Tetrahedron. 1967. Vol. 23, pp. 845 to 862. Pergamon Press Ltd. Printed in Northern Ireland

SLIDE RULE COMPUTATION OF HÜCKEL MOLECULAR ORBITALS

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(*Received in U.S.A.* 28 *May* 1966; *accepted for publication* 16 *June* 1966)

Abstract—Manual computation of Hückel molecular orbitals Ψ_J and of their corresponding orbital energies ε_J involves the solving of a secular determinant and of sets of linear equations, if carried out in the usual manner. This time consuming procedure has to be used because the set of n atomic orbitals ϕ_μ used is n-fold degenerate. It is shown that the a priori knowledge of certain mathematical properties which the HMOs Ψ_J must satisfy allows the construction of a set of basis functions φ_J (called qualitative molecular orbitals QMO) which are no longer degenerate (at least inside one irreducible representation). Starting from such functions φ_J one can obtain excellent approximations to the exact HMOs Ψ_J and their orbital energies ε_J by second order perturbation methods and with a considerable saving in computing time.

THE availability of large scale computing facilities and of tables of simple molecular orbitals[1] have made obsolete many of the techniques used in manual calculations of molecular orbitals. From a didactic point of view this is rather unfortunate and the student who relies exclusively on such aids is liable to lose much of the intuitive insight into the meaning and workings of even the simplest molecular orbital models, e.g. those calculated according to the Hückel-scheme[2]. He will often experience some difficulties in reading and in using the output of computations performed with readymade programs.[3] For this reason it is necessary to have him perform manual calculations for at least a few HMO-models of simple π-electron systems. These are usually carried out according to a tedious and lengthy procedure, involving the exact diagonalization of a matrix and the repeated solution of a system of linear equations. In this note we propose a considerably faster method, yielding approximations to the exact solution which are of sufficient accuracy for almost all practical purposes in theoretical organic chemistry.

The basis functions of Hückel molecular orbitals ψ[HMO] for a π-electron system of n centers are atomic orbitals (AO) ϕ_μ ($\mu = 1, 2, \ldots$ n) which form an orthonormal set:

$$\psi = c_1\phi_1 + c_2\phi_2 + \ldots + c_n\phi_n \tag{1}$$

$$\int \phi_\mu\phi_\nu \, dv = \delta_{\mu\nu} = \begin{cases} 1 \text{ if } \mu = \nu \\ 0 \text{ if } \mu \neq \nu \end{cases} \tag{2}$$

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[1] C. A. Coulson and A. Streitwieser Jr., *Dictionary of π-Electron Calculations*. Pergamon Press, Oxford (1965); A. Streitwieser Jr. and J. I. Brauman, *Supplemental Tables of Molecular Orbital Calculations*. Pergamon Press, Oxford (1965); E. Heilbronner and P. A. Straub, *HMO-Hückel Molecular Orbitals*. Springer Verlag, Heidelberg (1966).

[2] E. Hückel, *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*. Verlag Chemie Heidelberg (1938). A. Streitweiser Jr., *Molecular Orbital Theory for Organic Chemists*. Wiley, New York (1961).

[3] Such programs, among others, are given in: K. Wiberg, *Physical Organic Chemistry*, Interscience, New York (1965); E. Heilbronner and P. A. Straub Ref. 1; Programs can be obtained from: *Quantum Chemistry Program Exchange*, Department of Chemistry, (Dr. F. Prosser) Indiana University, Bloomington, Indiana.

With respect to a suitable energy operator $\mathscr{H}$ the AOs ϕ_μ (assumed to be real functions) yield the matrix elements

$$H_{\mu\nu} = \int \phi_\mu \mathscr{H} \phi_\nu \, dv \tag{3}$$

For unsaturated or aromatic hydrocarbons, zeroth order HMO-theory postulates that

$$H_{\mu\mu} = \alpha, \qquad H_{\mu\nu} = \beta \tag{4}$$

for all centers μ and all bonds μ, ν between nearest neighbours. $H_{\mu\nu}$ is set equal to zero for non-bonded pairs of centers.

According to (4) the AOs $\phi_1, \phi_2, \ldots, \phi_n$ define a basis which is n-fold degenerate. Therefore, the corresponding eigenvalue problem,

$$\mathscr{H}\psi = \varepsilon\psi \tag{5}$$

leads, according to the rules for perturbation treatments of highly degenerate systems,[4] to a secular determinant of order n:

$$\|H_{\mu\nu} - \varepsilon\delta_{\mu\nu}\| = 0 \tag{6}$$

This is often transformed into its equivalent standard form, the so called Hückel determinant

$$\|B_{\mu\nu} - x\delta_{\mu\nu}\| = 0 \tag{7}$$

where $B_{\mu\nu} = 1$ for bonded centers μ, ν and $B_{\mu\nu} = 0$ otherwise. The solution of (7), that is the n eigenvalues $x_1, x_2, \ldots, x_J, \ldots, x_n$ which define the orbital energies

$$\varepsilon_J = \alpha + x_J\beta \qquad (J = 1, 2, \ldots, n) \tag{8}$$

and the coefficients $c_{J\mu}$ underlying the corresponding linear combinations (HMOs)

$$\psi_J = c_{J1}\phi_1 + c_{J2}\phi_2 + \ldots + c_{Jn}\phi_n \tag{9}$$

are easily obtained with the help of modern computing facilities, even for high orders of n.

In all textbooks on the subject, essentially the same procedure is recommended for obtaining ε_J and ψ_J by hand. The necessary steps are:

(1) The Hückel determinant (7) (written in terms of x) is expanded into a polynominal P(x) of order n.

(2) The n roots of the equation $P(x) = 0$ are computed.

(3) The coefficients $c_{J\mu}$ of the linear combinations (8) are obtained by solving the secular equations for each root x_J.

Factorization of the determinant (7) may precede step 2, if the system has the appropriate symmetry. A desk calculator is needed for performing the lengthy computations involved in steps (2) and (3).

This procedure implicitely assumes that the only information available *a priori* for obtaining the HMOs of a given π-electron system is that which is needed for the establishment of the Hückel determinant: e.g. the topology of the π-electron system. However, this is not the case: It is well known that for mathematical reasons the HMOs must comply to a series of rules, some of which can be summarised as follows:[5]

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[4] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics.* McGraw-Hill, New York (1935).

[5] A more complete set of rules has been given by: M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

Rule a. A π-electron system consisting of n AOs ϕ_μ ($\mu = 1, \ldots, n$) has n orthonormal HMOs ψ_J ($J = 1, \ldots, n$), which we assume to be numbered according to increasing orbital energies ε_J.

Rule b. In the HMO ψ_1 of lowest energy ε_1 all coefficients $c_{1\mu}$ of the linear combination (9) have the same (positive) sign.

Rule c. In purely linear systems the number of nodes in the HMO ψ_J is equal to J-1. For a pure perimeter the number of nodes in the pair of degenerate HMOs ψ_J and ψ_{n-J} is equal to 2J ($J = 1, 2, \ldots$). In a general way the number of nodes in the HMOs ψ_J of a given π-electron system increases with increasing orbital energy ε_J. (This last rule has exceptions.) In the cyclic systems the single HMO ψ_0 of lowest energy ε_0 has no nodes and for even n the highest HMO $\psi_{n/2}$ has n nodes.

Rule d. In alternant systems[6] there belongs to each HMO ψ_J an alternant HMO ψ_{n-J+1} which differs from ψ_J only in that the sign of the coefficients of the set of starred (or unstarred) AOs is reversed:

$$\begin{aligned} \psi_J &= \sum_\mu{}^{*} c_{J\mu}\phi_\mu + \sum_\nu{}^{\circ} c_{J\nu}\phi_\nu \\ \psi_{n-J+1} &= \sum_\mu{}^{*} c_{J\mu}\phi_\mu - \sum_\nu{}^{\circ} c_{J\nu}\phi_\nu \end{aligned} \tag{10}$$

As a consequence the corresponding energies satisfy the following conditions:

$$\varepsilon_J = \alpha + x_J\beta; \quad \varepsilon_{n-J+1} = \alpha - x_J\beta, \text{ that is } x_{n-J+1} = -x_J \tag{11}$$

Rule e. Alternant systems with an odd number n of AOs have at least one nonbonding HMO $\psi_{n.b.}$ of energy $\varepsilon_{n.b.} = \alpha$ ($x_{n.b.} = 0$). In the linear combination $\psi_{n.b.}$ (9) the coefficients of the smaller set of AOs (starred or unstarred) are zero.

More precisely, the number of non-bonding orbitals in an alternant system is equal to or larger than the difference between the number of starred and unstarred atomic orbitals.[6]

Rule f. The HMO ψ_J of a π-electron system having symmetry, must be either symmetric or antisymmetric with respect to symmetry elements of order 2 (e.g. twofold axis, mirror planes and centers of inversion).

In a more general way, the HMOs of a system of given symmetry must belong to one of the irreducible representations of the group. The number of HMOs belonging to each irreducible representation can be established a priori by the usual methods of group theory[7] or, in most cases of interest to us, by simple inspection.

Rule g. For isoconjugate π-electron systems, the distance between two consecutive nodes in a given HMO ψ_J (measured in bond-length or number of AOs) is roughly a constant.

These rules—which are needed to develop the procedure described in this paper—are only a selection from the more complete set of rules given by Dewar.[5]

We shall now demonstrate that a very convenient method for calculating satisfactory approximations to ε_J and ψ_J results if we make use of the following simple and rather obvious basis transformations:

(1) Replace the AOs ϕ_μ by a set of new basis functions φ_J ($J = 1, 2, \ldots, n$)

$$\varphi_J = N_J(a_{J1}\phi_1 + a_{J2}\phi_2 + \ldots + a_{Jn}\phi_n) \tag{12}$$

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[6] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **36**, 193 (1940); H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 275 (1950). See also Ref. 5.

[7] For example: F. A. Cotton. *Chemical Applications of Group Theory*. Wiley, New York (1963).

such that the coefficients $a_{J\mu}$ are either $+1$, -1 or zero. N_J is the appropriate normalisation constant. Such functions φ_J will be called "qualitative molecular orbitals" (QMO).

(2) Incorporate as many of the rules *a* to *g* as possible into the set of basis functions φ_J. Due to the incorporation of the rules *a* to *g*, the QMOs φ_J in themselves will turn out to be in many cases useful, if somewhat crude, approximations to the set of exact HMOs ψ_J. Especially from a didactic point of view the construction of such QMOs for a series of simple model systems will yield considerable intuitive insight into the workings of HMO theory. Examples will be given in the next paragraph.

(3) Make sure that the basis set is complete, that is that the φ_J are linearly independent. (This condition is automatically satisfied if the rules *a* to *g* are applied correctly).

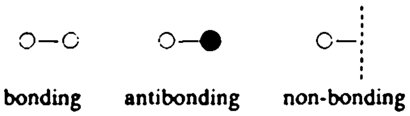
It is easy to show (and in a way rather obvious) that such QMOs will have the property that members φ_J belonging to the same irreducible representation (symmetry type) are no longer degenerate, i.e. that their energies

$$E_J = \alpha + y_J\beta \tag{13}$$

are all different. (We assume for the moment that the system has no symmetry elements of order higher than 2).

Qualitative Molecular Orbitals (*QMO*)

We introduce the following definitions and symbols: If in a particular QMO ψ_J two bonded AOs ϕ_μ and ϕ_ν occur in the linear combination (12) with the same (opposite) sign, we call this a bonding (antibonding) interaction between nearest neighbours. If either ϕ_μ or ϕ_ν (or both) are affected with coefficients zero, the interaction is non-bonding. AOs affected with opposite sign are represented graphically by contrasting colours (here open and filled circles). Bonding, antibonding and non-bonding interactions are given as:



(Nodes through AOs are represented as vertical dotted lines).

Let Z_b, Z_a and Z_n be the number of bonding, antibonding and non-bonding interactions in a given QMO. If Z is the number of bonds in the system, we have obviously

$$Z = Z_a + Z_b + Z_n \tag{14}$$

(the number of nodes across bonds is Z_a and the number of nodes through centers usually $Z_{n/2}$.)

The normalising factor N_J of the linear combination φ_J (12) is equal to the inverse square root of the number of coefficients $a_{J\mu}$ different from zero:

$$\boxed{N_J = \Big(\sum_{\mu} |a_{J\mu}|\Big)^{-1/2}} \tag{15}$$

It is easy to show that the energy E_J (13) associated with a given basis function φ_J is

$$E_J = \int \varphi_J \mathscr{H} \varphi_J \, dv = \alpha + 2\beta N_J^2(Z_b - Z_a) \tag{16}$$

or according to (13)

$$\boxed{y_J = 2N_J^2(Z_b - Z_a)} \tag{17}$$

Example A. We give as a first trivial example the QMOs for the alternant chain of six AOs ("hexatriene"): $\overset{*}{C}H_2{=}CH{-}\overset{*}{C}H{=}CH{-}\overset{*}{C}H{=}CH_2$.

J			Sym.	N_J	Z_b	Z_a	Z_n	y_J
6	φ_6	●—○—●—○—●—○	B	$1/\sqrt{6}$	0	5	0	$-1\frac{2}{3}$
5	φ_5	●—○—●—●—○—●	A	$1/\sqrt{6}$	1	4	0	-1
4	φ_4	●···⋮ -○—●—⋮— ○	B	$\frac{1}{2}$	0	1	4	$-\frac{1}{2}$
3	φ_3	● — ⋮—○—○—⋮ ●	A	$\frac{1}{2}$	1	0	4	$\frac{1}{2}$
2	φ_2	●—●—●—○—○ ··○	B	$1/\sqrt{6}$	4	1	0	1
1	φ_1	●—●—●—●—● ·●	A	$1/\sqrt{6}$	5	0	0	$1\frac{2}{3}$

The choice of basis functions φ_1 is obvious: φ_1 is determined by rule *b* and its alternant basis function φ_6 according to *d*, that is by changing the signs on all unstarred centers. Rules *c* and *f* require φ_2 and hence φ_5 (according to *d*). Finally φ_3 has to have two nodes (rule *c*) arranged symmetrically (rule *f*) and again φ_4 follows from *d*. There are two reasonable choices for φ_3 with coefficients 1, 0, −1, −1, 0, 1 and 1, 1, −1, −1, 1, 1 of which the former is to be preferred. According to rule *a* this completes the set.

In the diagram the basis functions have been arranged according to their energy. A and B denote whether the diagram for φ_J is symmetric or antisymmetric with respect to a reflection in a plane through the middle and perpendicular to the center bond. The parameters Z_b, Z_a, Z_n and N_J defined previously in formulae (14) and (15) have been indicated. From them the coefficient y_J of the energy E_J is calculated according to (17). (Example: The coefficient y_2 of the energy E_2 of φ_2 is $y_2 = 2(\frac{1}{2})^2(4\text{-}1) = 1\frac{1}{2}$. From (11) we deduce that $y_5 = -y_2 = -1\frac{1}{2}$.)

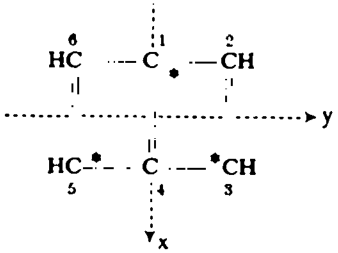
Another compact way to represent the QMOs φ_J consists in listing the coefficients $a_{J\mu}$ in form of a matrix $A - (a_{J\mu})$ which, in our example would read:

$$A = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & 0 & -1 & -1 & 0 & 1 \\ 1 & 0 & -1 & 1 & 0 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 \end{pmatrix}$$

If $N = (N_J)$ is the diagonal matrix of the normalising constants then NA contains the normalised coefficients of the QMOs φ_J.

Example B. As a second example we give here the QMOs for the hypothetical, alternant system of 1,4-dehydrobenzene, the simplest nontrivial example for a

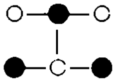
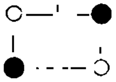
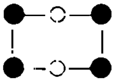
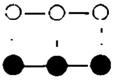
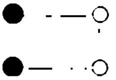
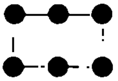
π-electron system of D_{2h}-symmetry:



Here simple group theoretical arguments (rule *f*) are sufficient for the establishment of the six QMOs of this system, which has only two sets of equivalent AOs: $\{\phi_1, \phi_4\}$, $\{\phi_2, \phi_3, \phi_5, \phi_6\}$. These must transform either symmetrically (s) or antisymmetrically (a) under the influence of a reflection in the mirror plane $\sigma(x, z)$ or $\sigma(y, z)$. Of course no contribution from $\{\phi_1, \phi_4\}$ can be included in QMOs which are antisymmetric with respect to $\sigma(x, z)$. Using a character table for D_{2h} or simply by inspection we get:

Number of QMOs	Behaviour relative to $\sigma(x, z)$	$\sigma(y, z)$	Irreducible Rep. (D_{2h})
2	s	s	B_{1u}
2	s	a	B_{2g}
1	a	s	B_{3g}
1	a	a	A_u

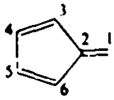
QMOs:

J		Sym	N_J	Z_b	Z_a	Z_n	y_J
6	φ_6 	B_{3g}	$1/\sqrt{6}$	0	7	0	$-2\frac{1}{2}$
5	φ_5 	A_u	$\frac{1}{2}$	0	2	5	-1
4	φ_4 	B_{1u}	$1/\sqrt{6}$	3	4	0	$-\frac{1}{2}$
3	φ_3 	B_{2g}	$1/\sqrt{6}$	4	3	0	$\frac{1}{2}$
2	φ_2 	B_{3g}	$\frac{1}{2}$	2	0	5	1
1	φ_1 	B_{1u}	$1/\sqrt{6}$	7	0	0	$2\frac{1}{2}$

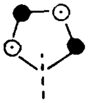
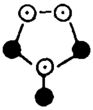
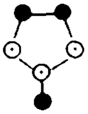
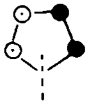
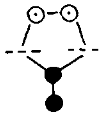
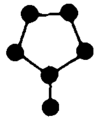
Note that all rules (a) to (g) are satisfied by this set of QMOs. Their A-matrix is:

$$A = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & -1 & -1 & 0 & 1 & 1 \\ -1 & -1 & 1 & 1 & 1 & -1 \\ -1 & 1 & 1 & -1 & 1 & 1 \\ 0 & 1 & -1 & 0 & 1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 \end{pmatrix}$$

Example C. As an example of a non alternant π-electron system we take fulvene (symmetry C_{2v}):



Elementary group theory demands four functions φ_J of symmetry type B′ and four functions of symmetry type A″. This, together with rules (b, f and g) yields the QMOs given below. Notice that the y_J do not form a symmetric pattern with respect to zero (non alternant system.).

J			Sym	N_J	Z_b	Z_a	Z_n	y_J
6	φ_6		A″	½	0	3	3	−1½
5	φ_5		B′	$1/\sqrt{6}$	1	5	0	−1⅓
4	φ_4		B′	$1/\sqrt{6}$	3	3	0	0
3	φ_3		A″	½	2	1	3	½
2	φ_2		B′	½	2	0	4	1
1	φ_1		B′	$1/\sqrt{6}$	6	0	0	2

$$A = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & -1 & -1 & 0 \\ 0 & 0 & 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 \\ 0 & 0 & 1 & 1 & 1 & -1 \end{pmatrix}$$

We conclude by remarking that the parameters y_J of our QMOs do already constitute a crude approximation to the HMO-values x_J, as shown in the following Table:

	A		B		C	
J	hexatriene		1,4-dehydrobenzene		fulvene	
	y_J	x_J	y_J	x_J	y_J	x_J
1	1·67	1·80	2·33	2·41	2·00	2·11
2	1·00	1·25	1·00	1·00	1·00	1·00
3	0·50	0·45	0·33	0·41	0·50	0·62
4	−0·50	−0·45	−0·33	−0·41	0·00	−0·25
5	−1·00	−1·25	−1·00	−1·00	−1·33	−1·86*
6	−1·67	−1·80	−2·33	2·41	−1·50	−1·62*

* φ_5 corresponds to ψ_6 and φ_6 to ψ_5 (see later).

Computation of approximate HMOs ψ_J'

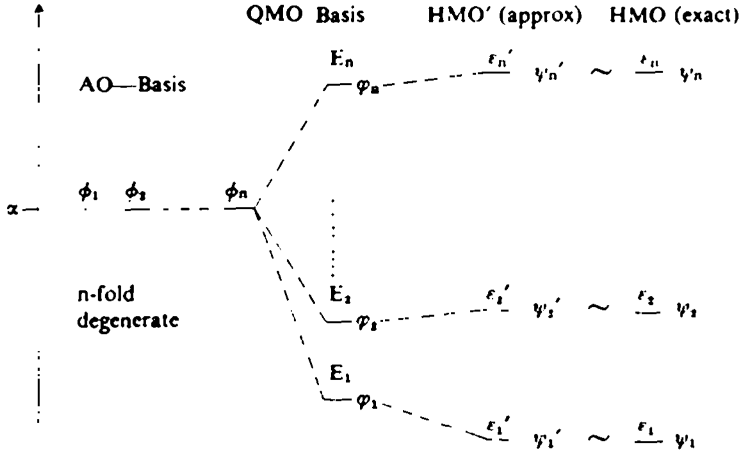
Obviously the major drawback of a standard HMO calculation is that the orthonormal set of basis AOs ϕ_μ in the LCAO-MO ψ (1) is n fold degenerate, and that it leads therefore to a secular determinant of order n. In contrast to this, the equivalent linear combination

$$\psi = c_1\varphi_1 + c_2\varphi_2 + \ldots c_n\varphi_n \tag{18}$$

is based on QMOs φ_J which are not degenerate (at least inside one irreducible representation). Furthermore the interaction terms $H_{\mu\nu} = \beta$ between bonded AOs ϕ_μ and ϕ_ν (3, 4) are large, while the corresponding matrix elements

$$h_{JK} = \int \varphi_J \mathscr{H} \varphi_K \, dv \tag{19}$$

are expected to be small, in view of the close relationship of the φ_J to the exact interaction free HMOs ψ_J. We therefore expect that a second order perturbation treatment starting from the φ_J and their energies E_J will yield approximate orbital energies ε_J' and approximate functions ψ_J' which will be close enough to the exact HMO-values ε_J and ψ_J for most practical purposes:



To obtain from the basis φ_J the approximations ψ_J' to the true HMOs ψ_J we write for a particular orbital of index R

$$\boxed{\psi_R' = M_R\Big(\varphi_R + \sum_{J \neq R} b_{RJ}\varphi_J\Big)} \tag{20}$$

making use of second order perturbation theory for the determination of the coefficients b_{RJ} and renormalising the linear combination by multiplying with a suitable factor M_R. The corresponding energies $\varepsilon_R' = \alpha + x_R'\beta$ (c.f. (8)) are calculated according to

$$\varepsilon_R' = E_R + \sum_{J \neq R} \Delta E_{RJ} \tag{21}$$

or

$$\boxed{x_R' = y_R + \sum_{J \neq R} \Delta y_{RJ}} \tag{22}$$

where the ΔE_{RJ} or the Δy_{RJ} are the second order perturbation due to the interaction of φ_R and φ_J under the influence of the operator $\mathscr{H}$. Obviously b_{RJ} and ΔE_{RJ} are different from zero only when φ_R and φ_J belong to the same irreducible representation.

Such calculations yield approximations which are quite satisfactory for most organic chemical applications. They involve only whole numbers or simple fractions and can be performed on a slide rule or with the help of a table of squares and square roots. The calculations require very little time, especially if only approximations to particular orbitals are needed (e.g. the highest bonding and lowest antibonding HMOs of a system). The procedure is best outlined with reference to simple examples.

In general it will be found that the QMOs φ_J deduced from the rules *a* to *g* form a set of normalised basis functions φ_J which are *not* all orthogonal to each other, so that the matrix of the overlaps

$$S_{JK} = \int \varphi_J \varphi_K \, dv \tag{23}$$

differs from the unit matrix. However, this will not complicate the calculation in a noticeable way. Also, in most cases, only a few of the matrix elements S_{JK} with $J \neq K$ are different from zero.

The overlaps are computed according to

$$\boxed{S_{JK} = N_J N_K \sum_{\mu} a_{J\mu} a_{K\mu}} \tag{24}$$

a sum which can be carried out by inspection, the products $a_{J\mu}a_{K\mu}$ being either $+1$, -1 or zero.

Taking hexatriene (A) as an example we find that the overlap S_{15} between φ_1 and φ_5 (both of symmetry A) is

$$S_{15} = \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{6}} (1 - 1 + 1 + 1 - 1 + 1) = \tfrac{1}{3}.$$

The complete matrix $S = (S_{JK})$ reads:

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 & \frac{1}{3} & 0 \\ 0 & 1 & 0 & 0 & 0 & \frac{1}{3} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ \frac{1}{3} & 0 & 0 & 0 & 1 & 0 \\ 0 & \frac{1}{3} & 0 & 0 & 0 & 1 \end{pmatrix}$$

The next step consists in calculating the energy crossterms

$$\boldsymbol{h}_{JK} = \int \varphi_J \mathscr{H} \varphi_K \, dv = S_{JK}\alpha + h_{JK}\beta \tag{25}$$

between two basis functions belonging to the same irreducible representation (otherwise the crossterm will be zero). The factor

$$h_{JK} = N_J N_K \sum_{\mu} \sum_{\substack{\nu \text{ bonded} \\ \text{to } \mu}} a_{J\mu} a_{K\nu} \tag{26}$$

is best obtained as a sum of contributions due to each of the bonds between nearest neighbours:

$$\boxed{h_{JK} = N_J N_K \sum_{\substack{\text{bonds} \\ (\mu,\nu)}} i(\mu, \nu)} \tag{27}$$

To determine the individual contributions $i(\mu, \nu)$, the bond μ, ν in φ_J is to be compared to the same bond in φ_K. The following situations may arise:

	●—●	●—○	○—●	○—○	●- -⋮	○· ·⋮	⋮—●	⋮—○
●—●	+2	0	0	−2	+1	−1	+1	−1
●—○	0	−2	+2	0	−1	+1	+1	−1
○—●	0	+2	−2	0	+1	−1	−1	1
○—○	−2	0	0	+2	−1	+1	−1	1
●—⋮	+1	−1	+1	−1	0	0	+1	−1
○ - ⋮	−1	+1	−1	+1	0	0	−1	+1
⋮- ●	+1	+1	−1	−1	+1	−1	0	0
⋮-- ○	−1	−1	+1	+1	−1	+1	0	0

For example, the interaction terms h_{13} and h_{16} for the QMOs φ_1, φ_3 and φ_6 of hexatriene (A) are computed as shown:

φ_3 ●—⋮—○—○—⋮—●
φ_1 ●—●—●—●—●—●
$i(\mu, \nu)$ 1 −1 −2 −1 1

$$h_{13} = \left(\frac{1}{\sqrt{6}}\right)\frac{1}{2}(1 - 1 - 2 - 1 + 1) = \frac{-1}{\sqrt{6}}$$

φ_6 ●—○—●—●—○—●
φ_1 ●—●—●—●—●—●
$i(\mu, \nu)$ 0 0 2 0 0

$$h_{16} = \left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right)(0 + 0 + 2 + 0 + 0) = \frac{1}{3}$$

The complete matrix $\mathbf{h} = (h_{JK})$ for our example reads (reminder: $h_{JJ} \equiv y_J$):

$$\mathbf{h} = \begin{pmatrix} 1\frac{2}{3} & 0 & -1/\sqrt{6} & 0 & \frac{1}{3} & 0 \\ 0 & 1 & 0 & 1/\sqrt{6} & 0 & -\frac{1}{3} \\ -1/\sqrt{6} & 0 & \frac{1}{2} & 0 & -1/\sqrt{6} & 0 \\ 0 & 1/\sqrt{6} & 0 & -\frac{1}{2} & 0 & 1/\sqrt{6} \\ \frac{1}{3} & 0 & -1/\sqrt{6} & 0 & -1 & 0 \\ 0 & -\frac{1}{3} & 0 & 1/\sqrt{6} & 0 & -1\frac{2}{3} \end{pmatrix}$$

The second order perturbation terms b_{RJ} and Δy_{RJ} of the formulae (20 and 22) are written in terms of the matrix elements S_{JK} and h_{JK} according to well known relations,[8] remembering that $h_{JJ} = y_J$:

$$b_{RJ} = \frac{h_{RJ} - S_{RJ}y_R}{y_R - y_J} \tag{28}$$

$$\begin{aligned} \Delta y_{RJ} &= \frac{(h_{RJ} - S_{RJ}y_R)^2}{y_R - y_J} \\ &= b_{RJ}(h_{RJ} - S_{RJ}y_R) \end{aligned} \tag{29}$$

Insertion of (28) and (29) into (20) and (22) yields:

$$\psi_R' = M_R\left(\varphi_R + \sum_{J \neq R}\left(\frac{h_{RJ} - S_{RJ}y_R}{y_R - y_J}\right)\varphi_J\right) \tag{30}$$

$$x_R' = y_R + \sum_{J \neq R} \frac{(h_{RJ} - S_{RJ}y_R)^2}{y_R - y_J} \tag{31}$$

For practical purposes it is more convenient to rewrite expression (30) in terms of the AOs ϕ_μ:

$$\psi_R' = c_{R1}'\phi_1 + c_{R2}'\phi_2 + \ldots + c_{Rn}'\phi_n \tag{32}$$

where the coefficients $c_{R\mu}'$ are defined as

$$c_{R\mu}' = M_R(a_{R\mu}N_R + \sum_{J \neq R} b_{RJ}a_{J\mu}N_J) \tag{33}$$

The expression in parenthesis is compiled first and then the normalisation constant M_R is chosen such that

$$c_{R1}'^2 + c_{R2}'^2 + \ldots + c_{Rn}'^2 = 1 \tag{34}$$

While these formulae may seem rather complicated, their application is extremely simple as only small rational numbers are involved. For hexatriene (A) the approximation x_1' to the coefficient of the true eigenvalue ε_1 is according to (31)

$$x_1' = 1\tfrac{2}{3} + \frac{\left(-\frac{1}{\sqrt{6}} - 0 \cdot 1\frac{2}{3}\right)^2}{1\frac{2}{3} - \frac{1}{2}} + \frac{(\frac{1}{3} - \frac{1}{3} \cdot 1\frac{2}{3})^2}{1\frac{2}{3} - (-1)} = 1{\cdot}83$$

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[8] For example: J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*. Methuen, London (1963).

and the linear combination $\psi_1{}'$ according to (30)

$$\psi_1{}' = \mathrm{M}_1\left(\varphi_1 + \frac{\left(-\frac{1}{\sqrt{6}} - 0\,.\,1\frac{2}{3}\right)}{1\frac{2}{3} - \frac{1}{2}}\,\varphi_3 + \frac{\left(\frac{1}{3} - \frac{1}{3}\,.\,1\frac{2}{3}\right)}{1\frac{2}{3} - (-1)}\,\varphi_5\right)$$

$$\psi_1{}' = \mathrm{M}_1(\varphi_1 - 0{\cdot}350\,\varphi_3 - 0{\cdot}083\,\varphi_5).$$

From this result (i.e. the coefficients $b_{13} = -0{\cdot}350$, $b_{15} = -0{\cdot}083$) and the known values of the coefficients $a_{1\mu}$, $a_{3\mu}$ and $a_{5\mu}$ of the AOs ϕ_μ in φ_1, φ_3 and φ_5, the unnormalised coefficients of the AOs ϕ_μ in $\psi_1{}'$ are computed as follows. (This corresponds to the bracket in expression 33.)

	μ	1	2	3	4	5	6
φ_1	$\mathrm{N}_1 \cdot a_{1\mu}$ =	0·408	0·408	0·408	0·408	0·408	0·408
φ_3	$-0{\cdot}350\,\mathrm{N}_3 a_{3\mu}$ =	−0·175	0	0·175	0·175	0	−0·175
φ_5	$-0{\cdot}083\,\mathrm{N}_5 a_{5\mu}$ =	−0·034	0·034	−0·034	−0·034	0·034	−0·034
unnormalised $c'_{1\mu}$		0·199	0·442	0·549	0·549	0·442	0·199

From these the normalised linear combination is obtained as

$$\psi_1{}' = 0{\cdot}19\phi_1 + 0{\cdot}43\phi_2 + 0{\cdot}53\phi_3 + 0{\cdot}53\phi_4 + 0{\cdot}43\phi_5 + 0{\cdot}19\phi_6$$

In the following table the approximate results $\psi_J{}'$, $x_J{}'$ for hexatriene are compared to the exact HMO figures ψ_J and x_J. Only the values for the bonding orbitals ψ_1, ψ_2, ψ_3 are given. The others follow from the alternancy principle.

J		c_{J1}	c_{J2}	c_{J3}
1	$x_1 = 1{\cdot}80$	$\psi_1 = 0{\cdot}23$	0·42	0·52
	$x_1{}' = 1{\cdot}83$	$\psi_1{}' = 0.19$	0·43	0·53
2	$x_2 = 1{\cdot}25$	$\psi_2 = 0{\cdot}42$	0·52	0·23
	$x_2{}' = 1{\cdot}28$	$\psi_2{}' = 0{\cdot}45$	0·52	0·17
3	$x_3 = 0{\cdot}45$	$\psi_3 = 0{\cdot}52$	0·23	−0·42
	$x_3{}' = 0{\cdot}47$	$\psi_3{}' = 0{\cdot}50$	0·24	−0·44

As can be seen, the approximation is quite sufficient for most practical purposes.

The calculation becomes almost trivial if the system is highly symmetrical, such as the one given in our example B (1,4-dehydrobenzene). In this particular case only φ_1 and φ_4 (belonging to the irreducible representation B_{1u}) or φ_3 and φ_6 (belonging to B_{2g}) can interact. Furthermore, as φ_1 and φ_6 as well as φ_3 and φ_4 are paired, alternant QMOs, the perturbation calculation needs to be carried out only once, for one of the irreducible representations (e.g. for B_{1u}). The rules given above yield:

$$x_1{}' = x_1 + \frac{(h_{14} - S_{14}x_1)^2}{x_1 - x_4} = 2\tfrac{1}{3} + \frac{(\frac{1}{3} - \frac{1}{3}\,\frac{7}{3})^2}{\frac{7}{3} + \frac{1}{3}} = 2{\cdot}407$$

$$x_4{}' = x_4 + \frac{(h_{14} - S_{14}x_4)^2}{x_4 - x_1} = -\tfrac{1}{3} - \frac{(\frac{1}{3} + \frac{1}{3}\,\frac{1}{3})^2}{\frac{8}{3}} = -0{\cdot}407$$

$$\psi_1{}' = \mathrm{M}_1\left(\varphi_1 + \frac{h_{14} - S_{14}x_1}{x_1 - x_4}\,\varphi_4\right) = \mathrm{M}_1(\varphi_1 - \tfrac{1}{6}\varphi_4)$$

$$\psi_4{}' = \mathrm{M}_1\left(\varphi_4 + \frac{h_{14} - S_{14}x_4}{x_4 - x_1}\,\varphi_1\right) = \mathrm{M}_1(\varphi_4 - \tfrac{1}{6}\varphi_1)$$

After renormalisation of ψ_1' and ψ_4' the results obtained compare favourably to the exact HMO-values x_J and ψ_J:

J		
1	$x_1 = 2{\cdot}414$ $x_1' = 2{\cdot}407$	$\psi_1 = 0{\cdot}354(\phi_2 + \phi_3 + \phi_5 + \phi_6) + 0{\cdot}500(\phi_1 + \phi_4)$ $\psi_1' = 0{\cdot}355(\phi_2 + \phi_3 + \phi_5 + \phi_6) + 0{\cdot}497(\phi_1 + \phi_4)$
2	$x_2 = 1{\cdot}000$ $x_2' = 1{\cdot}000$	$\psi_2 = 0{\cdot}500(\phi_2 + \phi_3 - \phi_5 - \phi_6)$ $\psi_2' = 0{\cdot}500(\phi_2 + \phi_3 - \phi_5 - \phi_6)$
3	$x_3 = 0{\cdot}414$ $x_3' = 0{\cdot}407$	$\psi_3 = 0{\cdot}354(\phi_2 - \phi_3 - \phi_5 + \phi_6) + 0{\cdot}500(\phi_1 - \phi_4)$ $\psi_3' = 0{\cdot}355(\phi_2 - \phi_3 - \phi_5 + \phi_6) + 0{\cdot}497(\phi_1 - \phi_4)$

All other values follow from the alternancy principle (rule *d*, formulae (10), (11)).

We now summarise the actual numerical procedure involved in calculating the approximations x_J' and ψ_J', using example C (fulvene).

STEP I: Derive a QMO-basis for the system, which satisfies rules *a* to *g*.

This has been done above. The QMOs φ_J, belong to two irreducible representations of the group C_{2v}: φ_1, φ_2, φ_4, φ_5 to B′, φ_3, φ_6 to A″. It is useful—but not necessary—to rearrange the corresponding **A**-matrix in such a way that the coefficients of the QMOs belonging to the same irreducible representation are in adjacent lines, as shown here:

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{B'} \\ \hdashline \mathbf{A}_{A''} \end{pmatrix}$$

$$\mathbf{A}_{B'} = \left(\begin{array}{rrrrrr} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & -1 & -1 & 0 \\ 1 & -1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 \end{array}\right)\begin{array}{l} \varphi_1 \\ \varphi_2 \\ \varphi_4 \\ \varphi_5 \end{array} \qquad \mathbf{A}_{A''} = \left(\begin{array}{rrrrrr} 0 & 0 & -1 & -1 & 1 & 1 \\ 0 & 0 & -1 & 1 & -1 & 1 \end{array}\right)\begin{array}{l} \varphi_3 \\ \varphi_6 \end{array}$$

The matrices $\mathbf{N}_{B'}$ and $\mathbf{N}_{A''}$ which would yield the normalised QMO-coefficients according to $\mathbf{N}_{B'} . \mathbf{A}_{B'}$ and $\mathbf{N}_{A''} . \mathbf{A}_{A''}$ are therefore:

$$\mathbf{N}_{B'} = \begin{pmatrix} 1/\sqrt{6} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1/\sqrt{6} & 0 \\ 0 & 0 & 0 & 1/\sqrt{6} \end{pmatrix} \qquad \mathbf{N}_{A''} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$$

STEP II: Compute the overlap matrix **s**.

As a consequence of the rearrangement of **A**, the overlap matrix is obtained in a factorised form

$$\mathbf{s} = \left(\begin{array}{c:c} \mathbf{s}_{B'} & 0 \\ \hdashline 0 & \mathbf{s}_{A''} \end{array}\right)$$

0 standing for a zero matrix of order 4 × 2. By inspection we obtain from the QMOs:

$$\mathbf{s}_{B'} = \begin{array}{c} \begin{array}{cccc} 1 & 2 & 4 & 5 \end{array} \\ \left(\begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & -1/\sqrt{6} & 1/\sqrt{6} \\ 0 & -1/\sqrt{6} & 1 & -\frac{1}{3} \\ 0 & 1/\sqrt{6} & -\frac{1}{3} & 1 \end{array}\right) \end{array} \begin{array}{l} \\ 1 \\ 2 \\ 4 \\ 5 \end{array} \qquad \mathbf{s}_{A''} = \begin{array}{c} \begin{array}{cc} 3 & 6 \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{array} \begin{array}{l} \\ 3 \\ 6 \end{array}$$

STEP III: Compute the interaction matrix $\mathbf{h}$.

Again $\mathbf{h}$ is obtained in a factorised form:

$$\left(\begin{array}{c:c} \mathbf{h}_{B'} & 0 \\ \hdashline 0 & \mathbf{h}_{A''} \end{array}\right)$$

$$\mathbf{h}_{B'} = \begin{pmatrix} 2 & 0 & \frac{1}{3} & -\frac{1}{3} \\ 0 & 1 & -1/\sqrt{6} & -1/\sqrt{6} \\ -\frac{1}{3} & -1/\sqrt{6} & 0 & 0 \\ -\frac{1}{3} & 1/\sqrt{6} & 0 & -1\frac{1}{3} \end{pmatrix} \qquad \mathbf{h}_{A''} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{3}{2} \end{pmatrix}$$

Note that the diagonal elements h_{JJ} are identical with y_J and the off diagonal terms h_{JK} are obtained according to the rules given by matching the individual bonds in QMOs φ_J and φ_K.

STEP IV: Compute the coefficients x_J' according to formula (31), using the matrix elements of $\mathbf{s}$ and $\mathbf{h}$.

For our example we obtain the following values of x_J', which are compared with the correct HMO coefficients x_J of fulvene. (It is noteworthy that our perturbation treatment has switched the sequence of the orbitals ψ_5' and ψ_6' relative to the sequence of φ_5, φ_6 and that agreement with the correct sequence of states has been obtained.)

J	y_J	x_J'	x_J	Sym.
1	2	2·09	2·11	B'
2	1	1·00	1·00	B'
3	$\frac{1}{2}$	0·63	0·62	A''
4	0	−0·22	−0·25	B'
5	$-1\frac{1}{3}$	1·90	−1·86	B'
6	$-1\frac{1}{2}$	−1·63	1·62	A''

STEP V: Compute the coefficients b_{JK} for the linear combination ψ_J' (20) according to formula (28), using the matrix elements of $\mathbf{s}$ and $\mathbf{h}$.

The coefficients b_{JK} can be collected in a matrix $\mathbf{b} = (b_{JK})$ which, in our particular example, factorises in the same way as $\mathbf{s}$ or $\mathbf{h}$:

$$\mathbf{b} = \left(\begin{array}{c:c} \mathbf{b}_{B'} & 0 \\ \hdashline 0 & \mathbf{b}_{A''} \end{array}\right)$$

$$\mathbf{b}_{B'} = \begin{pmatrix} 1 & 0 & -\frac{1}{6} & -\frac{1}{10} \\ 0 & 1 & 0 & 0 \\ \frac{1}{6} & 1/\sqrt{6} & 1 & 0 \\ \frac{1}{10} & -1/\sqrt{6} & \frac{1}{3} & 1 \end{pmatrix} \qquad \mathbf{b}_{A''} = \begin{pmatrix} 1 & \frac{1}{4} \\ -\frac{1}{4} & 1 \end{pmatrix}$$

The elements b_{JJ} are set equal to one. This is the factor of the basis function φ_J of the same index as ψ_J', as shown in the expression (30). The normalising factor M_J will be taken care of in the next step.

STEP VI: Compute the coefficients $c_{J\mu}'$ of the linear combination ψ_J' (32) from the matrix elements of $\mathbf{A}$ and $\mathbf{b}$.

This is done, according to the procedure outlined above. As shown, the coefficients $c_{J\mu}'$ of ψ_J' are obtained by first multiplying each row K of $\mathbf{A}$ by b_{JK}, adding the numbers so obtained column by column and normalising them (see (20) and (33)). As the matrix A contains only the entries 1, -1 and 0, the first part involves only additions and subtractions of the b_{JK}'s.

For our example C (fulvene) we obtain: (The values $c_{J\mu}$ given in the bottom half of the following table are the results obtained according to the exact HMO procedure.)

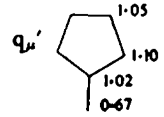
J	1	2	4	5	3	6
c_{J1}'	0·30	0·50	0·73	0·41	0	0
c_{J2}'	0·51	0·50	0·15	−0·77	0	0
c_{J3}'	0·43	0	−0·37	0·34	−0·61	−0·36
c_{J4}'	0·38	−0·50	0·29	−0·03	−0·36	0·61
c_{J5}'	0·38	−0·50	0·29	−0·03	0·36	−0·61
c_{J6}'	0·43	0	−0·37	0·34	0·61	0·36
c_{J1}	0·25	0·50	0·75	0·36	0	0
c_{J2}	0·52	0·50	−0·19	−0·66	0	0
c_{J3}	0·43	0	−0·35	0·44	−0·60	−0·37
c_{J4}	0·39	−0·50	0·28	−0·15	−0·37	0·60
c_{J5}	0·39	−0·50	0·28	−0·15	0·37	−0·60
c_{J6}	0·43	0	−0·35	0·44	0·60	0·37

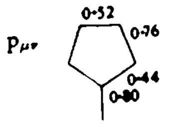
(Orbital 5 is of higher energy than orbital 6!)

STEP VII: Compute charge densities, bond orders etc. according to the traditional rules of HMO theory.

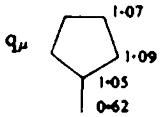
In the following diagrams the results obtained for the charge populations q_μ' and the bond orders $p_{\mu\nu}'$ of fulvene from the set of coefficients $c_{J\mu}'$ given above, have been compared with those calculated according to the standard HMO procedure.

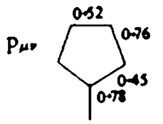
Approximate methode





Standard HMO





Iterative refinement of the results

If desired, the coefficients $c_{J\mu}'$ of ψ_J' and the values of x_J' can be refined, using the same technique as before with ψ_J' and x_J' playing the role of the QMOs φ_J and of y_J. It is of advantage to use a matrix formulation at this stage. Again all numbers will be simple rational numbers so that only a few multiplications and divisions are involved in the last stages of the computation. Usually a single iteration step will yield values for the coefficients of the linear combinations and for the approximation to x_J which are identical to the exact HMO values, inside the usual slide rule precision.

If the $a_{J\mu}$ are the coefficients $+1, 0, -1$ of the AOs ϕ_μ in the QMOs φ_J and N_J their normalisation constant, then the matrix

$$\boldsymbol{\alpha} = (N_J a_{J\mu}) \tag{35}$$

lists the coefficients of the normalised QMOs φ_J. The overlap matrix $\mathbf{s}$ is given by

$$\mathbf{s} = \boldsymbol{\alpha} . \boldsymbol{\alpha}^T \tag{36}$$

$\boldsymbol{\alpha}^T$ being the transposed matrix $\boldsymbol{\alpha}$. The matrix of the interactions h_{JK} between QMOs φ_J and φ_K (27) is obtained according to

$$\mathbf{h} = (h_{JK}) = \boldsymbol{\alpha}\mathbf{B}\boldsymbol{\alpha}^T \tag{37}$$

where $\mathbf{B}$ is the Hückel matrix $\mathbf{B} = (B_{\mu\nu})$ (c.f. (7)) of the π-electron system. From the entries in $\mathbf{s}$ and $\mathbf{h}$ we calculate the elements b_{JK} (28) of the matrix $\mathbf{b} = (b_{JK})$ as shown above (STEP V of the procedure, page 14). These quantities define the improved linear combinations ψ_J' (30)

$$\psi_J' = M_J \sum_K b_{JK} \varphi_K = \sum_\mu c_{J\mu}' \phi_\mu$$

which we have shown to be good approximations to the HMOs ψ_J. M_J is the normalisation factor $M_J = \left(\sum_K \sum_L b_{JK} b_{JL} s_{KL}\right)^{-1/2}$, which however is calculated more conveniently according to the procedure outlined above $\left(\text{that is as } M_J^2 = \sum_\mu \left(\sum_K b_{JK} \alpha_{K\mu}\right)^2\right)$. If we define the matrix

$$\boldsymbol{\beta} = (M_J b_{JK}) \tag{38}$$

then the matrix $c' = (c_{J\mu}')$ of the coefficients $c_{J\mu}'$ in the linear combination ψ_J' can be written as

$$c' = \boldsymbol{\beta}\boldsymbol{\alpha}^T \tag{39}$$

We now substitute the QMOs φ_J in the method given in the previous paragraph by the improved orbitals ψ_J', and we compute the matrices $\mathbf{s}'$ and $\mathbf{h}'$ which take the place of $\mathbf{s}$ and $\mathbf{h}$ (36 and 37):

$$\mathbf{s}' = \boldsymbol{\beta}\boldsymbol{\beta}^T \tag{40}$$

$$\mathbf{h}' = \mathbf{c}'\mathbf{B}\mathbf{c}'^T = \boldsymbol{\beta}\mathbf{h}\boldsymbol{\beta}^T \tag{41}$$

If the elements of S' and $\mathbf{h}'$ are now used in the expressions (30) and (31) (note that $h_{JJ}' = x_J'$) in exactly the same way as those of $\mathbf{s}$ and $\mathbf{h}$, one obtains excellent approximations to the exact HMO values of the coefficients $c_{J\mu}$ of ψ_J and the corresponding eigenvalue x_J. We show this without further comment for the example C fulvene.

$$\mathbf{B} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & -1 & -1 & 0 \\ 1 & -1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 \\ 0 & 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & 1 & -1 \end{pmatrix}$$

$$\mathbf{s} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1/\sqrt{6} & 1/\sqrt{6} & 0 & 0 \\ 0 & -1/\sqrt{6} & 1 & -\frac{1}{3} & 0 & 0 \\ 0 & 1/\sqrt{6} & -\frac{1}{3} & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{h} = \begin{pmatrix} 2 & 0 & -\frac{1}{3} & -\frac{1}{3} & 0 & 0 \\ 0 & 1 & -1/\sqrt{6} & 1/\sqrt{6} & 0 & 0 \\ -\frac{1}{3} & -1/\sqrt{6} & 0 & 0 & 0 & 0 \\ -\frac{1}{3} & 1/\sqrt{6} & 0 & -1\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{3}{2} \end{pmatrix}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\ \frac{1}{2} & \frac{1}{2} & 0 & -\frac{1}{2} & -\frac{1}{2} & 0 \\ 1/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} \\ 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{3}{2} \end{pmatrix}$$

$$\mathbf{s}' = \begin{pmatrix} 1{\cdot}000 & 0{\cdot}027 & 0{\cdot}047 & 0 & 0 & 0 \\ 0{\cdot}027 & 1{\cdot}000 & 0 & -0{\cdot}148 & 0 & 0 \\ 0{\cdot}047 & 0 & 1{\cdot}000 & 0{\cdot}150 & 0 & 0 \\ 0 & -0{\cdot}148 & 0{\cdot}150 & 1{\cdot}000 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1{\cdot}000 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1{\cdot}000 \end{pmatrix}$$

$$\mathbf{h}' = \begin{pmatrix} 2{\cdot}108 & 0{\cdot}027 & 0{\cdot}028 & -0{\cdot}122 & 0 & 0 \\ 0{\cdot}027 & 1{\cdot}000 & 0 & -0{\cdot}148 & 0 & 0 \\ 0{\cdot}028 & 0 & -0{\cdot}258 & 0{\cdot}043 & 0 & 0 \\ -0{\cdot}122 & -0{\cdot}148 & 0{\cdot}043 & -1{\cdot}729 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0{\cdot}618 & -0{\cdot}029 \\ 0 & 0 & 0 & 0 & -0{\cdot}029 & -1{\cdot}618 \end{pmatrix}$$

$$\mathbf{c}' = \begin{pmatrix} 0{\cdot}295 & 0{\cdot}510 & 0{\cdot}430 & 0{\cdot}376 & 0{\cdot}376 & 0{\cdot}430 \\ 0{\cdot}500 & 0{\cdot}500 & 0 & -0{\cdot}500 & -0{\cdot}500 & 0 \\ 0{\cdot}733 & -0{\cdot}147 & -0{\cdot}367 & 0{\cdot}293 & 0{\cdot}293 & 0{\cdot}367 \\ 0{\cdot}415 & -0{\cdot}771 & 0{\cdot}341 & -0{\cdot}030 & -0{\cdot}030 & 0{\cdot}341 \\ 0 & 0 & 0{\cdot}606 & 0{\cdot}364 & -0{\cdot}364 & -0{\cdot}606 \\ 0 & 0 & 0{\cdot}364 & -0{\cdot}606 & 0{\cdot}606 & -0{\cdot}364 \end{pmatrix}$$

The following improved approximations x_J'' and $c_{J\mu}''$ to the correct HMO-quantities x_J and $c_{J\mu}$ are obtained, if the entries s_{JK}' and h_{JK}' of the matrices s' and h' are used in the formulae (31, 28 and 33) instead of the corresponding imprimed quantities.

J	y_J	x_J'	h_{JJ}'	x_J''	x_J
1	2·000	2·089	2·108	2·115	2·115
2	1·000	1·000	1·000	1·000	1·000
3	0	−0·222	−0·258	−0·254	−0·254
4	−1·333	−1·904	1·729	−1·855	−1·861
5	0·500	0·625	0·618	0·618	0·618
6	−1·500	−1·625	−1·618	−1·618	1·618

$$C'' = \begin{pmatrix} 0{\cdot}247 & 0{\cdot}526 & 0{\cdot}431 & 0{\cdot}382 & 0{\cdot}382 & 0{\cdot}431 \\ 0{\cdot}500 & 0{\cdot}500 & 0 & -0{\cdot}500 & -0{\cdot}500 & 0 \\ 0{\cdot}745 & -0{\cdot}197 & -0{\cdot}352 & 0{\cdot}283 & 0{\cdot}283 & -0{\cdot}352 \\ 0{\cdot}355 & -0{\cdot}664 & 0{\cdot}439 & -0{\cdot}155 & -0{\cdot}155 & 0{\cdot}439 \\ 0 & 0 & 0{\cdot}602 & 0{\cdot}372 & -0{\cdot}372 & -0{\cdot}602 \\ 0 & 0 & 0{\cdot}372 & -0{\cdot}602 & 0{\cdot}602 & -0{\cdot}372 \end{pmatrix}$$

$$C = \begin{pmatrix} 0{\cdot}247 & 0{\cdot}523 & 0{\cdot}429 & 0{\cdot}385 & 0{\cdot}385 & 0{\cdot}429 \\ 0{\cdot}500 & 0{\cdot}500 & 0 & -0{\cdot}500 & -0{\cdot}500 & 0 \\ 0{\cdot}749 & -0{\cdot}190 & -0{\cdot}351 & 0{\cdot}280 & 0{\cdot}280 & 0{\cdot}351 \\ 0{\cdot}357 & -0{\cdot}664 & 0{\cdot}439 & -0{\cdot}153 & -0{\cdot}153 & 0{\cdot}439 \\ 0 & 0 & 0{\cdot}602 & 0{\cdot}372 & -0{\cdot}372 & -0{\cdot}602 \\ 0 & 0 & 0{\cdot}372 & -0{\cdot}602 & 0{\cdot}602 & -0{\cdot}372 \end{pmatrix}$$

A comparison of x_J'' with x_J and of C'' with C shows that the approximation so obtained is excellent and quite sufficient for most practical purposes.

This work was supported by the Schweizerischer Nationalfonds (Projekt Nr. 3745).