Theoret. chim. Acta (Berl.) 13, 421–427 (1969)

A Modified Hückel Method for Calculating Ring Current Contributions to the Diamagnetic Susceptibilities of Conjugated Hydrocarbons

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Received December 10, 1968

SCF calculations of the ring current contributions to the diamagnetic susceptibilities of certain conjugated hydrocarbons are compared with the Hückel values. It is shown that discrepancies arise because of the inherent inability of the Hückel formalism to allow for two-electron terms in the Hamiltonian. A modified Hückel scheme is proposed which rectifies this omission while still retaining the fundamental simplicity of the theory.

La contribution des courants cycliques à la susceptibilité diamagnétique des hydrocarbures conjugués est calculée par la méthode SCF-MO et comparée avec les valeurs obtenues par la méthode de Hückel. On montre que les désaccords proviennent de l'inaptitude propre au formalisme de Hückel de tenir compte des termes biélectroniques contenus dans l'hamiltonien. On propose une méthode de Hückel modifiée qui corrige cette omission tout en conservant la simplicité de la théorie.

Der Anteil des Ringstroms an der diamagnetischen Suszeptibilität konjugierter Kohlenwasserstoffe wurde mit der SCF-MO-Methode berechnet und mit den mittels Hückelmethode erhaltenen verglichen. Es wird gezeigt, daß die Unterschiede daher rühren, daß im Hückelformalismus die Zweielektronenterme des Hamiltonoperators nicht richtig berücksichtigt sind. Ein modifiziertes Hückelschema, das diese Terme berücksichtigt, aber die fundamentale Einfachheit der Theorie beibehält, wird angegeben.

Introduction

The first acceptable quantum mechanical theory of the ring current contribution to the magnetic susceptibilities of conjugated molecules was due to London [1]. Based on the Hückel approximation, his theory is very easy to apply and many calculations have been made using it [1—5]. In recent years, however, with the general tendency to replace Hückel theory by the self-consistent version of molecular orbital theory, there have been a number of calculations of magnetic susceptibilities using this latter method [6—8]. It has been usual to present numerical results in a relative form (with benzene as the reference molecule) rather than by giving the absolute values. Consequently, it does not seem to be generally known that the two methods give very different results. This is illustrated in Table 1 where the first two columns give the Hückel values for the ring current part, χ^R, of the susceptibilities for a number of molecules. The second two columns give the self-consistent results[1]. Both sets of results are given in absolute and relative

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[1] By SCF treatment, in this context, we refer to uncoupled Hartree-Fock perturbation theory with appropriate corrections c.f. Ref. [8].

Table 1. *Comparison of Hückel and* SCF *susceptibilities* χ^R *(units of* 10^{-6} *cgs emu)*

Molecule	SCF[a]		Hückel[b]		Modified Hückel	
	χ^R	ϱ[c]	χ^R	ϱ[c]	$\lambda = 0.5$	$\lambda = 0.55$
Benzene	−31.2	1	−56.8	1	−28.4	−31.2
Naphthalene	−67.5	2.16	−124.3	2.19	−62.2	−68.4
Azulene	−72.1	2.31	−128.3	2.26	−64.2	−70.6
Styrene	−29.8	0.96	−51.7	0.91	−25.9	−28.5
Diphenyl	−59.9	1.92	−106.1	1.87	−53.1	−58.4
Anthracene	−107.0	3.43	−195.8	3.45	−97.9	−107.7
Phenanthrene	−100.4	3.22	−184.5	3.25	−92.3	−101.5
Pyrene	−144.1	4.62	−260.0	4.58	−130.0	−143.0

[a] β and γ parameters chosen in Ref. [8].

[b] To allow direct comparison β (Hückel) was chosen to be −4.35 eV, being equal to the nearest neighbour entries in the SCF matrix for benzene[a].

[c] ϱ indicates ratio to benzene.

form. From the table it is clear that the two sets are in fairly good agreement when relative values are used. However, in absolute terms the Hückel results are approximately twice as big as the self-consistent ones[2].

It is the purpose of this note to give reasons for this and to show how Hückel theory may be modified in a simple way to give results in better agreement with the self-consistent ones.

As a further comment on the absolute values of χ^R we refer to a non-empirical calculation of this quantity for benzene made by Itoh, Ohno and Yoshizumi [9]. Their value for χ^R is −16.82 (10^{-6} c.g.s. e.m.u.). This tends to suggest that the Hückel values are much too large and that even the SCF results may need to be revised downwards. On the other hand, it is well known that many calculations on π-systems using non-empirical integrals give very unreliable results.

It is clearly not the purpose of this paper to join in the present controversy as to whether or not ring current calculations are valid (c.f. Ref. [10]). However, we should perhaps refer to the paper by Nowakowski [11] who finds that rather better agreement with experiment can be obtained using the ring current approach rather than that suggested by Musher [10].

Theory

Consider a zero-order wave function for the π-electrons in a conjugated molecule

$$\Psi_0 = |\phi_1^0 \alpha \phi^0{}_1 \beta \dots \phi_n^0 \alpha \phi_n^0 \beta| \,. \qquad (1)$$

The molecular orbitals $\{\phi_i^0\}$ are written as linear sums of atomic $2p_z$-like orbitals

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[2] This does, of course, depend on the choice of β-parameter in the Hückel method. We would argue that, for consistency, the Hückel β should correspond to the nearest-neighbour elements of the SCF Hamiltonian and we have chosen such a value (c.f. Footnote b of Table 1). Naturally, by choosing a different value of β the SCF and Hückel absolute values of χ^R can be made consistent but such a choice of β is completely lacking in any theoretical justification and, indeed, obscures the underlying differences between the two methods, which it is the purpose of this note to explore and, eventually, remove.

$\{\omega_r\}$ so that

$$\phi_i^0 = \sum_s a_{is}^0 \omega_s \,, \tag{2}$$

and are eigenfunctions of the one electron Hamiltonian F^0, i.e.

$$F^0 \phi_i^0 = \varepsilon_i^0 \phi_i^0 \tag{3}$$

where ε_i^0 is the orbital energy.

The form of F^0 will depend on whether Hückel or SCF theory is used. In the latter, F^0 consists of two parts, the first arising from the one electron terms in the total Hamiltonian and the second corresponding to Coulomb and exchange operators. In Hückel theory no such distinction is made, F^0 corresponding to a single entity. In practice, at least for alternant hydrocarbons, this difference in the two methods does not matter as far as the numerical values of a_{is}^0 and ε_i^0 are concerned since the two methods give similar results. The difference becomes important in the calculation of total energies, since the one electron terms have to be treated differently from the Coulomb and exchange terms. The Hückel method cannot do this, and therefore great care must be taken when using Hückel theory to find total energies[3].

In the presence of a uniform magnetic field $\boldsymbol{H}$, Ψ_0 will change to

$$\Psi = |\phi_1 \alpha \phi_1 \beta \ldots \phi_n \alpha \phi_n \beta| \tag{4}$$

where, following London, the $\{\phi_i\}$ are written as linear combinations of gauge-invariant atomic orbitals $\{\chi_s\}$

$$\phi_i = \sum_s a_{is} \chi_s \tag{5}$$

where $\chi_s = \omega_s \exp(-i\alpha \boldsymbol{A}_s \cdot \boldsymbol{r})$, $\boldsymbol{A}_s = \frac{1}{2} \boldsymbol{H} \times \boldsymbol{R}_s$, $\alpha = e/\hbar c$ and $\boldsymbol{R}_s$ is the position vector of atom s relative to the chosen origin of the vector potential, $\boldsymbol{A}$.

The $\{\phi_i\}$ now satisfy an equation analogous to (3)

$$F \phi_i = \varepsilon_i \phi_i \tag{6}$$

but where the matrix elements of F will now depend on the field $\boldsymbol{H}$.

At this point there is considerable divergence between the Hückel and self-consistent methods. For the former the matrix elements $\langle \omega_s | F | \omega_t \rangle = F_{st}$ of F are

$$F_{st}(\mathrm{H}) = F_{st}^0(\mathrm{H}) \exp(iL_{st}) \tag{7}$$

where $L_{st} = \frac{1}{2} (\boldsymbol{H} \times \boldsymbol{R}_s) \cdot \boldsymbol{R}_t$ while in the SCF treatment

$$F_{st}(\mathrm{S}) = H_{st}^0(\mathrm{S}) \exp(iL_{st}) + V_{st}(\mathrm{S}) \tag{8}$$

where V_{st}^0 corresponds to the two-electron terms in F_{st}^0, and H_{st}^0 to the one electron terms and in (7) and (8) H and S refer to Hückel and SCF. Moreover, by considering the derivations of (7) and (8) (c.f. Refs. [1, 7, 8]) it is clear that the difference is due to the inability of Hückel theory to allow for the exchange terms in F^0.

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[3] An example is the fact that ordinary Hückel theory predicts singlet and triplet states to have the same energy. This is because the difference between the two depends on two-electron integrals which are not considered in the simple form of the theory. For an empirical attempt to include such integrals in order to estimate triplet energies more accurately within the Hückel scheme see [12].

This is not the only difference between the two theories. In the Hückel method the total energy is, incorrectly, taken to be

$$2\sum_{i}^{\mathrm{occ}} \varepsilon_i\,. \tag{9}$$

Expanding all quantities in orders of the field and using primes to denote first and second order terms, we therefore obtain the Hückel expression for the ring current part of χ as

$$\begin{aligned}\chi^R(\mathrm{H}) &= -4\sum_{i}^{\mathrm{occ}} \varepsilon_i'' \\ &= -4\sum_{i}^{\mathrm{occ}} \langle \phi_i^0(\mathrm{H})|F'(\mathrm{H})|\phi_i'(\mathrm{H})\rangle - 4\sum_{i}^{\mathrm{occ}} \langle \phi_i^0(\mathrm{H})|F''(\mathrm{H})|\phi_i^0(\mathrm{H})\rangle\,.\end{aligned} \tag{10}$$

The self-consistent expression for χ^R will differ from this because i) F is given by (8) instead of (7) and ii) the correct expression for the total energy is used rather than (9). The net result is[4]

$$\chi^R(\mathrm{S}) = -8\sum_{i}^{\mathrm{occ}} \langle \phi_i^0(\mathrm{S})|F'(\mathrm{S})|\phi_i'(\mathrm{S})\rangle - 4\sum_{i}^{\mathrm{occ}} \langle \phi_i^0(\mathrm{S})|F''(\mathrm{S})|\phi_i^0(\mathrm{S})\rangle\,. \tag{11}$$

A Modification of the Hückel Method

It is clear from the previous section that some modification of Hückel theory is needed if it is to give numerical results for χ^R similar to those of SCF theory. It is also clear that this modification must amount to an introduction of exchange terms into the Hückel method. There are several ways in which this might be done but most of them destroy the simplicity which makes the Hückel method so attractive. We therefore propose to use the following rather naive idea which has the great advantage of retaining this simplicity.

An examination of the elements of an SCF Hamiltonian for nearest neighbour elements (corresponding to the off diagonal elements of a Hückel Hamiltonian) reveals that the ratio of the one electron terms to the two electron terms is fairly constant and, in fact, $H_{st}^0 \approx V_{st}^0$. If we assume that the Hückel Hamiltonian can also be divided into two parts such that the ratio of Coulomb and exchange terms to other terms is the same for all elements[5], i.e.

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

with

$$H_{st}^0 = \lambda F_{st}^0 \tag{12}$$

and

$$V_{st}^0 = (1-\lambda) F_{st}^0$$

then we shall have achieved our object of introducing two electron terms into Hückel theory in a very simple way. From the SCF results where, for nearest neighbours, $H_{st}^0(\mathrm{S}) \approx V_{st}^0(\mathrm{S})$ we can expect $\lambda \approx 0.5$.

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[4] Note that (11) is the uncoupled result plus correcting terms discussed in Ref. [8]. In fact (11) is just $E_{02} + \tilde{E}_{02}$ in the notation of [8].

[5] We note that (12) will only be suitable for off diagonal terms and not at all for the diagonal ones, but fortunately the latter do not enter the calculations since $L_{st} = 0$ for $s = t$.

Applying assumption (12) to Eq. (8) and using M.H. to indicate the modified Hückel method we have, instead of (7)

$$F_{st}(\mathrm{M.H.}) = \lambda F^0_{st}(\mathrm{H}) \exp(iL_{st}) + (1-\lambda) F^0_{st}(\mathrm{H}) \tag{13}$$

and instead of (10) we have

$$\begin{aligned}\chi^R(\mathrm{M.H.}) = &-8\lambda^2 \sum_i^{\mathrm{occ}} \langle \phi^0_i(\mathrm{H}) | F'(\mathrm{H}) | \phi'_i(\mathrm{H}) \rangle \\ &-4\lambda \sum_i^{\mathrm{occ}} \langle \phi^0_i(\mathrm{H}) | F''(\mathrm{H}) | \phi^0_i(\mathrm{H}) \rangle .\end{aligned} \tag{14}$$

We recall that $\lambda \approx 0.5$ so that $\lambda^2 \approx \frac{1}{2}\lambda$, thus giving

$$\begin{aligned}\chi^R(\mathrm{M.H.}) &= \lambda \left\{ -4 \sum_i^{\mathrm{occ}} \langle \phi^0_i(\mathrm{H}) | F'(\mathrm{H}) | \phi'_i(\mathrm{H}) \rangle - 4 \sum_i^{\mathrm{occ}} \langle \phi^0_i(\mathrm{H}) | F''(\mathrm{H}) | \phi^0_i(\mathrm{H}) \rangle \right\} \\ &= \lambda \chi^R(\mathrm{H}) .\end{aligned} \tag{15}$$

Since we expect $\chi^R(\mathrm{M.H.})$ to be approximately equal to $\chi^R(\mathrm{S})$ then we have

$$\chi^R(\mathrm{S}) \approx \chi^R(\mathrm{M.H.}) = \lambda \chi^R(\mathrm{H}) . \tag{16}$$

Equation (16) can be used to give an explanation of the first four columns of Table 1. For, since $\lambda \approx 0.5$, (16) implies that χ^R (Hückel) is approximately twice as big as $\chi^R(\mathrm{S})$ which is the case. Moreover, if we assume λ to be the same for all molecules (16) also implies that

$$\frac{\chi^R(\mathrm{S})}{\chi^R_{\mathrm{benzene}}(\mathrm{S})} \approx \frac{\chi^R(\mathrm{H})}{\chi^R_{\mathrm{benzene}}(\mathrm{H})}$$

which is also the case. This leads us to suppose that the modification suggested in Eq. (12) is likely to be useful in calculations of χ^R. We now give further numerical examples which reinforce this opinion.

Numerical Examples

The objection to using the figures in Table 1 to test the modified Hückel method is that the SCF and Hückel zero order Hamiltonians are different. To eliminate this we have taken the SCF F^0 matrix and used it as if it were a Hückel matrix. On this basis we have found $\chi^R(\mathrm{H})$, using (7) and (10). As expected and as shown in the first two columns of Table 2 this leads to much larger values than $\chi^R(\mathrm{S})$. We then calculated $\chi^R(\mathrm{M.H.})$ with $\lambda = 0.5$ (Table 2). $\chi^R(\mathrm{M.H.})$ and $\chi^R(\mathrm{S})$ are in quite good agreement although the former seem to be uniformly too small. Finally we chose λ to give the best fit between $\chi^R(\mathrm{S})$ and $\chi^R(\mathrm{M.H.})$. This is for $\lambda = 0.55$ [6] and the $\chi^R(\mathrm{M.H.})$ for this value are given in the third column of the table. It is seen that there is quite good agreement with the self-consistent values.

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[6] This contradicts the step leading from (14) to (15). However, a term by term numerical comparison of (14) with the corresponding SCF values indicates that agreement is best when λ^2 is replaced by $\frac{1}{2}\lambda$ even with $\lambda = 0.55$. Presumably this is due to the fact that (12) is an approximation so that the use of $\frac{1}{2}\lambda$ rather than λ^2 represents some adjustment due to a small accumulation of errors.

Table 2. *Comparison of Hückel*[a] *and* SCF *susceptibilities* χ^R *(units of* 10^{-6} *cgs emu)*

Molecule	SCF	Hückel[a]		
			χ^R (M.H.)	
	χ^R	χ^R (H)	$\lambda=0.5$	$\lambda=0.55$
Benzene	−31.2	−54.1	−27.1	−29.8
Naphthalene	−67.5	−119.6	−59.8	−65.8
Azulene	−72.1	−137.4	−68.7	−75.6
Styrene	−29.8	−57.3	−28.7	−31.6
Diphenyl	−59.9	−112.3	−56.3	−61.9
Anthracene	−107.0	−191.5	−95.8	−105.4
Phenanthrene	−100.4	−181.2	−90.6	−99.7
Pyrene	−144.1	−253.7	−126.9	−153.8

[a] Treating the SCF zero-order Hamiltonian as a Hückel Hamiltonian.

This seems final confirmation that the modified Hückel procedure can allow for the satisfactory incorporation of two electron terms into Hückel theory. We return to Table 1 to see if, by a λ scaling, the true Hückel values can be brought into reasonable coincidence with the SCF values. The fifth column of Table 1 gives the values obtained when $\lambda=0.5$ and the last column for $\lambda=0.55$. The latter was again chosen to give the best fit. As can be seen χ^R(H) and χ^R(S) agree very well using this method. Thus, it seems that the λ scaling is more or less unaffected by the fact that the SCF and Hückel F^0 are rather different.

Conclusion

We have pointed out that the ring current contributions to χ as calculated by the Hückel and SCF methods differ by a factor of two when absolute values are considered although the relative values are much the same. We have shown that this is due to the lack of identifiable exchange terms in the Hückel Hamiltonian, which can be rectified by a simple modification. This leads to the result that $\chi^R(\mathrm{S}) \approx \lambda\chi^R(\mathrm{H})$ where $\lambda \approx 0.5$. A numerical comparison indicates that this relation holds rather well for a fairly large number of conjugated molecules so that the modified Hückel method can take into account not only the exchange terms but also the fact that the Hückel and SCF zero order Hamiltonians differ.

Since the Hückel method is so much easier to apply than the SCF method, we have, therefore, the very useful practical result that, provided they are scaled by a factor of approximately 0.55, the Hückel χ^R will prove to be perfectly satisfactory for most molecules.

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