sum_{B}^{\text{atoms}} \sum_{q}^{B} 2R_{qq}{}^{r}\gamma_{AB} - R_{pp}{}^{r}F^{0} \\ G_{pp}{}^{i} &= 0 \end{aligned} \tag{A.5}$$

where p is taken to be on atom A and $F^{0} = \gamma_{AA}$. Also

$$\begin{aligned} G_{sp_\alpha}{}^{r} &= R_{sp_\alpha}{}^{r}(G^{1} - F^{0}) \\ G_{sp_\alpha}{}^{i} &= R_{sp_\alpha}{}^{i}\left(F^{0} - \frac{1}{3}G^{1}\right) \\ G_{p_\alpha p_\beta}{}^{r} &= R_{p_\alpha p_\beta}{}^{r}\left(\frac{11}{25}F^{2} - F^{0}\right) \\ G_{p_\alpha p_\beta}{}^{i} &= \frac{1}{2}R_{p_\alpha p_\beta}{}^{i}\left(F^{0} - \frac{1}{5}F^{2}\right) \end{aligned} \tag{A.6}$$

where s and p refer to s and p type atomic orbitals centered on the same atom and G^{1} and F^{2} are the Slater–Condon parameters given in ref 34. If p and q are centered on different atoms A and B, then

$$\begin{aligned} G_{pq}{}^{r} &= -R_{pq}{}^{r}\gamma_{AB} \\ G_{pq}{}^{i} &= R_{pq}{}^{i}\gamma_{AB} \end{aligned} \tag{A.7}$$

Semiempirical Magnetic Susceptibilities of Benzene Derivatives[1]

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Abstract: We applied a previously derived semiempirical theory of diamagnetic susceptibilities to a series of conjugated hydrocarbons that are composed of phenyl groups and saturated or unsaturated hydrocarbon chains. With the exception of diphenylethylene and mesitylene the agreement between theoretical and experimental values is better than 0.5%.

In a previous series of papers we developed a semiempirical theory of the diamagnetic susceptibilities of organic molecules. In the first paper[2a] we applied the theory to saturated hydrocarbons, in the second paper[2b] to oxygen containing molecules, and in the third paper[3] to polyacenes. In each of these calculations we applied the theory to all molecules of a given type for which the experimental susceptibility values are known and we expressed the susceptibilities in terms of a small number of adjustable parameters. In the present paper we extend the theory to conjugated hydrocarbon molecules which are not polyacenes; these are molecules such as toluene, styrene, biphenyl, etc. Again, we consider all molecules of this type for which the experimental diamagnetic susceptibilities are known.

We follow the same procedure as in the treatment of the polyacenes.[3] We represent the diamagnetic susceptibility of a molecule as a sum of bond contributions and of bond-bond interactions; in addition, we must also consider the π-electron susceptibility. For example, the susceptibilities χ_{benzene} and χ_{toluene} of benzene and toluene are written as

$$\begin{aligned} \chi_{\text{benzene}} = {} & 6\chi_{C} + 6\chi_{\sigma} + 6\chi_{CH} - 6\chi_{\sigma,\sigma} - \\ & 12\chi_{\sigma,CH} - 6\chi_{\pi,CH} - 12\chi_{\sigma.\pi} + D \\ \chi_{\text{toluene}} = {} & 7\chi_{C} + 7\chi_{\sigma} + 8\chi_{CH} - 8\chi_{\sigma,\sigma} - 13\chi_{\sigma,CH} - \\ & 5\chi_{\pi,CH} - 13\chi_{\sigma,\pi} - 3\chi_{CH,CH} + K_{\text{toluene}}D \end{aligned} \tag{1}$$

Here, the π-electron susceptibility is calculated by means of a method that was proposed by London[4] and it is expressed in terms of the π-electron susceptibility D of the benzene molecule. In this way we use the ratios of the London-type π-electron results between different molecules; we feel that these ratios are much more reliable than the absolute values.

We have found that the many parameters in these expressions occur in certain fixed combinations so that the molecular susceptibilities can usually be expressed in terms of a relatively small numbers of parameters. In the present case, where we consider the molecules that are listed in Table I, we can express the susceptibilities in terms of some parameters that we have introduced previously and in terms of some additional,

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[2] (a) H. F. Hameka, *J. Chem. Phys.*, 34, 1996 (1961); (b) P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, 92, 25 (1970).

[3] P. S. O'Sullivan and H. F. Hameka, *ibid.*, 92, 1821 (1970).

[4] F. London, *J. Phys. Radium*, 8, 397 (1937).