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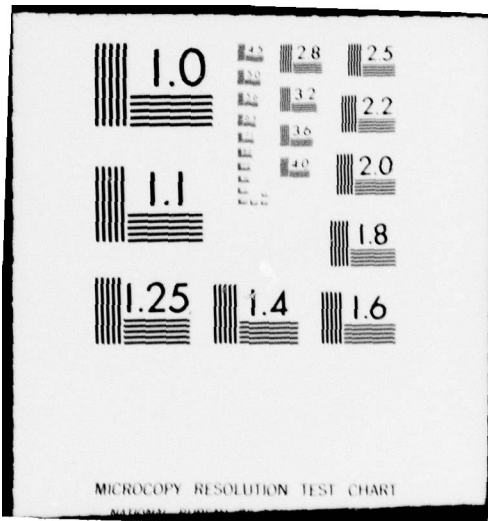
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6 The Theory of Chemical Shifts in the Hartree-Fock Approach.

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Introduction

The general theory of chemical shifts has been well known since the paper of Ramsey⁽¹⁾ in 1950. With the development of improved methods for obtaining new Hartree-Fock wave functions interest has again been rekindled to theoretically determine the chemical shift tensor in this approximation. Although the final equations are well established they have derived by several different routes and often in different formalisms. Since one's ultimate goal is to not only correctly predict the chemical shift but also to understand the origins of its various contributions, it is clearly important to have a good feel for how the various theoretical terms arise. The purpose of the present discussion is to present what we believe to be a thorough and, hopefully, clear derivation of the theoretical expressions in what we also believe to be the most transparent approach. A variety of background material is included and we delve somewhat more deeply into some of the steps than would one in a formal journal article. Following a brief review of the pertinent Hamiltonian the Hellmann-Feynmann theorem^(2,3) is used to establish the general shift expression. This is followed by a discussion of London's approach⁽⁴⁾ to the origin-gauge problem and perturbed Hartree-Fock theory in a variable basis set. Finally, we derive the chemical shift equations employing London's approach and show how they are trivially modified for the case where London orbitals are not used.

The Hamiltonian

In the semi-classical treatment of the interaction of a molecular system with electromagnetic radiation the usual Born-Oppenheimer electronic Hamiltonian is given by

$$\mathcal{H} = \sum_i \frac{1}{2m_i} (p_i + \frac{e}{c} A_i)^2 + V - \mu_N \cdot H \quad (1)$$

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for a nucleus N coupled directly to an external magnetic field H. $A_{\mathbf{i}}$ is the vector potential of the i^{th} electron while V contains all other interactions being considered including all of the attractive and repulsive coulomb interactions.

The vector potential consists of two parts:

$$A_{\mathbf{i}} = \frac{1}{2} H \times (r_{\mathbf{i}} - R) + \frac{\mu_N \times (r_{\mathbf{i}} - R_N)}{|r_{\mathbf{i}} - R_N|^3} \quad (2)$$

The first part is due to the presence of the external field H and contains an arbitrary vector R due to the fact that in the selection of $A_{\mathbf{i}}$ we are free to select any gauge which, in this example, is an arbitrary reselection of the origin of the coordinate system. No such freedom of relative origin exists for the second term, however, which is the contribution to $A_{\mathbf{i}}$ of the nuclear moment μ_N and where distances are measured with respect to R_N , the location of μ_N . The form exhibited can further be modified by the addition of an arbitrary term of the type $\text{grad}(f(r_{\mathbf{i}}))$ since $\text{curl}(\text{grad}(f(r_{\mathbf{i}}))) = 0$ and does not change the physical total magnetic field. In any complete calculation the choice of gauge is, like the choice of coordinate system, immaterial. Epstein⁽⁵⁾ has shown that the approximate unrestricted coupled Hartree-Fock theory is also gauge invariant within any given set of trial functions in the sense of yielding identical energies for an arbitrary choice of gauge. The general problem is, of course, that exact calculations are not currently possible for most molecular systems of interest and Hartree-Fock calculations usually employ either a limited basis set or approximations to the necessary integrals.

Since the direct nucleus-field coupling is easily treated, the presence of the vector potential yields a perturbation of the form (electron subscript and sum repressed)

$$\begin{aligned} \mathcal{H}_p &= \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{e^2}{2mc^2} \mathbf{A} \cdot \mathbf{A} \\ &= \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2mc^2} \mathbf{A} \cdot \mathbf{A} \end{aligned} \quad (3)$$

where the coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) has been selected⁽⁶⁾.

For a system with multiple perturbations such that

$$\mathcal{H} = \mathcal{H}_0 + \alpha \mathcal{H}^{(\alpha)} + \beta \mathcal{H}^{(\beta)} + \alpha\beta \mathcal{H}^{(\alpha, \beta)} + \dots \quad (4)$$

where α, β are the usual ordering (expansion) parameters, we may expand both the wavefunction and energy in a similar series:

$$|\psi\rangle = |\psi_0\rangle + \alpha |\psi^{(\alpha)}\rangle + \beta |\psi^{(\beta)}\rangle + \alpha\beta |\psi^{(\alpha, \beta)}\rangle + \dots \quad (5)$$

$$\epsilon = \epsilon_0 + \alpha \epsilon^{(\alpha)} + \beta \epsilon^{(\beta)} + \alpha\beta \epsilon^{(\alpha, \beta)} + \dots \quad (6)$$

so that, for example,

$$\epsilon^{(\alpha, \beta)} = \left. \frac{\partial^2 \epsilon}{\partial \alpha \partial \beta} \right|_{\alpha=\beta=\dots=0} \quad (7)$$

$$\epsilon^{(\alpha)} = \left. \frac{\partial \epsilon}{\partial \alpha} \right|_{\alpha=\beta=\dots=0} \quad (8)$$

The Hellman-Feynman theorem^(2,3) yields the result

$$\frac{\partial \epsilon}{\partial \alpha} = \langle \psi | \frac{\partial \mathcal{H}}{\partial \alpha} | \psi \rangle \quad (9)$$

so that further differentiation leads to

$$\frac{\partial^2 \epsilon}{\partial \alpha \partial \beta} = \langle \frac{\partial \psi}{\partial \beta} | \frac{\partial^2 \mathcal{H}}{\partial \alpha} | \psi \rangle + \langle \psi | \frac{\partial^2 \mathcal{H}}{\partial \alpha} | \frac{\partial \psi}{\partial \beta} \rangle + \langle \psi | \frac{\partial^2 \mathcal{H}}{\partial \alpha \partial \beta} | \psi \rangle \quad (10)$$

or, since the mixed derivative is independent of the order of differentiation

$$\frac{\partial^2 \epsilon}{\partial \beta \partial \alpha} = \left\langle \frac{\partial \psi}{\partial \alpha} \left| \frac{\partial \mathcal{H}}{\partial \beta} \right| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \mathcal{H}}{\partial \beta} \right| \frac{\partial \psi}{\partial \alpha} \right\rangle + \left\langle \psi \left| \frac{\partial^2 \mathcal{H}}{\partial \alpha \partial \beta} \right| \psi \right\rangle \quad (11)$$

a result which Moccia⁽⁷⁾, referring to earlier work by Dalgarno and Steward⁽⁸⁾, calls the interchange theorem. Accordingly, we find

$$\epsilon^{(\alpha, \beta)} = \left\langle \psi^{(\alpha)} \left| \mathcal{H}^{(\beta)} \right| \psi_0 \right\rangle + \left\langle \psi_0 \left| \mathcal{H}^{(\beta)} \right| \psi^{(\alpha)} \right\rangle + \left\langle \psi_0 \left| \mathcal{H}^{(\alpha, \beta)} \right| \psi_0 \right\rangle \quad (12)$$

where the second term is the hermitian adjoint of the first term.

If we write the chemical shift tensor σ such that the nuclear spin Hamiltonian is

$$\mathcal{H}^{\text{spin}} = -H \cdot (1 - \sigma) \cdot \mu_N \quad (13)$$

then

$$\begin{aligned} \sigma_{ij} &= \left. \frac{\partial^2 \epsilon}{\partial H_i \partial \mu_{Nj}} \right|_{H=\mu_N=0} = \left\langle \psi^{(H_i)} \left| \mathcal{H}^{(\mu_{Nj})} \right| \psi_0 \right\rangle + \left\langle \psi_0 \left| \mathcal{H}^{(\mu_{Nj})} \right| \psi^{(H_i)} \right\rangle \\ &+ \left\langle \psi_0 \left| \mathcal{H}^{(H_i, \mu_{Nj})} \right| \psi_0 \right\rangle \end{aligned} \quad (14)$$

and we can calculate the general i - j element of the tensor σ from a knowledge of $|\psi_0\rangle$ and the first-order perturbative effect of the external field H on $|\psi\rangle$. Use of the interchange theorem reverses the H and μ symbols but must lead to the same physical answer.

The particular choice above of finding the first order external-field-perturbed wavefunction has the practical advantage that for a system of many nuclei it need be carried out only once whereas had we chosen to determine $\psi^{(\mu_{Nj})}$ a calculation would be required for each nucleus N .

London Orbitals

The freedom to select an arbitrary gauge would seem to add flexibility to the chemical shift calculation in terms of choosing a gauge that leads to a particularly transparent physical interpretation. The fact that most approximate calculations are not gauge invariant diminishes this flexibility and presents one with the problem of which gauge is "best" in a particular situation. The usually trivial choice of coordinate system origin is now more important since this constitutes one class of gauge choice. One solution to this particular problem is to follow London⁽⁴⁾ and replace the orbital $\phi_n(r)$ centered at R_n by what we shall term a London orbital⁽⁹⁾ (LO)

$$\chi_n(r) = e^{\frac{-ie}{\hbar c} A(R_n) \cdot r} \phi_n(r) \equiv |n_L\rangle \quad (15)$$

since now

$$\left(p + \frac{e}{c}A\right)\chi_n = e^{\frac{-ie}{\hbar c} A(R_n) \cdot r} \left(p + \frac{e}{c}(A - A(R_n))\right)\phi_n \quad (16)$$

and the vector potential term in the remaining operator becomes

$$A - A(R_n) = \frac{1}{2}\hbar x(r - R_n) + \frac{\mu_N x(r - R_N)}{|r - R_N|^3} \quad (17)$$

Now, in both terms in the operator (applied to a particular orbital n), a specific reference origin is referenced: still the nucleus N for the second term and now R_n , the center of orbital n , for the first term. The use of London orbitals thus suppresses any arbitrariness in selection of origin; one has, in fact, for each choice of origin made a unitary transformation of the basis so that so long as one uses the same basic orbital set $\{\phi_n\}$ the gauge invariance is, as Epstein⁽¹⁰⁾ puts it, "enforced". Epstein points out that this resulting gauge invariance within a given set of functions is not important for just that point, but rather that the physical significance lies in the

fact that $e^{-ieA(\mathbf{R}_n) \cdot \mathbf{r}/\hbar c} \phi_n(\mathbf{r})$ is through first order in H the exact eigenfunction of a one-electron, one center uniform magnetic field problem which has ϕ_n as an eigenfunction when $H=0$. Since London orbitals (sometimes called GIAO) account for only the translational invariance, some feel ⁽¹¹⁾ that the gauge problem can be overcome only by the use of large basis sets, despite some recent successes ⁽¹²⁾ obtained by use of the London basis.

Perturbed Hartree Fock Theory and Variable Basis Sets

Use of London orbitals is an example of working with a variable basis, that is, a basis set in which one or more perturbation parameters are explicitly contained in the description of the wave functions employed. Moccia ⁽⁷⁾ has treated this problem and presents general formulas which are very useful not only for the variable basis set problem but for the more conventional approach in which the perturbation ordering parameters appear only in the Hamiltonian. One purpose of this section is to briefly review the general procedure, to establish notation, and finally to present expressions which allow the determination of $\psi^{(H_i)}$ presented before in the general formula for the chemical shift tensor (equation 14).

We consider a closed shell system described by a set of doubly-occupied molecular orbitals $\psi_i(\mathbf{r})$ written as a single Slater determinant. The total energy is given by

$$E = \sum_i^{\text{occ}} 2f_{ii} + \sum_{i,j}^{\text{occ}} (2J_{ij} - K_{ij}) \quad (18)$$

where f_{ii} is the expectation value of all the one-electron terms with ψ_i and $J_{ij} = (ii/jj)$ and $K_{ij} = (ij/ji)$ are the usual coulomb and exchange integrals in the MO(ψ_i) basis:

$$(ij|kl) = \int \psi_i^*(\mathbf{r}_1) \psi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_1) \psi_l(\mathbf{r}_2) dV_1 dV_2 \quad (19)$$

Requiring E to be stationary with respect to an arbitrary change $\delta\psi_i$ in ψ_i subject to maintenance of the MO orthogonality leads to the Fock equations

$$\sum_n \langle m|f|n\rangle C_{ni} + \sum_j \sum_{r,s,n} C_{rj}^* C_{sj} C_{ni} \{2\langle mn|rs\rangle - \langle ms|rn\rangle\} = \sum_{n,j} \epsilon_{ij} C_{nj} \langle m|n\rangle \quad (20)$$

where the MO $|\psi_i\rangle$ has been expanded in a general atomic orbital basis $|n\rangle$ where

$$|\psi_i\rangle = \sum_n |n\rangle C_{ni} \quad (21)$$

and $\langle m|n\rangle$ is an overlap integral in the basis $|n\rangle$. Since for this case (doubly occupied orbitals) the density matrix P can be written

$$P_{mn} = \sum_j^{\text{occ}} 2C_{nj}^* C_{mj} \quad (22)$$

we can rewrite the Fock equation in matrix form as

$$\{F + G(P)\}C_i = \sum_j \epsilon_{ij} SC_j \quad (23)$$

where

$$\begin{aligned} F_{mn} &= \langle m|f|n\rangle \\ G(P)_{mn} &= \sum_{rs} P_{sr} \{ \langle mr|g|ns\rangle - \frac{1}{2} \langle mr|g|sn\rangle \} \\ S_{mn} &= \langle m|n\rangle \end{aligned} \quad (24)$$

and C_i is the column vector representation of ψ_i in the AO basis $\{|n\rangle\}$. The self-consistent nature of the approach is apparent; one assumes an initial density matrix and iterates until self-consistency is reached. Usually, the matrix ϵ (of elements ϵ_{ij}) is presumed diagonal. If one is to carry out a

perturbed Hartree-Fock procedure, this may be presumed to be so in zeroth order but not in higher orders.

Following Moccia ⁽⁷⁾, consider the first order perturbation equation in $\mathcal{H}^{(\alpha)}$ for the Hartree-Fock procedure:

$$(F^0 + G^0(P))C_i^\alpha + (F^{(\alpha)} + G^{(\alpha)}(P))C_i^0 = \epsilon_i^0 S^0 C_i^\alpha + \epsilon_i^0 S^{(\alpha)} C_i^0 + \sum_j^{\text{occ}} \epsilon_{ij}^{(\alpha)} S^0 C_j^0 \quad (25)$$

Here we have used a diagonalized ϵ_{ij} in zeroth order. By rearrangement we obtain

$$(F^0 + G^0(P) - \epsilon_i^0 S^0)C_i^\alpha + (F^{(\alpha)} + G^{(\alpha)}(P) - \epsilon_i^0 S^{(\alpha)})C_i^0 = \sum_j^{\text{occ}} \epsilon_{ij}^{(\alpha)} S^0 C_j^0 \quad (26)$$

Note that $G(P)$ may contain a first-order contribution from both the density matrix P and the electron repulsion terms $\langle mr|g|ns \rangle$ if a variable basis set is employed. By a procedure similar to ordinary perturbation theory, C_i^α , may be projected on both the occupied and unoccupied orbitals to obtain

$$C_i^\alpha = \sum_k^{\text{occ}} \left(-\frac{1}{2} C_k^{\text{o}+} S^{(\alpha)} C_i^0 \right) C_k^0 + \sum_k^{\text{vac}} \frac{C_k^{\text{o}+} [F^{(\alpha)} + G^{(\alpha)}(P) - \epsilon_k^0 S^{(\alpha)}] C_i^0}{\epsilon_i^0 - \epsilon_k^0} C_k^0 \quad (27)$$

where, we note, both the occupied and vacant (in zeroth order) MO's enter into the expression for C_i^α , and where

$$G^{(\alpha)}(P)_{mn} = \sum_{r,s} [P_{sr}^{(\alpha)} \{ \langle mn|g|ns \rangle^0 - \frac{1}{2} \langle mr|g|sn \rangle^0 \} + P_{sr}^0 \{ \langle mr|g|ns \rangle^{(\alpha)} - \frac{1}{2} \langle mr|g|sn \rangle^{(\alpha)} \}] \quad (28)$$

Since an iterative solution to $P^{(\alpha)}$ is desired where

$$P = 2 \sum_j^{\text{occ}} C_j C_j^\dagger$$

$$P^{(\alpha)} = 2 \sum_j^{\text{occ}} [C_j^0 (C_j^\alpha)^\dagger + C_j^\alpha (C_j^0)^\dagger] \quad (29)$$

it is useful to rewrite the expression for C_i^α as

$$C_i^\alpha = -\frac{1}{2} \sum_k^{\text{occ}} C_k^0 C_k^{\text{ot}(\alpha)} S^{(\alpha)} C_i^0 + \sum_k^{\text{vac}} \frac{C_k^0 C_k^{\text{ot}}}{(\epsilon_i^0 - \epsilon_k^0)} \cdot (F^{(\alpha)} - \epsilon_k^0 S^{(\alpha)}) C_i^0$$

$$+ \sum_k^{\text{vac}} \frac{C_k^0 C_k^{\text{ot}}}{(\epsilon_i^0 - \epsilon_k^0)} \cdot G^{(\alpha)}(P) C_i^0 \quad (30)$$

so that in the first term one may recognize $P^0 = 2 \sum_k^{\text{occ}} C_k^0 C_k^{\text{ot}}$ and in terms two and three the term $C_k^0 C_k^{\text{ot}} / (\epsilon_i^0 - \epsilon_k^0)$ which need be calculated only once, as indeed is true for the entire second term. Indeed, if we neglect the third term we have what is referred to as uncoupled Hartree-Fock perturbation theory. (13) It is the electrostatic integrals that couple the various C_i^α equations that require the iterative procedure in perturbed Hartree-Fock and lead to this approach being referred to as "coupled" Hartree-Fock.

While our procedure requires us to determine the C_{ni}^α (or C_i^α) in the general wave-function expansion

$$|\psi_i\rangle = \sum_n |n\rangle C_{ni} = \sum_n |n^0\rangle C_{ni}^0 + |n^\alpha\rangle C_{ni}^\alpha + |n^{\alpha\alpha}\rangle C_{ni}^{\alpha\alpha} + \dots \quad (31)$$

use of a variable basis introduces the perturbation parameters in the basis and thus into a variety of integrals. For example, in employing London orbitals

for the chemical shift problem

$$S_{mn} = \int (\phi_m e^{\frac{-ie}{\hbar c} A(R_m) \cdot r})^* (\phi_n e^{\frac{-ie}{\hbar c} A(R_n) \cdot r}) dV \quad (32)$$

and, since $A(R_n) = \frac{1}{2} H \times R_n$

$$S_{mn}^{(H_j)} = \frac{ie}{2\hbar c} \int \phi_m^* \phi_r ((R_m - R_n) \times r)_j dV \quad (33)$$

Similar terms enter in the $F^{(\alpha)}$ and $G^{(\alpha)}$ matrices. The general manipulation of such terms will become more apparent as the next section is developed.

The Chemical Shift Expression

We wish to write out explicitly the various contributions to the chemical shift tensor and exhibit their origin in terms of the general expression given in equation 14. We will assume that London orbitals are to be employed but will be able to see also the resulting expression when ordinary AO's are used

$$1. \quad \langle \psi_0 | \mathcal{L}^{(H_i, \mu_{Nj})} | \psi_0 \rangle \equiv (I_1)_{ij}$$

The simplest term to consider is that in which only the unperturbed wavefunction enters and the bilinear $H-\mu$ term arises in the perturbing Hamiltonian.

$$\frac{e^2}{2mc^2} (H \times r) \cdot \frac{\mu_N \times r_N}{r_N^3} = \frac{e^2}{2mc^2} [(H \cdot \mu_N)(r \cdot r_N) - (H \cdot r_N)(\mu_N \cdot r)] \frac{1}{r_N^3} \quad (34)$$

where $r_N = r - R_N$. Accordingly,

$$\mathcal{L}^{(H_i, \mu_{Nj})} = \frac{e^2}{2mc^2} [(r \cdot r_N) \delta_{ij} - (r_N)_i (r)_j] \frac{1}{r_N^3} \equiv \mathcal{L}_{ij}^{(1,1)} \quad (35)$$

If we define the row vector χ_0 as the gaugeless basis vector whose components are $\phi_n \equiv |n\rangle$ the various zeroth order MO's k become $\chi_0 C_k^0$ and I_1 becomes

$$\begin{aligned} (I_1)_{ij} &= 2 \sum_k^{\text{occ}} C_k^{0\dagger} \chi_0^\dagger \mathcal{H}_{ij}^{(1,1)} \chi_0 C_k^0 = \text{Tr} \sum_k^{\text{occ}} 2 C_k^0 C_k^{0\dagger} (\chi_0^\dagger \mathcal{H}_{ij}^{(1,1)} \chi_0) \\ &= \sum_{n,m} P_{nm}^0 \langle m | \mathcal{H}_{ij}^{(1,1)} | n \rangle \end{aligned} \quad (36)$$

We remind ourselves again that $|n\rangle, |m\rangle$ are gaugeless, non-LO orbitals.

$$2. \quad \langle \psi^{(H_1)} | \mathcal{H}^{(\mu_{NJ})} | \psi_0 \rangle + \text{h.a.} \equiv (I_2 + I_3)_{ij}$$

As we finally evaluate I_2 and I_3 to complete the calculation, the desirability of dividing the integral into two parts will become apparent. Since the perturbed wave function is now involved, the perturbed MO's $\chi_0 C_k^{(H_1)} + \chi^{(H_1)} C_k^0$ are composed of two parts.

$$\begin{aligned} (I_2)_{ij} &= \sum_k^{\text{occ}} 2 C_k^{(H_1)\dagger} (\chi_0^\dagger \mathcal{H}^{(\mu_{NJ})} \chi_0) C_k^0 + \text{h.a.} \\ &= \text{Tr} \sum_k^{\text{occ}} 2 C_k^0 C_k^{(H_1)\dagger} (\chi_0^\dagger \mathcal{H}^{(\mu_{NJ})} \chi_0) + \text{h.a.} \end{aligned} \quad (37)$$

Since

$$\begin{aligned} P &= \sum_k^{\text{occ}} 2 C_k C_k^\dagger \\ P^{(H_1)} &\equiv P_1^{(1,0)} = \sum_k^{\text{occ}} 2 (C_k^0 C_k^{(H_1)\dagger} + C_k^{(H_1)} C_k^{0\dagger}) \\ \mathcal{H}^{(\mu_{NJ})} &= \frac{e}{mc} \frac{(\mathbf{r}_N \cdot \mathbf{p})_j}{r_N^3} \end{aligned} \quad (38)$$

we finally obtain (the Hermitian adjoint now explicitly included)

$$(I_2)_{ij} = \sum_{n,m} (P_{nm}^{1,0})_i \langle m | \frac{e}{mc} \frac{(r_N^{xp})_j}{r_N^3} | n \rangle \quad (39)$$

I_3 will contain $\chi^{(H_1)}$ which contributes the H_1 part of the $H-\mu$ bilinear term. The derivation must be done carefully since the perturbation operator is a derivative operator and will act on the $\chi^{(H_1)}$. I_3 can quickly be put in the form

$$(I_3)_{ij} = \text{Tr } P^0 [(\chi^{(H_1)})^\dagger \mathcal{H}^{(\mu_N j)} \chi_0 + (\chi_0^\dagger \mathcal{H}^{(\mu_N j)} \chi^{(H_1)})] \quad (40)$$

Since

$$\begin{aligned} \frac{e}{mc} A \cdot p e^{\frac{-ie}{\hbar c} A(R_n) \cdot r} \phi_n &= e^{\frac{-ie}{\hbar c} A(R_n) \cdot r} \left\{ \frac{e}{mc} A \cdot p | n \rangle \right. \\ &\left. + \frac{e}{mc} A \cdot \left(\frac{\hbar}{i} \right) \left(\frac{-ie}{\hbar c} A(R_n) \right) | n \rangle \right\} \quad (41) \end{aligned}$$

the contribution from the second term takes on a different form and we finally obtain

$$\begin{aligned} (I_3)_{ij} &= \text{Tr } P_{nm}^0 \langle m | \frac{ie^2}{\hbar mc^2} [(R_m - R_n)_{xj}]_i \cdot \frac{(r_N^{xp})_j}{r_N^3} | n \rangle \\ &- \text{Tr } P_{nm}^0 \langle m | \frac{e^2}{2mc^2} \cdot \frac{(R_n \cdot r_N) \delta_{ij} - (r_N)_i (R_n)_j}{r_N^3} | n \rangle \quad (42) \end{aligned}$$

where we note the resemblance in form of the second part of the expression for I_3 to that for I_1 in equations 36 and 35; indeed, they may be combined.

Expressing $p = -i\hbar\nabla$ we may combine all terms to finally obtain

$$\begin{aligned}
\sigma_{ij} = & \sum_{n,m} \{ P_{nm}^0 \langle m | \frac{e^2}{2mc^2} \frac{(r-R_n) \cdot r_N \delta_{ij} - (r_N)_i (r-R_n)_j}{r_N^3} | n \rangle \\
& + P_{nm}^0 \langle m | \frac{e^2}{2mc^2} ((R_m - R_n) \times r)_i \frac{(r_N \times V)_j}{r_N^3} | n \rangle \\
& + \frac{1}{i} (P_{nm}^{1,0})_i \langle m | \frac{e\hbar}{mc} \frac{(r_N \times V)_j}{r_N^3} | n \rangle \} \quad (43)
\end{aligned}$$

Having specified a particular perturbation - the external H-field and internal μ -field - the perturbation expressions may also be explicitly given. The general matrix element for $S^{(H_i)}$ has been given in equation 33. For $F^{(H_i)}$ we obtain

$$\begin{aligned}
F_{mn}^{(H_i)} = & \frac{ie}{2\hbar c} \langle m | ((R_m - R_n) \times r)_i \mathcal{H}_{core} | n \rangle \\
& + \frac{1}{i} \langle m | \frac{e\hbar}{2mc} ((r-R_n) \times V)_i | n \rangle \quad (44)
\end{aligned}$$

where \mathcal{H}_{core} is the usual unperturbed 1-electron part of the Hamiltonian. The $G^{(H_i)}$ term is given by replacing in equation 28 $P_{rs}^{(\alpha)}$ by $P_{rs}^{(H_i)}$ where, for example,

$$\begin{aligned}
\langle m_L r_L | g | n_L s_L \rangle^{(H_i)} = & \langle m r | g \frac{ie}{2\hbar c} [((R_m - R_n) \times r_1)_i \\
& + ((R_r - R_s) \times r_2)_i] | n s \rangle \quad (45)
\end{aligned}$$

Equation 43 represents the general results for the i-j element of the shielding tensor calculated from the coupled perturbed Hartree-Fock approach. For solution work we may desire only the isotropic part of σ obtained by

setting $i=j$, and taking one-third the sum over i .

$$\sigma_{\text{iso}} = \frac{1}{3} \text{Tr}(\sigma) \quad (46)$$

To obtain the proper result for the case where we do not use London orbitals one simply sets R_n, R_m equal to zero in equation 43. Similar simplifications occur in the perturbation part of the calculation; in equations 33, 44, and 45 one sets R_m, R_n, R_r, R_s all equal to zero. $S^{(H_i)}$ vanishes as does the \mathcal{H} core term in 44, and $G^{(H_i)}$ is considerably simplified. Translational invariance is lost, of course, and one's answer may now depend upon the choice of origin. A convenient choice often employed is to locate the origin at the nucleus of interest; this has the effect of replacing r in the final equations 33, 43, 44, and 45 by $r_N = r - R_N$.

1. N. F. Farnsey, Phys. Rev. 78, 699 (1950).
2. H. Hellmann, "Einführung in die Quantenchemie", F. Deuticke and Co., Leipzig, 1937.
3. R. P. Feynman, Phys. Rev., 56, 340 (1939).
4. F. London, J. Phys. Radium 8, 397 (1937).
5. S. T. Epstein, J. Chem. Phys., 42, 2897 (1965).
6. See H. F. Hammett, "Advanced Quantum Chemistry", Chapter 1, for a good discussion of the gauge of the electromagnetic potentials.
7. R. Moccia, Chem. Phys. Lett. 5, 260 (1970).
8. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. A247, (1958).
9. These are sometimes called GIAO (gauge invariant atomic orbitals) or, as proposed by Pople (J. A. Pople, Discuss. Faraday Soc. 34, 7 (1969)), gauge-dependent atomic orbitals.
10. S. T. Epstein, J. Chem. Phys. 58, 1592 (1973).
11. P. Lazzeretti and R. Zanasi, Int. J. Quant. Chem., 12, 93 (1977).
12. R. Ditchfield, Mol. Phys. 27, 789 (1974).
13. See, for example, P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).