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Self-consistent Perturbation Theory for Conjugated Molecules

I. General Theory and Method of Calculation

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The theory of one-electron perturbations is developed in the context of the self-consistent LCAO treatment of molecular wavefunctions. A numerical method of calculating changes in the charge and bond order matrix due to one-electron perturbations is described. The method is used to compute self-consistent atom-atom polarizabilities for a number of conjugated hydrocarbons. The results are applied to spin-density calculations and to a discussion of chemical reactivity.

Im Rahmen des SCF–LCAO-Verfahrens wird eine Einteilchen-Störung behandelt und ein numerisches Verfahren zur Berechnung der Änderung der Matrix der Bindungsordnung angegeben. In der vorliegenden Arbeit wird diese Methode benützt, um Atom-Atom-Polarisierbarkeiten und Spindichten für eine Anzahl von Kohlenwasserstoffen zu berechnen sowie ihre chemische Reaktivität zu diskutieren.

La théorie des perturbations monoélectroniques est developpée au contexte du procédé LCAO autocohérent de fonctions d'ondes moléculaires. On décrit une méthode numérique pour le calcul de changements dans la matrice de charge et d'ordre de liaison dûs aux perturbations monoélectroniques. Suivant cette méthode sont calculées les polarisabilités atome-atome autocohérentes pour un nombre d'hydrocarbures conjugués. A l'aide des résultats on calcule des densités de spin, et discute la réactivités chimiques.

1. Introduction

Perturbation theory plays a most useful part in the quantum mechanical theory of molecules. In particular, the perturbation theory introduced by Coulson and Longuet-Higgins [2] into the Hückel theory of conjugated molecules has enabled electronically similar molecules to be related to one another. The theory enables changes in the charge and bond order matrix arising from small changes in the α or β integrals to be computed. This is especially appropriate for a discussion of the inductive effects produced when a heteroatom is substituted into a hydrocarbon. The theory has also been applied to certain problems in the theory of chemical reactivity [*3, 18*].

The Hückel theory of conjugated molecules is now known to be an unreliable approximation and has been superceded by the self-consistent form of the LCAO theory. A perturbation theory analogous to that of Coulson and Longuet-Higgins is therefore needed in this new context. Self-consistent perturbation theories based on the Hartree-Fock equations have been developed earlier [*8, 14*] and some applications to conjugated systems have been made [*4, 9, 15*].

In this paper we describe an iteration method for the direct calculation of first and second order changes in the bond order matrix, the total energy, the various molecular orbitals and their energies produced by a perturbation which is the sum of one-electron operators. The method is used to compute atom-atom polarizabilities for a number of hydrocarbons. These polarizabilities should be of direct use in discussions of the shifts of charge when a heteroatom is substituted into one of these hydrocarbons. We have used them to discuss the spin densities of hydrocarbon ions and the relative susceptibilities of the different atoms to attack by free radicals.

Self-consistent perturbation theory can also be used to discuss such topics as electric polarizabilities of conjugated molecules and the spectra of heteromolecules. Some of these topics will be taken up in following papers.

2. Perturbation by One-Electron Operators

In the molecular orbital theory the ground state of a conjugated molecule is represented by a determinant of doubly occupied orbitals. Such a wave function is stable with respect to perturbations which are the sum of one-electron operators [*5*] and consequently the perturbed wave function can be represented, to the same approximation, as a determinant of perturbed molecular orbitals. The first and higher order corrections to the original molecular orbitals can be obtained by applying perturbation theory to the molecular orbital equations.

If the molecular orbitals are expressed as linear combinations of atomic orbitals ω_r,

$$\psi_i = \sum \omega_r \, a_{ir}$$

the equations determining the $\{a_{ir}\}$ and the orbital energies E_i will be [*6*, *16*]

$$\sum_s (F_{rs} - E_i \, S_{rs}) \, a_{is} = 0 \tag{2.1}$$

where

$$S_{rs} = \int \omega_r^* \, \omega_s \, d\tau \tag{2.2}$$

$$F_{rs} = h_{rs} + \tfrac{1}{2} \sum_{ut} P_{ut} \, \{2(tr \mid us) - (tr \mid su)\} \tag{2.3}$$

and

$$(tu \mid rs) = \int \omega_t^* (1) \, \omega_u^* (2) \frac{1}{r_{12}} \omega_r (1) \, \omega_s (2) \, d\tau_{12}$$

$$h_{rs} = \int \omega_r^* \left(-\tfrac{1}{2}\nabla^2 - \sum_a z_\alpha / r_\alpha \right) \omega_s \, d\tau \, . \tag{2.4}$$

The charge density and bond order matrix $\boldsymbol{P}$ is defined by

$$P_{rs} = 2 \sum_{\substack{\text{occupied} \\ \text{orbitals}}} a_{ir} \, a_{is}^* \tag{2.5}$$

and is related to the spinless first order density matrix for the unperturbed molecule by

$$P_1 (1, 1') = \sum_{rs} P_{sr} \, \omega_r^* (1) \, \omega_s (1') \, . \tag{2.6}$$

The one electron operators in the Hamiltonian will be changed in the perturbed equations by an amount

$$\lambda \sum_i \mathscr{L} (i)$$

so that the effect of the perturbation is to change h_{rs} to $h_{rs} + \lambda z_{rs}$ where

$$z_{rs} = \int \omega_r^* \mathscr{L} \omega_s \, d\tau \,. \tag{2.7}$$

The first order change in F_{rs} will not be simply z_{rs} for there will be first order changes in P_{rs} which must be included.

To proceed further, therefore, we write all our quantities as power series in the perturbation parameter λ. Including terms up to second order we have

$$F_{rs} = F^0_{rs} + \lambda F'_{rs} + \lambda^2 F''_{rs} \tag{2.8}$$

$$a_{ir} = a^0_{ir} + \lambda a'_{ir} + \lambda^2 a''_{ir} \tag{2.9}$$

$$P_{rs} = P^0_{rs} + \lambda P'_{rs} + \lambda^2 P''_{rs} \tag{2.10}$$

$$E_i = E^0_i + \lambda E'_i + \lambda^2 E''_i \tag{2.11}$$

and by substituting in (2.3) and (2.5) we obtain

$$F^0_{rs} = h_{rs} + \tfrac{1}{2} \sum_{ut} P^0_{ut} \{2\,(tr \mid us) - (tr \mid su)\} \tag{2.12a}$$

$$F'_{rs} = z_{rs} + \tfrac{1}{2} \sum_{ut} P'_{ut} \{2\,(tr \mid us) - (tr \mid su)\} \tag{2.12b}$$

$$F''_{rs} = \qquad \tfrac{1}{2} \sum_{ut} P''_{ut} \{2\,(tr \mid us) - (tr \mid su)\} \tag{2.12c}$$

and

$$P^0_{rs} = 2 \sum_{\substack{\text{occupied}\\ \text{orbitals}}} a^0_{ir}\, a^{0*}_{is} \tag{2.13a}$$

$$P'_{rs} = 2 \sum_{\substack{\text{occupied}\\ \text{orbitals}}} (a^0_{ir}\, a'^*_{is} + a'_{ir}\, a^{0*}_{is}) \tag{2.13b}$$

$$P''_{rs} = 2 \sum_{\substack{\text{occupied}\\ \text{orbitals}}} (a'_{ir}\, a'^*_{is} + a^0_{ir}\, a''^*_{is} + a''_{ir}\, a^{0*}_{is}) \,. \tag{2.13c}$$

The orbitals used in the derivation of (2.1) are assumed orthonormal and this imposes restrictions on the a'_{ir} and a''_{ir} .In particular we have that

$$\sum_{rs} a^{0*}_{ir}\, S_{rs}\, a'_{is} = 0 \qquad \text{all } i \,. \tag{2.14}$$

By substituting Eq. (2.11), 2.12) and (2.13) into (2.1) we obtain the equations determining the coefficients a^0_{ir}, a'_{ir}, a''_{ir}. These are

$$\sum_r (F^0_{sr} - S_{sr} E^0_i)\, a^0_{ir} = 0 \tag{2.15a}$$

$$\sum_r (F^0_{sr} - S_{sr} E^0_i)\, a'_{ir} = \sum_r (E'_i\, S_{sr} - F'_{sr})\, a^0_{ir} \tag{2.15b}$$

$$\sum_r (F^0_{sr} - S_{sr} E^0_i)\, a''_{ir} = \sum_r (E'_i\, S_{sr} - F'_{sr})\, a'_{ir} + \sum_r (E''_i\, S_{sr} - F''_{sr})\, a^0_{ir} \,. \tag{2.15c}$$

Note that Eq. (2.15b) is linear in the a'_{ir} which implies that the value of a'_{ir} due to two perturbations acting simultaneously is the sum of the a'_{ir} due to each perturbation acting by itself. From (2.15b) and (2.15c) the relations

$$E'_i \sum_{rs} a^{0*}_{is}\, S_{sr}\, a^0_{ir} = \sum_{rs} a^{0*}_{is}\, F'_{sr}\, a^0_{ir} \tag{2.16a}$$

and

$$E''_i \sum_{rs} a^{0*}_{is}\, S_{sr}\, a^0_{ir} = \sum_{rs} a^{0*}_{is}\, (F''_{st}\, a^0_{ir} + F'_{sr}\, a'_{ir} - E'_i\, S_{sr}\, a'_{ir}) \tag{2.16b}$$

can be obtained.

3. Iterative Solution of the Equations

Although (2.15b) and (2.15c) are linear equations they involve all the unknown coefficients simultaneously and so it is much simpler to solve them iteratively. A straightforward way of solving them would be as follows:

(i) Calculate F^0_{rs} and the a^0_{ir} in the usual way.

(ii) Guess the first order corrections to the orbitals, a'_{ir}.

(iii) From these form the P'_{rs} and F'_{rs}. [Alternatively (ii) may be omitted and P'_{rs} guessed instead].

(iv) For each occupied orbital i find E'_i from (2.16a) and substitute in (2.15b) to find an improved set of a'_{ir}. Note that (2.15b) may be written in matrix form

$$(\boldsymbol{F}^0 - E^0_i\,\boldsymbol{S})\,\boldsymbol{a}'_i = (E'_i\,\boldsymbol{S} - \boldsymbol{F}')\,\boldsymbol{a}^0_i \tag{3.1}$$

from which is obtained

$$\boldsymbol{a}'_i = (\boldsymbol{F}^0 - E'_i\,\boldsymbol{S})^{-1}\,(E^0_i\,\boldsymbol{S} - \boldsymbol{F}')\,\boldsymbol{a}^0_i\,. \tag{3.2}$$

Since E^0_i satisfies the equation $|\,\boldsymbol{F}^0 - E^0_i\,\boldsymbol{S}\,| = 0$ (3.1) can only be solved subject to the condition (2.14). In practice equation (2.14) needs to be substituted for one of the equations in (3.1). This substitution must be asssumed if the expression involving the inverse matrix in (3.2) is to be properly defined. If there is degeneracy among the E^0_i there is a further difficulty in solving (3.1) and the proper zero order orbitals must be chosen and the problem treated as it is when degeneracy occurs in ordinary perturbation theory.

(v) Once the new set of orbitals $\boldsymbol{a}'_i$ have been found the whole process must be repeated until they are consistent.

The main difficulty with the above procedure is that for each occupied orbital i a different matrix has to be inverted to substitute in (3.2). This can be avoided by applying an idea used in ordinary perturbation theory. Suppose, for convenience, that the atomic orbitals are orthonormal. If they are not, as when Slater orbitals are used, they can be made so with Löwdin's procedure [*10*]. When this is done $\boldsymbol{S}$ becomes the unit matrix $\boldsymbol{I}$. The zero order orbitals and orbital energies will then be the eigenvectors and eigenvalues of $\boldsymbol{F}^0$. The unitary matrix $\boldsymbol{U}$ which is formed from these eigenvectors will diagonalize $\boldsymbol{F}^0$.

Multiplying (3.1) on the left by $\boldsymbol{U}^\dagger$ and writing $\boldsymbol{b}'_i$ for $\boldsymbol{U}^\dagger\,\boldsymbol{a}'_i$ gives

$$(E^0_j - E^0_i)\,(\boldsymbol{b}'_i)_j = -\,(\boldsymbol{U}^\dagger\,\boldsymbol{F}'\,\boldsymbol{U})_{ji} \qquad i \neq j$$

so that

$$(\utilde{\boldsymbol{b}}'_i)_j = \frac{(\utilde{\boldsymbol{U}}^\dagger\;\utilde{\boldsymbol{F}}'\;\utilde{\boldsymbol{U}})_{ji}}{E^0_i - E^0_j} \qquad j \neq i \tag{3.3}$$

while (2.14) implies that $(\boldsymbol{b}'_i)_i = 0$.

These expressions can be used to find the $\boldsymbol{b}'_i$ very quickly without having to invert matrices. The matrix $\boldsymbol{P}'$ can then be found from the relations

$$\boldsymbol{P}' = 2(\boldsymbol{q} + \boldsymbol{q}^\dagger)$$

where

$$\boldsymbol{q} = \boldsymbol{U}\,\boldsymbol{r}\,\boldsymbol{U}^\dagger \tag{3.4}$$

and

$$r_{ij} = (\boldsymbol{b}_i)_j^* \text{ if } i \text{ is an occupied orbital}$$
$$= 0 \qquad \text{otherwise}.$$

Our experience with using an electronic computer to solve these equations has been that (3.3) and (3.4) lead to saving in time both in programing and computing. Even so a fair number of iterations are usually needed for convergence although naturally this depends on how good the choice of starting orbitals is. The rate of convergence can be accelerated by employing an extrapolation formula such as that found useful in HALL and HARDISSON's work in a similar context [7]. As a practical point, however, we have found it better to let the iterations settle down a little before using the extrapolation formula since otherwise a bad choice of starting orbitals can lead to some trouble.

4. The Total Energy

The total energy W for the ground state is given by the formula

$$W = \tfrac{1}{2} \sum_{rs} P_{sr} (F_{rs} + h_{rs}) . \tag{4.1}$$

Expressing W as a power series in λ i.e.

$$W = W^0 + \lambda W' + \lambda^2 W'' + \ldots \tag{4.2}$$

we can obtain the first order and second order corrections as

$$W' = \tfrac{1}{2} \sum_{rs} (F^0_{rs} + h_{rs}) P'_{sr} + \tfrac{1}{2} \sum_{rs} (F'_{rs} + z_{rs}) P^0_{sr} = \sum_{rs} z_{rs} P^0_{sr} \tag{4.3}$$

and

$$W'' = \tfrac{1}{2} \sum_{rs} P''_{sr} (F^0_{rs} + h_{rs}) + \tfrac{1}{2} \sum_{rs} P'_{sr} (F'_{rs} + z_{rs}) + \tfrac{1}{2} \sum_{rs} P^0_{sr} F''_{rs} = \tfrac{1}{2} \sum_{sr} z_{rs} P'_{sr} \tag{4.4}$$

so that W' depends only on the zero order $\boldsymbol{P}^0$ and W'' only on the first order $\boldsymbol{P}'$.

5. Atom-Atom Polarizabilities of Conjugated Molecules

For π electron systems the Pariser-Parr-Pople schemes enable the expressions for $\boldsymbol{F}^0$ and $\boldsymbol{F}'$ to be simplified to

$$F^0_{rs} = \beta_{rs} + \delta_{rs} \sum_u P^0_{uu} \gamma_{ur} - \tfrac{1}{2} P^0_{rs} \gamma_{rs}$$

$$F'_{rs} = z_{rs} + \delta_{rs} \sum_u P'_{uu} \gamma_{ur} - \tfrac{1}{2} P'_{rs} \gamma_{rs}$$

where the $\{\gamma_{rs}\}$ are the usual Pariser-Parr integrals and

$$\beta_{rr} = - \sum_{u \neq r} \gamma_{ur}$$

$$\beta_{rs} = 0.5\, \beta \qquad \text{if } r, s \text{ refer to neighbouring atoms}$$
$$= 0 \qquad \text{otherwise.}$$

The overlap matrix $\boldsymbol{S}$ is assumed to be the unit matrix. In the calculations presented in this paper the integrals were given the values $\gamma_{rr} = - 2.301\, \beta$ and $\gamma_{rs} = - 1.485\, \beta$ where r and s refer to neighbouring atoms and $\beta = - 4.78$ eV. The remaining integrals were computed using the method described by SNYDER and AMOS [*17*].

The atom-atom polarizabilities π_{ur} have been defined for Hückel perturbation theory by COULSON and LONGUET-HIGGINS [*2*] and represent the changes in the charge of the rth atom due to a perturbation at the uth atom of $\lambda z_{uu} = \beta$. In the self-consistent case we have the analogous definition that $\pi_{ur} = P'_{rr}$ when $z_{vt} = \beta$, $v = t = u$ and $z_{vt} = 0$ otherwise. Similarly the self-consistent bond-atom polarizabilities and bond-bond polarizabilities can be defined but they are not so important as the atom-atom polarizabilities.

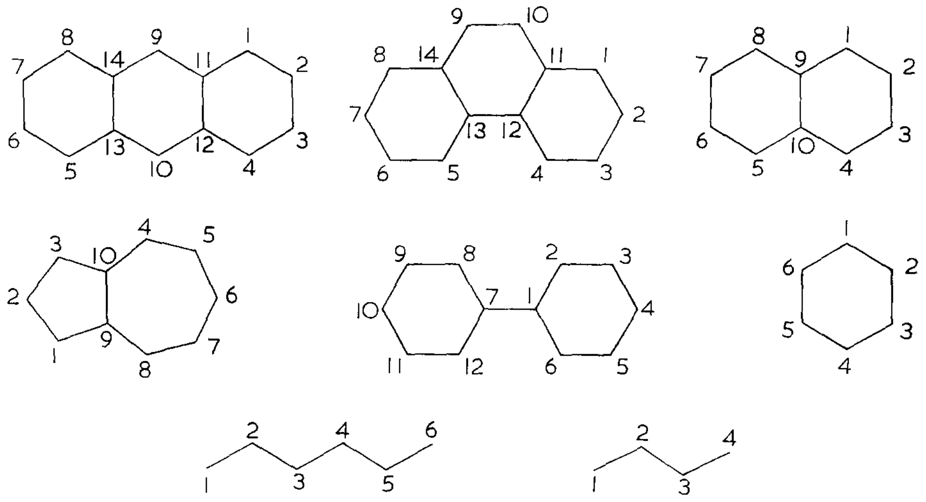

Fig. 1. Molecules considered in this paper

Table 1. *Self-consistent atom-atom polarizabilities* π_{ur}

	u
r	1
1	.560
2	−.276
3	.054
4	−.116

Benzene

	u	
r	1	2
1	.601	−.478
2	−.478	.513
3	−.003	−.031
4	−.120	−.003

Butadiene

	u		
r	1	2	3
1	.620	−.471	.016
2	−.471	.513	−.050
3	.016	−.050	.552
4	−.102	−.006	−.410
5	.020	−.006	−.006
6	−.083	.020	−.102

Hexatriene

	u				
r	1	2	4	5	6
1	.607	−.292	.054	−.075	.044
2	−.292	.588	−.075	.047	−.071
3	.065	−.292	.018	−.082	.044
4	.054	−.075	.623	−.307	.078
5	−.075	.047	−.307	.617	−.305
6	.044	−.071	.078	−.305	.615
7	−.082	.047	−.111	.084	−.305
8	.018	−.075	.054	−.111	.078
9	−.236	.061	−.087	.056	−.089
10	−.104	.061	−.247	.077	−.089

Azulene

	u	
r	1	2
1	.595	−.345
2	−.345	.569
3	.064	−.225
4	−.150	.064
5	.008	.010
6	.010	−.036
7	−.017	.007
8	−.023	−.017
9	−.176	.043
10	.034	−.071

Naphthalene

Table 1 (Continued)

r	u 2	3	4
1	−.255	.048	−.113
2	.590	−.285	.063
3	−.285	.567	−.277
4	.063	−.277	.576
5	−.115	.054	−.277
6	.054	−.115	.063
7	.005	.014	.018
8	−.051	.003	−.014
9	.003	−.007	−.004
10	−.014	−.004	−.017
11	.006	−.004	−.004
12	−.002	.006	−.014

Diphenyl

r	u 1	2	9
1	.598	−.362	−.020
2	−.362	.570	−.029
3	.066	−.207	.013
4	−.157	.066	.006
5	.001	.001	.006
6	.001	−.015	.013
7	−.005	−.004	−.029
8	−.002	−.005	−.020
9	−.020	−.029	.647
10	.006	.013	−.199
11	−.146	.037	−.234
12	.024	−.055	.041
13	.009	−.020	.041
14	−.011	.011	−.234

Anthracene

r	u 1	2	3	4	10
1	.595	−.323	.064	−.137	−.023
2	−.323	.572	−.245	.063	−.004
3	.064	−.245	.575	−.319	.015
4	−.137	.063	−.319	.594	.013
5	.011	−.012	.010	−.049	.005
6	−.010	−.002	−.018	.010	−.042
7	.001	−.015	−.002	−.012	.005
8	−.011	.001	−.010	.011	−.021
9	−.021	.005	−.042	.005	−.400
10	−.023	−.004	.015	.013	.585
11	−.207	.047	−.088	.040	−.135
12	.041	−.088	.051	−.214	.031
13	.007	.015	−.003	.000	−.079
14	.011	−.014	.012	−.005	.048

Phenanthrene

We have calculated atom-atom polarizabilities for the hydrocarbons shown in Fig. 1. All C–C bond lengths were assumed to be 1.4 Å and all angles 120° except for azulene whose rings were taken to be regular polygons. The molecules were all taken as planar although this is rather a bad approximation for diphenyl.

The values of the π_{ur} are given in Tab. 1. The overall pattern agrees quite well with previous calculations [*4*, *9*, *15*] although the numerical values differ slightly due to different values of the Pariser and Parr integrals. The self consistent atom-atom polarizabilities are generally much larger than the corresponding Hückel ones and some of the characteristic properties of Hückel polarizabilities — such as, for example, the alternation in sign — are no longer to be found in the self consistent ones.

6. Applications

In this section we consider three rather simple applications of the perturbation method. Further applications will be dealt with in future papers.

Firstly we have considered the charge distribution in a benzene ring due to the inductive effect of a heteroatom substituted for the C–H bond at position 1. We have assumed that the presence of the hetero-atom can be represented completely by changing the value of h_{rr} in Eq. (2.3). This change is then represented by a perturbation λz_{11}. We have computed the charge distribution for several values of λ ($z_{11} \equiv \beta$) using both the perturbation method taken to first order and the exact method in which the original LCAO equations are solved again. The results are given in Tab. 2. The table shows clearly that for values of $|\lambda|$ up to about 0.5 second order perturbation theory gives results which are almost identical to the exact calculations. Beyond this point the two treatments begin to diverge presumably because third order effects become important. Even so, when $\lambda \simeq \pm 1$ the overall charge distributions predicted by the two methods are qualitively similar although the quantitative agreement is no longer very good.

Table 2. *Comparison of Charges Calculated by Accurate and Perturbation Methods for monosubstituted Benzene*

λ	± 0.1		± 0.3		± 0.5		± 0.75		± 1.0	
	P	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*
q_1	.056	.057	.168	.168	.280	.275	.420	.399	.560	.507
q_2	.028	.028	.083	.083	.138	.136	.207	.196	.276	.249
q_3	.005	.006	.016	.016	.027	.027	.040	.039	.054	.049
q_4	.012	.012	.035	.035	.058	.058	.087	.084	.116	.108

q_1, q_2, q_3, q_4 are the charges at atoms 1, 2, 3, 4.
$P \equiv$ perturbation method; $E \equiv$ exact calculation. The signs of q_1 and q_3 are the same as that of λ and the signs of q_2 and q_4 opposite to that of λ.

As well as changing h_{rr} to allow for the substituent at the rth atom it seems likely that γ_{rr} should be changed and probably also the values of β_{rs} and γ_{rs} for the bonds between the substituent and the nearest neighbour carbon atoms. In so far as these change the off-diagonal elements of F_{rs} they will not change the charge densities to first order. However, if we expand the γ_{rs} in terms of the parameter λ and substitute into the diagonal elements of F^0 and F' we obtain

$$\begin{aligned} F^0_{ss} &= \beta^0_{ss} + \sum_u P^0_{uu}\gamma^0_{us} - \tfrac{1}{2} P^0_{ss}\gamma^0_{ss} \\ F'_{ss} &= z_{ss} + \sum_u P'_{uu}\gamma^0_{us} - \tfrac{1}{2} P'_{ss}\gamma^0_{ss} + \sum_{u\neq s}(P^0_{uu}-1)\gamma'_{us} + \tfrac{1}{2} P^0_{ss}\gamma'_{ss} \end{aligned} \qquad (6.1)$$

so that the variation in the γ_{rs} can be allowed for by replacing the perturbation z_{ss} by

$$z_{ss} + \sum_{u\neq s}(P^0_{uu}-1)\gamma'_{us} + \tfrac{1}{2} P^0_{ss}\gamma'_{ss}\,. \qquad (6.2)$$

For alternant hydrocarbons this simplifies to

$$z_{ss} + \tfrac{1}{2}\gamma'_{ss} \qquad (6.3)$$

since $P^0_{uu} \equiv 1$ all u. Also since z_{ss} and γ'_{ss} will be zero except at the substituted atom, the change in the Coulomb integral can be allowed for either by changing z_{rr} or by leaving this alone and changing λ. For example the work of McWeeny and Peacock [*13*] on nitrogen heterocyclics suggests that with z_{rr} at the substituent equal to β, λ will equal 0.35. With this value of λz_{rr} they change γ_{rr} by approximately $-0.30\,\beta$ so that γ'_{rr} $-0.86\,\beta$. Therefore we can either set $\lambda = 0.35$ and $z_{rr} = 0.57\,\beta$ or $\lambda = 0.20$ and $z_{rr} = 1.0\,\beta$, in both cases thus allowing for the variation in γ_{rr}.

As a second application we have considered the spin density distribution in the negative ions of naphthalene and anthracene. It is well known that the simplest treatments of this problem lead to computed spin density distributions which are not very satisfactory. McLachlan has introduced a most convenient approximate method for calculating spin densities which agree quite well with experiment [*12*]. The formula obtained by McLachlan for the spin density at the rth carbon atom is

$$\varrho_r = c_{or}^2 - M \sum_s \pi_{rs}^h c_{os}^2 \tag{6.4}$$

where the $\{c_{os}\}$ are the Hückel coefficients of the lowest unoccupied orbital in the ground state and π^h_{rs} are the Hückel atom-atom polarizabilities. The parameter M was given an empirical value between 1.0 and 1.2.

Table 3. *Comparison of Spin-densities Calculated by McLachlan's Method and Experiment*

Molecule	Atom	Calculated McLachlan	Calculated This paper	Experimental
Naphthalene	1	.222	.209	.203
	2	.047	.054	.076
	9	−.037	−.027	(−.058)
Anthracene	1	.118	.108	.113
	2	.032	.040	.064
	9	.256	.235	.230
	11	−.028	−.015	(−.042)

Work by Snyder and Amos [*17*] implies that an equivalent formula holds if the Hückel coefficients and polarizabilities are replaced by self-consistent ones provided M is given a value between $\frac{1}{3}$ and $\frac{2}{3}$. Setting $M = \frac{1}{2}$ we have computed ϱ_r for naphthalene and anthracene from (6.4) using self consistent values for the c_{os} and π_{rs}. The results are given in Tab. 3 and for comparison the results of McLachlan's original calculation using Hückel parameters and the 'experimental' values obtained from e.s.r. hyperfine splitting data [*1*] via the McConnell relation [*11*] are also included. Our new values agree reasonably well with experiment and are slightly better than McLachlan's Hückel ones. They could probably be further improved by a different choice of M coupled with the use of a more elaborate relation to obtain the 'experimental' spin densities from the e.s.r. data.

A rather naive approach to chemical reactivity suggests that the most reactive site in a molecule with respect to an attacking positive reagent is that with the largest charge density q_r. For alternant hydrocarbons $q_r = 0$ at all positions so that the next measure of reactivity will be the auto polarizabilities π_{rr}. In fact the Hückel polarizabilities do correlate reasonably well with experimental evidence of reactivity so it is interesting to examine it self consistent polarizabilities are equally successful. In Tab. 4 we include the reactivity constants for electrophilic aromatic substitution taken from a table of results obtained by Streitwieser [18] from a consideration of the available experimental evidence and these experimental reactivities may be compared with the Hückel and self-consistent auto polarizabilities. Unfortunately the experimental results are not accurate enough to enable any general conclusions to be drawn. Both the Hückel and self-consistent autopolarizabilities seem able to distinguish between very reactive and very unreactive positions and this is probably all that can be expected. There are, however, some anomalies namely the 2 position of anthracence, the 4 position of phenanthrene and the 2 and 4 positions of diphenyl. The last three are almost certainly due to steric effects and the fact that diphenyl is not planar casts some doubts on the theoretical values of π_{rr} for this molecule. The 2 position of anthracene is rather more puzzling and further experimental data on this would be welcome.

Table 4. *Index of Chemical Reactivity versus Autopolarizabilities*

Hydrocarbon	Position	Experimental Reactivity[a]	Auto-Polarizabilities[a]	
			S.C.F.	Hückel
Benzene	1	−7.8	−.035	−.045
Naphthalene	1	0	0	0
	2	−3.4	−.026	−.038
Anthracene	1	1.1	+.003	+.011
	2	0	−.025	−.032
	9	8.1	+.052	+.083
Phenanthrene	1	−0.2	0	−.004
	2	−2.5	−.023	−.040
	3	−0.5	−.020	−.034
	4	−2.7	−.001	−.014
	9	0.5	−.010	−.001
Diphenyl	2	−1.7	−.005	−.019
	4	−1.7	−.019	−.032

[a] Relative to the 1-position of naphthalene.

References

[1] Carrington, A., F. Dravnieks, and M. C. R. Symons: J. chem. Soc. 947 (1959).

[2] Coulson, C. A., and H. C. Longuet-Higgins: Proc. Roy. Soc. **A 191**, 39; **A 192**, 16 (1947); **A 193**, 447 (1948).

[3] Daudel, R., R. Lefebvre, and C. Moser: Quantum chemistry, methods and applications. New York: Wiley (Interscience) 1959.

[4] Greenwood, H. H., and T. H. J. Hayward: Mol. Physics **3**, 495 (1960).

[5] Hall, G. G.: Philos. Mag. **6**, 249 (1961).

[6] — Proc. Roy. Soc. **A 205**, 541 (1951).

[7] —, and A. Hardisson: Proc. Roy. Soc. **A 268**, 328 (1962).

[8] —, and J. E. Lennard-Jones: Proc. Roy. Soc. **A 202**, 155 (1950).

[9] Lefebvre, R., and C. Moser: Calcul des fonctions d'onde moleculaire, p. 109. Paris: Centre National de la Recherche Scientifique 1958.

[10] Löwdin, P.-O.: J. chem. Physics **18**, 365 (1950).

[*11*] McConnell, H. M.: J. chem. Physics **24**, 632, 764 (1956).
[*12*] McLachlan, A. D.: Mol. Physics **3**, 233 (1960).
[*13*] McWeeny, R., and T. E. Peacock: Proc. Phys. Soc. **A 70**, 41 (1957).
[*14*] Peng, H. W.: Proc. Roy. Soc. **A 178**, 499 (1941).
[*15*] Pople, J. A., and P. Schofield: Proc. Roy. Soc. **A 233**, 233, 241 (1955).
[*16*] Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
[*17*] Snyder, L. C., and A. T. Amos: J. chem. Physics **41**, 1773 (1964); **42**, 3670 (1965).
[*18*] Streitwieser, A., Jr.: Molecular orbital theory for organic chemists New York: Wiley 1961.

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