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Basis of Extended Hückel Formalism

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It is shown that the LCAO molecular Hartree-Fock equations for a closed-shell configuration can be reduced to a form identical with that of the Hoffmann extended Hückel approximation if (i) we accept the Mulliken approximation for overlap charge distributions, and (ii) we assume a uniform charge distribution in calculating two-electron integrals over molecular orbitals. Numerical comparisons indicate that this approximation leads to results which, while unsuitable for high accuracy calculations, should be reasonably satisfactory for molecules that cannot at present be handled with facility by standard LCAO molecular Hartree-Fock methods.

Es wird gezeigt, daß die Hartree-Fock Gleichungen für eine abgeschlossene Schale unter der Voraussetzung, daß (i) die Mulliken-Näherung und (ii) zur Berechnung der zwei Zentrenintegrale eine gleichmäßige Ladungsverteilung angenommen werden können, in eine mit der EH-Näherung übereinstimmende Form gebracht werden können. Ein numerischer Vergleich ergibt dann Resultate, die für Moleküle, die nach der LCAO-HF-Methode nicht behandelt werden können, ausreichend genau sind.

On montre que les équations moléculaires de Hartree-Fock L.C.A.O. pour une configuration à couches complètes peuvent être réduites à une forme identique à celle de l'approximation Hückel Etendu de Hoffman, si (1) on admet l'approximation de Mulliken pour les distributions de charge de recouvrement et (2) on suppose une distribution de charge uniforme lors du calcul des intégrales biélectroniques entre orbitales moléculaires. Des comparaisons numériques indiquent que cette approximation conduit à des résultats qui, sans pouvoir servir à des calculs très précis, sont raisonnablement satisfaisants pour des molécules qui ne peuvent actuellement être facilement étudiées par les méthodes moléculaires standard de Hartree-Fock.

1. Introduction

Molecular-orbital theory has taken many forms, and has been dealt with by many approximations. In 1963 Hoffmann [1] presented a formalism which he referred to as "extended Hückel" (EH). In the 1930's, however, this formalism would simply have been called "molecular-orbital", since it is a straightforward application of molecular orbital (MO) theory, using a one-electron Hamiltonian. Hoffmann referred to it as "extended Hückel" because it did not limit itself to π-electron systems, and was able to deal with saturated molecules by including all overlap integrals. In these respects it did "extend" the usual, or "simple Hückel" method, which was customarily applied to π-electrons, and assumed complete $\pi-\sigma$ separability.

In the Hoffmann formalism each MO is assumed to be of the form

$$\phi_j = \sum_p C_{jp} \chi_p \tag{1}$$

where the C_{jp} are LCAO coefficients, and the χ_p are normalized atomic orbitals. If we use the variation method with an effective one-electron Hamiltonian h,

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these coefficients are given by the secular equations

$$\sum_q (h_{pq} - \varepsilon_j S_{pq})\, C_{jq} = 0\,, \quad j = 1, 2, \ldots; \quad p = 1, 2, \ldots \tag{2}$$

where the ε_j are the orbital energies, the S_{pq} are atomic overlap integrals, and the h_{pq} are the matrix components of h, defined by

$$h_{pq} = \int \chi_p^* \, h \chi_q \, d\tau\,. \tag{3}$$

Throughout this paper subscripts i, j will refer to molecular orbitals, and p, q, r, s to atomic orbitals. These latter orbitals may be of π or of σ type.

Elimination of the C_{jq} in (2) leads to the typical secular determinantal equation

$$\| h_{pq} - \varepsilon S_{pq} \| = 0 \tag{4}$$

from which the orbital energies ε_j are found, if the S_{pq} and h_{pq} are known. When Slater orbitals are used it is easy to compute the S_{pq}. But since the precise form of h cannot be written down in a one-electron model, we make no attempt to compute the h_{pq} directly. Instead Hoffmann argues that h_{pp} should be identified with the valence-state ionization potential of χ_p, and that h_{pq} should be proportional to S_{pq}, so that

$$h_{pq} = k\left(\frac{h_{pp} + h_{qq}}{2}\right) S_{pq}\,. \tag{5}$$

In (5) k is a constant subsequently to be chosen in such a way as to give best results for the total energy [1]. In any one-electron model such as this, the total energy is taken to be the sum of the orbital energies.

An alternative way of evaluating the h_{pq} in the EH method has recently been proposed by Newton, Boer, Palke and Lipscomb [21, 22]. It is clear that h is itself the sum of a kinetic energy operator and a potential energy term (in which nuclear attractions, Coulomb repulsions and exchange interactions are all involved). Newton *et al.* calculate the kinetic energy part of h_{pq} exactly, and use a Mulliken approximation for the potential energy part. Diagonal elements and proportionality constants for this part were estimated from SCF procedures for small, chemically similar, molecules. Their approach was designed to see how well they could reproduce the SCF secular determinant within the EH formalism. In this paper we proceed in the opposite direction; our starting points are the elements of the SCF secular determinant, which are examined to see what approximations must be made within the SCF scheme in order to reduce the SCF equations to EH form.

There are, of course, certain circumstances in which the SCF equations can easily be shown to reduce to Hückel-type equations. Thus in the standard-excited-state equations of Hall [9] for π-electron aromatic hydrocarbons, it can be shown that the LCAO coefficients are often precisely the same as in the Hückel scheme. However, this particular state is not of direct value for our purposes. Further, Pople [23] has shown that if the Pariser-Parr approximation of zero differential overlap is accepted then apart from some (usually) small terms in inverse internuclear distances, the total π-electron energy is given by an expression (Eq. 2.20) identical in form to that of Hückel theory. Both of these writers adopt the approxi-

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[1] Our conclusions in this paper would not be significantly altered if, instead of the arithmetic mean in (5), we used the Wolfsberg-Helmholtz-Mulliken geometrical-mean formula $h_{pq} = k\sqrt{(h_{pp} h_{qq})}\, S_{pq}$ recently advocated by Allen and Russel [1].

mation of neglecting all overlap integrals. This is particularly serious with σ-orbitals, in which an overlap integral may be as large as 0.8. We have therefore thought it worthwhile to make an independent study of the equivalence of SCF and EH equations, in which overlap is not neglected from the start.

2. Significance of the Overlap Integrals S_{pq}

The EH method is designed to take advantage of the fact that modern computers can solve complete secular determinants very readily, so that there is no need to neglect any of the off-diagonal elements in the secular determinants. It aims to produce reasonable values for important electronic properties by semi-empirical methods; and its success must depend on how well it can approximate the more accurate SCF Hamiltonian matrix elements. Central to the EH method is the approximation of making the off-diagonal matrix elements h_{pq} proportional to the corresponding overlap integrals S_{pq}.

This particular assumption was introduced, as early as 1942, by Wheland [28], who used it in π-electron calculations, but without any theoretical justification. He applied it to near-neighbour overlaps, neglecting all further interactions. Mulliken [19] reported an empirical observation that for the π-electrons of ethylene the calculated values of the ratio β/S varied by only about 10 % when the carbon-carbon distance changed from 0.998 to 1.664 Å. He also noted, empirically, that this ratio did not undergo large variations for the cases of H_2 and benzene. Within a very short time thereafter the proportionality of matrix elements h_{pq} to overlap integrals S_{pq} developed from being a method of estimating small changes in resonance integrals between adjacent atoms to being a method for estimating all off-diagonal elements h_{pq} [2, 5, 12, 13, 16, 17, 18, 29]. In this sense the method was already in use before it was referred to as the "extended" Hückel method. Nevertheless it is an appropriate label for a method of sufficient generality which embodies in the MO framework the following features:

(i) use of LCAO representation of molecular orbitals,
(ii) use of a one-electron Hamiltonian
(iii) overlap integrals not neglected,
(iv) h_{pq} proportional to S_{pq},
(v) usable for saturated as well as unsaturated π-electron molecules. In order that this method may give reliable predictions it is necessary that the corresponding secular determinant (4) should be almost identical with the SCF secular determinant. For then both orbital energies and LCAO coefficients given by the two methods will be closely similar. It is the way in which this equivalence depends upon feature (iv) above that provides the main concern of this paper. We shall first deal with the general theory, and shall then conclude with a numerical study of some illustrative examples.

3. General Theory

In the Roothaan form [25] of the SCF MO equations, we suppose that the total electronic wave function is of single-determinant Slater form, in which the molecular spinorbitals are products of space orbitals ϕ_j, as in (1), and conventional spin functions. The basic equations are

$$\sum_q (F_{pq} - \varepsilon_j S_{pq})\, C_{jq} = 0\,, \tag{6}$$

so that the orbital energies ε_j are found from the determinantal equation

$$\|F_{pq} - \varepsilon S_{pq}\| = 0 . \tag{7}$$

In (6) and (7) F_{pq} is usually written as

$$F_{pq} = H_{pq} + G_{pq} \tag{8}$$

where H_{pq} (to be distinguished from our previous Hückel h_{pq}) comes from the 1-electron part of the total Hamiltonian and G_{pq} from the 2-electron part. Thus, if V_α is the potential due to nucleus α

$$H_{pq} = \int \chi_p^* \left\{ -\frac{1}{2} \nabla^2 - \sum_\alpha V_\alpha \right\} \chi_q \, d\tau \tag{9a}$$

$$G_{pq} = \sum_i \{2(pq/ii) - (pi/iq)\} \tag{9b}$$

where the i-summation is over all doubly-occupied orbitals ϕ_i, and

$$(pq/ij) = \int \chi_p^*(1)\, \chi_q(1) \frac{1}{r_{12}} \phi_i^*(2)\, \phi_j(2)\, d\tau_1 \, d\tau_2 . \tag{10}$$

Our question is: under what conditions will the F_{pq} of (7) and (8) be the same as the h_{pq} of (4)?

Now Mulliken [19] has shown that, to a good approximation, multicentre electron repulsion integrals involving atomic orbitals p, q, r, s may be simplified by putting

$$(pq/rs) \approx \tfrac{1}{4} S_{pq} S_{rs} \{(pp/rr) + (pp/ss) + (qq/rr) + (qq/ss)\} . \tag{11}$$

With this approximation the first term in (9b) becomes

$$\sum_i 2(pq/ii) = \sum_i 2 \cdot \frac{S_{pq}}{2} \cdot \{(pp/ii) + (qq/ii)\} .$$

The term (pp/ii) is the Coulomb repulsion between an electron in the atomic orbital χ_p and an electron in the molecular orbital ϕ_i. But molecules have resonably uniform charge distributions, and in particular, as the Coulson-Rushbrooke theorem proves, alternant hydrocarbons have exactly uniform atomic charge densities in their ground states. We may therefore expect the sum $\sum_i (pp/ii)$ will be approximately the same, regardless of which atom p we have chosen. Thus we find that

$$\sum_i 2(pq/ii) \approx \text{constant } x \ S_{pq} . \tag{12}$$

Applying the Mulliken approximation to the second term of (9b), we have

$$\sum_i (pi/iq) \approx \sum_i \tfrac{1}{4} S_{pi} S_{iq} \{(pp/ii) + (pp/qq) + (ii/ii) + (ii/qq)\} . \tag{13}$$

On the assumption of a reasonably uniform charge distribution as before, the summations over i in $(pp|ii)$, $(ii|ii)$ and $(ii|qq)$ would be expected to give constants independent of p and q. But the presence of the additional term $(pp|qq)$ and the factors $S_{pi} S_{iq}$ in the summation means that there is no strictly analogous formula to (12) which applies to the exchange term (13). Fortunately however (see later) it appears from numerical calculations for linear H_6, ethylene, butadiene and benzene that the first term in G_{pq} is much larger than the second. If this is true generally, it will be approximately true to say that $G_{pq} \alpha S_{pq}$. The numerical justification for this is given in chapter 5.

We now turn to H_{pq}. Equation (9a) shows this to be the sum of a kinetic energy term and a core-attraction term. Numerical study of the kinetic energy term shows it to be large if $p \equiv q$, small if p and q are adjacent atoms, and negligible otherwise. This is illustrated for s and p_π orbitals in Table 1.

This still leaves the core-attraction terms, to which Barker and Eyring [3] have applied the Mulliken approximation, and found inaccuracies of about 10–20 %. Some of the deviations were positive, others were negative. In general, however, this term gives

Table 1. *Values of kinetic energy integral,* $\int \chi_p^* (-\frac{1}{2} \nabla^2) \chi_q \, d\tau$ *as a function of the* $p-q$ *separation, using Slater orbitals*

1s orbitals (orbital exponent 1)			p_π orbitals (orbital exponent 3.18)		
Separation (au)	Kinetic energy (au)	Overlap integral	Separation (au)	Kinetic energy (au)	Overlap integral
0	0.5000	1.000	0	0.5000	1.000
2	0.1128	0.586	2.64	0.0373	0.258
4	−0.0030	0.189	5.28	−0.0068	0.017
6	−0.0060	0.047	7.92	−0.0006	0.0017
8	−0.0021	0.010			
10	−0.0005	0.002			

$$\int \chi_p^* \left(\sum_\alpha \frac{1}{r_\alpha} \right) \chi_q \, d\tau \approx \frac{1}{2} S_{pq} \left\{ \int \chi_p^* \left(\sum_\alpha \frac{1}{r_\alpha} \right) \chi_p \, d\tau + \int \chi_q^* \left(\sum_\alpha \frac{1}{r_\alpha} \right) \chi_q \, d\tau \right\}. \quad (14)$$

Now $\sum_\alpha \frac{1}{r_\alpha}$ will have approximately the same value at all nuclei of the molecule, except for the end atoms of a chain, for which the number of close neighbour nuclei is less than for "internal" atoms. Thus, except possibly for such edge atoms, the potential energy part of H_{pq} is approximately proportional to S_{pq}.

Combining the various results just described we may therefore conclude that

(i) if p and q are no closer than second-neighbours, F_{pq} should be closely proportional to S_{pq},

(ii) if p and q are first-neighbours there should be a small variation from proportionality due chiefly to the kinetic energy operator,

(iii) if p and q are the same atom, the kinetic energy part of F_{pq} shifts the numerical value right out of the sequence of other F_{pq} matrix elements.

Thus the EH formalism of putting $h_{pq} \alpha S_{pq}$ $(p \neq q)$ is reasonably justified, and the necessity of the constant k in (5), with k not having the expected value of 1, is seen to arise from the kinetic-energy part of the Hamiltonian, which affects the diagonal terms differently from the off-diagonal ones. The importance of the kinetic-energy contribution to these off-diagonal elements has recently been recognized by Jørgensen [14] and by Radtke and Fenske [24] in some studies of transition metal complexes. These latter authors wrote: "terms of considerable magnitude which do not vary as functions of overlap integrals, make substantial contributions to off-diagonal elements". Our discussion has shown just what these are, and why it is not possible to choose $k = 1.75$ in (5), as originally suggested by Hoffmann, nor to put $k = 2 - S_{ij}$ as urged by Carroll and McGlynn [4]. We can also see why Newton *et al.* [21, 22] found it necessary to use a different value of k for each type of bond, and why Cusachs [6] who did not consider any two-electron terms, adopted different variations for the kinetic- and potential-energy matrices, putting [2]

$$T_{ij} \approx S_{ij}\,|S_{ij}| \left(\frac{T_{ii} + T_{jj}}{2}\right), \qquad U_{ij} \approx S_{ij} \left(\frac{U_{ii} + U_{jj}}{2}\right).$$

4. Total Energy Expressions, and Electronic Spectra

The discussion in chapter 3 dealt with the equivalence of orbital energies and LCAO coefficients in SCF and EH methods. This equivalence, however, does not imply equivalence of total energy E. In the SCF scheme there are the relations [25]

$$E = 2 \sum_i H_i + \sum_{i,j} (2J_{ij} - K_{ij}) \tag{15}$$

$$E = 2 \sum_i \varepsilon_i - \sum_{i,j} (2J_{ij} - K_{ij}) \tag{16}$$

$$E = \sum_i \varepsilon_i + \sum_i H_i \,. \tag{17}$$

The single summations are over all doubly-occupied molecular orbitals ϕ_i, and the double ones are over all ϕ_i and ϕ_j including $i = \mathrm{j}$. These equations show that although the Hückel energy is a good approximation for the various ionization potentials, it is bad for the total energy. For example for linear H_6 (see chapter 5 for an explanation of the calculation) the simple electronic energy is $2 \sum_i \varepsilon_i = -3.23$ a.u. whereas in the SCF scheme the total energy from Eq. (17) is -7.42 a.u. If we are interested in total energies there seems no alternative to the calculation of the exchange and Coulomb integrals; if we have used the EH procedure to get the ε_i and LCAO coefficients, then we can determine the F matrix in terms of various atomic integrals. All those that involve the kinetic energy, and the diagonal elements for the nuclear attractions and r_{12}-integrals, can readily be evaluated numerically; and it is in the spirit of this approximation to put the remaining off-diagonal elements proportional to overlap, or – as suggested by Newton *et al.* [21, 22] – estimate their values by comparison with suitable reference compounds. We shall show in chapter 5 that both procedures give a reasonable reproduction of the F matrices calculated by direct evaluation of all integrals.

In the evaluation of E, Eq. (17) is preferred to either (15) or (16), since the ε_i are already determined in solving the secular determinant; and only one-electron terms are involved in computing the H_i.

It is natural to estimate electronic excitation energies from the ground state, as suggested by Roothaan [25], by using the virtual orbitals of the ground-state calculation as excited-state orbitals. However an improvement of 5–20% has been indicated [7, 15] if new orbitals are calculated for each excited state. But in view of the approximations inherent in the EH method, it is doubtful if this extra labour is justified. Moreover, most u.v. excitations lead to a displacement of charge, so that, except for situations such as the p-band of alternant hydrocarbons, in which no gross redistribution of charge occurs [20], the assumption of a uniform

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[2] Further comment on the Cusachs approximation can be found in M. D. Newton, J. chem. Physics **45**, 2716 (1966) and L. C. Cusachs, ibid. 2717 (1966).

charge distribution, required in our justification of the EH formalism, is in general less valid for excited states than for the ground state.

5. Numerical Comparisons

We turn to some numerical illustrations of our general conclusions in chapter 3. First we have considered a linear complex H_6, using Slater 1*s* orbitals on each atom. We have made a SCF-LCAO-MO calculation for the system. Using Roothaan's equations, and an internuclear spacing of 2 a.u. in this calculation, all one- and two-centre integrals were obtained from standard tables [27]; the three- and four-centre electron-repulsion integrals were obtained with the Mulliken approximation [19]; the three-centre nuclear attraction integrals were taken from Hirschfelder and Weygandt [10]. We found agreement, both as regards energies and LCAO coefficients, with previous calculations using similar methods for H_4 and H_6 [8, 26]. Table 2 gives comparisons of matrix elements calculated in this way and with the assumption of proportionality to overlap. In this table $G_{pq} = G'_{pq} + G''_{pq}$, where G'_{pq} is the first (i.e. Coulomb) part of G_{pq} given by (9b) and (12); and G''_{pq} is the second (i.e. exchange) part of G_{pq} as in (9b) and (13). A comparison of entries, particularly in the last two columns of the table, shows that for linear H_6 off-diagonal matrix elements of F are reasonably well represented by terms proportional to overlap.

Table 2. *Comparison of matrix elements calculated from Roothaan's equations with elements which are proportional to overlap for the case of linear* H_6

q	G'_{1q}	$\frac{G'_{12}}{S_{12}}\cdot S_{1q}$	G''_{1q}	$\frac{G''_{12}}{S_{12}}\cdot S_{1q}$	G_{1q}	$\frac{G_{12}}{S_{12}}\cdot S_{1q}$	H_{1q}	$\frac{H_{12}}{S_{12}}\cdot S_{1q}$	F_{1q}	S_{1q}
1	1.69	1.86	−0.46	−0.66	1.23	1.19				
2	1.09	(1.09)	−0.39	(−0.39)	0.696	(0.696)	−1.164	(−1.164)	−0.465	0.586
3	0.36	0.35	−0.14	−0.13	0.224	0.224	−0.409	−0.375	−0.185	0.189
4	0.090	0.87	−0.030	−0.031	0.060	0.056	−0.130	−0.093	−0.069	0.047
5	0.019	0.019	−0.0065	−0.0068	0.012	0.012	−0.023	−0.019	−0.010	0.010
6	0.0034	0.0037	−0.0052	−0.0001	−0.0018	0.0023	−0.0035	−0.003	−0.005	0.002

Linear H_6 is a rather theoretical system. So we have made various similar calculations for the more realistic systems ethylene, trans-butadiene and benzene. The results are shown in Tables 3, 4 and 5. Again there is a reasonable (but far from perfect) correspondence for the off-diagonal elements.

Some confirmation of our general conclusions can be found from the work of Newton *et al.* [21] on methane. These writers found a close correspondence between matrix elements calculated from Roothaan's formulae and elements calculated by adding together (i) a purely theoretical kinetic energy term, and (ii) a potential energy term of which the diagonal elements were taken over from

Table 3. *Comparison of matrix elements calculated from Roothaan's equations with elements which are proportional to overlap, for the case of ethylene*

G'_{12}	$S_{12}G'_{11}$	G''_{12}	$S_{12}G''_{11}$	G_{12}	$S_{12}G_{11}$	V_{12}[a]	$S_{12}V_{11}$
0.268	0.268	−0.256	−0.106	0.012	0.162	0.95	1.05

[a] V denotes the core attraction term in H_{pq} as in Eq. (14).

Table 4. *Comparison of matrix elements calculated from Roothaan's equations with elements which are proportional to overlap, for the case of trans-butadiene*

q	G'_{12}	$\frac{G'_{12}}{S_{12}} \cdot S_{1q}$	G''_{1q}	$\frac{G''_{12}}{S_{12}} \cdot S_{1q}$	G_{1q}	$\frac{G_{12}}{S_{12}} \cdot S_{1q}$	H_{1q}	$\frac{H_{12}}{S_{12}} \cdot S_{1q}$	F_{1q}	$\frac{F_{12}}{S_{12}} \cdot S_{1q}$
1	1.30	1.49	−0.35	−0.95	0.95	0.53				
2	0.39	(0.39)	−0.25	(−0.25)	0.14	(0.14)	−0.419	(−0.419)	−0.276	(−0.276)
3	0.047	0.044	−0.033	−0.028	0.014	0.016	−0.049	−0.047	−0.035	−0.024
4	0.0028	0.0107	+0.013	−0.007	0.016	0.004	−0.0107	−0.0115	−0.0054	−0.0059

Table 5. *Comparison of matrix elements calculated from Roothaan's equations with elements which are proportional to overlap, for the case of benzene*

q	G'_{1q}	$\frac{G'_{12}}{S_{12}} \cdot S_{1q}$	G''_{1q}	$\frac{G''_{12}}{S_{12}} \cdot S_{1q}$	G_{1q}	$\frac{G_{12}}{S_{12}} \cdot S_{1q}$
1	1.95	1.95	−0.39	−0.76	1.56	1.19
2	0.508	(0.508)	−0.20	(−0.20)	0.309	(0.309)
3	0.076	0.076	−0.037	−0.030	0.038	0.046
4	0.035	0.035	+0.015	−0.014	0.050	0.021

Roothaan-type calculations for ethane, and the off-diagonal elements were made proportional to overlap.

The following conclusions follow from our present study:

1. Molecular LCAO Hartree-Fock equations can be reduced to the extended-Hückel form if we adopt Mulliken's approximation for an overlap-charge distribution, and assume an approximately uniform charge distribution in the molecule.

2. There is an advantage in distinguishing between the kinetic energy terms (which are not proportional to overlap) and the other items (most of which are much more closely proportional to overlap).

3. The origin of the difficulty with the numerical scale factor k in the Wolfsberg-Helmholtz formula (5) lies chiefly in the variation of kinetic-energy matrix elements with distance apart of the two atoms involved.

4. Numerical calculation for systems with σ or with π electrons indicate that the approximations considered produce results which, while not appropriate for a requirement of high accuracy, should be reasonably satisfactory for molecules that cannot at the present time be conveniently handled by full molecular Hartree-Fock methods.

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