Theoret. chim. Acta (Berl.) 15, 293—302 (1969)

SCF-π-Electron Calculations Using Orthogonalised Atomic Orbitals

III. An Approach to Non-Empirical Calculations

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Received June 2, 1969

SCF-LCAO-π-electron calculations are made for a number of representative hydrocarbon systems by a non-empirical variant of the Adams-Miller technique. The essential modifications introduced are: – (i) the determination of the H^0 parameters by direct calculation instead of from experimental data, and (ii) the use of a properly orthogonalised set of electron repulsion integrals. Results are considered for two different values of the one-centre repulsion integral, (pp/pp): – (a) using 11.13 eV, as derived from $(pp/pp) = I - A$, and (b) using 9.82 eV, as given by direct calculation with Saturno's operator. The latter is found overall to give significantly better values for singlet state excitation energies, and these compare quite favourably with the results of semi-empirical methods. The need for the explicit calculation of all penetration integral terms occurring in the H^0 parameters is demonstrated, and the dependence of the results on the assumed value of Z investigated. Variations arising from the choice of hydrogenic or Slater-type $2s$ orbitals for evaluating the penetration integrals are described.

Für eine Anzahl repräsentativer Kohlenwasserstoffsysteme werden mit Hilfe einer nicht-empirischen Variante der Adams-Miller-Technik SCF-LCAO-π-Elektronenrechnungen durchgeführt. Dabei werden im wesentlichen folgende Änderungen vorgenommen: (i) Die Bedingung des H^0-Parameters erfolgt durch direkte Berechnung und nicht aus experimentellen Daten. (ii) Es wird ein geeignet orthogonalisierter Satz an Elektronenwechselwirkungsintegralen benutzt. Die Ergebnisse werden für zwei verschiedene Werte des Einzentrenwechselwirkungsintegrals (pp/pp) diskutiert: (a) Aus der Beziehung $(pp/pp) = I - A$ erhält man für (pp/pp) den Wert 11,13 eV. (b) Die direkte Berechnung mit Saturno's Operator ergibt für (pp/pp) einen Wert von 9,82 eV. Mit dem letzten Wert erhält man wesentlich bessere Werte für die Anregungsenergien einfach angeregter Zustände und überaus gute Übereinstimmung mit den Ergebnissen semi-empirischer Methoden. Die Möglichkeit einer expliziten Berechnung aller Überlappungsintegrale, die in dem H^0-Parameter enthalten sind, wird gezeigt und die Abhängigkeit der Ergebnisse von dem angenommenen Z-Wert untersucht. Unterschiede, die durch die Wahl von Wasserstoff- oder Slater-Typ-$2s$-Funktionen für die Berechnung der Überlappungsintegrale entstehen, werden dargestellt.

On effectue des calculs SCF-LCAO sur les systèmes π d'un certain nombre d'hydrocarbures représentatifs dans une version non empirique de la technique de Adams-Miller. Les principales modifications introduites sont (i) la détermination des paramètres de H^0 par un calcul direct au lieu de l'utilisation de données expérimentales; (ii) l'utilisation d'un jeu convenablement orthogonalizé d'intégrales de répulsion électronique.

On considère les résultats pour 2 valeurs différentes de l'intégrale de répulsion monocentrique (pp/pp): (a) 11.13 eV, déduite de la formule $(pp/pp) = I - A$ et (b) 9,82 eV, déduite du calcul direct par l'opérateur de Saturno. Cette dernière valeur donne au total des valeurs nettement meilleures des énergies de transition singulet, qui se comparent assez bien avec les résultats des méthodes semi-empiriques. On démontre la nécessité du calcul explicite de toutes les intégrales de pénétration qui interviennent dans les paramètres H^0. On analyse la dépendance des résultats à la valeur adoptée pour Z. On décrit l'influence du choix d'orbitales $2s$ hydrogenoïdes ou du type Slater sur l'évaluation des intégrales de pénétration.

Introduction

In the first paper of this series [1] a critical analysis was made of the semi-empirical SCF-LCAO-π-electron method introduced by Adams and Miller [2], and encouraging preliminary results obtained when the H^0 parameters were evaluated non-empirically, using $Z = 3.25$. For simplicity the presumed equivalence of localised and orthogonalised repulsion integrals was then retained, but we have now refined the method by using properly orthogonalised repulsion integrals for the $\boldsymbol{H}^\lambda$ to $\boldsymbol{F}$ conversion and localised integrals for that from $\boldsymbol{H}^0$ to $\boldsymbol{H}$.

In addition we have examined alternative choices for the value of the one-centre integral. We consider especially 11.13 eV, as given empirically by $(pp/pp) = I - A$, and 9.82 eV, as calculated using the Saturno operator [3], $1/(r_1 + r_2)$ (instead of $1/r_{12}$), by which model the consequences of electron correlation can be included theoretically. Using the theoretical integral we initially approximated H^0_{pq} as a polynomial in r_{pq}, but the explicit calculation of the penetration terms was later found to be necessary.

Finally we studied the effects of small variations in Z on the H^0 parameters and on the excitation energies derived. The contributions of the penetration terms are here rather important, and for this reason the results of calculating penetration integrals using Slater 2*s* orbitals instead of the usual hydrogenic functions were also investigated.

Method

The original method of Adams and Miller [2], analysed in Part I [1], is used with two main modifications. The first of these concerns the parameters H^0_{pp} and H^0_{pq}, which are now calculated directly from the relationships [1]

$$H^0_{pp} = E_p - \sum_{r \neq p} (U^0_r : pp)$$

and

$$H^0_{pq} = \tfrac{1}{2} S_{pq}(E_p + E_q) - \tfrac{1}{2} \left\{ \sum_{r \neq p} (U^0_r : pq) + \sum_{r \neq q} (U^0_r : pq) \right\}$$

instead of being derived from experimental data [2]. In the above the two-centre Coulombic and exchange penetration integrals were evaluated using the formulae of Lofthus [4], and the three-centre exchange penetration integrals similarly in conjunction with the Mulliken approximation. The value of E_p was taken as the negative of the valence state ionisation potential for a *p* electron of an sp^2 hybridised carbon atom.

The second modification relates to the use of proper bases for the repulsion integrals required for the $\boldsymbol{H}^0 \rightarrow \boldsymbol{H}$ and $\boldsymbol{H}^\lambda \rightarrow \boldsymbol{F}$ conversions. In a localised basis (non-orthogonal atomic orbitals) the core terms, H_{pp}, H_{pq}, are related to the H^0 parameters by the equations [2]

$$H_{pp} = H^0_{pp} - \sum_{r \neq p} (pp/rr)$$

and

$$H_{pq} = H^0_{pq} - \tfrac{1}{2} \left\{ \sum_{r \neq p} (pq/rr) + \sum_{r \neq q} (pq/rr) \right\}$$

in which the repulsion integrals clearly relate to a localised basis set. The core terms in an orthogonalised basis are then obtained from the relationship

$$\boldsymbol{H}^{\lambda} = \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}}$$

when the localised atomic orbitals, χ, are transformed to an orthogonalised set, λ, according to $\lambda = \chi \boldsymbol{S}^{-\frac{1}{2}}$. The elements of the Fock matrix, $\boldsymbol{F}$, are then derived using

$$F_{pp} = H_{pp}^{\lambda} + \sum_{k} P_{kk}(pp/kk)^{\lambda} - \tfrac{1}{2} P_{pp}(pp/pp)^{\lambda}$$

and

$$F_{pq} = H_{pq}^{\lambda} - \tfrac{1}{2} P_{pq}(pp/qq)^{\lambda}$$

in which the repulsion integrals now relate to an orthogonalised basis.

In the original Adams-Miller method this distinction was ignored, but for systems up to ten atoms it proved quite feasible to construct a properly orthogonalised set of repulsion integrals using the relationship given by Chong [5],

$$(pq/rs)^{\lambda} = \sum_{k} \sum_{l} \sum_{m} \sum_{n} (kl/mn)\, S_{kp}^{-\frac{1}{2}} S_{lq}^{-\frac{1}{2}} S_{mr}^{-\frac{1}{2}} S_{ns}^{-\frac{1}{2}}$$

and we have therefore used localised and orthogonalised integrals as appropriate throughout our calculations.

Apart from the two major changes described above our method differs from that used previously [1] only in the use of a configuration interaction treatment involving all singly excited states for the calculation of the singlet transition energies.

Parameters

Since the principal object of this investigation was to approach as closely as possible to a non-empirical SCF-π-electron calculation, we have examined critically all the required parameters and procedures in order to provide adequate theoretical justification for their use. We consider them as follows: –

(a) Orbital exponent and related quantities. – Initially we adopted the Slater's rules value of $Z_{\mathrm{eff}} = 3.25 = 2\xi$; the Slater screening constants, s, minimise the total energy, via the virial theorem, using the hydrogenic approximation [6] for the kinetic energy integral, $E = \sum (Z - s)^2/n^2$. (A slightly smaller value, $Z_{\mathrm{eff}} = 3.136$, is derived [7] when the total energy is minimised using an SCF procedure with a minimum basis set of Slater-type prbitals).

The orbital energy of an electron in a $2p$ orbital on atom p, E_p, can be calculated from the total energies [6] of C and C^{+}, but the figure derived, -11.46 eV, represents a relatively small difference between two large calculated energies, and we therefore preferred the value $E_p = -11.16$ eV, as derived by Hinze and Jaffé [8] from experimental data. Our calculations showed only insignificant differences when -11.46 eV was used.

(b) H^0 parameters. – Since in this work we are using theoretical values of H_{pp}^0 and H_{pq}^0 throughout, we give first our reasons for rejecting the calculation of these values from experimental data. To begin with we repeated Adams and Miller's [2] derivation of H_{pp}^0, in which the equivalence of localised and orthogonalised repulsion integrals is assumed, and confirmed that the H_{pp}^0 vs. Z curves for ethylene and benzene cross at $Z = 2.81$. When however due allowance is made to distinguish between localised and orthogonalised quantities we find that the curves do *not* cross and that even when corrections are applied [1] for the difference between the penetration terms for ethylene and benzene the curves intersect only just above or just below $Z = 3.75$, depending on whether Slater-type or hydrogenic 2*s* orbitals are assumed for evaluating the penetration integrals. These values are manifestly too high and were therefore discarded.

Turning now to the direct calculation of the H^0 parameters it is important to consider here whether Slater-type or the conventional [9] hydrogenic 2*s* orbitals should be used for finding the penetration integrals. For our first two sets of calculations we used hydrogenic 2*s* orbitals, with $Z = 3.25$, for the penetration terms to derive H^0_{pp}, and obtained H^0_{pq} from a polynomial in r_{pq} which reproduced the H^0_{12}, H^0_{13}, and H^0_{14} calculated for benzene. All our other sets of results are though obtained by calculating the H^0_{pp} and H^0_{pq} terms by explicit evaluation of all the penetration integrals which appear, using the appropriate formulae as given by Lofthus [4].

(c) Electron repulsion integrals. – The critical quantity here is the one-centre repulsion integral, since all the others are directly derived from it. Thus the two-centre integrals were determined by the Mataga-Nishimoto [10] relationship, $(pp/qq) = 1/(a_{pq} + r_{pq})$ where $a_{pq} = 2/((pp/pp) + (qq/qq))$, and the three- and four-centre terms from these, via Mulliken's approximation. We have therefore tested two methods of obtaining the one-centre integral, first of all semi-empirically using the expression $(pp/pp) = I - A$, and secondly using the formula derived with Saturno's operator, $(pp/pp) = 2\xi/(4n + 1)$.

(i) Semi-empirical value. – The value used for (pp/pp) was 11.13 eV $= 11.16 - 0.03$, as taken from the data of Hinze and Jaffé [8].

(ii) Theoretical value. – It has long been recognised that the value derived theoretically for the one-centre integral, (pp/pp), using Slater-type orbitals, with the operator $1/r_{12}$, is substantially too high and it has recently been shown by Saturno [3] that its replacement by the operator $1/(r_1 + r_2)$ leads to a very much smaller value, 9.82 eV, when $Z = 3.25$. There are also reasons [11] for believing that this form of the operator imposes theoretically the necessary constraint to allow for the effects of electron correlation (or at least represents a lower bound for the integral), and although the values of (pp/pp) obtained are usually 1–2 eV less than the $I - A$ results it is not clear that they are therefore necessarily too low.

A fuller test of the Saturno formula by actual application was therefore carried out, and this also allows the use of the Mataga-Nishimoto approximation to be justified. Writing the operator for the two-centre situation as $1/(r_1 + r_2 + R)$ Coulson obtained [12] $(pp/qq) = 2\xi e^{2\xi R} E_{4n+2}(2\xi R)$ for the homonuclear case, and it has been shown [11] that this expression closely reproduces the values given by Mataga and Nishimoto's equation. Thus we may infer that the Mataga-Nishimoto approximation does take account of correlation effects and is therefore particularly suitable for calculations of singlet state energies. Conversely the procedure is not appropriate for triplet states, and consequently we have not carried out calculations for such states.

In our calculations with the Saturno value for the one-centre integral we have used the relationship $(pp/qq) = 0.98\ (pp/qq)_{\mathrm{MN}}$ since this adequately reproduces the purely theoretical values at the distances concerned. Also, for calculations using different Z values, the one-centre integral is varied according to $(pp/pp) = 2\xi/(4n+1)$. It is found throughout that the three- and four-centre integrals closely obey the predictions of Fischer-Hjalmars [13] when they are converted to an orthogonalised basis. All terms of the form $(pp/rs)^{\lambda}$, and $(pq/rs)^{\lambda}$ are vanishingly small and can thus be neglected in the calculations with the orthogonalised basis set.

Results and Discussion

Our principal sets of calculations have been carried out on ten compounds: – ethylene, benzene, butadiene, hexatriene, octatetraene, decapentaene, styrene, fulvene, naphthalene, and azulene. For these, three series of calculations were made with the parameters and procedures listed.

Method 1. $Z = 3.25$, $E_p = -11.16$ eV, $(pp/pp) = 11.13$ eV, hydrogenic 2s orbitals for penetration integrals, H^0_{pq} derived from polynomial, two-centre integrals obtained by the Mataga-Nishimoto equation.

Method 2. As for (1) but with $(pp/pp) = 9.822$ eV, and the two-centre integrals as 0.98 times the Mataga-Nishimoto value.

Method 3. As for (2) but with all H^0 terms calculated explicitly.

In addition other modified calculations were carried out on four compounds – butadiene, styrene, naphthalene, and azulene – which were taken as representative examples of different types of hydrocarbon – polyene, mixed polyene-aromatic, alternant hydrocarbon, and nonalternant hydrocarbon. For these compounds the methods used were as follows, the theoretical (Saturno) value of (pp/pp) being employed all through.

Method 4. As for (3) but with $Z = 3.15$ and $(pp/pp) = 9.522$ eV.

Method 5. As for (3) but using Slater-type 2s orbitals for penetration integrals.

Method 6. As for (5) but with $Z = 3.15$ and $(pp/pp) = 9.522$ eV.

In this paper we have not attempted to incorporate any VBO-type modifications, such as were used in Part II [14], since this would have proved unduly time consuming in computation because of the need to re-orthogonalise the repulsion integrals after each cycle of the SCF iteration. Instead we simply used fixed input geometries for each molecule, taking these as far as possible from crystallographic data.

For ethylene we took [15] the bond length 1.338 Å, and for benzene 1.397 Å, and for the polyenes we assumed the long and short bonds to be 1.450 and 1.348 Å respectively, with the regular trans-conformation and the 120° angle. For fulvene we used a set of bond lengths given by a simple VBO-PPP calculation, these being $1-2 = 1.459$, $2-3 = 1.354$, $3-4 = 1.446$, and $1-6 = 1.351$ Å, where atom 1 is the tertiary and atom 6 the exocyclic carbon. For working out non-neighbour distances we adjusted the angles of the five-membered ring so as to correspond to a realistic geometry, although very little change in the results ensues if the angles are all taken as 108°.

As an initial test for our modified method we calculated the singlet state excitation energies for the molecules of ethylene and benzene, using the equations quoted by Adams and Miller [2]. By Method 1 the calculated values were all too high by a substantial amount (ca. 0.7 eV), and this was generally true to a greater

Table. *Comparison of experimental and calculated singlet excitation energies*

	Experimental[b–f]		Adams and Miller[a]		Present work[g]	
	ΔE	f	ΔE	f	ΔE	f
Ethylene, D_{2h}						
$^1B_{1u}(z)$	7.60[b]	—	—	—	6.80	0.540
Butadiene, C_{2h}						
$^1B_u(x, y)$	5.71[b]	0.470[b]	5.48	1.054	5.18	0.909
$^1B_u(x, y)$	—	—	9.32	0.286	8.84	0.320
Hexatriene, C_{2h}						
$^1B_u(x, y)$	4.63[b]	—	4.49	1.516	4.38	1.276
$^1B_u(x, y)$	—	—	6.50	0.003	6.40	0.001
$^1B_u(x, y)$	—	—	7.78	0.026	7.51	0.064
$^1B_u(x, y)$	—	—	8.31	0.328	7.87	0.309
Octatetraene, C_{2h}						
$^1B_u(x, y)$	4.08[b]	—	3.90	1.945	3.92	1.616
$^1B_u(x, y)$	5.84[b]	—	5.96	0.004	5.87	0.001
$^1B_u(x, y)$	—	—	6.97	0.112	6.60	0.162
$^1B_u(x, y)$	—	—	7.33	0.213	7.06	0.180
Decapentaene, C_{2h}						
$^1B_u(x, y)$	3.71[b]	—	3.50	2.344	3.61	1.929
$^1B_u(x, y)$	—	—	5.48	0.004	5.43	0.001
$^1B_u(x, y)$	—	—	6.31	0.198	5.98	0.223
$^1B_u(x, y)$	—	—	6.64	0.156	6.48	0.138
Fulvene, C_{2v}						
$^1B_1(x)$	3.32[c]	0.012[c]	3.17	0.034	3.21	0.035
$^1A_1(z)$	5.12[c]	0.320[c]	4.90	0.524	4.71	0.604
$^1A_1(z)$	—	—	6.38	0.432	6.46	0.271
Styrene, C_s						
$^1A'(x, y)$	4.34[b]	—	—	—	4.45	0.000
$^1A'(x, y)$	5.06[b]	—	—	—	4.85	0.609
$^1A'(x, y)$	—	—	—	—	5.84	0.364
$^1A'(x, y)$	—	—	—	—	6.04	0.602
Naphthalene, D_{2h}						
$^1B_{3u}(x)$	3.97[b,d]	0.002[b,d]	4.01	0.016	4.07	0.013
$^1B_{2u}(y)$	4.51[b,d]	0.180[b,d]	4.33	0.235	4.38	0.240
$^1B_{3u}(x)$	5.63[b,d]	1.700[b,d]	5.72	2.113	5.57	1.802
$^1B_{2u}(y)$	6.51[b,d]	0.210[b,d]	6.21	0.562	6.09	0.578

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[a] Ref. [16].

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[e] Plattner, P. A., and E. Heilbronner: Helv. chim. Acta **30**, 910 (1947); **31**, 804 (1948).

[f] Geometry – Hansen, A. W.: Acta crystallogr. **19**, 19 (1965).

[g] Method 3; details of the results derived using the other methods described may be obtained on application to the authors.

Table (continued)

	Experimental[b–f]		Adams and Miller[a]		Present work[g]	
	ΔE	f	ΔE	f	ΔE	f
Azulene, C_{2v}						
$^1B_1(x)$	1.96[e,f]	0.045[e,f]	2.07	0.019	2.16	0.029
$^1A_1(z)$	3.66[e,f]	0.080[e,f]	3.43	0.015	3.42	0.010
$^1B_1(x)$	4.48[e,f]	—	—	—	4.27	0.219
$^1A_1(z)$	4.52[e,f]	1.100[e,f]	4.86	2.055	4.70	1.977
$^1B_1(x)$	5.24[e,f]	0.380[e,f]	5.60	0.200	5.56	0.269
$^1B_1(x)$	6.42[e,f]	—	6.36	0.686	6.17	0.302
$^1A_1(z)$	—	—	—	—	6.57	0.366

or lesser extent for all the molecules studied, with the exception of fulvene and the two longest polyenes. On the other hand calculations by Method 2, using the theoretical (pp/pp) value, gave a much better overall agreement with experiment, and with the results of other calculations. For ethylene and benzene we obtain $^1\Delta E_1(C_2H_4)=7.31$ eV, and $^1\Delta E_1$, $^1\Delta E_2$, and $^1\Delta E_3(C_6H_6)=5.28$, 5.91, and 7.19 eV respectively, as against the experimental values of 7.60 eV and 4.91, 6.19 and 7.02 eV, and these results are now in agreement to within ca. 0.3 eV. Furthermore the values for styrene, naphthalene, and azulene, were now much closer to the experimental energies than were the results of Method 1, and although the excitation energies for fulvene and the polyenes were appreciably (ca. 0.5 eV) underestimated by Method 2, this result is due at least in part to the inadequacy of the polynomial formula for H^0_{pq}.

The results, especially those obtained by Method 2, were considered sufficiently encouraging, for an essentially non-empirical calculation, to justify an attempt to improve the method in detail, and in particular to study the effects of (i) explicit calculations of all penetration terms appearing in the H^0 parameters, (ii) the testing of both hydrogenic and Slater-type 2*s* orbitals in this evaluation, and (iii) the variation of the assumed Z value. In the Table we show therefore the results of calculations using Method 3, together with those of Adams and Miller taken from their second paper [16], and the experimental values. This is seen to yield overall a very satisfactory agreement with the experimental figures, and for most of the molecules studied substantial improvements over Method 2 were found, for example for the first transition of styrene, the first and third transitions of naphthalene, and the fifth transition of azulene, all of which were also appreciably overestimated in previous Adams-Miller type [1, 2, 14] calculations. In fact only for ethylene and butadiene does Method 3 lead to generally poorer results than Method 2. (For benzene the results of Method 2 and 3 are identical since the polynomial reproduced the explicit H^0_{pq} values, but the H^0_{12} value for ethylene is not adequately given by the expression and a significant difference is found between the results of the two procedures.) With these exceptions, the only transition whose position is significantly less well predicted is the fourth transition of naphthalene, which is now overestimated by 0.42 eV, but in this case there is some uncertainty about the position of the origin of the very high energy band.

The marked difference between the results of Methods 2 and 3 indicates clearly that the penetration terms involved affect the H^0 parameters and the calculated excitation energies in a quite critical manner. Any attempt therefore to represent the variation of H^0_{pq} as a simple function of r_{pq} is thus necessarily a rather inaccurate approximation: each H^0 term must be calculated explicitly with due regard to the molecular environment of the atoms concerned if the method is to be regarded in any way as non-empirical.

A comparison of the results of Methods 3, 4, 5, and 6 also showed that the assumed value of Z has a marked effect upon the calculated excitation energies. Thus the change to $Z = 3.15$ in Method 4 led to markedly inferior results overall, especially for those transitions whose energies were noticeably improved in Method 3. Furthermore, the results of Methods 3 and 5 showed that the calculation of the penetration integrals with Slater-type, instead of hydrogenic, 2*s* orbitals also led to a much poorer correlation between theory and experiment, when the Z value is maintained at 3.25. When however the Z value was reduced to 3.15 (Method 6), the values calculated with the Slater-type 2*s* orbitals were very close indeed to those given by Method 3, and the two sets of results did not in fact diverge by more than 0.15 eV.

If then we take the results of Method 3 as a whole, the agreement with experiment is extremely satisfactory, except for ethylene and butadiene, for which the lowest singlets are underestimated by 0.80 and 0.53 eV respectively. It is though noteworthy that the discrepancy between the theoretical and experimental values of the lowest singlet excitation energies decreases regularly as the length of the carbon chain in the polyenes is increased, and that the results for ethylene and butadiene with $(pp/pp) = 11.13$ eV (Method 1) are rather better than in the same calculation using $(pp/pp) = 9.822$ eV (Method 2). Since on the other hand Method 1 greatly overestimates the excitation energies for the aromatic compounds, for which Method 2 was much more satisfactory, there is evidence to suggest that for compounds which show the greatest degree of electron delocalisation, e.g. aromatics, a smaller value of the one-center integral may be appropriate than for compounds in which the double bonds are in effect fixed and electron delocalisation minimal.

In essence this idea is not new. Dewar and Schmeising [17], dealing with the interpretation of resonance theory on a molecular orbital basis, showed that certain of the apparent discrepancies could be traced to a neglect of vertical correlation effects. Thus they concluded that for a polyene such as butadiene, the electrons should tend to correlate in pairs, above and below the nodal plane, corresponding to the formal double bond structures, whereas in an aromatic compound such as benzene the electrons should tend to adopt an alternating one up – one down arrangement around the ring. It thus follows, if we accept this picture, that the electron repulsion terms for systems showing the strongest double-bond fixation could be appreciably larger than for purely aromatic systems, and we can therefore understand the tendency for the theoretical Saturno value of (pp/pp) somewhat to underestimate the transition energies for some of the polyenes. Similarly the extent to which the electron pairs would be expected to congregate exclusively in this way at the formal double bonds should decrease sharply as the length of the polyene chain is increased, and this is here reflected in the steadily improving fit of theory and experiment as the chain is extended. Thus the behaviour of fulvene and the higher polyenes is readily rationalised, and styrene, although not a purely aromatic system by virtue of the vinyl substituent, would be expected to behave dominantly in the same way as benzenoid structures. Likewise azulene is not an alternant hydrocarbon, but if we regard it on the perimeter model it can clearly approximate to the one up – one down disposition of electrons.

At present, because of the N^4-type problem presented by the orthogonalisation of the repulsion integrals, the limits of our computational facilities have hindered the extension of our calculations to systems containing more than ten atoms. Work on larger systems is though intended, and we have also recently incorporated a Variable Electronegativity (VE) routine into our program. This latter should have little effect for alternant hydrocarbons, but judging from previous experience [1, 14], it seems likely that some slight decrease in the lowest transition energies should result for non-alternant systems.

We are also in the process of extending our non-empirical treatment to heteroatom systems, especially nitrogen containing molecules, in which we expect that the penetration integrals will play at least as important a role as for the hydrocarbon molecules. For this reason we are not enthusiastic about the recent modifications made to their method by Adams and Miller [16], in their calculations on heteroatomic compounds, wherein the H^0_{pp} parameters were approximated simply as the negative of the appropriate valence state ionisation potentials. Whilst this may be very satisfactory *as a purely empirical procedure*, our results indicate quite definitely that the penetration terms are of vital importance, and consequently there can be no theoretical justification for their complete neglect. Moreover, although Adams and Miller's new procedure does produce quite good I.P.s *and* singlet state excitation energies for both hydrocarbon and heteroatomic systems, it still suffers from the same drawbacks as indicated previously [1] and above.

Conclusions

The results of the calculations described herein lead to the following conclusions: –

(i) Satisfactory singlet state excitation energies *can* be obtained when the H^0 parameters are evaluated theoretically.

(ii) Localised or orthogonalised repulsion integrals must be correctly used in the appropriate situations.

(iii) Substantially better agreement with experiment is obtained when the one-centre integral is derived theoretically via Saturno's operator than when the semi-empirical value is used.

(iv) Explicit calculation of all penetration terms involved in the H^0 parameters produces much better results than when H^0_{pq} is approximated as a polynomial in r_{pq}.

(v) The results are strongly dependent on the assumed Z value, and on whether hydrogenic or Slater-type 2*s* orbitals are used to evaluate the penetration terms.

(vi) The best overall set of results is obtained using $Z = 3.25$, with hydrogenic $2s$ orbitals (Method 3).

(vii) The agreement with experiment thereby obtained is extremely satisfactory for a non-empirical type calculation and compares favourably with most semi-empirical methods.

Computation

The calculations described were carried out by means of programs written by us in FORTRAN IV. To avoid non-convergence problems the starting vectors for the orthogonalised Fock matrix iteration were obtained from a simple PPP-SCF calculation. From the input geometry, Z, E_p, and (pp/pp), the program finds the overlap matrix and its root inverse, the localised repulsion integrals, the penetration integrals, the $\boldsymbol{H}^0$ matrix, the $\boldsymbol{H}^\lambda$ matrix, the orthogonalised repulsion integrals, and the $\boldsymbol{F}$ matrix, to self-consistency. Diagonalisation is followed by construction of the complete singlet CI matrix for singly excited states, and output of the singlet excitation energies and the corresponding oscillator strengths.

Acknowledgements. The computations were carried out on the English Electric 450 computer at the University College Cardiff Computing Centre.
One of us (G.R.) thanks the S.R.C. for financial support.

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