Self-consistent perturbation theory of diamagnetism

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Published online: 22 Aug 2006.

To cite this article: Robert Ditchfield (1974) Self-consistent perturbation theory of diamagnetism, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, 27:4, 789-807, DOI: 10.1080/00268977400100711

To link to this article: http://dx.doi.org/10.1080/00268977400100711

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Self-consistent perturbation theory of diamagnetism
I. A gauge-invariant LCAO method for N.M.R. chemical shifts

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(Received 13 July 1973)

An ab initio gauge-invariant molecular orbital theory is developed for nuclear magnetic shielding. The molecular orbitals are written as linear combinations of gauge-invariant atomic orbitals, the wavefunctions in the presence of a uniform external magnetic field being determined by self-consistent field perturbation theory. The final magnetic shielding result is broken up into contributions which can be related to various features of electronic structure. Calculated magnetic shielding constants are presented using three sets of atomic orbitals, all of which are taken as contracted gaussian-type functions. The first two sets are minimal and the third is slightly extended. All three levels of theory give good descriptions of shielding at first row and hydrogen atoms. Carbon and hydrogen chemical shifts calculated at the extended level are in excellent agreement with experimental values.

1. INTRODUCTION

The application of Fourier transform techniques in Nuclear Magnetic Resonance (N.M.R.) has established that $^{13}$C spectra can be obtained for many types of molecule with sampling times nearly comparable to those required for $^1$H spectra [1]. This has already resulted in the collection of a large body of data and the $^{13}$C N.M.R. literature is growing at a rapid pace. This highlights the need for a theoretical framework within which carbon N.M.R. chemical shifts and the results for shielding at protons and other first row atoms can be understood.

In order that such a theory form a useful independent study, it is essential that as little empirical data as possible be incorporated into it. Thus, while semi-empirical methods [2–13] have led to useful qualitative ideas, quantitative agreement with experiment has usually been poor despite the adjustment of empirical parameters. In addition, certain types of shielding effect have not been interpreted by semi-empirical theories.

An ab initio theory, on the other hand, while clearly attractive as an unbiased method, must be simple enough to permit application to moderately sized molecules without excessive computational effort. If quantitatively successful, such a theory would be useful not only in a predictive way but also it would allow a critical evaluation of the various qualitative ideas that have arisen from simpler theories. Indeed, this type of approach may well provide a better understanding of the more important features which must be included in any semi-empirical model of magnetic shielding.
To ensure that such a theory represents an advance over current methods it is important that it satisfy certain minimum requirements. Some of these are the following:

(i) it should give calculated magnetic shielding constants which are independent of the gauge [14] of the vector potential describing the magnetic field;
(ii) it should be applicable to closed-shell molecules containing up to at least three first-row atoms;
(iii) it should be equally applicable to all types of nuclei;
(iv) in order to be a useful quantitative tool, it should give calculated chemical shifts which are accurate to ten per cent (or better) of the observed range. For example, 20 p.p.m. for $^1$C, 50 p.p.m. for $^{19}$F and 1 p.p.m. for $^1$H;
(v) the theory should be developed in such a way that the results can be interpreted in detail and used to support or discount qualitative hypotheses. For example, it would be useful if the calculated shielding constants could be related to features of electronic structure such as electronic charge distribution and types of bonding.

Previous work [15] has suggested that (i) is an essential requirement, since theories which do not satisfy this condition have been shown [16] to give results which depend linearly on the gauge of the vector potential. This leads to problems when comparing magnetic shielding constants, both for different nuclei in the same molecule (e.g. $^1$C$_a$ and $^1$C$_b$ in $^1$C$_a$H$_3$$^1$C$_b$H$_2$-CH$_3$) and for nuclei in different polyatomic molecules [15].

In early important work Stevens, Pitzer and Lipscomb [17, 18] calculated magnetic shielding constants for some diatomic molecules using self-consistent field (SCF) perturbation theory. The wavefunctions, $\Psi$, in the presence and the absence of a magnetic field were taken in single determinant form

$$\Psi = |\phi_1\bar{1}_1 \ldots \phi_n\bar{1}_n|, \quad (1.1)$$

where the bar indicates that $\phi_j$ is associated with a $\beta$ spin function. In addition, the molecular orbitals $\psi_j$ were written as linear combinations of real atomic orbitals (LCAO) $\phi_r$

$$\psi_j = \sum_r c_{jr} \phi_r, \quad (1.2)$$

These workers attempted to achieve gauge-invariant results for magnetic shielding constants by using a basis set of atomic orbitals, $\phi_r$, which was large enough to be considered close to being complete. However, with this approach even diatomic molecules require considerable computational effort and at the present time this method does not appear too attractive as a general theory of magnetic shielding.

One possible alternative is to use gauge-invariant atomic orbitals (GIAO)$^\dagger$ $X_r$, where the real atomic basis functions $\phi_r$ are modified by a multiplicative complex factor which depends on the gauge of the vector potential $A(r)$

$$X_r = \exp \left( -\frac{i}{\epsilon} A(r) \cdot r \right) \phi_r, \quad (1.3)$$

$^\dagger$ This is an unfortunate term since these orbitals include a factor which depends on the gauge. A better description is that proposed by Pople [4] of 'gauge-dependent atomic orbitals'.

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Use of such functions in problems of molecular diamagnetism was first made by London [19] in connection with ring currents in aromatic hydrocarbons and they have since been employed in more general studies of magnetic properties by many workers [3–6, 13, 20–26].

In this paper we present an \textit{ab initio} theory of magnetic shielding using GIAO within the framework of SCF perturbation theory. As a result, requirement (i) is automatically satisfied for any choice of atomic functions $\phi_p$ [24]. In § 2 we develop the quantum mechanical theory and show how the final gauge-invariant magnetic shielding result can be divided up into contributions which are related to various features of electronic structure. Within this framework several levels of theory may be defined which differ only in the choice of $\phi_p$. In this study we consider three possible sets of basis functions. The first two sets are minimal\textdagger sets of $\phi$-functions, whilst the third is a small extended set. The results obtained with these basis sets are presented in § 3 where we discuss each level of theory and attempt to evaluate its performance in terms of requirements (ii), (iii) and (iv) outlined above. The main conclusions of this work are summarized in § 4.

2. Theory

The electronic hamiltonian describing a closed-shell molecule in the total magnetic field due to a uniform external magnetic field $\mathbf{H}$ and the dipole fields arising from nuclear magnetic moments $\mu_B$, $\mu_D$, ... situated at fixed nuclear positions $\mathbf{R}_B$, $\mathbf{R}_D$, ... has the form (in atomic units)

\begin{equation}
\mathcal{H}(\mathbf{H}, \mu) = \left(\frac{1}{2}\right) \sum_j \left[ (p_j + (1/c) \mathbf{A}'(r_j))^2 - 2 \sum_B Z_B r_{jB}^{-1} \right] + \sum_j \sum_{\alpha \neq j} r_{ji}^{-1} + \sum_B \sum_D Z_B Z_D R_{BD}^{-1}. \tag{2.1}
\end{equation}

Here $c$ is the velocity of light, $\sum_j$ is a sum over all electrons and $\sum_B$ is a sum over all nuclei. The last three terms represent the electron–nucleus, electron–electron and nucleus–nucleus contributions, respectively, to the potential energy. The vector potential describing the total magnetic field at the position of electron $j$, $\mathbf{A}'(r_j)$, is given by

\begin{equation}
\mathbf{A}'(r_j) = \left(\frac{1}{2}\right) \mathbf{H} \times r_j + \sum_B (\mu_B \times r_{jB}) r_{jB}^{-3}
= \mathbf{A}(r_j) + \sum_B (\mu_B \times r_{jB}) r_{jB}^{-3}. \tag{2.2}
\end{equation}

In the above equations $r_j$ is the distance vector from electron $j$ to some arbitrary origin, $r_{jB}$, $r_{jB}$, $r_{BD}$ are the vectors $(r_j - R_B)$, $(r_j - R_l)$ and $(R_B - R_D)$, respectively, and $Z_B$ is the charge on nucleus $B$.

Substituting equation (2.2) into (2.1), replacing the quantum mechanical momentum $p_j$ by $-i \nabla_j$ and working in the coulomb gauge [14] (div $\mathbf{A} = 0$) leads to equation (2.3):

\begin{equation}
\mathcal{H}(\mathbf{H}, \mu_B) = \mathcal{H}^{(0)} + \sum_a H_a \mathcal{H}_a^{(1, 0)} + \mu_B \mathcal{H}_a^{(0, 1)} + \left(\frac{1}{2}\right) \sum_{\alpha \beta} \sum_{\alpha \beta} H_{aB} \mathcal{H}_{aB}^{(2, 0)} + \sum_{\alpha} \sum_{\beta} H_{aB} \mathcal{H}_{aB}^{(1, 1)} \mu_{B\beta}. \tag{2.3}
\end{equation}

\textdagger A minimal basis set is considered to consist of the least number of atomic orbitals required to describe the atomic ground state (1s for hydrogen, 1s, 2s, 2px, 2py, 2pz for carbon, etc.). If a larger number of $\phi$-functions is used the basis set is usually described as extended.
To simplify the notation, from this point on we consider a single nuclear magnetic moment $\mu_\alpha$ only. Extension to several nuclear magnetic moments is straightforward. In equation (2.3), $H_\alpha$ and $H_\beta$ are components of the external magnetic field and

$$H^{(0)} = \sum_j (-\frac{1}{2} \nabla_j^2 - \sum_B Z_B r_{jB}^{-1}) + \sum_{j \neq l} r_{jl}^{-1} + \sum_{B \neq D} Z_B Z_D R_{BD}^{-1},$$  

$$H_{\alpha}^{(1, 0)} = -\frac{i}{2c} \sum_j L_{ja},$$  

$$H_{\alpha\beta}^{(2, 0)} = \frac{1}{4c^2} \sum_j (r_j \delta_{\alpha\beta} - r_{ja} r_{j\beta}),$$  

$$H_{B\alpha}^{(0, 1)} = -\frac{i}{c} \sum_j L_{jB\alpha} r_{jB}^{-3},$$  

$$H_{B\beta}^{(1, 1)} = \frac{1}{2c^2} \sum_j (r_j \cdot r_{jB} \delta_{\alpha\beta} - r_{ja} r_{jB\beta}) r_{jB}^{-3},$$  

$$L_{ja} = (r_j \times \nabla_j)_{\alpha},$$  

$$L_{jB\alpha} = (r_{jB} \times \nabla_j)_{\alpha}.$$  

Here $\delta_{\alpha\beta}$ is the Kronecker delta and $\alpha$, $\beta$ are used to indicate cartesian coordinates $x$, $y$ or $z$.

The energy $E(H, \mu_B)$ associated with this hamiltonian can be found by solving the Schroedinger equation

$$\mathcal{H}(H, \mu_B) \Psi(H, \mu_B) = E(H, \mu_B) \Psi(H, \mu_B),$$  

where $\Psi(H, \mu_B)$ is the wavefunction describing the molecule in the presence of $H$ and $\mu_B$. For small values of $H$ and $\mu_B$, $E(H, \mu_B)$ and $\Psi(H, \mu_B)$ can be expanded as Taylor series about their zero-field values:

$$\Psi(H, \mu_B) = \Psi^{(0)} + \sum_{\alpha} \left( \frac{\partial \Psi(H, \mu_B)}{\partial H_\alpha} \right)_{0} H_\alpha + \sum_{\alpha, \beta} \left( \frac{\partial^2 \Psi(H, \mu_B)}{\partial H_\alpha \partial H_\beta} \right)_{0} H_\alpha H_\beta + \ldots (2.12)$$  

and similarly

$$E(H, \mu_B) = E^{(0)} + \sum_{\alpha} E_\alpha^{(1, 0)} H_\alpha + \sum_{\alpha, \beta} E_{B\alpha}^{(0, 1)} H_\alpha H_\beta + \frac{1}{2} \sum_{\alpha} H_\alpha E_{B\alpha}^{(2, 0)} H_\alpha + \frac{1}{4} \sum_{\alpha, \beta} H_\alpha H_\beta E_{B\alpha\beta}^{(0, 2)} H_\alpha H_\beta + \ldots (2.13)$$  

An alternative expression for the energy is given in equation (2.14):

$$E(H, \mu_B) = E^{(0)} - \sum_{\alpha} \gamma_\alpha H_\alpha - \sum_{\alpha} \mu_{B\alpha} H_\alpha - \frac{1}{2} \sum_{\alpha} H_\alpha \gamma_{\alpha\beta} H_\beta + \sum_{\alpha} \sum_{\beta} H_\alpha \sigma_{B\alpha\beta} H_\beta + \ldots (2.14)$$
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Here \( \gamma \) is a component of the permanent magnetic moment of the molecule. For singlet state molecules with zero orbital angular momentum \( \gamma \) is zero. The third term in (2.14) represents the direct interaction between the nuclear magnetic moment and the external magnetic field. The fourth term describes the diamagnetic polarization of the molecule; the total magnetic moment (in direction \( \alpha \)) associated with the electronic currents induced by the external magnetic field is \( \sum \chi_{\alpha \beta} H_{\beta} \), where \( \chi_{\alpha \beta} \) is a component of the molecular diamagnetic susceptibility tensor \( \chi \). The secondary magnetic field (in direction \( \alpha \)) at nucleus B due to these electronic currents is \( \sum \sigma_{\alpha \beta} H_{\beta} \), where \( \sigma_{\alpha \beta} \) is a component of the magnetic shielding tensor \( \sigma \). Thus the total magnetic field experienced by nucleus B which determines its N.M.R. frequency is given by

\[
H_B = H(1 - \sigma_B). \tag{2.15}
\]

It is clear from comparing equations (2.13) and (2.14) that the calculation of \( \sigma_{\alpha \beta} \) requires the determination of \( E_{\alpha \beta} \).

In SCF perturbation theory one seeks a solution \( \Psi(H, \mu_B) \) to the Schrödinger equation (2.11) as a single determinant of MO's \( \psi_j(H, \mu_B) \):

\[
\Psi(H, \mu_B) = \sum \psi_j(H, \mu_B) \psi_j(H, \mu_B) ... \psi_n(H, \mu_B) \psi_n(H, \mu_B). \tag{2.16}
\]

In the absence of a magnetic field, it is usual to write each MO in LCAO form, as in equation (1.2), where the \( \phi \) are taken in real form. Attempts to use such an LCAO expansion of real field-independent atomic orbitals for determining \( \Psi(H, \mu_B) \) leads to the problems discussed in § 1. In fact, in the presence of a magnetic field such a theory does not give a correct description of an isolated atom. To remedy this defect, we follow London [19] and write each MO as a linear combination of GIAO \( \chi_\alpha \):

\[
\psi_j(H, \mu_B) = \sum \chi_\alpha(H) \psi_j(H, \mu_B) \chi_\alpha(H), \tag{2.17}
\]

where, as indicated previously,

\[
\chi_\alpha(H) = \exp \left(-\frac{(i/e)A_\alpha}{c} \cdot r\right) \phi_\alpha \tag{2.18}
\]

In equation (2.18), \( A_\alpha = \frac{1}{2} H \times R_\alpha \) is the value of the vector potential \( A \) at the nuclear position, \( R_\alpha \), of atomic orbital \( \phi_\alpha \). It should be noted that the LCAO coefficients \( c_j(\mu_B) \) are also allowed to become complex in the presence of a magnetic field.

Application of the variational principle to the energy \( E(H, \mu_B) \) associated with \( \Psi(H, \mu_B) \) of equation (2.16) leads to the modified Roothaan [27] equations

\[
\sum_\lambda \left[ F_{\alpha \lambda}(H, \mu_B) - \epsilon_j(H, \mu_B) S_{\alpha \lambda}(H) \right] c_{\lambda j}(H, \mu_B) = 0. \tag{2.19}
\]

In equation (2.19), the Fock matrix elements \( F_{\alpha \lambda}(H, \mu_B) \) are given by

\[
F_{\alpha \lambda}(H, \mu_B) = H_{\alpha \lambda}(H, \mu_B) + G_{\alpha \lambda}(H, \mu_B), \tag{2.20}
\]

where

\[
H_{\alpha \lambda}(H, \mu_B) = \chi_\alpha \left\{ \left(\frac{i}{\hbar}\right) (-i \nabla + (1/e) A'(r))^2 - \sum B Z_B \right\} \chi_\lambda, \tag{2.21}
\]
The overlap integral $S_{p\lambda}(H)$, density matrix $P_{\rho\sigma}(H, \mu_B)$ and two-electron integral $(\chi_\rho^\ast \chi_\lambda|\chi_\rho^\ast\chi_\sigma)$ are given by equations (2.23), (2.24) and (2.25), respectively:

$$S_{p\lambda} = \int \chi_\rho^\ast \chi_\lambda \, d\tau,$$

$$P_{\rho\sigma}(H, \mu_B) = 2 \sum_{j} \langle \rho|j(H, \mu_B) \rangle \langle \sigma|j(H, \mu_B) \rangle,$$

$$\chi_\rho^\ast\chi_\lambda|\chi_\rho^\ast\chi_\sigma = \int \chi_\rho^\ast(1)|\chi_\lambda(1)|\chi_\rho^\ast(2)|\chi_\sigma(2) \, d\tau_1 \, d\tau_2.$$

The energy associated with MO $\psi_j(H, \mu_B)$ is $\epsilon_j(H, \mu_B)$. It is worthy of note that the use of GIAO leads to one- and two-electron integrals with an explicit magnetic field dependence. The energy $E(H, \mu_B)$ is given by

$$E(H, \mu_B) = \sum_{p\lambda} P_{p\lambda}(H, \mu_B)|H_{p\lambda}(H, \mu_B) + (\frac{1}{2})G_{p\lambda}(H, \mu_B)|.$$

Introducing expansions of $c_{\rho \lambda}$ and $P_{p\lambda}$ similar to those of equations (2.12) and (2.13) we may write

$$c_{\rho \lambda}(H_{\alpha}, \mu_{B\alpha}) = c_{\rho \lambda}^{(0)} + iH_{\alpha}(c_{\rho \lambda}^{(1 , 0)})_{\alpha} + i\mu_{B\alpha}(c_{\rho \lambda}^{(0 , 1)})_{\alpha} + \cdots \tag{2.27}$$

and

$$P_{p\lambda}(H_{\alpha}, \mu_{B\alpha}) = P_{p\lambda}^{(0)} + iH_{\alpha}(P_{p\lambda}^{(1 , 0)})_{\alpha} + i\mu_{B\alpha}(P_{p\lambda}^{(0 , 1)})_{\alpha} + \cdots \tag{2.28}$$

from which it is clear that

$$P_{p\lambda}^{(0)} = 2 \sum_{j} c_{\rho j}^{(0)} c_{\lambda j}^{(0)} \tag{2.29}$$

and

$$(P_{p\lambda}^{(1 , 0)})_{\alpha} = 2 \sum_{j} [c_{\rho j}^{(0)}(c_{\lambda j}^{(1 , 0)})_{\alpha} - (c_{\rho j}^{(1 , 0)})_{\alpha} c_{\lambda j}^{(0)}]. \tag{2.30}$$

Differentiating equation (2.26) with respect to $\mu_{B\beta}$ and using equations (2.29) and (2.30) leads to

$$(\delta E(H, \mu_B)|\delta \mu_{B\beta})_0 = E_{B\beta}^{(0 , 1)} = i \sum_{p\lambda} [(P_{B\rho\lambda}^{(0 , 1)})_{\beta}(H_{p\lambda}^{(0)} + G_{p\lambda}^{(0)})$$

$$+ P_{p\lambda}^{(0)}(H_{B\rho\lambda}^{(0 , 1)})_{\beta}], \tag{2.31}$$

since the atomic orbitals do not depend on the nuclear magnetic moments. This expression can be simplified by using the fact that the solutions of the modified Roothaan equation (2.19) are constrained to be orthonormal for all values of $H$ and $\mu_B$, i.e.

$$\sum_{p\lambda} c_{\rho j}^{\ast}(H, \mu_B) c_{\lambda j}(H, \mu_B) S_{p\lambda}(H) = \delta_{j\ell}. \tag{2.32}$$
Differentiating equation (2.32) with respect to $\mu_{B\beta}$ and using equation (2.27) gives
\[
i \sum \{c_{ij}^{(0)}(c_{B\alpha}^{(0, 1)})_\beta S_{\alpha \lambda}^{(0)} - (c_{B\alpha}^{(0, 1)})_\beta c_{ij}^{(0)} S_{\alpha \lambda}^{(0)}\} = 0. \tag{2.33}
\]
Using these results allows equation (2.31) to be simplified to
\[
E_{B\beta}^{(0, 1)} = i \sum P_{\alpha \lambda}^{(0)} (H_{B\alpha \lambda}^{(0, 1)})_\beta, \tag{2.34}
\]
where
\[
(H_{B\alpha \lambda}^{(0, 1)})_\beta = -(1/c) \langle \phi_\rho | L_{B\rho \beta} r_B^{-3} | \phi_\lambda \rangle. \tag{2.35}
\]
Similar equations may be obtained for $E_{B\beta}^{(1, 0)}$. An important point to note about equation (2.34) is that the expression for $E_{B\beta}^{(0, 1)}$ depends only on the zero-order coefficients $c_{ij}^{(0)}$. Thus the calculation of the magnetic shielding tensor $\sigma_B$ requires the coefficients $c_{ij}(H, \mu_B)$ correct to first-order in the external magnetic field $H$.

Recalling the relationship between $E_{B\alpha \beta}^{(1, 1)}$ and $\sigma_{B\alpha \beta}$ we can write
\[
\sigma_{B\alpha \beta} = \sum \{P_{\alpha \lambda}^{(0)} (H_{B\alpha \lambda}^{(1, 1)})_\beta + (P_{\alpha \lambda}^{(1, 0)})_\beta (H_{B\alpha \lambda}^{(0, 1)})_\beta\}, \tag{2.36}
\]
where
\[
(H_{B\alpha \lambda}^{(1, 1)})_\beta = (H_{B\alpha \lambda}^{(1, 1)})_\beta d + (H_{B\alpha \lambda}^{(1, 1)})_\beta p, \tag{2.37}
\]
and
\[
(H_{B\alpha \lambda}^{(1, 1)})_\beta d = \left(\frac{1}{2} c^2\right) \langle \phi_\rho | [r_\lambda \cdot r_B \delta_{\alpha \beta} - (r_\lambda)_\alpha (r_B)_\beta] r_B^{-3} | \phi_\lambda \rangle, \tag{2.38}
\]
\[
(H_{B\alpha \lambda}^{(1, 1)})_\beta p = \left(\frac{1}{2} c^2\right) \langle Q_{\alpha \lambda} \rangle_\alpha \langle \phi_\rho | L_{B\rho \beta} r_B^{-3} | \phi_\lambda \rangle + \langle (T_{\alpha \lambda})_\alpha \phi_\rho | L_{B\rho \beta} r_B^{-3} | \phi_\lambda \rangle. \tag{2.39}
\]
In equation (2.38)
\[
r_\lambda = r - R_\lambda, \tag{2.40}
\]
and in deriving these equations we have made use of the relationship
\[
\langle \chi_\rho | (\frac{1}{2}(-i\nabla + (1/c)A(r))^2 | \chi_\lambda \rangle = \langle \chi_\rho | \phi_\rho | (\frac{1}{2}(-i\nabla + (1/c)A(r))^2 | \phi_\lambda \rangle. \tag{2.41}
\]
The gauge factor product in equation (2.41) is given by
\[
f_r * f_\lambda = \exp \{(i/c)(A_\rho - A_\lambda) \cdot r\} \tag{2.42}
\]
and we have written equation (2.39) in terms of the vector quantities $Q_{\alpha \lambda}$ and $T_{\alpha \lambda}$ which are defined by equations (2.43) and (2.44) :
\[
Q_{\alpha \lambda} = R_\lambda \times R_\lambda, \tag{2.43}
\]
\[
T_{\alpha \lambda} = R_\lambda \times R_\rho. \tag{2.44}
\]
The first-order coefficients $c_{ij}^{(1, 0)}$ required to calculate $\sigma$ are determined by expanding the perturbed Roothaan equation (2.19), separating orders with respect to $H$ and solving the first-order (in $H$) equation [28]
\[
\sum \lambda \{(F_{\alpha \lambda}^{(0)} - \epsilon_j^{(0)})S_{\alpha \lambda}^{(0)}\} c_{ij}^{(1, 0)} + (F_{\alpha \lambda}^{(1, 0)} - \epsilon_j^{(0)})S_{\alpha \lambda}^{(1, 0)} c_{ij}^{(0)}\} = 0. \tag{2.45}
\]
The elements $F_{\alpha\lambda}(1,0)$ are given by

$$F_{\alpha\lambda}(1,0) = H_{\alpha\lambda}(1,0) + \sum_{\rho\sigma} \{ P_{\rho\sigma}^{(0)} G_{\alpha\lambda,\rho\sigma}(1,0) + P_{\rho\sigma}^{(1,0)} G_{\alpha\lambda,\rho\sigma}^{(0)} \}, \quad (2.46)$$

where, for example,

$$\langle H_{\alpha\lambda}^{(1,0)} \rangle_\alpha = \left( \frac{1}{2c} \right) \langle \phi_\alpha | L_\alpha^\Lambda | \phi_\lambda \rangle - \langle Q_{\alpha\lambda} \rangle_\alpha H_{\alpha\lambda}^{(0)}$$

$$- \langle T_{\alpha\lambda} \rangle_\alpha \phi_\lambda | H^{core} | \phi_\lambda \rangle, \quad (2.47)$$

$$L_\alpha^\Lambda = (r_\alpha \times \nabla)_\alpha, \quad (2.48)$$

and

$$H^{core} = - \left( \frac{1}{2} \right) \nabla^2 - \sum_B Z_B r_B^{-1}. \quad (2.49)$$

The terms $G_{\alpha\lambda,\rho\sigma}(1,0)$ are defined in an analogous manner to $S_{\alpha\lambda}(1,0)$. Using standard perturbation theory gives the projection of $c_{\alpha\lambda}(1,0)$ on the vacant orbitals. Since the atomic basis functions $X_\alpha$ depend on the external magnetic field, there is a further contribution to $c_{\alpha\lambda}(1,0)$ from the occupied orbitals. This can be determined from the orthonormality condition of equation (2.32). Thus the total result for $c_{\alpha\lambda}(1,0)$ is

$$c_{\alpha\lambda}(1,0) = c_{\alpha\lambda}(1,0)(\text{occ}) + c_{\alpha\lambda}(1,0)(\text{vac} 1) + c_{\alpha\lambda}(1,0)(\text{vac} 2), \quad (2.50)$$

where

$$c_{\alpha\lambda}(1,0)(\text{occ}) = \sum_{\nu \rho} \sum_{\nu} \sum_{\rho} \left( - \left( \frac{1}{2} \right) c_{\nu\rho}^{(0)} \right) S_{\nu\rho}^{(1,0)} \rho_{\nu\rho}^{(0)} c_{\lambda\lambda}^{(0)}, \quad (2.51)$$

$$c_{\alpha\lambda}(1,0)(\text{vac} 1) = \sum_{\nu \rho} \sum_{\nu} \sum_{\rho} \langle \epsilon_\nu^{(0)} - \epsilon_\nu^{(0)} \rangle^{-1} \langle c_{\nu\rho}^{(0)} F_{\nu\rho}^{(1,0)} \rho_{\nu\rho}^{(0)} \rangle c_{\lambda\lambda}^{(0)}, \quad (2.52)$$

$$c_{\alpha\lambda}(1,0)(\text{vac} 2) = - \sum_{\nu \rho} \sum_{\nu} \sum_{\rho} \langle \epsilon_\nu^{(0)} - \epsilon_\nu^{(0)} \rangle^{-1} \langle c_{\nu\rho}^{(0)} S_{\nu\rho}^{(1,0)} \rho_{\nu\rho}^{(0)} \rangle c_{\lambda\lambda}^{(0)}, \quad (2.53)$$

These formulae clearly reduce to the fixed basis set results [15, 17] if the gauge factors are set equal to unity.

Equation (2.36) can be written in the alternate form

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^d + \sigma_{\alpha\beta}^p, \quad (2.54)$$

where

$$\sigma_{\alpha\beta}^d = \sum_{\nu \lambda} P_{\nu\lambda}^{(0)} (H_{\nu\lambda}^{(1,1)})_{\alpha\beta} \quad (2.55)$$

and

$$\sigma_{\alpha\beta}^p = \sum_{\nu \lambda} \{ P_{\nu\lambda}^{(0)} (H_{\nu\lambda}^{(1,1)})_{\alpha\beta} + (P_{\nu\lambda}^{(1,0)})_{\alpha} (H_{\nu\lambda}^{(0,1)})_{\beta} \}. \quad (2.56)$$

The first contribution $\sigma^d$ depends on the unperturbed atomic basis functions $\phi_\alpha$ and the unperturbed density matrix $P^{(0)}$, where $\sigma^p$ involves either the perturbed basis functions or the perturbed density matrix. The two parts $\sigma^d$ and $\sigma^p$ may be described as diamagnetic and paramagnetic contributions in this gauge-invariant LCAO theory, but they are not to be directly compared with the two parts of the original Ramsey [29] equation.
Although equation (2.54) provides a theoretical value for the magnetic shielding constant, in this particular form it gives no indication of the important mechanisms by which shielding occurs. It is important in a calculation of this type to analyse the contributions to $\sigma_B$ in terms of atomic (local and non-local) and interatomic parts. To illustrate how $\sigma_B$ can be separated into such parts we consider the contribution to $\sigma_B$ from $c_{ij}^{(1,0)}(\text{vac} \ 1)$ as an example. For each occupied orbital $\psi_j$, we define a matrix $\mathbf{W}^j$, the elements of which are given by

$$W_{\lambda \nu}^j = \sum_{\xi} (\epsilon_j^{(0)} - \epsilon_\xi^{(0)})^{-1} c_{\lambda \xi}^{(0)} c_{\nu \xi}^{(0)}. \quad (2.57)$$

Equation (2.52) can now be written as

$$c_{ij}^{(1,0)}(\text{vac} \ 1) = \sum_{\nu, \rho} \sum_{\mu} W_{\lambda \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)}. \quad (2.58)$$

Since the matrices $\mathbf{W}$ and $\mathbf{F}$ can be blocked into atomic and interatomic parts, equation (2.58) can be split up as follows:

$$c_{ij}^{(1,0)}(\text{vac} \ 1) = \sum_{\nu, \rho} \sum_{\mu} W_{\lambda \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)} + \sum_{\delta \neq \lambda, \nu, \rho} W_{\lambda \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)}$$

$$+ \sum_{\omega \neq \lambda, \nu, \rho} W_{\lambda \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)} \lambda, \nu \text{ and } \rho \text{ on } B; \sigma, \tau \text{ on } D; \omega \text{ on } E; \delta \text{ on } F. \quad (2.59)$$

Similarly the first-order density matrix corresponding to these coefficients may be written in the form

$$P_{\mu \lambda}^{(1,0)}(\text{vac} \ 1) = P_{\mu \lambda}^{(1,0)B B B B}(\text{vac} \ 1) + \sum_{D \neq B} P_{\mu \lambda}^{(1,0)B D D B}(\text{vac} \ 1)$$

$$+ \sum_{E \neq F} P_{\mu \lambda}^{(1,0)B E F B}(\text{vac} \ 1). \quad (\mu \text{ and } \lambda \text{ on } B). \quad (2.60)$$

Here

$$P_{\mu \lambda}^{(1,0)B B B B}(\text{vac} \ 1) = 2 \sum_{\psi} \sum_{\nu, \rho} (c_{\mu \nu}^{(0)} c_{\rho \psi}^{(0)} W_{\lambda \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)} - c_{\lambda j}^{(0)} W_{\mu \nu}^j F_{\nu \rho}^{(1,0)} c_{\rho j}^{(0)}). \quad (2.61)$$

is a purely intra-atomic term and represents a contribution to the electronic currents at atom B due to the external magnetic field acting on atom B. The second term $P_{\mu \lambda}^{(1,0)B D D B}(\text{vac} \ 1)$ is defined similarly and contributes to the electronic currents at atom B which arise from the external magnetic field acting on atom D. The final term describes a contribution to the currents at atom B due to the magnetic field acting on the pair of atoms E and F.

In a similar manner we can define $P_{\mu \lambda}^{(1,0)D B B D}(\text{vac} \ 1)$, $P_{\mu \lambda}^{(1,0)D D D D}(\text{vac} \ 1)$ and $P_{\mu \lambda}^{(1,0)D E F D}(\text{vac} \ 1)$ terms where $\mu$ and $\lambda$ are both situated on atom D, and $P_{\mu \lambda}^{(1,0)}(\text{vac} \ 1)$ terms where $\mu$ and $\lambda$ are on different atoms. The former terms describe currents on atoms other than B, whilst the latter term represents a purely interatomic contribution. A similar division may be made for the contributions to $\sigma_B^p$ arising from $c_{ij}^{(1,0)}(\text{occ})$ and $c_{ij}^{(1,0)}(\text{vac} \ 2)$. It should be
noted, however, that because of the nature of $S^{(1,0)}$ such contributions can only be of BEFB, DEFD or purely interatomic type. The first term in equation (2.56) can also be broken up in this way. However, since $(H_{B\alpha\beta}^{(1,1)})^p$ is only non-zero if $\nu$ and $\lambda$ are orbitals on different centres this contribution is purely interatomic in character. Treating $\sigma_{B\beta}^d$ in an analogous way gives

$$\sigma_{B\beta}^d = (\sigma_{B\beta}^{BBBB})^d + \sum_{D \neq B} (\sigma_{B\beta}^{DDDD})^d + (\sigma_{B\beta}^{interatomic})^d,$$

where

$$\sigma_{B\beta}^{BBBB})^d = \sum_{\nu, \lambda} \int \rho_{\nu\lambda}^0 (H_{B\nu\lambda}^{(1,1)})_{\alpha\beta}^d \quad (\nu \text{ and } \lambda \text{ on } B),$$

$$\sigma_{B\beta}^{DDDD})^d = \sum_{\rho, \sigma} \int \rho_{\rho\sigma}^0 (H_{B\rho\sigma}^{(1,1)})_{\alpha\beta}^d \quad (\rho \text{ and } \sigma \text{ on } D),$$

and

$$(\sigma_{B\beta}^{interatomic})^d = \sum_{\tau, \omega} \int \rho_{\tau\omega}^0 (H_{B\tau\omega}^{(1,1)})_{\alpha\beta}^d \quad (\tau \text{ and } \omega \text{ on different atoms}).$$

The corresponding expression for $\sigma_{B\beta}^p$ is given by

$$\sigma_{B\beta}^p = (\sigma_{B\beta}^{BBBB})^p + \sum_{D \neq B} (\sigma_{B\beta}^{DDDD})^p + \sum_{E \neq F} (\sigma_{B\beta}^{BEFB})^p$$

$$+ \sum_{D \neq B} \{ \sum_{E \neq D} \sigma_{B\beta}^{DEED})^p + \sigma_{B\beta}^{DDDD})^p + \sum_{E \neq F} (\sigma_{B\beta}^{DEFD})^p\}$$

$$+ (\sigma_{B\beta}^{interatomic})^p,$$

where

$$\sigma_{B\beta}^{BBBB})^p = \sum_{\nu, \lambda} \int \rho_{\nu\lambda}^0 (H_{B\nu\lambda}^{(0,1)})_{\alpha\beta}^p,$$

$$\sigma_{B\beta}^{DDDD})^p = \sum_{\rho, \sigma} \int \rho_{\rho\sigma}^0 (H_{B\rho\sigma}^{(0,1)})_{\alpha\beta}^p,$$

$$\sigma_{B\beta}^{BEFB})^p = \sum_{\nu, \lambda} \int \rho_{\nu\lambda}^0 (H_{B\nu\lambda}^{(0,1)})_{\alpha\beta}^p,$$

$$\sigma_{B\beta}^{DEED})^p = \sum_{\rho, \sigma} \int \rho_{\rho\sigma}^0 (H_{B\rho\sigma}^{(0,1)})_{\alpha\beta}^p,$$

$$\sigma_{B\beta}^{DDDD})^p = \sum_{\rho, \sigma} \int \rho_{\rho\sigma}^0 (H_{B\rho\sigma}^{(0,1)})_{\alpha\beta}^p,$$

and

$$(\sigma_{B\beta}^{interatomic})^p = \sum_{\tau, \omega} \int \rho_{\tau\omega}^0 (H_{B\tau\omega}^{(1,1)})_{\alpha\beta}^p$$

$$+ \rho_{\tau\omega}^0 (H_{B\tau\omega}^{(0,1)})_{\alpha\beta}^p.$$

The total magnetic shielding constant for nucleus B is a sum of all these terms which may be interpreted as follows:

(1) $(\sigma_{B}^{BBBB})^d$ is the contribution to the screening field at nucleus B due to the diamagnetic Langevin-type currents on atom B itself. For an isolated spherical atom, it is the only contribution and is given by the Lamb [30] formula. From equation (2.63) it is clear that this contribution depends on the charge density on atom B.
Calculation of N.M.R. chemical shifts

(2) \((\sigma_B^{BBBB})^p\), \((\sigma_B^{BDDB})^p\) and \((\sigma_B^{BEFB})^p\) are contributions due to the paramagnetic-type currents on atom B. The first term is a purely intraatomic contribution. \((\sigma_B^{BDDB})^p\) arises because the external magnetic field acting on atom D mixes in certain excited electronic states of the molecule and thereby induces a current flow on atom B. Clearly this contribution is rather sensitive to the type of bonding between B and D and to the availability of low-lying excited electronic states. Within the framework presented here this contribution is the analogue of the multiple-bond term defined by Pople [5]. \((\sigma_B^{BEFB})^p\) has rather similar origins and describes the shielding effect of currents on atom B which arise from the external magnetic field acting on the pair of atoms E and F.

(3) \((\sigma_B^{DDDD})^d+(\sigma_B^{DDDD})^p\) is the total contribution made to the screening at atom B by the atomic circulations (on D) produced by the magnetic field acting on atom D. This term may be compared with the neighbour-anisotropy contribution of the independent electron LCAO treatment of Pople [4]. Within such an approach [4], if the magnetic effects of these neighbouring currents are treated in a dipole approximation, this term involves only the anisotropy of the local susceptibility on atom D.

(4) \((\sigma_B^{DRED})^p\) and \((\sigma_B^{DRED})^p\) are contributions to the secondary magnetic field at B due to the paramagnetic-type currents on atom D which arise from the magnetic field acting on atom E, and on the pair of atoms E and F, respectively.

(5) Finally \((\sigma_B^{interatomic})^d+(\sigma_B^{interatomic})^p\) is the contribution to the screening due to currents which cannot be localized on any atom.

It is possible to achieve an even more detailed analysis by defining

\[
W_{\lambda\nu}^{j+1} = (\epsilon_j^{(0)} - \epsilon_j^{(0)})^{-1}c_{\lambda l}^{(0)}c_{\nu l}^{(0)}
\]

and repeating the above procedure for each occupied–unoccupied pair of orbitals. By considering such individual orbital excitations we can identify the types of magnetic field induced orbital mixings which make important contributions to nuclear magnetic shielding.

Within this framework various levels of theory can be defined which differ only in the choice of the real basis functions \(\phi\). Three basis sets will be considered. The first two sets (STO–5G and LEMAO–5G) are minimal sets, consisting of a single function for hydrogen (1s) and five functions for each first row atom (1s, 2s, 2p). The third is a more flexible extended set (4–31G). All \(\phi\) are taken as contracted gaussian functions chosen as follows.

A. Basis set 1 (STO–5G)

The first basis set is closely related to a minimal basis of Slater-type atomic orbitals (STO) [31]. Each \(\phi\) is obtained by rescaling a five gaussian least squares representation of the standard type STO with \(\zeta = 1\). Thus,

\[
\phi_{\lambda}(\zeta, r) = \zeta^{\frac{3}{2}}\phi_{\lambda}(1, \zeta r).
\]
B. Basis set 2 (LEMAO-5G)

The second basis set is one which corresponds to a minimal set of Hartree-Fock atomic orbitals in the atomic limit. These orbitals are referred to as least energy minimal atomic orbitals (LEMAO) and are specified in full elsewhere [33]. The valence shell $\zeta$ values were treated as additional variational parameters in the unperturbed molecular calculations to allow for changes in the atomic size depending on the molecular environment. Details of these optimum $\zeta$ values which were determined in the LEMAO-4G representation have been given previously [34]. For the magnetic properties reported in this work we have used the LEMAO-5G basis. It is shown in Appendix A that results based on LEMAO-5G are close to the limit appropriate to LEMAO-NG type functions.

C. Basis set 3 (4-31G)

The third basis set is slightly extended. The inner shells are represented by a single sum of four gaussians. However, the valence shells, hydrogen 1s and heavy atom 2s, 2p are split into inner and outer parts which are sums of three and one gaussian, respectively. Thus there are two $\phi$-functions per hydrogen and nine per heavy atom. The valence shell functions are rescaled by standard scale factors chosen as averages of optimized values for some small molecules. This basis set is denoted by 4-31G and is fully described elsewhere [35].

Once the basis set is specified it is clear from equation (2.36) that the magnetic shielding tensors for all the nuclei in a molecule can be obtained from one unperturbed and three ($\zeta = x, y, z$) perturbed wavefunction calculations. These wavefunctions are determined by the usual iterative procedures which are terminated when the root-mean-square difference between two successive density matrices is less than $10^{-4}$. The construction of the Fock matrix $F^{(t, 0)}$ of equation (2.46) requires the evaluation of integrals involving GIAO. The methods used to calculate such integrals are briefly described in Appendix B.

3. Results and Discussion

The theoretical method described in the previous section has been applied to the molecules listed in table 1 using the STO-5G, LEMAO-5G and 4-31G basis sets. This table lists the calculated total magnetic shielding constants for chemically non-equivalent nuclei. In table 2 we present the calculated chemical shifts together with the corresponding experimental values. All calculated values are for geometries in which the nuclei are fixed in the experimentally determined equilibrium configurations.

The results clearly indicate that all three SCF GIAO methods calculate magnetic shielding constants moderately well. This is reflected in the mean absolute differences between theory and experiment shown in table 3. It is also apparent that the extended 4-31G basis generally gives more accurate results than the minimal sets. This is particularly evident for $^{13}$C and $^1$H chemical shifts which are described very accurately at the 4-31G level. Although the STO and LEMAO methods differ in the way in which they describe individual shieldings, the minimal basis set results show very similar mean absolute differences indicating comparable overall agreement with experiment.

† For details of the experimental geometries used see reference [34].
Calculation of N.M.R. chemical shifts

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Nucleus of interest</th>
<th>STO–5G opt. scale</th>
<th>LEMAO–5G opt. scale</th>
<th>4–31G</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>C</td>
<td>232.5</td>
<td>232.8</td>
<td>204.8</td>
</tr>
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<td>H</td>
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<td>235.0</td>
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<td>H</td>
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<td>32.93</td>
<td>32.38</td>
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<td>182.0</td>
<td>157.8</td>
<td>139.4</td>
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<tr>
<td></td>
<td>F</td>
<td>470.7</td>
<td>585.3</td>
<td>485.7</td>
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<td>29.61</td>
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<td>33.03</td>
<td>33.59</td>
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<td>384.1</td>
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<td>32.79</td>
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<td>F</td>
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<td>456.6</td>
<td>411.7</td>
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<td></td>
<td>H</td>
<td>34.60</td>
<td>28.74</td>
<td>30.61</td>
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</table>

Table 1. Total magnetic shielding constants‡.
‡ Units are parts per million.

A number of comments can be made about individual chemical shifts. The deshielding of the methane carbon when H is replaced by CH₃, which is usually termed the ‘α effect’, is well described at 4–31G. The STO result is qualitatively satisfactory but the shift is somewhat overestimated at this level. The LEMAO set provides no interpretation of this effect.

The large deshielding effect experienced by the methane carbon when H is replaced by F is reproduced by all three methods. Although underestimated to some extent, the 4–31G result is in moderately good agreement with the experimental value. The LEMAO–5G value is in excellent agreement with experiment. The STO–5G basis, on the other hand, underestimates this type of low field shift quite markedly.

The difference in shielding at a carbon atom in a C–C single and a C–C double bond is described very well by the 4–31G method. Experimentally carbon atoms in C–C triple bonds are found to resonate at fields intermediate between alkanes and alkenes. This trend is qualitatively reproduced at all three levels. It is apparent from table 2 that the deshielding of carbon atoms in multiply-bonded systems is consistently overestimated by the LEMAO–5G method and consistently underestimated at the STO–5G level. By contrast the 4–31G results for C₂H₆, C₂H₄ and C₂H₃ are in excellent quantitative agreement with experiment. In addition the extended level results are in good agreement with experimental values for H₂CO and HCN. Thus the method appears capable of describing the screening at carbon nuclei which form multiple bonds to electronegative atoms.
Table 2. N.M.R. chemical shifts†

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Nucleus of interest</th>
<th>STO-5G opt. scale</th>
<th>LEMAO-5G opt. scale</th>
<th>4-31G</th>
<th>Experiment‡</th>
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<td>CH₄</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0 [38]</td>
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<tr>
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<td>0.00</td>
<td>0.00 [39]</td>
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<tr>
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<tr>
<td></td>
<td>F</td>
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<td>128.7</td>
<td>74.0</td>
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</tbody>
</table>

† Units are parts per million.
‡ 13C chemical shifts are given relative to CH₄, 14N shifts relative to NH₃, 17O shifts relative to H₂O and 19F shifts relative to HF. A negative value indicates a downfield shift.

The experimental 13C shift of CH₄ relative to TMS is 2.1 p.p.m. All 1H shifts are given relative to CH₄. The experimental 1H shift of CH₄ relative to TMS is -0.23 p.p.m.

Table 3. Mean absolute deviations between theory and experiment† (p.p.m.)

<table>
<thead>
<tr>
<th></th>
<th>STO-5G</th>
<th>LEMAO-5G</th>
<th>4–31G</th>
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<td>13C chemical shifts</td>
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<tr>
<td>1H chemical shifts</td>
<td>1.31</td>
<td>0.83</td>
<td>0.43</td>
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</table>

† Chemical shifts relative to CH₄.

Examples in table 2 of shielding at other first row atoms are fairly limited. The 4–31G results for the 14N shift of HCN relative to NH₃ and the 19F shift of CH₃F relative to HF are in excellent agreement with experiment. While these limited data give no conclusive evidence as to the general applicability of this type of method for shielding at nitrogen and fluorine nuclei it certainly suggests that a more extensive study would be worthwhile. All calculated values for the 17O shift in H₂CO relative to H₂O are in poor agreement with experiment. Although at present there is no accurate experimental chemical shift value available for H₂CO it appears likely that this shift is rather overestimated by all three methods. This defect of the method deserves further investigation.
The accurate calculation of $^1$H N.M.R. chemical shifts has previously proved to be extremely difficult, deviations between theory and experiment often being larger than 10 p.p.m. Thus all the $^1$H results in table 2 represent a considerable improvement over previous methods. The mean absolute deviation of 0.43 p.p.m. for the 4-31G results indicates the excellent agreement between $^1$H chemical shifts calculated at this level and experiment. The deshielding effects of adjacent C–C, C–O and C–N groups are all well described at 4-31G. It is worth noting that the low field $^1$H shift of ethane is calculated correctly only at the extended basis set level.

All three levels of theory differentiate correctly between the shielding effects associated with adjacent C–C, C–O and C–N groups. The LEMAO–5G and 4-31G $^1$H chemical shifts for CH$_3$F are in good agreement with experiment. The STO level, however, considerably underestimates this downfield shift. The $^1$H chemical shifts of the first row hydrides are also reproduced moderately well at the LEMAO and 4-31G levels. The values obtained using the STO basis are again in somewhat poorer agreement with experiment.

Although the results presented in table 2 cannot be regarded as exhaustive, they do illustrate that the theory presented here is capable of describing quantitatively the main types of shielding effect. The overall excellent agreement between the 4–31G level of theory and experiment suggests that a detailed analysis of these results in terms of the contributions outlined in § 2, should provide a critical test of current qualitative ideas about shielding. Such an analysis will be presented in a future paper.

4. CONCLUSIONS

From the study presented here we draw the following conclusions:

1. It is feasible to calculate gauge-invariant magnetic shielding constants at an ab initio level comparable to that routinely used for other types of ground state property.

2. N.M.R. chemical shifts calculated using minimal and slightly extended sets of contracted gaussian functions are in good agreement with experimental values. The calculated values show a substantial improvement when the minimal basis is replaced by the slightly extended set of atomic functions.

3. The main types of shielding effect at carbon and hydrogen are extremely well described at the extended level. The excellent quantitative agreement between this level of theory and experiment suggests that this method has promise as a predictive tool.

4. Limited data for shielding at other first row atoms are also in good agreement with experimental values except for $^{17}$O. Thus it appears likely that this type of approach will be generally applicable to most first row atoms.

5. More studies are clearly required to define further the predictive capabilities of this method. In view of the small amount of computational effort required for polyatomic molecules containing two first row atoms, systematic applications of this approach to larger systems should not present computational difficulties.

It is a pleasure to thank Dr. P. C. Hariharan for useful discussions and for his generous advice on efficient procedures for evaluating two-electron integrals.
Thanks are also due to the Director and Staff of Kiewit Computation Center for their assistance in this project.

APPENDIX A

To assess the convergence of magnetic shielding constants with respect to the number of gaussian functions used in the LEMAO expansion, we have examined the diamagnetic and paramagnetic shielding contributions for the molecules listed in table 4. Calculations were performed at the LEMAO-3G, LEMAO-4G, LEMAO-5G and LEMAO-6G levels using the standard scale factors reported in reference [36] and experimental geometries †. Calculated values of $\sigma^d$ and $\sigma^p$ are given in tables 4 and 5, respectively. The diamagnetic contribution $\sigma^d$ converges rapidly for all types of nuclei. The paramagnetic contribution $\sigma^p$ to shielding at first row atoms, however, converges much more slowly. As shown in table 5, the LEMAO-5G results are probably within five per cent of the LEMAO limit. We therefore conclude that the LEMAO-5G level provides a description of magnetic shielding close to that which would be obtained if the LEMAO-NG (large N) level were used. The paramagnetic contribution to shielding at protons converges rather more rapidly. For $^1$H chemical shifts the LEMAO-4G basis set provides results which are close to the LEMAO-NG limit.

<table>
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<th>Molecule</th>
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<th>LEMAO-3G</th>
<th>LEMAO-4G</th>
<th>LEMAO-5G</th>
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Table 4. LEMAO-NG studies for $\sigma^d$.

† For details of the experimental geometries used see reference [34].
The first-order correction to the Fock matrix is given by
\[
(F^{(1,0)}_{\nu\lambda})_x = (H^{(1,0)}_{\nu\lambda})_x + \sum_{\rho\sigma} \{P_{\rho\sigma}^{(0)}(G_{\nu\lambda\rho\sigma}^{(1,0)})_x + (P_{\rho\sigma}^{(1,0)})_x G_{\nu\lambda\rho\sigma}^{(0)}\}
\]  (B 1)

The most time-consuming part of the construction of this matrix is the evaluation of the two-electron integrals \(\{x_\nu^*x_\lambda^{|x_\rho^*x_\sigma}\}_x\). If such integrals had to be evaluated using the full form of the GIAO \(x_{\nu\rho}\), then the construction of \(F^{(1,0)}_{\nu\lambda}\) would be a formidable task. However, as shown in §2 we only require \(G_{\nu\lambda\rho\sigma}^{(1,0)}\) and thus we merely need the values of the two-electron integrals correct to first-order in the external magnetic field \(H\). Expanding \((x_\nu^*x_\lambda|x_\rho^*x_\sigma)\) in a similar manner to the other integrals we can write
\[
\{x_\nu^*x_\lambda|x_\rho^*x_\sigma\}_x = (\phi_\nu\phi_\lambda|\phi_\rho\phi_\sigma) + iH_x\{[(\phi_\nu\phi_\lambda|\phi_\rho\phi_\sigma)^{(1,0)}]_x + ...\}
\]  (B 2)

Here \((\phi_\nu\phi_\lambda|\phi_\rho\phi_\sigma)\) is the unperturbed two-electron integral and \((x_\nu^*x_\lambda|x_\rho^*x_\sigma)^{(1,0)}\) is the first-order correction. We can write the gauge factor product \(f_\nu^*f_\lambda\) of equation (2.42) in the form
\[
f_\nu^*f_\lambda = 1 + (i/c)(A_\nu - A_\lambda) \cdot r + ...
\]
\[
= 1 + iH_x[(1/c)(Q_{\nu\lambda})_x + (T_{\nu\lambda})_x] + ...\]  (B 3)

Thus the first-order correction to the two-electron integral becomes
\[
\{x_\nu^*x_\lambda|x_\rho^*x_\sigma\}^{(1,0)}_x = (1/c)[[(Q_{\nu\lambda})_x + (Q_{\rho\sigma})_x](\phi_\nu\phi_\lambda|\phi_\rho\phi_\sigma)
\]
\[
+ (T_{\nu\lambda})_x\phi_\nu\phi_\lambda|\phi_\rho\phi_\sigma) + (\phi_\nu\phi_\lambda|(T_{\rho\sigma})_x\phi_\rho\phi_\sigma).\]  (B 4)
Recalling $Q_{\alpha}$ and $T_{\alpha}$ from equations (2.43) and (2.44), respectively, we obtain

$$\langle Q_{\alpha} \rangle = \langle \phi_{\alpha} | \phi_{\beta} \rangle = \{ Y_{\rho}Z_{\lambda} - \tilde{Z}_{\rho}Y_{\lambda} \} \langle \phi_{\alpha} | \phi_{\beta} \rangle$$  \hspace{1cm} (B 5)

and

$$\langle (T_{\alpha}) Z_{\rho}Y_{\lambda} \phi_{\rho} \phi_{\sigma} \rangle = Y_{\rho}(z_{\rho} \phi_{\alpha} | \phi_{\beta} \phi_{\sigma}) - Z_{\rho}(y_{\rho} \phi_{\alpha} | \phi_{\beta} \phi_{\sigma}).$$  \hspace{1cm} (B 6)

It is clear that the contribution of equation (B 5) involves only the unperturbed two-electron integrals and the nuclear coordinates. It is worth noting that these quantities are required for the prior calculation of the unperturbed electronic energy.

The second contribution (equation (B 6)), however, involves the evaluation of two-electron integrals of the type $\langle z_{\rho} \phi_{\alpha} | \phi_{\beta} \phi_{\sigma} \rangle$. If the real basis functions for first row and hydrogen atoms are restricted to 1s, 2s, 2px, 2py, and 2pz type orbitals then the most complicated integrals required for the perturbed wavefunction calculation are of the type $(d|pp)$ where $d$ signifies a d-type function. In this work we use $\phi$-functions taken as fixed linear combinations of gaussian-type functions. The $\phi_{2p}$ and $\phi_{2d}$ functions share common gaussian exponents for reasons of computational efficiency [33]. As a result, the $\phi_{2p}$ (from $\phi_{2s}$) and $\phi_{2d}$ (from $\phi_{2p}$) type functions which arise in equation (B 6) also share the same set of gaussian exponents. Thus one set of values of error and exponential functions suffices for $9 \times 4^2 = 576$ distinct integral values and allows the $(\chi_{d} \phi_{\alpha} | \chi_{d} \phi_{\beta})^{(1,0)}$ integrals to be computed rapidly. It should also be noted that integrals of the type $\langle (T_{\alpha}) Z_{\rho}Y_{\lambda} \phi_{\rho} \phi_{\sigma} \rangle$ are non-zero only if $\phi_{\alpha}$ and $\phi_{\beta}$ are located on different atoms. First-order corrections to one-electron integrals are evaluated in a similar way. All types of integral are calculated using methods originally due to Boys [37].

References

Calculation of N.M.R. chemical shifts