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Commentationes

SCF-π-Electron Calculations Using Orthogonalised Atomic Orbitals

I. An Assessment of a Recent Approach

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An analysis is made of a recently developed semi-empirical SCF-LCAO-π-method in which an orthogonalised basis set of atomic orbitals is used. The reasons underlying the relative success of this method are investigated, and a less empirical approach to the estimation of the basic parameters is described.

Eine kürzlich entwickelte, halbempirische SCF-LCAO-π-Methode, in der ein orthogonalisierter Basissatz aus Atomorbitalen benutzt wird, wird analysiert. Die Gründe für die relativ guten Ergebnisse dieser Methode werden untersucht. Ein Weg zu einer weniger empirischen Parameterwahl wird beschrieben.

Analyse d'une méthode semi-empirique SCF-LCAO-MO récemment élaborée et utilisant une base orthogonale d'orbitales atomiques. Les raisons qui sont à la base du succès relatif de cette méthode sont recherchées et un procédé moins empirique d'évaluation des paramètres de base est décrit.

Introduction

In the past few years numerous semi-empirical π-electron calculations using variants of the Pariser-Parr-Pople [1, 2] method have been made for conjugated hydrocarbon systems. In many cases however it has been found that the choice of parameters required to give optimum agreement with experiment is specific for a particular property, or for a restricted class of compounds, and cannot therefore be generally extended to other situations. In particular, it has frequently been noted [3] that parameters which yield excellent values for excited state energies usually overestimate ionisation potentials by at least some 2–3 eV.

Recently, a method using an orthogonalised basis set of atomic orbitals, obtained by the Löwdin procedure, was developed by Adams and Miller [4], which appeared to overcome many of these difficulties, and which yielded, simultaneously, satisfactory values for ionisation potentials and for singlet and triplet excitation energies. Although certain aspects of their technique have been criticised by Bloor,

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Gilson, and Brearley [5], the method has been extended with some degree of success to heteroatomic systems by Greenshields and his co-workers [6]. Since any π-electron method which takes definite account of non-orthogonality should be especially relevant to heteroatomic systems, we therefore thought it necessary, initially, to examine more closely the basic assumptions of the Adams-Miller procedure as applied to hydrocarbons.

Our examination falls into two parts. Firstly we have studied the theoretical implications of the way in which the parameters are derived from experimental data – for example, the choice of orbital exponent, the appropriateness of the use of Mataga integrals, the validity of Koopmans' theorem etc. Secondly, we have considered how the basic parameters could be calculated in a less empirical way, and report the results of some preliminary work on these lines.

Analysis of Method

1. Method

The standard Adams-Miller procedure adopts the usual π-electron approximation and represents the wave functions as Slater determinants in the normal way [7]. The molecular orbitals are linear combinations of Löwdin atomic orbitals [8], the latter being related to the ordinary Slater-type orbitals by

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

where λ is the array of Löwdin orbitals, χ that of Slater-type orbitals and $S^{-\frac{1}{2}}$ the root inverse of the overlap matrix. Expansion of the core Hamiltonian by the Goeppert-Meyer and Sklar procedure [9] then yields

$$H_{pp} = \langle \chi_p(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle - \left\{ \sum_{r \neq p} (pp/rr) + \sum_{r \neq p} (U_p^0 : pp) \right\}$$

and

$$\begin{aligned} H_{pq} = {} & \tfrac{1}{2} \{ \langle \chi_p(i) | T(i) + U_q^+(i) | \chi_q(i) \rangle + \langle \chi_q(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle \} \\ & - \tfrac{1}{2} \left\{ \sum_{r \neq p} (pq/rr) + \sum_{r \neq q} (pq/rr) + \sum_{r \neq p} (U_r^0 : pq) + \sum_{r \neq q} (U_r^0 : pq) \right\} \end{aligned}$$

where the integrals (pp/rr), (pq/rr), are the two- and three-centre repulsion integrals over Slater-type orbitals, and $(U_r^0 : pp)$ and $(U_r^0 : pq)$ are neutral atom penetration integrals.

The parameter H_{pp}^0 and H_{pq}^0 are now defined as

$$H_{pp}^0 = \langle \chi_p(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle - \sum_{r \neq p} (U_r^0 : pp)$$

and

$$\begin{aligned} H_{pq}^0 = {} & \tfrac{1}{2} \{ \langle \chi_p(i) | T(i) + U_q^+(i) | \chi_q(i) \rangle + \langle \chi_q(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle \} \\ & - \tfrac{1}{2} \left\{ \sum_{r \neq p} (U_r^0 : pq) + \sum_{r \neq q} (U_r^0 : pq) \right\} \end{aligned}$$

whence

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

the three-centre integrals being evaluated by the Mulliken approximation.

The parameters H_{pp}^{0} and H_{pq}^{0} are evaluated from experimental data for ethylene and benzene: they are simply related to the quantities H_{pp} and H_{pq}, which are in turn related to the core integrals over Löwdin orbitals by the expression [8]

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

where $\boldsymbol{H}^{\lambda}$ is the matrix containing the elements H_{pq}^{λ} and $\boldsymbol{H}$ contains the elements H_{pq}.

The one-centre repulsion integrals are evaluated in the conventional fashion [1] as the difference between the valence state ionisation potential, I_p, and the electron affinity A_p, of atom p, but the resulting value is assumed to relate to a repulsion integral over *Löwdin orbitals:* i.e.

$$I_p - A_p = (pp/pp)^{\lambda}.$$

The two-centre integrals, $(pp/qq)^{\lambda}$ are then derived using the familiar Mataga-Nishimoto relationship. The elements of the Fock matrix, $\boldsymbol{F}$, are now readily derived [4], using the Roothaan closed-shell formulation [10] as simplified by Pople [2]. (The ZDO approximation is not in fact needed here since three- and four-centre integrals over Löwdin orbitals are known to be extremely small).

If Koopmans' theorem [11] is now assumed to be valid, expressions for the ionisation potentials of ethylene and benzene can be written involving only quantities of the form H_{pp}^{λ}, H_{pq}^{λ}, $(pp/pp)^{\lambda}$, and $(pp/qq)^{\lambda}$. Combining these with similar expressions for singlet excitation energies, the values of H_{pp}^{λ}, H_{pq}^{λ} etc. in the two systems can readily be found and thence the parameters H_{pp}^{0} and H_{pq}^{0}. The values of H_{pp}^{0} and H_{pq}^{0} obtained are dependent on the value of the orbital exponent $\zeta(=Z/2)$ chosen for the $2p\pi$ Slater-type orbitals: the value $Z=2.81$ gave identical values for H_{11}^{0} in ethylene and benzene and was therefore taken as the standard parameter. From the values of H_{12}^{0}, H_{13}^{0}, and H_{14}^{0} for benzene and that of H_{12}^{0} for ethylene, the variation of H_{pq}^{0} with r_{pq} could be determined.

In the original calculations [4] the $\boldsymbol{F}$ matrices were constructed as described and the self consistent ground state solutions obtained by the usual iterative diagonalisation. Limited configuration interaction involving the two highest occupied and the two lowest unoccupied ground state molecular orbitals was superimposed on the ground state solution for the calculation of the excited state energies, singly excited states only being considered.

2. *Analysis*

The results presented [4] showed very satisfactory agreement with experiment for ionisation potentials as well as for both singlet and triplet excitation energies. However, a detailed scrutiny of the procedure reveals a number of disquieting points:

1. The Assumption of $Z=2.81$. Very nearly all semi-empirical π-electron calculations on hydrocarbons have, up to the present, been made [3] with the value $Z=3.25$, or thereabouts, as given by Slater's rules [12]. Whilst both SCF orbitals [13] and the Clementi double zeta functions [14] produce larger overlap integrals than the standard Slater orbitals at the usual nearest neighbour distances, and thereby imply lower effective Z values, the framework of the π-electron approximation is probably better served by the adoption of a minimum basis set of Slater-type orbitals for which Clementi and Raimondi [15] have shown the orbital exponent to conform extremely closely to Slater's rules (for carbon they find $Z=3.136$). The value of 2.81 therefore rests only upon the reported insensitivity of the results to the actual value of Z used, and on the equality of the H^0_{pp} values for ethylene and benzene. The former feature is not particularly surprising, in view of the method of derivation of H^0_{pp} and H^0_{pq}, especially when only benzenoid polycyclics and polyenes were investigated.

Examination of the plot of H^0_{pp} as a function of Z [4] is also not reassuring. At $Z=3.25$, $H^0_{pp}(C_6H_6)=-11.50$ eV and $H^0_{pp}(C_2H_4)=-11.71$ eV. Since we may write

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

where E_p (which may be assumed the same for ethylene and benzene) is the orbital energy of an electron in a $2p\pi$ carbon AO, then

$$H^0_{pp}(C_6H_6)-H^0_{pp}(C_2H_4)\simeq(H:CC)-(C:CC)$$

Empirically the result is $+0.21$ eV, but calculation of the penetration integrals yields -0.18 eV. Furthermore, the calculated value of $H^0_{pp}(C_6H_6)$ is -13.32, nearly 2 eV more negative than the empirical result. At $Z=2.81$ the situation is worse: the value of (C:CC) increases rapidly as Z decreases yielding $H^0_{pp}(C_6H_6)=-14.51$ as against the empirical -11.96, and the calculated value of (H:CC) $-$ (C:CC) is now -0.63 eV.

Most of these inconsistencies arise from the incorrect use of Koopmans' theorem: there is no real case for $Z=2.81$, and we show later that quite good singlet excitation energies can be obtained using $Z=3.25$ and *calculating* H^0_{pp} and H^0_{pq}, whereas $Z=2.81$ yields very poor results indeed.

In view of the other uncertainties involved, the assumption that $H^0_{pp}(C_6H_6)=H^0_{pp}(C_2H_4)$ in the standard Adams-Miller method probably leads only to trivial errors. Where calculated H^0_{pp} values are used (with $Z=3.25$) allowance could readily be made for the difference in penetration terms, but our own experience, varying H^0_{pp} by ca. 0.2 eV, suggests that the effect is almost negligible.

2. *The Validity of Koopmans' Theorem.* A striking feature of the Adams-Miller method is its success in calculating ionisation potentials. Almost all previous calculations, although adequately predicting excited state energies, led to excessively high values for the ionisation energy, and this has been shown by Hoyland and Goodman [16, 17, 18] to be due to the failure of Koopmans' theorem when the $\Sigma-\Pi$ separability condition is imposed. Thus the derivation of H^0_{pp} by equating the energy of the highest occupied molecular orbital with the negative of the experimental ionisation potential cannot really be justified, except in an empirical sense, and one must therefore consider just why the Adams-Miller parameters work so well.

Hoyland and Goodman showed that three factors were usually neglected in the application of Koopmans' theorem to conjugated hydrocarbons: (i) the effect of π-electron ionisation on the $2p\pi$ basis functions (Π deformation), (ii) its effect on the σ-framework (Σ-deformation) and (iii) changes in the π-M.O.'s which would result on construction of a new Hartree-Fock Hamiltonian for the ionised state, and subsequent reminimisation. They showed that the first of these terms led to a constant (negative) correction to the Koopmans' theorem value of the I.P., and they postulated that the orbital energies of the $2p\pi$ functions should vary with π-electron density as should also the electron repulsion integrals. The I.P. was then expressed as the energy difference between the ionised and ground states, these being written in terms of (a) core and (b) electron repulsion (J and K) integrals. The results showed a substantial negative correction due to core energy changes and a smaller positive correction due to repulsion energy changes, *the difference being roughly constant* for a considerable number of closed-shell systems. It is therefore because of this approximate constancy of the corrections to the Koopmans' theorem I.P.'s that the Adams-Miller method operates so satisfactorily: once the H^0_{pp} parameter has been adjusted to fit the experimental I.P.'s for ethylene and benzene, it would naturally be expected to give good values for other hydrocarbons. A similar method of circumventing the breakdown of Koopmans' theorem was used earlier by Skancke [19, 20] in a ZDO SCF calculation, his empirical W_p values being derived from the experimental I.P. for ethylene. Adams and Miller also showed [4] that *theoretical* evaluation of H^0_{pp} indicated that $\langle \chi_p(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle$ should be regarded as equivalent to the ionisation potential of a methyl radical, a conclusion fully in line with Skancke's observations.

Thus, although the Adams-Miller method produces good I.P.'s directly from the F matrix diagonalisation, these are no more significant theoretically than the values obtained by empirically correcting the high results from simpler SCF methods. Since, then, the original method is essentially a compromise between calculating satisfactory I.P.'s and satisfactory excited state energies, we are led to conclude that it would be better to accept the limitations of Koopmans' theorem and to concentrate attention on a less empirical approach to the determination of the energies of the excited states.

3. The Extent of Configuration Interaction: Triplet State Excitation Energies. The amount of configuration interaction originally imposed is probably less than is desirable even for the singlet states of small molecules, and quite significant errors may arise for the higher excited levels. For triplet states moreover the position is worse since the effect of C.I. is known to be much more substantial, especially when the Mataga-Nishimoto [21, 22] repulsion integrals are used [5]. In fact, Bloor, Gilson, and Brearley [5] showed that the excellent values obtained [4] for the lowest triplet levels of the polycyclic benzenoid systems were due to the restricted C.I. used. When a substantially greater measure is imposed, the calculated values are reduced by ca. 0.4–0.5 eV, and the agreement with experiment is much poorer (see Part II, Table 6). For the polyenes Adams and Miller reported only the calculated results for ${}^3\Delta E_1$, but these are much smaller than the experimental values where the latter are available [23] e.g. butadiene 1.20 (3.20), hexatriene 1.25 (2.60), and a greater amount of C.I. reduces the theoretical values still further.

No ${}^3\Delta E_1$ values were reported for the reference compounds benzene and ethylene [4], but it is readily shown that for ethylene ${}^3\Delta E_1 = 1.94$ eV and for benzene ${}^3\Delta E_1 = 2.49$ eV as against the experimental values of 4.6 and 3.9 eV respectively. For the simple case of ethylene it is readily shown that if the parameters are chosen to fit the experimental ${}^1\Delta E_1$ value of 7.60 eV, then it is *not* possible to obtain a satisfactory value for ${}^3\Delta E_1$, *using the Mataga-Nishimoto integrals.* [$(11/11)^\lambda = 11.13$ eV, $(11/22)^\lambda = 5.47$ eV, whence $K = \frac{1}{2}(11.13 - 5.47)$, and ${}^3\Delta E_1 = {}^1\Delta E_1 - 2K = 1.94$ eV.]

The Mataga-Nishimoto repulsion integrals are, in general, markedly superior to other formulations in reproducing singlet excitation energies, as was shown by Adams and Miller themselves [4]. The most significant feature is their relatively low value in the region corresponding to the normal nearest-neighbour and next nearest-neighbour distances, which suggests that two-electron correlation is being taken into account somehow. Consequently the values would be expected to be less appropriate for triplet than for singlet level calculations.

We conclude therefore that: (i) the C.I. imposed in the standard method is inadequate, (ii) the calculated ${}^3\Delta E_1$ values (with fuller C.I.) are *not* in satisfactory agreement with experiment, and (iii) the latter feature is due to the use of Mataga-Nishimoto repulsion integrals.

In addition to the three main points discussed above, a few other items require clarification. These deal mainly with details of the derivation of the parameters and do not therefore impinge so fundamentally on the validity of the method. We consider them as follows:

A. The Assumption $I_p - A_p = (pp/pp)^\lambda$. In the original treatment it was assumed that the one-centre repulsion integral, obtained as above [9], referred to repulsions over Löwdin orbitals rather than, as usual, over localised Slater-type orbitals. In fact, the one- and two-centre repulsion integrals over Löwdin orbitals are roughly equal to the corresponding localised quantities [24, 25], and by itself, this assumption would not be very significant in view of the fairly wide range of values in current use for the one-centre integral. However, in the derivation of H^0_{pp} and H^0_{pq}, it is tacitly assumed that the one- and two-centre repulsion integrals over Slater-type orbitals are equivalent to the corresponding orthogonalised values. Thus, in converting, H_{pp} and H_{pq} to H^0_{pp} and H^0_{pq} respectively, the integrals (pp/rr) and (pq/rr), which clearly are localised quantities, are evaluated by ascribing to (pp/pp) and (pp/rr) the same values as for orthogonalised integrals. This is manifestly inconsistent and we therefore examine the magnitude of the errors thereby produced in the parameters H^0_{11} and H^0_{12}, in the example of ethylene.

Let us assume that $I_p - A_p = 11.13$ eV refers, as it normally would, to the one-centre repulsion integral over Slater-type orbitals, $(11/11)$. We readily find $(11/22) = 5.471$ eV for $r_{12} = 1.338$ Å, and for $Z = 2.81$, $S_{12} = 0.3607$. Using the Mulliken approximation for $(11/12)$ and $(12/12)$ ($= 2.994$ and 1.080 eV respectively) we obtain, putting $\lambda = \chi S^{-\frac{1}{2}}$ and expanding the orthogonalised integrals in terms of localised quantities, $(11/11)^\lambda = 11.554$ and $(11/22)^\lambda = 5.048$ eV. (Note that it is not correct to obtain $(11/22)^\lambda$ from $(11/11)^\lambda$ by direct application of the Mataga-Nishimoto formula.) If we now fit our experimental ${}^1\Delta E_1$ and I.P. values as before, we obtain $H^\lambda_{11} = -16.745$ (instead of -16.535) and $H^\lambda_{12} = -2.175$ (-2.385) eV. Converting to H_{11} and H_{12} using $\boldsymbol{H} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{H}^\lambda\boldsymbol{S}^{\frac{1}{2}}$ we find $H_{11} = -17.528$ (-17.396) and $H_{12} = -8.213$ (-8.350) eV, whence, using *localised* repulsion integrals, we have $H^0_{11} = -12.057$ (-11.925) and $H^0_{12} = -5.219$ (-5.356) eV.

Obviously the discrepancies are not large, but the corrections will certainly affect the variation of H^0_{pp} with Z and therefore alter the value of Z at which H^0_{pp}

for ethylene and benzene become equal. Clearly this factor as well as the differences in the penetration integral summation between primary and secondary carbon atoms should be taken into account when fixing the value of Z. Finally, the slightly erroneous values of H^0_{11} and H^0_{12} etc. used may be a contributary reason for the small but appreciable values of H_{pq} found by some authors for non-nearest-neighbour terms.

B. The Neglect of Non-Nearest-Neighbour H^λ_{pq} Terms. In their review of SCF MO π-electron calculations, Bloor, Gilson and Brearley [5] reported the results of their use of the Adams-Miller method and criticised the assumption that all non-neighbour H^λ_{pq} terms could be set equal to zero. They found that all the H^λ_{pq} elements did not fall off in magnitude as r_{pq} is increased and that some even became positive. Furthermore, the result of including such matrix elements could be appreciable and was sensitive to the precise mode of evaluation of the H^0_{pq} terms.

Our own experience is not dissimilar: in many cases H^λ_{pq} terms for non-neighbour atoms differ significantly from zero (although they are always small by comparison with nearest neighbour terms) and are often positive. We have nevertheless here and in Part II adhered to the original procedure in setting all such elements equal to zero because we believe that theoretically this is necessary.

When the zero differential overlap approximation is used in normal semi-empirical methods, using localised orbitals, the following assumptions are usually made:

$$\langle\chi_p|S|\chi_q\rangle=\delta_{pq}\quad\langle\chi_p|H^{\text{core}}|\chi_p\rangle\neq 0\quad\langle\chi_p|H^{\text{core}}|\chi_q\rangle\neq 0\quad p,q\ \text{neighbours},$$

$$\langle\chi_p|H^{\text{core}}|\chi_q\rangle=0\quad p,q\ \text{non-neighbours},$$

$$\langle\chi_p^*\chi_q|e^2/r|\chi_r^*\chi_s\rangle=(pq/rs)=0\quad\text{unless } p=q \text{ and } r=s\,.$$

Fischer-Hjalmars [24] has shown that all these assumptions, which collectively constitute the ZDO approximation, can be rigorously deduced to the second order of approximation when an orthogonalised basis set is used, and that inclusion of non-neighbour $\langle\chi_p|H^{\text{core}}|\chi_q\rangle$ terms is not consistent with the rest of the ZDO conditions since it necessitates a higher order of approximation. It therefore follows that (i) in ordinary calculations with localised orbitals the inclusion of non-neighbour β terms is incompatible with the ZDO approximation, *whether or not* any improvement in results should ensue, and (ii) when an orthogonalised basis set is used, all non-neighbour H^λ_{pq} terms should essentially vanish.

Since all non-neighbour H^λ_{pq} terms do *not* become entirely negligible (even though they are usually very small) the original authors' procedure must contain some inadequacies. The confusion between localised and orthogonalised repulsion integrals in the determination of H^0_{pp} and H^0_{pq}, which has already been mentioned, most probably plays some part, and other possible causes are the neglect of the penetration integral summation difference for primary and secondary carbon atoms and the use of the Mulliken approximation to calculate three- and four-centre repulsion integrals. All these possibilities are currently under investigation but it now appears best to assume the non-neighbour H^λ_{pq} terms to be vanishingly small (as they should be) rather than include small elements which were merely artifacts of an imperfect method of parameter evaluation.

Clearly then, with an orthogonalised basis set, all the ZDO assumptions are adequately fulfilled: the parameters H^0_{pp} and H^0_{pq} refer to localised orbitals and no problem of parameter transferability [24] arises since the orthogonalised quantities are formed explicitly as required. In conclusion therefore we consider what bearing this has on the problem of the magnitude of the non-neighbour H^{core}_{pq} terms when a localised basis set is used.

Löwdin [26] showed that the formal neglect of differential overlap could be interpreted as implying that the various integrals should be taken over orthogonalised atomic orbitals rather than over the usual Slater-type orbitals. Thus the use of the ZDO approximation with localised orbitals is equivalent to regarding an orthogonalised basis set as a good approximation to the localised set, since all the integrals retained in the ZDO approximation are relatively little changed. The use, for localised basis set calculations, of the ZDO approximation, together with the inclusion of non-neighbour β terms would therefore appear to be unjustifiable, despite reports of significant improvements in the agreement of theoretical and experimental values.

Nevertheless, Flurry and his co-workers have reported extensive Pariser-Parr-Pople type calculations, using the usual Slater-type orbital basis set, in which non-neighbour β terms are used with the ZDO approximation [27, 28]. They found improvements in the calculated values of spectral excitation energies, together with significant charge separation in alternant hydrocarbon systems. The latter result is to be expected: Pople's extension of the Coulson-Rushbrooke theorem to his SCF method [2] shows that any treatment which destroys the exact equivalence of all the starred and all the unstarred atoms [e.g. inclusion of non-neighbour β terms, inclusion of different penetration integrals for (C : CC) and (H : CC) etc.] will result in departures from charge uniformity. The similarity of the results in this respect, upon which Flurry and Bell remarked [27], to those of Adams and Miller [4] is therefore understandable, but not significant, the inclusion of non-neighbour β terms being only an empirical approximation to a more satisfactory approach.

A recent review on zero differential overlap in π-electron theories [29] was also cited in support of the inclusion of non-neighbour β terms, but this seems to be based on a misconception. Fischer-Hjalmars [29] does indeed recommend the inclusion of non-neighbour β terms *in the Hückel method* since this approximation should reasonably correspond to a first order ZDO approximation, but this is only because, although the non-neighbour H^{core}_{pq} matrix elements will vanish, those corresponding to $-\frac{1}{2}P_{rs}(rr/ss)$ will not. Later in the same article it is emphasised that since all H^{core}_{pq} elements for non-neighbours are of the third order or smaller it is inconsistent to include them and yet still to assume that all three- and four-centre integrals vanish.

Approaches to Less Empirical Calculations

As we have indicated in the previous section, there is considerable evidence to suggest that the Z value of 2.81 assumed by Adams and Miller is both insecurely based and too low. Furthermore, the determination of H^0_{pp} by the use of Koopmans' theorem leads to values which are substantially smaller in magnitude than those obtained non-empirically. If we equate the quantity $\langle \chi_p(i)|T(i)+U_p^+(i)|\chi_p(i)\rangle$ with E_p, the $2p\pi$ trigonal valence state orbital energy for carbon, then

$$H_{pp}^0 = E_p - \sum_{r\neq p} (U_r^0 : pp)$$

and H_{pp}^0 can be calculated directly. E_p is obtained from the appropriate spectroscopic data [30] and the penetration integrals derived using the expression given by Lofthus [31, 32]. Similarly H_{pq}^0 can be determined from the relationship

$$H_{pq}^0 = \tfrac{1}{2}\{\langle \chi_p(i)|T(i)+U_q^+(i)|\chi_q(i)\rangle + \langle \chi_q(i)|T(i)+U_p^+(i)|\chi_p\rangle\} - \tfrac{1}{2}\left\{\sum_{r\neq p}(U_r^0 : pq) + \sum_{r\neq q}(U_r^0 : pq)\right\}.$$

We have therefore calculated the values of H_{pp}^0 and of H_{pq}^0 for the 1–2, 1–3, and 1–4 benzene distances for two values of Z : $Z=2.81$, as used by Adams and Miller, and (ii) $Z=3.25$, as given by Slater's rules. (We have, following Parr and Crawford, assumed hydrogenic $2s$ orbitals in evaluating the penetration integrals [33].)

The values obtained were:

$Z=2.81$ $H_{pp}^0 = -14.513$ $H_{pq}^0 = -6.900$ (1–2), -1.735 (1–3), -0.889 (1–4) eV.

$Z=3.25$ $H_{pp}^0 = -13.306$ $H_{pq}^0 = -4.835$ (1–2), -0.900 (1–3), -0.402 (1–4) eV.

In both cases the value of H_{pp}^0 is substantially more negative than the empirical figure of -11.92 eV, but clearly the H_{pq}^0 values using $Z=3.25$ correspond quite closely to those of Adams and Miller (-5.032, -1.332, and -0.548 eV), whereas, for $Z=2.81$, the values are considerably more negative.

Using a quadratic expression to fit the variation of H_{pq}^0 with r_{pq}, we carried out calculations on two test molecules – naphthalene and azulene – using the standard Adams-Miller method, except for the two sets of *non-empirical* H_{pp}^0 and H_{pq}^0 parameters, with the appropriate Z value, and the use of more extended C.I. (see Part II). For $Z=3.25$, we also made a calculation including our VBO and VE refinements (see Part II), starting with an assumed regular geometry. For this, following Brown and Heffernan [34], we took $Z=3.25$, 4.25, and 5.25 for C, N^+, and O^{++}, and obtained the relationship (for carbon in the trigonal valence state)

$$I_p = 0.3545\, Z_p^2 + 9.1583\, Z_p - 22.2487$$

which we used together with $Z_p = 3.60 - 0.35\, P_{pp}$ and $(pp/pp) = 3.4246\, Z_p$.

The more negative H_{pp}^0 values used in both series of calculations lead to predicted I.P.'s which are now substantially too high, but for $Z=3.25$ the off-diagonal elements of the $\boldsymbol{H}^0$ matrices are of comparable magnitude to those calculated by the original Adams-Miller method. Thus, since changing all the diagonal elements by a constant amount will have little effect on the excitation energies, the results for this Z value should be quite comparable with those given by the more empirical method. On the other hand, for $Z=2.81$, all the off-diagonal elements of $\boldsymbol{H}^0$ are appreciable more negative and considerable changes in the excitation energies should result.

The results, shown in the Table, substantially fulfil these expectations. All the excitation energies using $Z=2.81$ are very much in error, whereas the results with

Table. *Results of calculations using non-empirical H°-parameters*

Non-empirical						Empirical				Experiment	
$Z=3.25$				$Z=2.81$							
Fixed geometry[a]		VE-VBO		Fixed geometry		Fixed geometry		VE-VBO			
$^1\Delta E$(kK.)	f	$^1\Delta E$(kK.)	f	$^1\Delta E$(kK.)	f	$^1\Delta E$(kK.)	f	$^1\Delta E$(kK.)	f	$^1\Delta E$(kK.)	f
Naphthalene											
35.41	0.014	35.29	0.006	25.50	0.003	34.07	0.004	33.81	0.002	32.03	0.002
37.68	0.291	37.97	0.281	29.47	0.176	36.53	0.276	36.60	0.267	36.39	0.180
48.61	2.013	48.46	2.038	38.53	1.562	47.10	1.951	46.80	1.958	45.42	1.700
54.59	0.572	54.15	0.612	42.71	0.350	53.04	0.541	52.45	0.574	52.52	0.210
Azulene											
17.67	0.030	15.47	0.028	26.19	0.058	16.98	0.026	15.11	0.025	15.80	0.045
29.68	0.037	28.68	0.021	40.62	0.119	28.80	0.032	27.88	0.023	29.50	0.080
37.53	0.174	37.32	0.136	51.94	2.526	36.50	0.165	36.25	0.132	36.10	sh
40.24	1.958	39.65	1.987	52.05	0.325	39.23	1.889	38.67	1.901	36.47	1.100
48.82	0.319	48.61	0.397	66.65	0.473	47.60	0.287	47.31	0.339	42.30	0.380

[a] From crystallographic data. – Naphthalene: Cruickshank, D. W. J., and R. A. Sparks: Proc. Roy. Soc. (London) A **258**, 270 (1960). – Azulene: Hanson, A. W.: Acta crystallogr. **19**, 19 (1965).

$Z=3.25$ are quite satisfactory and differ little from those obtained by the standard procedure.

Strictly speaking, we should of course use a properly orthogonalised set of repulsion integrals when constructing the F matrices, rather than following Adams and Miller, but the effects of such corrections would be negligible compared to those resulting from changes in the magnitudes of the off-diagonal H^0 elements. Furthermore, since such an orthogonalisation is an "N^4" type problem, the requirements of computer time would be prohibitive for all but the smallest systems.

The critical quantities in calculating the H^0_{pp} and H^0_{pq} values are in fact the penetration integrals: as Z decreases these increase quite sharply and this is responsible for the too negative values of H^0_{pq} found with $Z=2.81$. (This effect would actually be greater if Slater rather than hydrogenic $2s$ orbitals were used [31, 32] and also raises the question whether Z_{2s} must necessarily be assumed equal to Z_{2p}). We are therefore directing our efforts towards optimising the choice of Z, and also towards allowing H^0_{pp} to vary according to the nature of the carbon atom concerned (i.e. primary, secondary, or tertiary). In the light of these investigations it will be possible to assess the utility of the VBO and VE refinements, which may be of particular significance in heteroatomic systems. Our present results are of course only preliminary but they do encourage belief in the possibility of performing satisfactory π-electron calculations with an orthogonalised basis set, without using as many empirical parameters.

Finally, we feel strongly that the determination of the H^0 parameters for hydrocarbons must have a much firmer theoretical basis than at present before heteroatomic molecules can be tackled. The empirical methods of evaluation that avail for hydrocarbons are not applicable for heteroatomic situations and current attempts [6] to determine H^0 values in such cases are therefore necessarily of a rather ad hoc type.

Conclusions

Analysis of the original method of Adams and Miller, using orthogonalised atomic orbitals leads to the following conclusions:

(i) The assumed Z_C value of 2.81 is too low, and a value nearer that given by Slater's rules (3.25) seems likely.

(ii) Neglect of the failure of Koopmans' theorem merely incorporates an empirical correction (for I.P.'s) *internally* rather than (as usual) externally.

(iii) The extent of configuration interaction adopted is inadequate.

(iv) Use of the Mataga-Nishimoto repulsion integrals prevents the method being applied to determine triplet state energies.

(v) The assumption of the equality of repulsion integrals over orthogonalised and over localised orbitals is not sufficiently accurate and leads to small errors in the H^0 parameters.

(vi) H^{λ}_{pq} terms corresponding to non-neighbour atoms are correctly assumed to be zero.

(vii) The results for spectral excitation energies, obtained when H^0_{pp} and H^0_{pq} are derived non-empirically, are in satisfactory agreement with the experimental values when Z is taken as 3.25, and support the view that this approach may be the most fruitful one for heteroatomic systems.

Appendix

The evaluation of the H^0_{pp} and H^0_{pq} quantities required the calculation of the neutral atom penetration integrals (C : CC) and (H : CC). Expressions for (C : CC) have been given by Lofthus [31, 32] but we were unable to discover similar formula for (H : CC) in the literature. It can, be readily shown that

$$\begin{aligned}(\mathrm{H}:\mathrm{CC}) = \alpha_1^5/16\, R\,[&\{(A_3 - A_1)(B_0 - B_2) - (A_2 - A_0)(B_1 - B_3)\} \\ &+ \tfrac{1}{2}\alpha\{(A_4 - A_2)(B_0 - B_2) - (A_2 - A_0)(B_2 - B_4)\}]\end{aligned}$$

where

$$A_m = A_m(\alpha + \alpha_1),\ \ B_n = B_n(\alpha - \alpha_1), \quad \text{with} \quad \alpha = \alpha_{\mathrm{H}} \quad \text{and} \quad \alpha_1 = \alpha_{\mathrm{C}}\,.$$

The symbols have the same meaning and are expressed in the same units as given by Lofthus.

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