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Relatio

On the Chemical Shifts in Conjugated Systems

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The calculation of the ring-current contribution to the proton chemical shifts in conjugated systems using uncoupled Hartree-Fock perturbation theory is improved by the inclusion of origin variation in the expression for the vector potential.

The proton chemical shifts in some conjugated hydrocarbons [1] and various heterocyclics [2] have been calculated using McWeeny's test-dipole procedure and applying uncoupled Hartree-Fock perturbation theory. However, the origin dependence of the vector potential was not taken into account and, as a result, no attention was given to any possible variation of the chemical shifts with choice of origin.

Eq. (1) of [1] may be more generally written as

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

where a tilde is used to denote that the origin of that particular vector may be chosen arbitrarily. The origin of $\boldsymbol{r}$ in the second term is fixed at the proton in question. Eq. (2) of [1] for the gauge-invariant orbitals is now expressed as

$$\chi_s = \omega_s \exp\{-i\alpha(\boldsymbol{A}_s^H \cdot \tilde{\boldsymbol{r}} + \boldsymbol{A}_s^m \cdot \boldsymbol{r})\},$$

where $\boldsymbol{A}_s^H = \frac{1}{2}\boldsymbol{H} \wedge \tilde{\boldsymbol{R}}_s$ and $\boldsymbol{A}_s^m = \frac{m\boldsymbol{n} \wedge \boldsymbol{R}_s}{R_s^3}$. The formalism now follows as in [1] the various perturbation and energy expressions being altered to those given in the revised Table 1. It is evident that the final chemical shifts will, in general, be dependent on the choice of the variable origin. The situation is precisely analogous to that for susceptibilities [3] and the conclusions exactly parallel those obtained for that property. Hence, if the geometric approximation is used there is usually very little origin dependence in the final values. The revised Table 2 of [1] gives the chemical shifts for an origin fixed at the centre of charge of the molecule. Part of the discrepancy between these results and those given in the original table arises from a slight units error and the remaining discrepancy is due to the change in the choice of origin (in [1] the variable origin was fixed at the proton). It may easily be shown that the Hückel results are independent of origin choice and hence discrepancies in these values arise solely from the units error.

Table 1. *Quantities used in the theory*

$$F_{st}(10) = i\alpha \tilde{S}_{st} H^0_{st}$$
$$F_{st}(01) = i\alpha S_{st} K_{st} H^0_{st}$$
$$F_{st}(11) = -\alpha^2 \tilde{S}_{st} S_{st} K_{st} H^0_{st}$$
$$E_{11} = -\alpha^2 \sum_{st} P^0_{st} \tilde{S}_{st} S_{st} K_{st} H^0_{st},$$
$$\text{where } P^0_{st} = 2 \sum_{j}^{\text{occ}} c^0_{js} c^0_{jt}$$
$$E_{011} = 4\alpha i \sum_{st} \sum_{j}^{\text{occ}} c^0_{js} c_{jt}(01) \tilde{S}_{st} H^0_{st}$$
$$E_{111} = 4 \sum_{st} \sum_{ij}^{\text{occ}} \gamma_{st} \delta_{stij},$$
$$\text{where } \delta_{stij} = c^0_{is} c^0_{js} c_{jt}(10) c_{it}(01) - c^0_{is} c^0_{jt} c_{js}(10) c_{it}(01)$$
$$S_{st} = \tfrac{1}{2}\boldsymbol{n}.(\boldsymbol{R}_s \wedge \boldsymbol{R}_t) \quad \tilde{S}_{st} = \tfrac{1}{2}\boldsymbol{n}.(\tilde{\boldsymbol{R}}_s \wedge \tilde{\boldsymbol{R}}_t) \quad \text{and} \quad K_{st} = R_s^{-3} + R_t^{-3}$$

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.[d]
Benzene		2.53	2.50	4.39	1	1	1	1
Naphthalene	1	3.26	3.22	5.75	1.29	1.28	1.31[c]	1.30
	2	2.93	2.87	5.14	1.16	1.15	1.17[c]	1.07
Azulene	1	2.96	3.10	5.00	1.17	1.23	1.14[a]	1.35
	2	3.49	3.43	5.58	1.38	1.37	1.27[a]	1.02
	3	3.34	3.32	5.88	1.32	1.32	1.34[a]	1.62
	4	3.11	2.99	5.36	1.23	1.18	1.22[a]	0.86
	5	3.08	2.92	5.27	1.22	1.16	1.20[a]	1.14
Styrene	1	0.42	0.48	0.79	0.17	0.19	0.18[a]	—
	2	0.21	0.17	0.26	0.08	0.07	0.06[a]	—
	3	0.35	0.37	0.61	0.14	0.15	0.14[a]	—
Anthracene	1	3.45	—	6.06	1.36	—	1.38[c]	1.43
	2	3.00	—	5.27	1.19	—	1.20[c]	1.08
	3	4.28	—	7.46	1.69	—	1.70[c]	1.70
Phenanthrene	1	3.73	—	6.59	1.47	—	1.50[c]	1.87
	2	3.12	—	5.49	1.23	—	1.25[c]	1.19
	3	3.10	—	5.40	1.23	—	1.23[c]	1.15
	4	3.39	—	6.01	1.34	—	1.37[c]	1.34
	5	3.15	—	5.62	1.25	—	1.28[c]	1.25
Pyrene	1	3.79	—	6.54	1.50	—	1.49[c]	1.43
	2	4.13	—	7.16	1.63	—	1.63[c]	1.54
	3	3.44	—	6.06	1.36	—	1.38[c]	1.47

[a] See Ref. [10] of [1].

[b] Hückel $\beta = -4.15$ eV. See Footnote 3 of [1].

[c] See Ref. [8] of [1].

[d] Based on an experimental estimate of 1.55 ppm for benzene. See Spiesecke, H., Schneider, W. G.: J. chem. Physics **35**, 731 (1961). Experimental results are from Haigh, C. W., Mallion, R. B.: Molecular Physics **18**, 737 (1970), except for azulene for which the results are from Meuche, D., Molloy, B. B., Reid, D. H., Heilbronner, E.: Helv. chim. Acta **46**, 2483 (1963).

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		2.53	4.39	2.20	2.20	2.51
Naphthalene	1	3.26	5.78	2.89	2.88	3.28
	2	2.93	5.20	2.60	2.57	2.93
Azulene	1	2.96	5.54	2.77	2.50	2.85
	2	3.49	6.09	3.05	2.79	3.18
	3	3.34	6.42	3.21	2.94	3.35
	4	3.11	6.44	3.22	2.68	3.06
	5	3.08	5.89	2.95	2.64	3.01
Styrene	1	0.42	1.23	0.62	0.40	0.45
	2	0.21	0.71	0.36	0.13	0.15
	3	0.35	0.71	0.36	0.31	0.30
Anthracene	1	3.45	6.07	3.04	3.03	3.45
	2	3.00	5.37	2.69	2.64	3.03
	3	4.28	7.98	3.99	3.73	4.26
Phenanthrene	1	3.73	6.58	3.29	3.30	3.76
	2	3.12	5.71	2.86	2.75	3.14
	3	3.10	5.65	2.83	2.70	3.08
	4	3.39	6.21	3.11	3.01	3.43
	5	3.15	5.73	2.87	2.81	3.20
Pyrene	1	3.79	6.66	3.33	3.27	3.72
	2	4.13	7.78	3.89	3.58	4.08
	3	3.44	6.02	3.01	3.03	3.45

[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 $\lambda = 0.57$, chosen to give the best fit with the SCF results.

Table 4. *Ring current properties of molecules A–G*

Molecule	Proton	Susceptibility		Chemical shift	
		Absolute[a]	Ratio[c]	Absolute[b]	Ratio[d]
A	2	31.5	1.01	2.55	1.01
	3			2.55	1.01
	4			2.55	1.01
B	2	31.2	1.00	2.53	1.00
	3			2.53	1.00
	5			2.53	1.00
C	1	30.9	0.99	2.45	0.97
D	2	11.4	0.36	0.89	0.35
	3			0.85	0.34
	4			0.84	0.33
	5			0.81	0.32
E	2	10.3	0.33	0.81	0.32
	3			0.79	0.31
F	1	18.5	0.59	0.94	0.37
G	1	16.4	0.53	0.88	0.35

[a] Units of -10^{-6} cgs emu.

[b] Units of ppm.

[c] Benzene value equals 31.2.

[d] Benzene value equals 2.53.

It may also be noted that we have taken the opportunity to update the experimental results. Table 3 of [1] is also shown in its revised form. There are no basic changes in the conclusions to be drawn from these tables.

The same errors occur in [2] and in Table 4 we give a corrected version of Table 2 of that paper for the heterocyclics $A-G$: -pyridine (*A*), pyrimidine (*B*), S-triazine (*C*), 1-methyl-2-pyridone (*D*), 1-methyl-4-pyridone (*E*), 1-methyl-2-cyclopentadienyl-1,2-dihydropyridine (*F*), 1-methyl-4-cyclopentadienyl-1,2-dihydropyridine (*G*). Again the general conclusions are unaffected by these changes but it may be noted that there are one or two large discrepancies between the "old" and "new" shifts e.g. molecule *G*. The reason for this is that the geometric approximation is only useful if the ratio $k = E_{111}/E_{011}$ is sensibly small [4], and, in fact, in most cases k is approximately 0.5 (this is always true for an origin fixed at the centre of charge). However, taking *G* as an example, and calculating the chemical shift at proton 1 with the variable origin fixed at this proton, k is found to have a value near to 1.0. It would be expected, therefore, that the geometric approximation would be much less accurate for such a choice of origin, thus explaining the large discrepancy in the calculated chemical shifts at this proton.

References

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