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Commentationes

Self-Consistent Perturbation Theory for Conjugated Molecules

V. Calculation of Bond Polarizabilities, Bond Lengths and Force Constants

A. T. Amos

Department of Mathematics, University of Nottingham

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Self-consistent bond polarizabilities are defined and computed for butadiene, benzene, naphthalene and anthracene. A self-consistent derivation of the bond order-bond length relationship is given and self-consistent formulae for force constants are obtained. Theoretical bond lengths for butadiene, naphthalene and anthracene are calculated in two ways; firstly by using the same values of β_{rs} and γ_{rs} for all bonds and secondly by allowing these to vary with bond length. The agreement with experiment is very satisfactory although in some respects the first set of results is to be preferred. Force constants for ethylene and benzene are found which have the correct orders of magnitude although the detailed agreement is not always very good and the interaction force constant between meta bonds in benzene is predicted to have the wrong sign.

Des polarisabilités de liaison self-consistantes sont définies et calculées pour le butadiène, le benzène, le naphtalène et l'anthracène. Une dérivation self-consistante de la relation entre l'indice de liaison et la longueur de liaison est obtenue, ainsi que des formules self-consistantes pour les constantes de force. Les longueurs théoriques des liaisons pour le butadiène, le naphtalène et l'anthracène sont calculées de deux manières: tout d'abord en utilisant les mêmes valeurs de β_{rs} et γ_{rs} pour toutes les liaisons, puis en les faisant varier avec la longueur de la liaison. L'accord avec l'expérience est très satisfaisant, quoique, d'un certain point de vue, le premier groupe de résultats doit être préféré à l'autre. Les constantes de force calculées pour l'éthylène et le benzène ont un ordre de grandeur correct quoique dans le détail l'accord ne soit pas toujours très bon et que la constante de force d'interaction entre liaisons en méta du benzène soit obtenue avec le signe contraire.

Es werden selbstkonsistente Bindungspolarisierbarkeiten definiert und für Butadiene, Benzol, Naphthalin und Anthrazen berechnet. Ebenso wird in diesem Rahmen eine Ableitung für eine Beziehung zwischen Bindungsordnung und Bindungslänge sowie ein Ausdruck für die Kraftkonstanten angegeben. Die Bindungslängen werden auf zwei Wegen berechnet: einerseits mit gleichen β_{rs} und γ_{rs} für alle Bindungen und andererseits mit Werten, die von der Bindungslänge abhängen. Letztere ergeben sich in befriedigender Weise, während bei den Kraftkonstanten in bezug auf Einzelheiten Abweichungen zu verzeichnen sind.

1. Introduction

Paper I [2] of this series described and developed a self-consistent perturbation theory for conjugated molecules. Although the theory is general enough to deal with any perturbation which is the sum of one electron terms, in I and the subsequent papers the only perturbations considered were those which changed the diagonal matrix elements of the one electron operator. In the present paper we shall extend the number of applications of the theory by considering perturbations which change the off-diagonal matrix elements corresponding to carbon-carbon bonds.

Just as it is possible to define self-consistent atom-atom polarizabilities analogous to Hückel atom-atom polarizabilities so it is possible to define self-consistent bond-bond polarizabilities which can be used to find changes in the carbon-carbon bond orders due to changes in the β_{rs} and γ_{rs} integrals between neighbouring carbons [*6*]. For example, the introduction of a heteroatom into a pure hydrocarbon will change these integrals although such changes are likely to be small and, therefore, much less important than the changes in β_{rr} and γ_{rr} at the heteroatom which were considered in papers III and IV [*1*]. A more interesting example concerns the calculation of bond orders taking into account the variations of the β_{rs} and γ_{rs} from their benzene values due to different equilibrium bond lengths.

One of the most satisfactory applications of Quantum Chemistry has been the use of bond orders to compute equilibrium bond lengths in hydrocarbons [*5*]. That there exists a relation between bond order and bond length can be proved easily for Hückel theory [*4, 8*]. A very similar proof can be given for self-consistent theory as we shall show. This involves expanding the π-electron part of the total energy as a Taylor series about the equilibrium bond lengths, which can partly be done using the expressions deduced in paper I for the first and second order terms in a perturbation expansion of the energy expression. These must, however, be slightly modified to allow for the changes in the two electron integrals γ_{rs}. The new expressions are obtained in the Appendix. The first order terms give the bond length-bond order relation while the second order terms are related to the stretching and interaction force constants so that self-consistent formulae can be obtained for these.

2. Bond Polarizabilities

Paper I [*2*] contains the equations which give the first order change $\boldsymbol{P}'$ in the bond order matrix $\boldsymbol{P}$ due to a perturbation $\boldsymbol{z}$ of the matrix elements of the one electron operators. If $z_{rs} = 0$ for all r, s except $r = s = u$ and $z_{uu} = 1$ in units of $\beta(\beta = -4.78 \text{ eV})$ then the diagonal elements of $\boldsymbol{P}'$ will be the self-consistent atom-atom polarizabilities

$$\text{i.e. } \pi_{uv} = P'_{vv} \,.$$

In a similar way the self-consistent bond polarizabilities can be defined. Suppose m and n and p and q refer to pairs of bonded carbons. If $z_{rs} = 0$ for all r and s except $r,s = m,n$ and $z_{mn} = z_{nm} = 1$ then the bond polarizabilities will be

$$\pi_{mn,pq} = P'_{pq} \,. \tag{2.1}$$

There will, of course, be other non-zero elements of $\boldsymbol{P}'$ apart from those referring to carbon-carbon bonds. However, for alternant hydrocarbons many of these are zero. For example, the diagonal elements of $\boldsymbol{P}'$ will be zero so that the atom-bond polarizabilities are zero

$$\text{i.e. } \pi_{mn,rr} = 0 \,.$$

They will not be zero for non-alternants, however.

Table 1. *Bond polarizabilities* $\pi_{mn,pq}$

Butadiene

	mn	
pq	1,2	23
12	.090	−.239
23	−.239	.636
34	.090	−.239

Benzene

	mn
pq	12
12	.507
23	−.447
34	.326
45	−.266

Naphthalene

	mn			
pq	12	23	19	9,10
12	.418	−.456	−.408	.146
23	−.456	.636	.327	−.119
34	.292	−.456	−.235	.146
56	−.078	.100	.109	.146
67	.100	−.112	−.148	−.119
78	−.092	.100	.156	.146
19	−.408	.327	.617	−.221
4.10	−.235	.327	.304	−.221
5,10	.109	−.148	−.142	−.221
8,9	.156	−.148	−.314	−.221
9,10	.146	−.119	−.221	.465

Table 1. Continued

Anthracene

	mn				
pq	12	23	1,11	9,11	11,12
12	.379	−.442	−.383	.170	.094
23	−.442	.666	.306	−.167	−.064
34	.268	−.442	−.207	.113	.094
56	−.026	.035	.037	−.082	.056
67	.035	−.044	−.053	.114	−.065
78	−.028	.035	.044	−.098	.056
1,11	−.383	.306	.638	−.348	−.151
4,12	−.207	.306	.269	−.148	−.151
5,13	.037	−.053	−.053	.116	−.085
8,14	.044	−.053	−.073	.169	−.085
9,11	.170	−.167	−.348	.590	−.275
10,12	.113	−.167	−.148	.321	−.275
10,13	−.082	.114	.116	−.251	.185
9,14	−.098	.114	.169	−.425	.185
11,12	.094	−.064	−.151	−.275	.507
13,14	.056	−.065	−.085	.185	−.079

It is sometimes useful to express the polarizabilities as partial derivatives of the bond orders with respect to the β_{rs} and γ_{rs} integrals. Clearly

$$\frac{\partial P_{pq}}{\partial \beta_{mn}} = \pi_{mn,pq} \tag{2.2}$$

and using the results of the appendix

$$\frac{\partial P_{pq}}{\partial \gamma_{mn}} = -\tfrac{1}{2} P_{mn} \pi_{mn,pq} . \tag{2.3}$$

Using the numerical method and integral values described in paper I the bond polarizabilities for butadiene, benzene, naphthalene and anthracene have been computed. The values are given in Tab. 1.

3. Series expansion of the π energy W

In order to deduce a bond order-bond length relationship and expressions for force constants in the context of the SCF method it is necessary to find the first and second order changes in W when CC bond lengths are changed from their equilibrium lengths. To do this Eqs. (A6) and (A7) of the Appendix may be used.

Any change in the CC bond lengths will change the integrals β_{rs} and γ_{rs}. We shall assume that a change in the bond length of the bond rs will change the integrals β_{rs} and γ_{rs} for that bond only and that these integrals are unique functions of the bond length of bond rs only. To make this more explicit it is convenient to use a single index to label the bonds, say i to label the bond rs, so that if R_i is the bond length

$$\beta_{rs} = \beta_i = \beta(R_i) \tag{3.1}$$

$$\gamma_{rs} = \gamma_i = \gamma(R_i) \tag{3.2}$$

and $\beta(R)$ and $\gamma(R)$ are the same functions for all bonds. It is important to notice that a sum over all indices r and s, referring to bonded carbons, equals twice the sum over all bonds i.

If a bond length changes from the equilibrium length R_i^0 to $R_i^0 + \Delta R_i$ the new values of β_i and γ_i will be given, correct to second order, by

$$\beta_i = \beta(R_i^0) + \beta'(R_i^0)\Delta R_i + \tfrac{1}{2}\beta''(R_i^0)(\Delta R_i)^2 \tag{3.3}$$

$$\gamma_i = \gamma(R_i^0) + \gamma'(R_i^0)\Delta R_i + \tfrac{1}{2}\gamma''(R_i^0)(\Delta R_i)^2 \tag{3.4}$$

where the primes denote derivatives of the functions defined by (3.1) and (3.2). Third and higher order terms for β_i and γ_i will not be needed here. Unfortunately (3.4) implies that there will also be changes in the quantity β_{ss} (see section 5 of paper I) since this is defined in terms of the γ_{rs}. It follows that

$$\beta_{ss} = \beta_{ss}^0 - \sum_i^s \gamma'(R_i^0)\Delta R_i - \tfrac{1}{2}\sum_i^s \gamma''(R_i^0)(\Delta R_i)^2 \tag{3.5}$$

where the sums are over all bonds which include the carbon atom s. Note that unlike β_i and γ_i the β_{ss} are, in general, functions of more than one of the bond lengths.

The change in W due to the changes in the β_{ss}, β_i and γ_i is obtained by using (A6) and (A7) with the following expressions for z_{rs}:

$$\begin{aligned} z_{ss} &= -\sum_i^s \gamma'(R_i^0)\Delta R_i - \tfrac{1}{2}\sum_i^s \gamma''(R_i^0)(\Delta R_i)^2 \\ z_i &= \beta'(R_i^0)\Delta R_i + \tfrac{1}{2}\beta''(R_i^0)(\Delta R_i)^2 \\ z_{tu} &= 0 \text{ otherwise} . \end{aligned} \tag{3.6}$$

Values for $g'(tr,us)$ are also needed. Except for $g'(sr,rs)$ and $g'(sr,sr)$ where s and r are bonded carbons they will be zero. The non-zero values are

$$\begin{aligned} g'(sr,sr) &= 2\gamma'(R_i^0)\,\Delta R_i + \gamma''(R_i^0)\,(\Delta R_i)^2 \\ g'(sr,rs) &= -\gamma'(R_i^0)\,\Delta R_i - \tfrac{1}{2}\gamma''(R_i^0)\,(\Delta R_i)^2 . \end{aligned} \tag{3.7}$$

If the final result is written in the form

$$W = W^0 + \sum_i W_i'\,\Delta R_i + \tfrac{1}{2}\sum_{i,j} W_{ij}''\,\Delta R_i\,\Delta R_j \tag{3.8}$$

then the expression for the W_i' is quite compact:

$$W_i' = c_i\,\gamma'(R_i^0) + 2P_i^0\,\beta'(R_i^0) - \tfrac{1}{2}(P_i^0)^2\,\gamma'(R_i^0) \tag{3.9}$$

where, if i is the bond rs,

$$c_i = P_{rr}^0\,P_{ss}^0 - P_{rr}^0 - P_{ss}^0 .$$

For alternants $P_{rr}^0 = P_{ss}^0 = 1$ so that

$$W_i' = -\gamma'(R_i^0) + 2P_i^0\,\beta'(R_i^0) - \tfrac{1}{2}(P_i^0)^2\,\gamma'(R_i^0) . \tag{3.10}$$

The expressions for W_{ij}'' are very complex especially for non-alternants. Therefore, we shall give them only for alternants since these are the only molecules to which they will be applied in this paper. The results are

$$\begin{aligned} W_{ii}'' = &-\gamma''(R_i^0) + 2P_i^0\,\beta''(R_i^0) - \tfrac{1}{2}(P_i^0)^2\,\gamma''(R_i^0) + \\ &+ 2[\beta'(R_i^0) - \tfrac{1}{2}\,P_i^0\,\gamma'(R_i^0)]^2\,\pi_{i,i} \end{aligned} \tag{3.11}$$

and

$$W_{ij}'' = 2[\beta'(R_i^0) - \tfrac{1}{2}\,P_i^0\,\gamma'(R_i^0)]\,[\beta'(R_j^0) - \tfrac{1}{2}\,P_j^0\,\gamma'(R_j^0)]\,\pi_{i,j} \tag{3.12}$$

where if i is the bond r,s and j the bond t,u, $\pi_{i,i} = \pi_{rs,rs}$ and $\pi_{i,j} = \pi_{rs,tu}$.

4. Bond Order-Bond Length Relations

To derive the bond order-bond length relationship the usual methods will be followed (see, for example, [*11*, *15*]) except that the SCF expression for the changes in W will be used. It will be assumed that the σ-electron energy is the sum of independent contributions from the CC bonds

$$F = \sum_i f(R_i) \tag{4.1}$$

where $f(R)$ is some unique function. Expanding to second order for changes from equilibrium lengths gives

$$F = \sum_i f(R_i^0) + \sum_i f'(R_i^0)\,\Delta R_i + \tfrac{1}{2}\sum_i f''(R_i^0)\,(\Delta R_i^0)^2 . \tag{4.2}$$

The total energy E will be the sum of F and W [Eq. (3.8)] so that the first order correction to E will be

$$\sum_i [f'(R_i^0) + c_i\,\gamma'(R_i^0) + 2P_i^0\,\beta'(R_i^0) - \tfrac{1}{2}(P_i^0)^2\,\gamma'(R_i^0)]\,\Delta R_i . \tag{4.3}$$

The condition that the R_i^0 are the equilibrium bond lengths is that (4.3) should be zero for any changes ΔR_i. This means that for all the bonds i,

$$f'(R_i^0) + c_i\,\gamma'(R_i^0) + 2P_i^0\,\beta'(R_i^0) - \tfrac{1}{2}(P_i^0)^2\,\gamma'(R_i^0) = 0 . \tag{4.4}$$

Since f, γ and β are unique functions of R_i Eq. (4.4) implies that there is a relation between R_i^0 and P_i^0 i.e. the bond order-bond length relation. To find the actual form of this relation f, γ and β need to be known explicitly as functions of R_i. More recent work, however, has tended to prefer empirical bond order-bond length relationships which can then be used in conjunction with (4.4) to express f in terms of γ and β [*5, 11, 15*]. An example of this for alternants, is the linear relation

$$R_i^0 = 1.517 - 0.180\, P_i^0 \tag{4.5}$$

(where R_i^0 is in Å) suggested by Coulson and Gołebiewski [*5*]. However, if $f(R_i)$ is assumed to have parabolic form and $\beta'(R_i)$ and $\gamma'(R_i)$ are taken to be essentially constant for the range of values of R_i which we need to consider, then, for alternants, (4.4) gives rise to the form

$$R_i^0 = A + B[P_i^0 + k(P_i^0)^2] \tag{4.6}$$

where k is $-\gamma'/4\beta'$. Except for a numerical factor in the value for k* this is a relation similar to that suggested by Binsch, Heilbronner and Murrell [*3*]. For reasons which will be discussed later we take $k = \frac{1}{8}$ and using this value and fitting the constants A and B to the experimental data for benzene and ethylene gives

$$R_i^0 = 1.505 - 0.149\, [P_i^0 + 0.125\, (P_i^0)^2]\,. \tag{4.7}$$

With the values normally obtained for P_i^0 there is little to choose between (4.7) and (4.5). This is shown in Tab. 2 where we have used the values of the P_i^0 for the various bonds in butadiene, naphthalene and anthracene to compute R_i^0 using both (4.5) and (4.7). There is very little difference between the two sets of values and both sets agree quite well with experiment. It is, however, worth pointing out that as $P_i^0 \to 0$, R_i^0 should tend to the bond length of a pure $sp^2 - sp^2$ single bond. Eq. (4.7) predicts this to be 1.505 Å which is probably fairly close to the correct value while (4.5) gives a value of 1.517 Å which is probably too large.

Although the agreement between the calculated and experimental bond lengths in Tab. 2 is quite good it is interesting to investigate one way in which it might be improved still further. It should be noted that the values of the P_i^0 given in Tab. 2 are SCF values computed on the assumption that the γ_i and β_i are the same for every bond. Since they are not an improvement might be obtained by recalculating the bond orders allowing for the variations in γ_i and β_i. To do this γ_i and β_i have to be written explicitly as functions of R. Since the expressions which have been given in the literature vary considerably and are usually rather complicated we shall simplify by taking only the first two terms of a Taylor series using the Pariser and Parr values of γ_i and β_i for benzene to fix two of the constants. This gives

$$\beta_i(R_i) = 0.5 + g(R_i - 1.397) \tag{4.8}$$

$$\gamma_i(R_i) = -1.485 + h(R_i - 1.397) \tag{4.9}$$

where the units of energy are those of $\beta = -4.78$ eV and of length Å. Clearly g and h equal the values of $\beta_i'(R_i)$ and $\gamma_i'(R_i)$ at the benzene equilibrium bond length and so the more complicated expressions given in the literature can be used to

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* This is due to the fact that in Ref. [*3*] W is taken to be twice the sum of the orbital energies for the occupied orbitals.

Table 2. *Comparison of Experimental and Theoretical Bond Lengths in Å*

Molecule	Bond	Experimental		Calculated with fixed γ_i and β_i			Calculated with variable γ_i and β_i	
		X-ray	Electron diffraction	$P^0{}_i$	$R_i(A)$	$R_i(B)$	$P^0{}_i + P'{}_i$	$R_i(A)$
Butadiene	1—2		1.337[a]	0.936	1.349	1.349	0.961	1.344
	2—3		1.483	0.352	1.454	1.450	0.286	1.466
Naphthalene	1—2	1.364[b]	1.371[c]	0.748	1.382	1.383	0.773	1.378
	2—3	1.415	1.412	0.581	1.413	1.412	0.549	1.418
	1—9	1.421	1.422	0.533	1.421	1.420	0.513	1.425
	9—10	1.418	1.420	0.553	1.418	1.417	0.586	1.412
Anthracene	1—2	1.368[b]	1.390[c]	0.770	1.378	1.379	0.811	1.371
	2—3	1.419	1.419	0.553	1.418	1.417	0.500	1.427
	1—11	1.436	1.420	0.499	1.427	1.426	0.458	1.435
	9—11	1.399	1.404	0.612	1.407	1.407	0.624	1.405
	11—12	1.428	1.425	0.510	1.425	1.424	0.529	1.422

Note that $R_i(A)$ are calculated using (4.5) and $R_i(B)$ using (4.7).

Experimental references:

[a] Almenningen, Bastiansen, and Traetteberg: Acta Chem. Scand. **12**, 1221 (1958).

[b] Cruickshank and Sparks: Proc. Roy. Soc. **A258**, 270 (1960).

[c] Bastiansen and Skancke: Adv. chem. Physics **3**, 323 (1961).

obtain these values. For γ_i the various polynomial expressions [*13*] which have been used all give a value for $\gamma'_i(1.397)$ close to -2 eV/Å so that we can put $h = 0.42$*. The most widely used expression for β_i is a constant times the overlap integral between $2p_z$ orbitals on the two carbons i.e. $\beta_i \propto S$. For benzene this gives $\beta'_i \sim 4$ eV/Å and therefore we can put $g = -0.84$. If the relationship suggested by Ruedenberg and Mehler [*14*] and Fisher-Hjalmers [*10*], i.e. $\beta_i \propto S(1 - S)$, is used $\beta'_i \sim 2.5$ eV/Å for benzene while if (4.8) is fitted to the Pariser and Parr value of β_i for ethylene [*13*], $\beta'_i \sim 9$ eV/Å so that to some extent $g = -0.84$ represents a compromise between these two extreme values. With the choice of $h = 0.42$ and $g = -0.84$ in (4.8) and (4.9) then γ'/β' will be constant and equal to $-\frac{1}{2}$. Hence the value of k in (4.6) will be $\frac{1}{8}$ as used in (4.7).

The expressions (4.8) and (4.9) could be used directly in the computation of the bond orders. After each cycle of the iterative procedure the bond orders could be used with (4.5) or (4.6) to find the bond lengths and hence, via (4.8) and (4.9) the values of β_i and γ_i which could be used for the next cycle, the iterations proceeding until there is consistency between the P^0_i, R^0_i, γ_i and β_i. In effect this is the method chosen by Dewar and Gleicher [*9*] in their recent calculations. We prefer to calculate the SCF values for P^0_i with all the β_i and γ_i equal and then use the bond polarizabilities to find corrections to these bond orders due to the differences in the β_i and γ_i. From (A5) it follows that the correction P'_i is given by

$$P'_i = \sum_j \left[g - \tfrac{1}{2} h P^0_j(0)\right] \left[R^0_j - 1.397\right] \pi_{i,j} \qquad (4.10)$$

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* The type of expression for γ_i suggested by Mataga and Nishimoto [*12*] would give a larger value for h but it would also give values for the γ_{rs}, between non-bonded carbons, which are smaller than those we have in fact used.

where $P_j^0(0)$ is the value computed with all the γ_i and β_i equal. Obviously (4.10) must be applied several times until the values of $P_i^0 + P_i'$ and R_i^0 are consistent with respect to whichever of (4.5) and (4.7) it is desired to use. This procedure is, therefore, equivalent in practice, although not in principle, to that used by Coulson and Gołebiewski [*5*].

The results of using (4.5) and (4.10) to calculate new bond orders and bond lengths for butadiene, naphthalene and anthracene are in Tab. 2. Unfortunately it cannot be said that the new values agree with experiment any better than the old ones and the average error between theory and experiment is much the same for both sets of theoretical values. Indeed while the new bond lengths for the 1 – 2 bonds are in rather better agreement with experiment this improvement is gained only at the cost of introducing quantitative and even qualitative error in some other bonds. In particular the new lengths for the 11 – 12 bond of anthracene and 9 – 10 bond of naphthalene are shorter than the corresponding 2 – 3 bonds in disagreement with both experiment and the previous theoretical results. A similar situation is found in the work of Dewar and Gleicher [*9*]. It is, of course, quite possible that these disagreements are due to experimental error and further refinements may lead to improved agreement. It seems more likely, however, that Eqs. (4.5), (4.8) and (4.9), which, after all, are trying to include σ effects in π theory, are not sophisticated enough for that purpose but it is difficult to see how they can be significantly improved without revising the whole of π electron theory.

5. Force Constants

The interaction force constant k_{ij} between bonds i and j is defined by

$$k_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j}\,. \tag{5.1}$$

With F taking the form of (4.1) there will be no contribution from $\partial^2 F/\partial R_i\,\partial R_j$ so that

$$\begin{aligned} k_{ij} &= \frac{\partial^2 W}{\partial R_i \partial R_j} = \tfrac{1}{2}(W''_{ij} + W''_{ji}) \\ &= 2[\beta'(R_i^0) - \tfrac{1}{2} P_i^0\,\gamma'(R_i^0)]\,[\beta'(R_j^0) - \tfrac{1}{2} P_j^0\,\gamma'(R_j^0)]\,\pi_{i,j}\,. \end{aligned} \tag{5.2}$$

The stretching force constant for the bond i is defined by

$$k_i = \frac{\partial^2 E}{\partial R_i^2} \tag{5.3}$$

which from (3.8), (3.11) and (4.1) will be

$$k_i = f''(R_i^0) + W''_{ii}\,. \tag{5.4}$$

Unfortunately (5.4) involves f'', γ'' and β''. However, following along the lines of Longuet-Higgins and Salem [*21*] the bond order-bond length relationship can be used to replace the terms in f'', γ'' and β''.

If Eq. (4.5) is used this gives

$$k_i = 5.556\,[2\beta'(R_i^0) - P_i^0\,\gamma'(R_i^0)] + 2[\beta'(R_i^0) - \tfrac{1}{2} P_i^0\,\gamma'(R_i^0)]^2\,\pi_{i,i} \tag{5.5}$$

while (4.7) leads to

$$\begin{aligned} k_i = 26.846\,[4 + P_i^0]^{-1}\,[2\beta'(R_i^0) - P_i^0\,\gamma'(R_i^0)] +& \\ + 2[\beta'(R_i^0) - \tfrac{1}{2} P_i^0\,\gamma'(R_i^0)]^2\,\pi_{i,i}\,.& \end{aligned} \tag{5.6}$$

Table 3. *Force constants in benzene* (dynes/cm·10^5)

	Theory		Experiment[b] [*16*]
	Using (5.5)[a]	Using (5.6)[a]	
Stretching force constant k_{11}	7.592	7.888	5.553, 5.757
Interaction force constants[c] k_{12}	0.657	0.657	0.633, 0.430
k_{13}	−0.479	−0.479	0.113, 0.317
k_{14}	0.391	0.391	0.573, 0.370
Vibrational modes[d] $K_{A_{1g}}$	8.339	8.634	7.620, 7.620
$K_{B_{2u}}$	4.929	5.225	3.940, 5.160

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[a] Only applicable for k_{11}, $k_{A_{1g}}$, $k_{B_{2u}}$.

[b] The first values quoted correspond to the assignments of Mair and Hornig for the B_{2u} frequencies [J. chem. Physics **17**, 1236 (1949)] and the second those of Herzfeld, Ingold and Poole [J. chem. Soc. (Lond.) **1946**, 316].

[c] The bonds are numbered consecutively so that bonds 2, 3 and 4 are respectively ortho, meta and para with respect to bond 1.

[d] A_{1g} and B_{2u} are respectively the symmetric and antisymmetric stretching modes.

The experimental determination of the force constants is rather difficult. For benzene, however, a complete set of values is available [*16*] and these are compared with the theoretical values in Tab. 3. On the whole the agreement is satisfactory. The only real failure is the wrong sign for the meta interaction constant k_{13} and this is almost certainly due to σ-terms of the form $\partial^2 F/\partial R_1\,\partial R_3$ which, using the simple expression (4.1), are taken to be zero.

The force constant for the CC stretching vibration of ethylene can be computed from (5.5) or (5.6) and the results are $8.93 \cdot 10^5$ dynes/cm [from (5.5)] and $8.63 \cdot 10^5$ dynes/cm [from (5.6)]. These compare reasonably well with the smaller of the two alternative values $10.99 \cdot 10^5$ dynes/cm and $8.84 \cdot 10^5$ dynes/cm suggested by Crawford, Lancaster and Inskeep [7].

The force constants calculated using SCF theory agree with experiment almost as well, therefore, as do those calculated using Hückel theory even though in the latter calculation parameters were adjusted to give the best agreement possible.

Appendix

The purpose of this appendix is to revise the equations given in paper I in order to allow for the possibility of a change in the two electron integrals. In practice most of the equations given in paper I still hold and, in particular, of the equations given in section 2 of that paper only Eq. (2.12) need be changed. Since the two electron integrals always occur in pairs it is convenient to write

$$g(tr,us) = 2(tr,us) - (tr,su) \tag{A1}$$

and to consider the changes in $g(tr,us)$.

If we write

$$g(tr,us) = g^0(tr,us) + \lambda g'(tr,us) \tag{A2}$$

and substitute into the SCF equations, the new versions of Eqs. (2.12 a, b, c) will be

$$F^0_{rs} = h_{rs} + \tfrac{1}{2} \sum_{ut} P^0_{ut}\, g^0(tr,us) \tag{A3a}$$

$$F'_{rs} = z_{rs} + \tfrac{1}{2} \sum_{ut} P'_{ut}\, g^0(tr,us) + \tfrac{1}{2} \sum_{ut} P^0_{ut}\, g'(tr,us) \tag{A3b}$$

$$F''_{rs} = \tfrac{1}{2} \sum_{ut} P''_{ut}\, g^0(tr,us) + \tfrac{1}{2} \sum_{ut} P'_{ut} g'(tr,us)\,. \tag{A3c}$$

Eq. (A3b) shows that the equations determining the changes in the orbital coefficients $\{a'_{ir}\}$ and hence P'_{rs} will still hold provided we replace z_{rs} everywhere by $\bar{z}_{rs}$ where

$$\bar{z}_{rs} = z_{rs} + \tfrac{1}{2} \sum_{ut} P^0_{ut}\, g'(tr,us)\,. \tag{A4}$$

Eq. (A3b) remains linear in the a'_{ir} so that the effect of several perturbations is additive. The elements of $\boldsymbol{P}'$ can, therefore, be written in terms of the polarizabilities $\pi_{mn,pq}$ and we have

$$P'_{pq} = \sum_{m \leq n} \bar{z}_{mn}\, \pi_{mn,pq}\,. \tag{A5}$$

Remembering that $g(tr,us)$ represents two electron terms which must be treated differently to the one electron terms in the formula for the total energy, expressions equivalent to (4.3) and (4.4) of paper I can be deduced for the first and second order energies W' and W''. The results are

$$W' = \sum_{rs} z_{rs}\, P^0_{sr} + \tfrac{1}{4} \sum_{\substack{rs\\tu}} P^0_{ut}\, P^0_{sr}\, g'(tr,us) \tag{A6}$$

and

$$W'' = \tfrac{1}{2} \sum_{rs} \bar{z}_{rs}\, P'_{sr} = \tfrac{1}{2} \sum_{\substack{rs\\t \leq u}} \bar{z}_{rs}\, \bar{z}_{tu}\, \pi_{rs,tu}\,. \tag{A7}$$

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Dr. A. T. Amos
The University Nottingham
Department of Mathematics
Nottingham, Great Britain