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Uncoupled Hartree-Fock Calculations of the Ring Current Contribution to the Chemical Shifts in Conjugated Hydrocarbons

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Uncoupled Hartree-Fock perturbation theory is adapted for the calculation of the ring current contribution to the chemical shifts in a number of conjugated hydrocarbons. The results compare favourably with those of the coupled form of the theory. It is also shown that the Hückel approach may be modified so as to give values close to those of the SCF theory.

Für einige konjugierte Kohlenwasserstoffe wird zur Berechnung des Anteils des Ringstroms an der chemischen Verschiebung die ungekoppelte Hartree-Fock-Störungstheorie verwandt. Die Ergebnisse stimmen gut mit denen überein, die man mit der gekoppelten Form der Theorie erhält. Ferner wird gezeigt, daß der Ansatz nach Hückel derart modifiziert werden kann, daß die Ergebnisse den aus der SCF-Theorie erhaltenen nahekommen.

La théorie de perturbation Hartree-Fock non couplé est adaptée pour le calcul de la contribution du «courant cyclique» aux déplacements chimiques dans un certain nombre d'hydrocarbures conjugués. Les résultats se comparent favorablement à ceux de la théorie de Hartree-Fock couplé. On montre que par ailleurs l'approximation de type Hückel peut être modifiée de manière à donner des valeurs proches de celles de la théorie SCF.

Introduction

The contributions to the total proton chemical shifts in conjugated molecules have been discussed by many authors [1, 2]. That due to the ring currents is the easiest to evaluate, the remaining contributions being largely of a local nature. In 1958, Pople [3] and McWeeny [4] independently developed theories to evaluate the ring current contributions and several calculations have been made using their techniques [5, 6, 7, 8]. However, both methods are based on the London theory of diamagnetic anisotropy [9] and are therefore restricted to being used within a Hückel framework. An SCF approach was first introduced by Hall and Hardisson [1, 10]. Their method is based on coupled Hartree-Fock perturbation theory and is, therefore, somewhat laborious to apply. In the case of diamagnetic susceptibilities we have already shown that the computational difficulties involved in the coupled approach may be circumvented by using the simpler uncoupled procedure [11]. We shall show that this is also the case for chemical shifts, so that no advantage is gained by using the more complex coupled theory.

In the case of hydrocarbons it has often been noted that, if the chemical shifts relative to benzene are evaluated, then the SCF and Hückel results are practically equal. However, the absolute values are found to differ by a factor of approximately two. In the final section we propose a modified Hückel scheme which seeks to explain and correct the divergences encountered.

Theory

The main steps of the theory correspond closely to those used in Ref. [11] for the calculation of diamagnetic susceptibilities. In particular the comparisons made there between the coupled and uncoupled formalisms carry over exactly to the case of chemical shifts. However, for completeness of discussion, we shall restate the equations used and indicate the modifications necessary for the calculation of the chemical shift.

The total π wavefunction is written as a Slater determinant of the form

$$\Psi = |\phi_1^0 \alpha\, \phi_1^0 \beta \ldots \phi_n^0 \alpha\, \phi_n^0 \beta| ,$$

i.e. each molecular orbital ϕ_i^0 $i = 1, \ldots, n$ is doubly occupied in the ground state. The molecular orbitals satisfy the SCF eigenvalue equations

$$F^0 \phi_i^0 = \varepsilon_i^0 \phi_i^0 , \qquad i = 1, \ldots, 2n$$

with $F^0 = (1/2m)\, p^2 + V$, where V is the self-consistent potential. It is further assumed that each ϕ_i^0 may be written as a linear combination of an orthonormal set of $2p_z$-like atomic orbitals $\{\omega_s\}$, one centred on each carbon atom i.e.

$$\phi_i^0 = \sum_s c_{is}^0 \omega_s .$$

In the presence of a uniform magnetic field $\boldsymbol{H}$ perpendicular to the plane of the molecule, and a field due to a magnetic dipole of moment m situated at an attached proton the total vector potential A for the system has the form

$$\boldsymbol{A} = \frac{1}{2} \boldsymbol{H} \wedge \boldsymbol{r} + \frac{m \boldsymbol{n} \wedge \boldsymbol{r}}{r^3} , \tag{1}$$

where the proton is chosen as the origin of $\boldsymbol{r}$ and $\boldsymbol{n}$ is a unit vector perpendicular to the molecular plane[1]. Following McWeeny [4] we may then identify the required chemical shift with the coefficient of $-Hm$ in the total perturbation energy expansion.

Adopting the uncoupled Hartree-Fock procedure we are required to solve

$$\left\{ \frac{1}{2m} \left(\boldsymbol{p} + \frac{e}{c} \boldsymbol{A} \right)^2 + V \right\} \phi_i = \varepsilon_i \phi_i , \qquad i = 1, \ldots, n$$

where the $\{\phi_i\}$ are the new molecular orbitals and V is the self-consistent potential for the unperturbed system.

Each ϕ_i is now written as a linear combination of guage-invariant orbitals $\{\chi_s\}$ i.e.

$$\phi_i = \sum_s c_{is} \chi_s ,$$

where

$$\chi_s = \omega_s \exp\{-i\alpha \boldsymbol{A}_s \cdot \boldsymbol{r}\} , \qquad s = 1, \ldots, 2n \tag{2}$$

and $\alpha = e/\hbar c$.

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[1] Note that the origin of the first term in (1) may be chosen arbitrarily. However, because the origin of the second term is fixed at the proton in question so also is the origin in (2). Therefore, the expression for F_{st} in (4) is not dependent on origin and we may fix A as in (1) without loss of generality.

A_s is the value of the vector potential A at the carbon atom s, with position vector $\boldsymbol{R}_s$, so that

$$A_s = \frac{1}{2} \boldsymbol{H} \wedge \boldsymbol{R}_s + \frac{m\boldsymbol{n} \wedge \boldsymbol{R}_s}{R_s^3} \tag{3}$$

The matrix elements of the field dependent Hamiltonian $\boldsymbol{F}$ will be

$$F_{st} = \int \chi_s^* \left\{ \frac{1}{2m} \left(\boldsymbol{p} + \frac{e}{c} A \right)^2 + V \right\} \chi_t \, \mathrm{d}\tau$$

In simplifying this integral the following approximations are made, corresponding to those used in the case of susceptibilities [11].

(a) $\int \omega_s \boldsymbol{p} \cdot (A - A_t) \, \omega_t \, \mathrm{d}\tau$ is neglected. Since ω_t is $2p_z$-like it may be argued that

$$\int \omega_s \boldsymbol{p} \cdot \tfrac{1}{2} \boldsymbol{H} \wedge (\boldsymbol{r} - \boldsymbol{R}_t) \, \omega_t \, \mathrm{d}\tau$$

is identically zero, $\boldsymbol{p} \cdot \boldsymbol{H} \wedge (\boldsymbol{r} - \boldsymbol{R}_t)$ being proportional to the z component of angular momentum around the atom t. By direct evaluation of the remaining terms it is seen that, if $s \neq t$, the integral may be neglected, provided the atomic orbitals $\{\omega_s\}$ are well localized. Terms arising when $s = t$ may be considered as being local in character.

(b) $\int \omega_s (A - A_t)^2 \, \omega_t \, \mathrm{d}\tau$ is neglected. The final arguments in (a) apply equally here, i.e. $s \neq t$ the localization of the atomic orbitals justifies neglect of the integral and, when $s = t$, the contributions are absorbed by the local terms.

(c) $\boldsymbol{r}$ is replaced by $\frac{1}{2}(\boldsymbol{R}_s + \boldsymbol{R}_t)$, following the usual London argument that the only non negligible contribution to the integral arises from this region [9].

(d) $\int \omega_s^2 \boldsymbol{r} \, \mathrm{d}\tau \approx 0$; $\int \omega_s^2 \boldsymbol{r}^2 \, \mathrm{d}\tau \approx 0$, i.e. the approximations of zero transition dipole and quadrupole moments are invoked.

With these approximations the matrix elements become

$$F_{st} = H_{st}^0 \exp \tfrac{1}{2} i\alpha (A_s - A_t) \cdot (\boldsymbol{R}_s + \boldsymbol{R}_t) + F_{st}^0 - H_{st}^0 \tag{4}$$

where $\boldsymbol{H}^0$ represents the one electron terms in the field free Hamiltonian.

In order to obtain the chemical shift, it is necessary to expand F_{st}, c_{is} and ε_i as double power series in H and m,

$$\begin{aligned} F_{st} &= F_{st}^0 + F_{st}(10) + F_{st}(01) + F_{st}(20) + F_{st}(11) + F_{st}(02) + \cdots \\ c_{is} &= c_{is}^0 + c_{is}(10) + c_{is}(01) + c_{is}(20) + c_{is}(11) + c_{is}(02) + \cdots \\ \varepsilon_i &= \varepsilon_i^0 + \varepsilon_i(10) + \varepsilon_i(01) + \varepsilon_i(20) + \varepsilon_i(11) + \varepsilon_i(02) + \cdots \end{aligned}$$

where the first entry in the brackets corresponds to the order of H, and the second to the order of m. The $F_{st}(pq)$ are obtained from (4) by substitution from (3) and expansion of the exponential. For convenience $F_{st}(01)$, $F_{st}(10)$, and $F_{st}(11)$ are listed in Table 1. Let

$$\phi_i(10) = \sum_s c_{is}(10) \, \omega_s$$

and

$$\phi_i(01) = \sum_s c_{is}(01) \, \omega_s ,$$

then $\phi_i(10)$ and $\phi_i(01)$ satisfy the equations

$$[\boldsymbol{F}^0 - \varepsilon_i]\,\phi_i(10) = -\boldsymbol{F}(10)\,\phi_i^0 \tag{5}$$

and

$$[\boldsymbol{F}^0 - \varepsilon_i]\,\phi_i(01) = -\boldsymbol{F}(01)\,\phi_i^0 \tag{6}$$

respectively ($\varepsilon_i(10)$ and $\varepsilon_i(01)$ are zero since *both* $\boldsymbol{F}(10)$ and $\boldsymbol{F}(01)$ are pure imaginary).

It is then easy to show that the coefficient of Hm in an expansion of the total energy E of the system is

$$E_{011} = E^a_{011} + E^b_{11}$$

where

$$E^b_{11} = 2\sum_i^{\text{occ.}} \langle \phi_i^0 | \boldsymbol{F}(11) | \phi_i^0 \rangle \tag{7}$$

and

$$E^a_{011} = 2\sum_i^{\text{occ.}} \langle \phi_i^0 | \boldsymbol{F}(10) | \phi_i(01) \rangle + 2\sum_i^{\text{occ.}} \langle \phi_i^0 | \boldsymbol{F}(01) | \phi_i(10) \rangle \,.$$

By virtue of Eqs. (5) and (6) the two summations in E^a_{011} are equal. Hence

$$E^a_{011} = 4\sum_i^{\text{occ.}} \langle \phi_i^0 | \boldsymbol{F}(10) | \phi_i(01) \rangle \,. \tag{8}$$

As was the case for susceptibilities, E^b_{11} will be identical in the coupled and uncoupled methods, since the Hamiltonian used in the coupled procedure is the same as (4). Therefore, any divergence between the two theories will arise from the E^a_{011} term. In fact, the use of E^a_{011} leads to total results which are of the wrong sign. It is, therefore, essential that correction terms, similar to those used in Ref. [11], are included if we are to obtain the coupled results. We may then write

$$E^a_{11}(\text{coupled}) = E^a_{011} + E^a_{111} + E^a_{211} + \cdots \tag{9}$$

The first term on the right is the uncoupled energy and the second term is the first order correction to it. Using arguments similar to those of Tuan *et al.* [12]

Table 1. *Quantities used in the theory*

$$F_{st}(10) = i\alpha S_{st} H^0_{st}$$

$$F_{st}(01) = i\alpha S_{st} K_{st} H^0_{st}$$

$$F_{st}(11) = -\alpha^2 S^2_{st} K_{st} H^0_{st}$$

$$E_{11} = -\alpha^2 \sum_{st} P^0_{st} S^2_{st} K_{st} H^0_{st}$$

where

$$P^0_{st} = 2\sum_j^{\text{occ.}} c^0_{js} c^0_{jt}$$

$$E_{011} = 4\alpha i \sum_{st} \sum_j^{\text{occ.}} c^0_{js} c_{jt}(01) S_{st} H^0_{st}$$

$$E_{111} = 4\sum_{st} \sum_{ij}^{\text{occ.}} \gamma_{st} \delta_{stij}$$

where

$$\delta_{stij} = c^0_{is} c^0_{js} c_{jt}(10) c_{it}(01) - c^0_{is} c^0_{jt} c_{js}(10) c_{it}(01)$$

$$S_{st} = \tfrac{1}{2}\boldsymbol{n}\cdot(\boldsymbol{R}_s \wedge \boldsymbol{R}_t) \quad \text{and} \quad K_{st} = R_s^{-3} + R_t^{-3}$$

it is easy to show that this term is given by

$$E^a_{111} = 4 \sum_{ij}^{\text{occ.}} \{(i(01)\,j^0\,|\,j(10)\,i^0) - (i(01)\,j(10)\,|\,j^0\,i^0)\}$$

where $i(01) \equiv \phi_i(01)$ etc.

Expressions for E^b_{11}, E^a_{011} and E^a_{111}, when the Pariser-Parr-Pople assumptions are made, are shown in Table 1.

However, inclusion of the first order correction term alone does not give a sufficiently good approximation to E^a_{11} (coupled). In some cases E_{11} is still of the wrong sign. It is therefore necessary to attempt a complete summation of the series (7). Fortunately a method of doing this is available in the form of the geometric approximation. This method has already proved of value in calculations of electric polarizabilities [13] and magnetic susceptibilities [17]. We suppose, then, that the series in (7) closely resembles a geometric progression so that

$$E^a_{11}(\text{coupled}) \approx E^a_{011}(1-k)^{-1}$$

where $k = E^a_{111}/E^a_{011}$.

By evaluating $\{c_{is}(10)\}$ and $\{c_{is}(01)\}$ from Eqs. (5) and (6) both E^a_{011} and E^a_{111} can be calculated, and hence we can find

$$E_{11}(\text{uncoupled}) = E^b_{11} + E^a_{011}(1-k)^{-1}\,. \tag{10}$$

The results may then be compared with those of the coupled theory.

Results

The uncoupled calculations were made on benzene[2] and the hydrocarbons illustrated in Fig. 1, where the proton labelling is also given. The β parameter was fixed at -2.39 eV and the two electron γ integrals were calculated by the method of Nishimoto and Mataga [14]. Molecular geometry was chosen as in Ref. [11]. In addition all C–H bond distances were fixed at 1.08 Å.

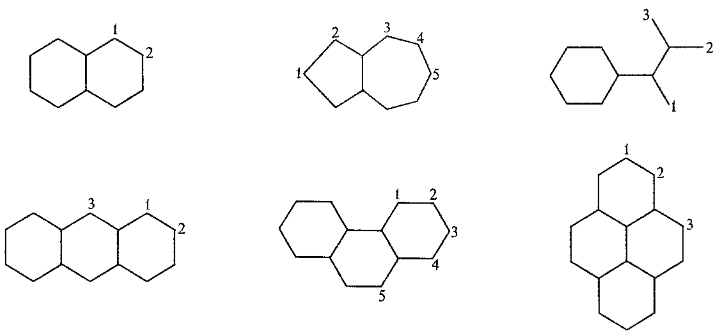

Fig. 1. Numbering system used in the tables

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[2] The interchange theorems [12] which are used in deducing the form of E^a_{111} break down in the case of benzene, since the latter has degenerate eigenvalues in its ground state. In the actual calculation it is, therefore, necessary to remove this degeneracy by varying one of the integral parameters about its correct benzene value. The result for benzene may then be obtained by extrapolation.

The chemical shift is the coefficient of $-Hm$ in the power series expansion of the total energy i.e. $-E_{11}$, and, in our theory, this will represent the ring current contribution to the total shift. However, we have specified a field perpendicular to the molecular plane whereas, in practice, the effect is averaged over all orientations. The final expression for the chemical shift, calculated using the geometric approximation, will therefore be $\sigma_{\text{geom}} = -\frac{1}{3}E_{11}$.

In Table 2 we have listed the results for the hydrocarbons considered. σ_{geom} is compared with σ_{coupled} and the ratios to benzene are also compared. In addition the absolute and relative values as calculated by the Hückel method are given[3]. The experimental results are also included although direct comparison between theory and experiment is not possible since the former takes no account of electrostatic and other effects.

It is seen that there is quite good agreement between σ_{geom} and σ_{coupled}, although the former seem to be a few per cent too small in most cases. This can be attributed to the differences in integral parameters used, particularly in the method used to evaluate the γ parameters[4]. Because of the ease with which σ_{geom} may be calculated, compared with σ_{coupled}, we may conclude that no advantage is gained by using the latter method.

In order to obtain a more direct comparison between theory and experiment in the case of azulene, a correcting term $\Delta\sigma$, arising from the net π-electron charge Δq on the adjacent carbon atom, should be added to the ring current contribution [20–22]. This correction is given by

$$\Delta\sigma = a\Delta q\,,$$

where a is a constant, taken to be 10.6 ppm [22]. The predicted chemical shifts (in ppm relative to benzene) for protons 1–5 of azulene are then −0.06, 0.55, −1.81, −0.11 and −1.03 respectively compared with the experimental −0.58, −0.07, −0.95, 0.28 and −0.17. Therefore, the theoretical values incorrectly predict even the general sequence of shifts. It has been suggested [1] that hybridization of the carbon atom could have a significant effect in the case of azulene

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[3] For consistency we have chosen the Hückel β to be equal to the nearest neighbour elements of the SCF Hamiltonian for benzene. In our case this means that the Hückel $\beta = -4.15$ eV. Note that in Ref. [19] this value was inadvertently taken to be −4.35 eV. The Hückel values in Table 1 of that paper should therefore be appropriately altered by 4.6 per cent. The scaling factor best suited to the Hückel values is then found to be 0.58. The general conclusions arrived at are not thereby affected.

[4] This is of particular relevance in the case of azulene were there is a non-uniformity in the π-electron charge distribution. The γ integrals used by Hall and Hardisson [10] are those of McWeeny and Peacock [15, 16] coupled with the Pariser and Parr formula [17]. The net π-electron charges using this method for azulene are given by Amos [18].

Atom	Amos	This paper
1	0.010	−0.004
2	−0.112	−0.107
3	0.130	0.108
4	−0.044	−0.019
5	0.084	0.076

Because of the differences in the above values the ring current contribution to the chemical shifts of azulene protons, as calculated in this paper, may be expected to differ from the coupled values of Hall and Hardisson by a larger per centage than in the case of the alternant hydrocarbons benzene, naphthalene and styrene.

Table 2. *Theoretical and experimental chemical shifts*

Molecule	Proton	Absolute values (in ppm)			Values relative to benzene			
		Geom.	Coupled[a]	Hückel[b]	Geom.	Coupled[a]	Hückel	Expt.[g]
Benzene		2.50	2.50	4.34	1	1	1	1
Naphthalene	1	3.22	3.22	5.69	1.28	1.28	1.31[c]	1.35[d]
	2	2.78	2.87	5.08	1.11	1.15	1.17[c]	1.12[d]
Azulene	1	2.60	3.10	4.95	1.04	1.23	1.14[a]	1.37[f]
	2	3.08	3.43	5.51	1.23	1.37	1.27[a]	1.04[f]
	3	3.17	3.32	5.82	1.27	1.32	1.34[a]	1.61[f]
	4	2.81	2.99	5.29	1.12	1.18	1.22[a]	0.82[f]
	5	2.72	2.92	5.21	1.09	1.16	1.20[a]	1.11[f]
Styrene	1	0.45	0.48	0.78	0.18	0.19	0.18[a]	—
	2	0.15	0.17	0.26	0.06	0.07	0.06[a]	—
	3	0.32	0.37	0.61	0.13	0.15	0.14[a]	—
Anthracene	1	3.28	—	5.99	1.31	—	1.38[c]	1.41[d]
	2	2.62	—	5.21	1.05	—	1.20[c]	1.08[d]
	3	4.24	—	7.38	1.69	—	1.70[c]	1.67[d]
Phenanthrene	1	3.69	—	6.51	1.48	—	1.50[c]	2.07[e]
	2	2.99	—	5.43	1.19	—	1.25[c]	1.39[e]
	3	3.05	—	5.34	1.22	—	1.23[c]	1.35[e]
	4	3.36	—	5.95	1.34	—	1.37[c]	1.54[e]
	5	3.03	—	5.56	1.21	—	1.28[c]	1.28[d]
Pyrene	1	3.61	—	6.47	1.44	—	1.49[c]	1.46[d]
	2	3.99	—	7.07	1.60	—	1.63[c]	1.57[d]
	3	3.21	—	5.99	1.28	—	1.38[c]	1.51[d]

[a] See Ref. [10].

[b] Hückel $\beta = -4.15$ eV. See Footnote 3.

[c] See Ref. [8].

[d] See Ref. [5].

[e] Batterham, T. J., L. Tsai and H. Ziffer: Austral. J. Chem. **18**, 1959 (1965).

[f] Pople, J. A., W. G. Schneider, and H. J. Bernstein: High resolution nuclear magnetic resonance. New York: McGraw-Hill 1959.

[g] Based on an experimental estimate of 1.55 ppm for benzene. See: Spiesecke, H., and W. G. Schneider: J. chem. Physics **35**, 731 (1961).

although, as yet, there is no indication as to how this should be incorporated into the theory.

Finally, we note that the Hückel ratios agree quite well with those of the SCF theory whereas the absolute values differ markedly. In the next section we propose a modified Hückel method which attempts to explain and correct the discrepancies in these absolute values.

Modified Hückel Method

It is found that the common ratio k can always be well approximated by 0.5 so that, from (10),

$$E_{11}(\mathrm{S}) \approx E_{11} + 2E_{011} = 2 \sum_{i}^{\mathrm{occ.}} \langle \phi_i^0(\mathrm{S}) | \boldsymbol{F}_s(11) | \phi_i^0(\mathrm{S}) \rangle + 8 \sum_{i}^{\mathrm{occ.}} \langle \phi_i^0(\mathrm{S}) | \boldsymbol{F}_s(10) | \phi_i^1(\mathrm{S}) \rangle ,$$

where S denotes SCF and $\phi_i^1 \equiv \phi_i(01)$.

In the Hückel(H) case the equivalent expression is

$$E_{11}(\mathrm{H}) = 2 \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(11) | \phi_i^0(\mathrm{H}) \rangle + 4 \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(10) | \phi_i^1(\mathrm{H}) \rangle . \tag{11}$$

The matrix elements of the SCF Hamiltonian $\boldsymbol{F}(\mathrm{S})$ may be written as

$$F_{st}(\mathrm{S}) = H_{s\,t}^0(\mathrm{S}) \exp(iL_{st}) + V_{st}^0(\mathrm{S}),$$

where $\boldsymbol{V}^0(\mathrm{S})$ corresponds to the two electron terms in $\boldsymbol{F}^0(\mathrm{S})$, and

$$L_{st} = \tfrac{1}{2}\alpha(\boldsymbol{A}_s - \boldsymbol{A}_t) \cdot (\boldsymbol{R}_s + \boldsymbol{R}_t).$$

The corresponding Hückel Hamiltonian has the form

$$F_{st}(\mathrm{H}) = F_{st}^0(\mathrm{H}) \exp(iL_{st}). \tag{12}$$

The differences between $E_{11}(\mathrm{S})$ and $E_{11}(\mathrm{H})$, $F_{st}(\mathrm{S})$ and $\mathrm{F}_{st}(\mathrm{H})$ arise from the inability of the Hückel formalism to allow for exchange terms in $\boldsymbol{F}^0$.

Evidently, we may expect different results from the two theories and if we are to modify the Hückel method so as to obtain results comparable with those of SCF theory then this must clearly involve introduction of exchange terms into the Hückel Hamiltonian.

Following Ref. [19], where we considered the same problem in the context of susceptibilities, we formally separate $F_{st}^0(\mathrm{H})$ into two parts corresponding to one and two electron terms i.e.

$$F_{st}^0(\mathrm{H}) = H_{st}^0(\mathrm{H}) + V_{st}^0(\mathrm{H})$$

with $H_{st}^0(\mathrm{H}) = \lambda F_{st}^0(\mathrm{H})$ and $V_{st}^0(\mathrm{H}) = (1-\lambda) F_{st}^0(\mathrm{H})$, where s and t are neighbours. If $s = t$ then there is no problem since $F_{tt}(\mathrm{H}) = F_{tt}(\mathrm{S}) = 0$. From our knowledge of off diagonal terms in the SCF Hamiltonian we shall expect $\lambda \approx 0.5$.

Denoting this modified Hückel method by M.H. we have, instead of (11), that

$$F_{st}(\mathrm{M.H.}) = \lambda F_{st}^0(\mathrm{H}) \exp(iL_{st}) + (1-\lambda) F_{st}^0(\mathrm{H})$$

and, instead of (12),

$$E_{11}(\mathrm{M.H.}) = 2\lambda \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(11) | \phi_i^0(\mathrm{H}) \rangle + 8\lambda^2 \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(10) | \phi_i^1(\mathrm{H}) \rangle .$$

Since $\lambda \approx 0.5$ then $\lambda^2 \approx \frac{1}{2}\lambda$. Therefore

$$\begin{aligned} E_{11}(\mathrm{M.H.}) &\approx \lambda \left\{ 2 \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(11) | \phi_i^0(\mathrm{H}) \rangle + 4 \sum_{i}^{\text{occ.}} \langle \phi_i^0(\mathrm{H}) | \boldsymbol{F}_{\mathrm{H}}(10) | \phi_i^1(\mathrm{H}) \rangle \right\} \\ &= \lambda E_{11}(\mathrm{H}). \end{aligned}$$

We will therefore expect that

$$\sigma(\mathrm{S}) \approx \sigma(\mathrm{M.H.}) \approx \lambda \sigma(\mathrm{H}).$$

Hence

$$\frac{\sigma_{\text{mol.}}(\mathrm{S})}{\sigma_{\text{benz.}}(\mathrm{S})} \approx \frac{\sigma_{\text{mol.}}(\mathrm{H})}{\sigma_{\text{benz.}}(\mathrm{H})},$$

which is confirmed in Table 2.

Table 3. *Comparison of Hückel and* SCF *chemical shifts (in ppm)*

Molecule	Proton	SCF	Hückel	Modified Hückel		
			A[a]	B[b]	C[c]	D[d]
Benzene		2.50	4.34	2.17	2.17	2.38
Naphthalene	1	3.22	5.72	2.86	2.85	3.13
	2	2.78	5.15	2.58	2.54	2.79
Azulene	1	2.60	5.49	2.75	2.48	2.72
	2	3.08	6.03	3.02	2.76	3.03
	3	3.17	6.36	3.18	2.91	3.20
	4	2.81	6.38	3.19	2.65	2.91
	5	2.72	5.83	2.92	2.61	2.87
Styrene	1	0.45	1.22	0.61	0.39	0.42
	2	0.15	0.70	0.35	0.13	0.14
	3	0.32	0.70	0.35	0.31	0.34
Anthracene	1	3.28	6.01	3.01	3.00	3.29
	2	2.62	5.32	2.66	2.61	2.87
	3	4.24	7.90	3.95	3.69	4.05
Phenanthrene	1	3.69	6.52	3.26	3.26	3.58
	2	2.99	5.65	2.83	2.72	2.99
	3	3.05	5.59	2.80	2.67	2.93
	4	3.36	6.15	3.08	2.98	3.27
	5	3.03	5.66	2.83	2.78	3.05
Pyrene	1	3.61	6.59	3.30	3.24	3.56
	2	3.99	7.71	3.86	3.54	3.89
	3	3.21	5.96	2.98	3.00	3.29

[a] Using the SCF Hamiltonian in the Hückel method.

[b] Modified A values with $\lambda = 0.5$.

[c] Modified Hückel values using $\lambda = 0.5$.

[d] Modified Hückel values using $\lambda = 0.55$, chosen to give the best fit with the SCF results.

Table 3 corresponds to Table 1 and 2 for susceptibilities. The first column gives the uncoupled results with the appropriate corrections. The remaining four columns deal with the modified Hückel method. Since the SCF and Hückel zero order Hamiltonians are different, the above theory is first tested by treating the SCF F^0 matrix as if it were a Hückel matrix. Column A of Table 3 gives the resulting values. As expected, the answers are much too large, but, if we adopt the above λ-technique with $\lambda = 0.5$, the values in column B are obtained. Taken as a whole these are in quite good agreement with the SCF results. This confirms that the modified Hückel method satisfactorily takes account of the exchange terms which were missing in the Hückel formulation. Finally, we consider an application of the same λ-scaling to the original Hückel values given in Table 2. Column C of Table 3 lists the results when $\lambda = 0.5$. The best fit for the complete set of values is obtained when λ is chosen to be 0.55. The results for this value of λ are given in column D. As can be seen, these agree very well with those of the SCF theory.

Conclusion

We have shown that uncoupled Hartree-Fock perturbation theory may be successfully applied to calculations of the ring current contribution to the proton chemical shifts in conjugated hydrocarbons. As was the case for magnetic susceptibilities, it is found that use of the geometric approximation is essential.

Further, we have shown that the Hückel procedure may be modified by identifying part of the Hamiltonian with the two electron terms of SCF theory. This leads to the result that $\sigma(\mathrm{SCF}) \approx \lambda\sigma(\text{Hückel})$. A choice of $\lambda = 0.55$ gives good agreement for the molecules considered.

Therefore, provided the Hückel values are scaled by a factor of 0.55 the results will prove to be quite satisfactory for most hydrocarbons.

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