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A New Semiempirical Approach to the Quantum Theoretical Study of Unsaturated Molecules¹

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A new semiempirical method is presented for the calculation of the π -electronic structure of unsaturated molecules. The method retains the basic simplicity of a Hückel molecular orbital treatment, yet it approximates the results of a self-consistent field-molecular orbital calculation. The essential feature of the method is the formulation of an effective Hamiltonian for a molecule under consideration from the matrix elements of self-consistent field Hamiltonians representing other molecules. The method is particularly useful for the quantum theoretical study of a related series of molecules or of large organic compounds.

I. Introduction

The Hückel molecular orbital (MO) theory and the self-consistent field-molecular orbital (SCF-MO) theory are the most generally utilized methods for calculating the π -electronic structure of unsaturated organic molecules.³ Although the approximations in the Hückel theory are rather severe, especially when applied to heterocyclic molecules, the method is widely used because the computational procedures involved are quite simple. The SCF-MO theory, on the other hand, is developed from a more rigorous theoretical foundation than is the Hückel theory and thus it enables one to describe more accurately the ground state and excited state properties of molecules.⁴ However, the additional complexity of the SCF-MO theory renders this method inconvenient for performing calculations on large molecules or for performing numerous calculations on a related series of molecules.

The crucial problem in any MO calculation is the construction of an effective Hamiltonian for the π -electronic system. A Hückel MO computation may be performed with relative ease because the matrix elements of the Hückel Hamiltonian $\mathbf{H}^{\text{Hückel}}$ are constructed without recourse to any calculation. The diagonal matrix elements $H_{rr}^{\text{Hückel}}$ and the off-diagonal matrix elements $H_{rs}^{\text{Hückel}}$ are expressed in the form⁵

$$H_{rr}^{\text{Hückel}} \equiv \alpha_r = \alpha_C + \delta_r \beta_{CC} \quad (1a)$$

$$H_{rs}^{\text{Hückel}} \equiv \beta_{rs} = \rho_{rs} \beta_{CC} \quad (1b)$$

Here α_C is the Coulomb integral for a carbon atom (C) in an alternant hydrocarbon, β_{CC} is the resonance integral for the π -electrons of an aromatic carbon-carbon double bond, and δ_r and ρ_{rs} are dimensionless parameters characteristic of an atom and its bonding in the mole-

cule under consideration. The matrix elements of the Hückel Hamiltonian are thus empirical parameters, which are assumed to retain their values from molecule to molecule.

The difficult evaluation of the matrix elements of the SCF Hamiltonian \mathbf{H}^{SCF} is one of the computational complexities that arises in the SCF-MO theory. In the Pariser-Parr approximation these matrix elements may be written as⁶

$$H_{rr}^{\text{SCF}} = \alpha_r + 1/2 P_{rr} \gamma_{rr} + \sum_{s(\neq r)} P_{rs} \gamma_{rs} \quad (2a)$$

$$H_{rs}^{\text{SCF}} \equiv \beta_{rs}^{\text{SCF}} = \beta_{rs} - 1/2 P_{rs} \gamma_{rs} \quad (2b)$$

Here P_{rs} are the elements of the charge and bond order matrix⁷ \mathbf{P} , β_{rs} are the so-called core resonance integrals, and γ_{rs} are the electronic repulsion integrals given by⁶

$$\gamma_{rs} = \iint |\phi_r(1)|^2 \frac{e^2}{R_{12}} |\phi_s(2)|^2 d\tau_1 d\tau_2$$

where $\phi(1)$ and $\phi(2)$ are the atomic $2p\pi$ -orbitals for electrons 1 and 2, and R_{12} is the distance between them. Finally, the SCF quantity α_r , which should not be confused with the Hückel empirical parameter α_r , is the so-called Coulombic core integral and its evaluation by different techniques is considered by some authors to be an essential feature in SCF-MO calculations.⁸⁻¹⁰

Once the Hamiltonian matrix \mathbf{H} is obtained for either type of MO calculation, the solution of the eigenvalue problem

$$\mathbf{H}\mathbf{c}_i = \epsilon_i \mathbf{c}_i \quad (3)$$

is sought. The eigenvalues ϵ_i of the Hamiltonian are the π -electronic MO energy levels. The eigenvectors \mathbf{c}_i are column matrices composed of the coefficients of the atomic orbitals ϕ_r that determine the molecular

(1) This study was supported by the Advanced Research Projects Agency under Contract SD-69.

(2) This work represents part of a thesis in Chemistry in partial fulfillment of the requirements for the Ph.D. degree from the University of Pennsylvania.

(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(4) H. C. Longuet-Higgins, in "Advances in Chemical Physics," Vol. I, I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 242.

(5) Reference 3, p. 117.

(6) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); (b) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(7) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(8) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc. (London)*, **A70**, 41 (1957).

(9) R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 319 (1959).

(10) R. L. Miller, P. G. Lykos, and H. N. Schmeising, *J. Am. Chem. Soc.*, **84**, 4623 (1962).

orbitals ψ_i in the linear combination of atomic orbitals (LCAO) approximation

$$\psi_i = \sum_r c_{ir} \phi_r \quad (4)$$

In a Hückel calculation, the Hückel Hamiltonian matrix is simply diagonalized, as indicated by eq. 3. In the SCF-MO treatment, however, the SCF Hamiltonian is a function of the coefficients c_{ir} through its dependence upon the charge and bond order matrix. Therefore, eq. 3 must be solved by an iterative procedure in the SCF-MO theory, thereby giving rise to a further complication in this method.

II. General Theory

In this article, we propose a semiempirical method for calculating the π -electronic structure of unsaturated molecules, a method which retains the simplicity of the Hückel treatment yet closely approximates the results of an SCF-MO calculation. This new method is a formalism by which one may reliably construct the desired Hamiltonians (hereafter called the constructed Hamiltonians) for molecules under consideration from the matrix elements of previously calculated SCF Hamiltonians (henceforth called framework Hamiltonians). For simplicity of discussion we designate the molecules which are represented by the constructed and framework Hamiltonians as the constructed and framework molecules, respectively.

The constructed molecule is regarded as being built up from framework molecules or parts of framework molecules. A framework molecule (or the fragment necessary for the construction) must contain atoms which are characterized by nearly the same chemical bonding and environment as the corresponding atoms in the constructed molecule. To describe this situation, we introduce the terminology that the framework molecule is "similar" to the constructed molecule. For example, furan, oxazole, pyrrole, and imidazole are considered "similar" molecules in this special sense. Furthermore, bicyclic purine is considered to be built up from pyrimidine and imidazole because these two monocyclic molecules are each "similar" to part of the purine molecule. As another example, *p*-benzoquinone may be regarded as built up from the "similar" molecules formaldehyde and *trans*-butadiene. On the other hand, six-membered heterocyclic molecules, for example, may not be regarded as a construction from segments of five-membered heterocycles because the bond angles, bond lengths, and electronic distributions in five-membered rings are not even approximately the same as those in six-membered rings.

The Hamiltonian matrix elements for a constructed molecule are determined from the actual SCF Hamiltonians for "similar" framework molecules according to the rules presented in the latter part of this section. Thus, the Hamiltonian for purine may be constructed from the SCF Hamiltonians of pyrimidine and imidazole, while the constructed *p*-benzoquinone Hamiltonian is obtained from the actual SCF Hamiltonians of formaldehyde and *trans*-butadiene. In general, the more "similar" the constructed molecule is to the framework molecules, the more accurately the constructed Hamiltonian approximates the actual SCF Hamiltonian for the molecule under consideration. In this respect, the constructed Hamiltonian might be considered as a quasi-SCF Hamiltonian.

We follow the formalism of McWeeny and Peacock⁸ by introducing an arbitrary zero level of energy into the Hückel and SCF Hamiltonians such that the diagonal matrix element H_{CC} equals zero for a carbon atom (C) in an alternant hydrocarbon. This manipulation is carried out by merely subtracting the numerical value

for H_{CC} from the diagonal matrix elements H_{rr} of the respective Hamiltonians. We further reduce all the matrix elements to "Hückel units"¹¹ by dividing both the diagonal and the off-diagonal elements of the Hamiltonian by β_{CC} in the case of the Hückel Hamiltonian and by β_{CC}^{SCF} in the case of the SCF Hamiltonian. The elements of the Hückel Hamiltonian now take the simplified form

$$H_{rr}^{Hückel} = \delta_r \quad (5a)$$

$$H_{rs}^{Hückel} = \rho_{rs} \quad (5b)$$

Although the algebraic formulation for the matrix elements of the SCF Hamiltonian is not simplified by these conventions, the numerical values for these elements may now be correlated with the Hückel parameters δ_r and ρ_{rs} . Accordingly, McWeeny and Peacock⁸ and Brown and Heffernan^{9,11,12} noted that the Hückel method might be improved by employing the matrix elements determined from SCF calculations as the appropriate Hückel parameters.

For discussion of the manner in which the matrix elements of the framework Hamiltonian might be utilized to formulate the constructed Hamiltonian, we categorize these elements into three classes: (1) off-diagonal matrix elements between neighboring or adjacent atoms, (2) off-diagonal matrix elements between non-adjacent atoms, and (3) diagonal matrix elements.

From eq. 2b, it may be seen that the off-diagonal matrix elements H_{rs}^{SCF} for neighboring atoms depend primarily upon atoms r and s and the bond between them. Therefore, it seems reasonable to assume that these elements may be carried over directly to the constructed Hamiltonian when the bond type and bond length are essentially the same in both the framework molecule and the constructed molecule.

The off-diagonal elements of the Hamiltonian matrix describing nonneighboring atoms are set equal to zero in the Hückel approximation and are given in SCF-MO theory by

$$-1/2 P_{rs} \gamma_{rs}$$

Although these SCF elements are small, they are often not negligible in comparison with the other SCF Hamiltonian matrix elements. We suggest that these matrix elements may also be carried over directly from the framework Hamiltonian to the constructed Hamiltonian. These off-diagonal matrix elements for non-adjacent atoms are insensitive to small changes in the distance between atoms r and s ; in fact, these elements are generally not sensitive to whether atoms r and s are carbon, nitrogen, or oxygen atoms, provided that these atoms are situated in similar geometrical environments.

We now turn our attention to the diagonal matrix elements of the Hamiltonian. With our choice for the zero level of energy, the numerical value for the diagonal matrix element representing a carbon atom in an alternant hydrocarbon is zero. However, the diagonal matrix elements corresponding to heteroatoms, to substituent groups, and to carbon atoms located near either heteroatoms or substituent groups are not zero. Since a substituent group may be regarded as an effective or pseudo-heteroatom¹³ in MO calculations, we use the term heteroatom in the following paragraph to include both genuine heteroatoms and pseudo-heteroatoms.

For the simple case where the constructed molecule has only one heteroatom, the diagonal elements for the heteroatom and the nearby carbon atoms are set equal

(11) R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 543 (1959).

(12) (a) R. D. Brown and M. L. Heffernan, *ibid.*, **12**, 554 (1959); (b) R. D. Brown and M. L. Heffernan, *ibid.*, **13**, 38 (1960); (c) R. D. Brown and M. L. Heffernan, *ibid.*, **13**, 49 (1960).

(13) Reference 3, p. 133.

to the corresponding diagonal matrix elements of the framework Hamiltonian. Usually a heteroatom affects the value of the matrix elements of the carbon atoms α and β to it, while the remaining carbon atoms are represented by a null matrix element. In the construction of the Hamiltonian for a molecule containing two or more heteroatoms, we suggest that the effect of these heteroatoms be considered as additive. That is, the diagonal matrix element representing *any* atom in the constructed molecule should be taken as the sum of the diagonal matrix elements representing the corresponding atom in the several framework Hamiltonians. In section III we present several illustrations of this construction, which is more clearly understood in conjunction with a specific example. We recognize that this approximation is not apparent from eq. 2a. McWeeny and Peacock⁸ demonstrated, however, that this approximation is excellent for the nitrogen heterobenzenes.

Once the constructed Hamiltonian is obtained, our method proceeds exactly as a Hückel calculation; *i.e.*, the constructed Hamiltonian is diagonalized for its eigenvalues and eigenvectors by solving eq. 3 directly without iteration. We show in section III that the constructed Hamiltonian is generally a very good approximation to the corresponding SCF Hamiltonian. Furthermore, it is demonstrated that numerous constructed Hamiltonians may be formulated from only a few framework Hamiltonians.

III. Applications

The details of our method may be more clearly understood and the validity of our approximations may be tested by a consideration of specific examples. Accordingly, in this section we present several illustrations of our method for constructing quasi-SCF Hamiltonians. Further, we compare the π -electronic MO energy levels and π -electronic charge densities obtained from the constructed Hamiltonian with those obtained from complete SCF-MO treatments and with those obtained from the Hückel MO method. Since the parameters employed in a Hückel calculation are empirical, we select the values suggested by Streitwieser.¹⁴

One might argue that a different selection of Hückel parameters could be made such that either the Hückel π -electronic energy levels or charge densities would better agree with the SCF values for these quantities. However, one could not choose any uniform set of Hückel parameters that would bring both these quantities into good agreement with their SCF counterparts, simply because the Hückel Hamiltonian, through its neglect of certain off-diagonal matrix elements, cannot accurately reproduce the SCF Hamiltonian. This difficulty is overcome in the constructed Hamiltonian.

Oxazole.—As our first application, we construct the Hamiltonian for oxazole. This molecule is sufficiently simple that it serves as a good illustrative example for our method. We choose furan and imidazole as the framework molecules for this construction because the oxygen atom in furan and the tertiary nitrogen atom in imidazole are characterized by chemical bonding and environment which is quite similar to the corresponding atoms in oxazole. The atoms in these three molecules are numbered as shown in Fig. 1.

In Table I we list the matrix elements of the SCF Hamiltonians for furan¹⁵ H^F and imidazole¹¹ H^I in Hückel units. These framework Hamiltonians depend, of course, upon the parameters employed in the SCF calculations. Consequently, the constructed Hamiltonian should approximate an SCF Hamiltonian which

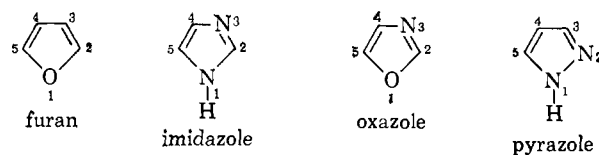


Fig. 1.—The numbering of ring atoms.

has been obtained from the same parameters that were used in the calculation of the framework Hamiltonian.

According to the principles outlined in section II, we make the following assignments for the neighboring diagonal matrix elements of the constructed Hamiltonian H^O for oxazole.

TABLE I
HAMILTONIAN MATRIX ELEMENTS (IN HÜCKEL UNITS) FOR
FURAN, IMIDAZOLE, AND OXAZOLE

Element ^a	SCF furan ^b	SCF imidazole ^c	Constructed oxazole	SCF oxazole ^d	Hückel oxazole ^e
11	0.84	1.34	0.84	0.83	2.00
12	.98	0.87	.98	1.05	0.80
13	-.19	-.18	-.19	-.20	.00
14	-.19	-.15	-.19	-.16	.00
15	.98	.85	.98	1.00	.80
22	.23	.24	.23	0.24	.00
23	1.21	1.05	1.05	.98	1.00
24	-0.07	-0.05	-0.05	-.08	0.00
25	-.15	-.21	-.15	-.19	.00
33	-.04	.10	.06	.06	.50
34	.72	.84	.84	.89	1.00
35	-.07	-.05	-.05	-.08	0.00
44	-.04	.00	-.04	-.10	0.00
45	1.21	1.17	1.21	1.18	1.10
55	0.23	0.24	0.23	0.31	0.00

^a The Hamiltonian matrices are symmetric. For the numbering of the atoms see Fig. 1. ^b M. K. Orloff and D. D. Fitts, *J. Chem. Phys.*, **38**, 2334 (1963). ^c R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 543 (1960). ^d M. K. Orloff and D. D. Fitts, *Tetrahedron*, in press. ^e The parameters used are those given by A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 135.

$$H_{12}^O = H_{12}^F$$

$$H_{23}^O = H_{23}^I$$

$$H_{34}^O = H_{34}^I$$

$$H_{45}^O = H_{45}^F$$

$$H_{15}^O = H_{15}^F$$

In similar fashion, the matrix elements for the non-neighboring atoms are identified as

$$H_{14}^O = H_{14}^F$$

$$H_{24}^O = H_{24}^I$$

$$H_{25}^O = H_{25}^F$$

$$H_{35}^O = H_{35}^I$$

Although there is no analogous matrix element in either framework Hamiltonian corresponding to H_{13}^O , the numerical values in Table I for this matrix element are almost identical in furan and imidazole; therefore, we may select

$$H_{13}^O = H_{13}^F \text{ or } H_{13}^I$$

Finally, we consider the diagonal matrix elements of the constructed Hamiltonian for oxazole. Examination of the framework Hamiltonian for furan reveals that the oxygen atom in a five-membered heterocyclic molecule affects the values of the diagonal matrix elements representing both the α - and β -carbon atoms. From the framework Hamiltonian for imidazole, we see that the secondary nitrogen atom affects only the matrix elements of the adjacent carbon atoms, while the tertiary nitrogen atom has no effect on the matrix elements cor-

(14) Reference 3, p. 135.

(15) M. K. Orloff and D. D. Fitts, *J. Chem. Phys.*, **38**, 2334 (1963).

responding to the carbon atoms in the molecule. Consequently, the diagonal matrix element representing position 3 in oxazole is the only element that must be constructed as the sum of the appropriate matrix elements appearing in the two framework Hamiltonians. Therefore, following the approximation discussed in section II, we construct the diagonal matrix elements for the oxazole Hamiltonian as

$$\begin{aligned} H_{11}^O &= H_{11}^F \\ H_{22}^O &= H_{22}^F \\ H_{33}^O &= H_{33}^I + H_{33}^F \\ H_{44}^O &= H_{44}^F \\ H_{55}^O &= H_{55}^F \end{aligned}$$

The constructed Hamiltonian thus obtained for oxazole is listed in Table I along with the actual SCF Hamiltonian¹⁶ and the Hückel Hamiltonian for purposes of comparison. The constructed Hamiltonian is clearly much closer to the SCF Hamiltonian than is the Hückel Hamiltonian. It is interesting to note that the poorest choice we could make for the constructed matrix element H_{13}^O from the framework matrix elements H_{13}^F and H_{13}^I represents a negligible error (0.02 Hückel unit). On the other hand, the neglect of this element by the Hückel approximation represents a significant error (0.20 Hückel unit).

The π -electronic MO energy levels ϵ_i and the π -electronic charge distribution as computed from the constructed, SCF, and Hückel Hamiltonians are listed in Tables II and III. Since the Hamiltonian matrix elements are given in Hückel units, the energy levels depend upon the value chosen for this unit. In this article, we adopt the value -4.79 e.v. for one Hückel unit.^{8,11} The constructed Hamiltonian reproduces the SCF energy levels to better than 0.20 e.v., which is well within the limits of the theory. The general features of the π -electronic charge distribution, such as the relative magnitudes of the densities at the carbon atoms, as calculated from the constructed Hamiltonian are also in good agreement with the SCF-MO treatment.

TABLE II

 π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR OXAZOLE

Energy level	Constructed	SCF ^a	Hückel
ϵ_1	-10.11	-10.21	-12.81
ϵ_2	-5.45	-5.62	-7.35
ϵ_3	-5.11	-5.08	-3.52
ϵ_4	6.69	6.74	4.37
ϵ_5	7.67	7.72	7.33

^a M. K. Orloff and D. D. Fitts, *Tetrahedron*, in press.

TABLE III

 π -ELECTRONIC CHARGE DENSITIES FOR OXAZOLE

Atom ^a	Constructed	SCF ^b	Hückel
1	1.48	1.44	1.78
2	1.15	1.15	0.86
3	1.14	1.17	1.28
4	1.07	1.03	1.05
5	1.16	1.21	1.02

^a For the numbering of the atoms see Fig. 1. ^b M. K. Orloff and D. D. Fitts, *Tetrahedron*, in press.

Pyrazole.—Using the framework Hamiltonian for imidazole once more, we may readily construct the Hamiltonian for pyrazole. Since imidazole and pyrazole are very "similar" molecules, one can expect the constructed Hamiltonian for pyrazole to be an excellent approximation to the SCF Hamiltonian.

In this construction, we encounter the same difficulty that arose in the oxazole calculation; we require off-diagonal matrix elements for the constructed pyrazole

(16) M. K. Orloff and D. D. Fitts, *Tetrahedron*, in press.

Hamiltonian H^P that have no exact counterpart in the framework Hamiltonian. In this case, however, two of the matrix elements in question, H_{12}^P and H_{34}^P (see Fig. 1 for numbering of the atoms) represent neighboring atoms. These elements are more sensitive to changes in bond length and bond type than are the elements for nonadjacent atoms so that slightly larger errors result here. We suggest that these two matrix elements of the constructed Hamiltonian be identified with the matrix elements of the framework Hamiltonian that represent the same bond from the standpoint of geometrical environment and not the same bond from the standpoint of component atoms. That is, for the constructed Hamiltonian matrix element H_{34}^P we select H_{34}^I and not say H_{45}^I ; similarly, for H_{12}^P we select H_{12}^I . Although some error is introduced in these particular assignments, the over-all results of our method in this calculation are excellent as is evidenced by the agreement between the constructed and SCF^{12c} values for the pyrazole Hamiltonian, energy levels, and charge distribution listed in Tables IV–VI.¹⁷

TABLE IV

HAMILTONIAN MATRIX ELEMENTS (IN HÜCKEL UNITS) FOR PYRAZOLE

Element ^a	Constructed	SCF ^b	Hückel
11	1.34	1.35	1.50
12	0.87	0.88	0.80
13	-.15	-.18	.00
14	-.15	-.16	.00
15	.85	.87	.80
22	.34	.36	.50
23	1.05	1.13	1.00
24	-0.05	-0.05	0.00
25	-.21	-.21	.00
33	.00	.01	.00
34	.84	.79	1.00
35	-.05	-.04	0.00
44	.00	.00	0.00
45	1.17	1.18	1.10
55	0.24	0.25	0.00

^a The Hamiltonian matrices are symmetric. For the numbering of the atoms see Fig. 1. ^b R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **13**, 49 (1960).

TABLE V

 π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR PYRAZOLE

Energy level	Constructed	SCF ^a	Hückel
ϵ_1	-10.61	-10.75	-11.62
ϵ_2	-6.00	-5.96	-5.79
ϵ_3	-5.48	-5.85	-4.12
ϵ_4	5.59	5.92	4.14
ϵ_5	7.30	7.21	7.80

^a R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **13**, 49 (1960).

TABLE VI

 π -ELECTRONIC CHARGE DENSITIES FOR PYRAZOLE

Atom ^a	Constructed	SCF ^b	Hückel
1	1.65	1.66	1.71
2	1.16	1.16	1.26
3	1.04	1.03	0.97
4	1.05	1.04	1.10
5	1.11	1.11	0.96

^a For the numbering of the atoms see Fig. 1. ^b R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **13**, 49 (1960); the value reported by these authors for position 4 is in error.

(17) In their Hückel treatment of pyrazole, H. Hamano and H. F. Hameka, *Tetrahedron*, **18**, 985 (1962), used a summation approximation to account for the inductive effect of the secondary nitrogen atom on the tertiary nitrogen atom. Their summation approximation is analogous to our method for obtaining the diagonal matrix elements of the constructed Hamiltonian.

Pyrimidine.—The application of our method to six-membered heterocyclic molecules is readily demonstrated with pyridine as the framework molecule.^{10,18} From pyridine, all the nitrogen heterobenzenes may be accurately constructed. As an example, we list in Tables VII and VIII the results for the π -electronic MO energy levels and charge distribution as calculated from the constructed, SCF,¹⁸ and Hückel Hamiltonians for pyrimidine. No new principles in the formulation of the constructed Hamiltonian for pyrimidine need be invoked. However, it is interesting to note that, in this example, our method is equivalent to determining the diagonal matrix elements of the constructed Hamiltonian for pyrimidine by appropriately superimposing one pyridine molecule upon another and summing the diagonal elements of the corresponding Hamiltonians. McWeeny and Peacock⁸ previously noted this effect.

TABLE VII

π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR PYRIMIDINE			
Energy level	Constructed	SCF ^a	Hückel
ϵ_1	-10.72	-10.60	-10.50
ϵ_2	-7.45	-7.36	-6.13
ϵ_3	-6.17	-6.00	-5.16
ϵ_4	5.67	5.78	3.74
ϵ_5	5.75	5.79	4.37
ϵ_6	9.65	9.46	8.90

^a R. L. Miller, P. G. Lykos, and H. N. Schmeising, ref. 10. These values were obtained from the Hamiltonian provided by R. L. Miller, private communication.

TABLE VIII

π -ELECTRONIC CHARGE DENSITIES FOR PYRIMIDINE			
Atom ^a	Constructed	SCF ^a	Hückel
1	1.24	1.24	1.20
2	0.78	0.78	0.84
3	1.24	1.24	1.20
4	0.83	0.83	0.87
5	1.10	1.10	1.01
6	0.83	0.83	0.87

^a The numbering of the atoms is the same as that of R. L. Miller, P. G. Lykos, and H. N. Schmeising, ref. 10.

Purine.—Of much greater importance than the preceding examples is the use of our method to construct the Hamiltonians for larger unsaturated molecules, which may be regarded as built up from segments of several smaller framework molecules. As an example of such an application, we formulate the constructed Hamiltonian for purine utilizing the SCF Hamiltonians of Miller, Lykos, and Schmeising^{10,18} for pyrimidine and pyrrole as the framework Hamiltonians.¹⁹ A somewhat better choice for framework molecules would include imidazole rather than pyrrole. However, we may not use the SCF Hamiltonian for imidazole as listed in Table I in conjunction with the SCF Hamiltonian for pyrimidine as calculated by Miller, Lykos, and Schmeising¹⁰ because these matrices were obtained by SCF-MO techniques employing different parameter values and approximations. In other words, there is a need for an "internal consistency" among the framework molecules for our method to be meaningful.

In the application of our method to the bicyclic molecule purine, we note that only one new problem arises in the formulation of the constructed Hamiltonian. The central bond in purine is common to both the five-membered and six-membered rings. For the value of the off-diagonal matrix element describing this

bond, we arbitrarily take the simple average of the matrix elements which represent the corresponding bonds in the framework Hamiltonians. The remaining off-diagonal matrix elements are taken directly from the framework molecules. The diagonal matrix elements are constructed by the method outlined in section II; the only novel feature here is that two of the carbon atoms are bonded to three rather than to two other ring atoms.

The matrix elements of the constructed, SCF, and Hückel Hamiltonians for purine are listed in Table IX. The constructed Hamiltonian for purine does not reproduce the SCF Hamiltonian¹⁸ quite as accurately as do the constructed Hamiltonians for monocyclic molecules. There are two reasons for this situation.

TABLE IX
HAMILTONIAN MATRIX ELEMENTS (IN HÜCKEL UNITS) FOR PURINE

Element ^a	Constructed	SCF ^b	Hückel	Element ^a	Constructed	SCF ^b	Hückel
11	0.53	0.48	0.50	39	0.00	0.01	0.00
12	1.15	.95	1.00	44	0.01	0.00	0.00
13	-0.02	-.03	0.00	45	1.14	1.10	1.00
14	-.15	-.15	.00	46	0.05	0.07	0.00
15	-.02	-.02	.00	47	.69	.72	.80
16	1.16	1.12	1.00	48	-.19	-.15	.00
17	0.00	0.03	0.00	49	-.03	-.05	.00
18	.00	.01	.00	55	-.03	.01	.00
19	.00	-.03	.00	56	1.01	.89	1.00
22	-.25	-.30	.00	57	-0.14	-.09	0.00
23	1.15	1.41	1.00	58	-.03	-.06	0.00
24	0.00	-0.01	0.00	59	.74	.86	1.00
25	-.18	-.13	.00	66	-.15	-.23	0.00
26	.00	.00	.00	67	.00	.01	.00
27	.00	-.03	.00	68	.00	-.06	.00
28	.00	.04	.00	69	.00	.00	.00
29	.00	.01	.00	77	1.63	1.68	1.50
33	.53	.48	.50	78	0.69	0.85	0.80
34	1.16	.96	1.00	79	-.14	-.15	.00
35	-0.02	-.02	0.00	88	-.04	.04	.00
36	-.15	-.15	.00	89	1.26	1.32	1.00
37	.00	-.05	.00	99	0.43	0.45	0.50
38	.00	.00	.00				

^a The Hamiltonian matrices are symmetric. The numbering of the atoms is the same as that of R. L. Miller, P. G. Lykos, and H. N. Schmeising, ref. 10. ^b Reference 10. These matrix elements were provided by R. L. Miller, private communication.

Firstly, in the constructed purine Hamiltonian, we neglected the off-diagonal matrix elements between atoms of the different ring systems, because such elements do not occur in the monocyclic framework molecules. As shown in Table IX, these neglected matrix elements lie in the range of 0.00 to 0.06 Hückel unit. This approximation is similar to, but not as severe as, the Hückel approximation of neglecting *all* off-diagonal matrix elements corresponding to nonneighboring atoms. However, this error may be substantially reduced by the selection of an appropriate bicyclic compound, such as indole in this example, as a framework molecule.

The second deficiency in the construction of purine from pyrimidine and pyrrole is the difference in bond length that may exist between adjacent atoms in isolated pyrimidine and in fused pyrimidine.¹⁰ This inadequacy cannot be corrected while maintaining the simplicity of our method. An extreme result of this effect is seen in the matrix elements H_{23} in Table IX.

Despite these two difficulties in our method, the π -electronic MO energy levels and charge densities for purine calculated from the constructed Hamiltonian agree rather well with those calculated from the SCF

(18) We wish to thank Prof. R. L. Miller for supplying us with the SCF Hamiltonian matrices used in ref. 10 for pyridine, pyrimidine, pyrrole, and purine.

(19) The numbering of the atoms in these three molecules is the same as that of ref. 10.

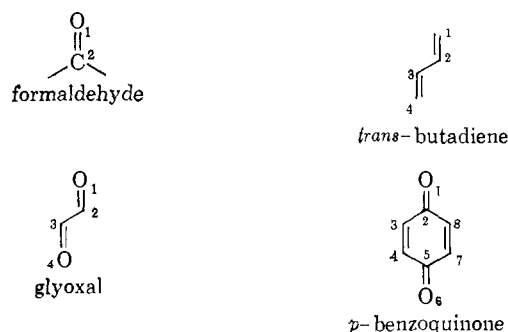


Fig. 2.—The numbering system for atoms adopted in this article.

Hamiltonian. These results are listed in Tables X and XI.

TABLE X

π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR PURINE			
Energy level	Constructed	SCF ^a	Hückel
ϵ_1	-11.60	-11.76	-12.35
ϵ_2	-9.60	-9.70	-9.25
ϵ_3	-8.13	-7.98	-7.45
ϵ_4	-6.75	-6.33	-5.28
ϵ_5	-5.09	-5.41	-3.55
ϵ_6	4.90	5.43	3.33
ϵ_7	6.34	5.90	4.55
ϵ_8	7.18	7.63	5.95
ϵ_9	10.03	9.82	9.67

^a R. L. Miller, P. G. Lykos, and H. N. Schmeising, ref. 10. These values were obtained from the Hamiltonian provided by R. L. Miller, private communication.

TABLE XI

π -ELECTRONIC CHARGE DENSITIES FOR PURINE			
Atom ^a	Constructed	SCF ^a	Hückel
1	1.24	1.27	1.22
2	0.79	0.79	0.87
3	1.25	1.24	1.23
4	0.93	0.94	0.90
5	1.03	1.05	1.02
6	0.85	0.78	0.89
7	1.83	1.78	1.74
8	0.87	0.91	0.83
9	1.23	1.23	1.31

^a The numbering of the atoms is the same as that of R. L. Miller, P. G. Lykos, and H. N. Schmeising, ref. 10.

Glyoxal.—As another example of the building up of an unsaturated molecule from smaller fragments, we formulate the constructed Hamiltonian for glyoxal using formaldehyde and *trans*-butadiene as the framework molecules²⁰ (see Fig. 2 for the numbering of the atoms). We select these framework molecules because they are "similar" to segments of the constructed molecule. That is, the carbon-oxygen bond in formaldehyde is similar to that in glyoxal, the central carbon-carbon bond in *trans*-butadiene is similar to that in glyoxal, and the carbon-carbon-carbon angle in *trans*-butadiene is approximately equal to the carbon-carbon-oxygen angle in glyoxal. Thus, in the construction of the glyoxal Hamiltonian H^G , we obtain the matrix elements $H_{13}^G (= H_{24}^G)$, H_{14}^G , and H_{23}^G from the framework Hamiltonian for *trans*-butadiene and we take the remaining elements from the formaldehyde Hamiltonian. As indicated in Tables XII and XIII, the energy levels and charge densities agree excellently with those calculated from SCF-MO theory.

Benzoquinone.—We now employ this constructed Hamiltonian for glyoxal and the *trans*-butadiene SCF

TABLE XII

π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR GLYOXAL			
Energy level	Constructed	SCF ^a	Hückel
ϵ_1	-8.92	-9.09	-9.35
ϵ_2	-7.28	-7.33	-6.85
ϵ_3	5.56	5.37	0.25
ϵ_4	8.05	7.69	6.37

^a J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

TABLE XIII

π -ELECTRONIC CHARGE DENSITIES FOR GLYOXAL			
Atom ^a	Constructed	SCF ^b	Hückel
1	1.15	1.16	1.37
2	0.85	0.84	0.63
3	0.85	0.84	0.63
4	1.15	1.16	1.37

^a For the numbering of the atoms see Fig. 2. ^b J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

Hamiltonian as the framework Hamiltonians from which the constructed Hamiltonian H^B for *p*-benzoquinone may be formulated. These framework molecules are appropriate for reasons analogous to those stated above in the construction of the Hamiltonian for glyoxal. The atoms in *p*-benzoquinone are numbered as in Fig. 2. For the matrix element $H_{34}^B (= H_{78}^B)$ we take the *trans*-butadiene matrix element H_{34} . All the other constructed matrix elements are taken from the glyoxal Hamiltonian. The results obtained from the constructed Hamiltonian for benzoquinone are again in good agreement with the SCF-MO values²⁰ (see Tables XIV and XV). Thus we have essentially reproduced the results of a complete SCF-MO calculation on *p*-benzoquinone utilizing in effect only formaldehyde and *trans*-butadiene as framework molecules. This example demonstrates the effectiveness of our method in building up a large molecule from two smaller molecules.

TABLE XIV

π -ELECTRONIC MO ENERGY LEVELS (IN E.V.) FOR BENZOQUINONE			
Energy levels	Constructed	SCF ^a	Hückel
ϵ_1	-9.42	-9.58	-10.71
ϵ_2	-8.45	-8.37	-8.64
ϵ_3	-6.56	-7.03	-5.27
ϵ_4	-5.76	-5.87	-4.97
ϵ_5	4.62	4.34	-0.68
ϵ_6	6.56	6.18	5.27
ϵ_7	7.33	6.94	5.63
ϵ_8	9.10	8.52	9.79

^a J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

TABLE XV

π -ELECTRONIC CHARGE DENSITIES FOR BENZOQUINONE			
Atom ^a	Constructed	SCF ^b	Hückel
1	1.15	1.15	1.43
2	0.86	0.87	0.71
3	.99	.99	.93
4	.99	.99	.93
5	.86	.87	.71
6	1.15	1.15	1.43
7	0.99	0.99	0.93
8	0.99	0.99	0.93

^a For the numbering of the atoms see Fig. 2. ^b J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

IV. Electronic Spectra

The electronic spectral transition energies relative to the ground state for the one-electron MO jump $\psi_i \rightarrow \psi_j$ are given in SCF-MO theory by²¹

$${}^1,{}^3E_{i \rightarrow j} = \epsilon_j - \epsilon_i - (J_{ij} - K_{ij}) \pm K_{ij} \quad (6)$$

(21) C. C. J. Roothaan, *Rev. Modern Phys.*, **23**, 61 (1951).

(20) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

where the superscripts 1 and 3 represent the singlet and triplet excitation energies, respectively, and the plus sign is to be taken with the singlet and the negative sign with the triplet transition. Here, J_{ij} and K_{ij} are molecular Coulomb and exchange integrals, respectively, and are defined by

$$J_{ij} = \iint |\psi_i(1)|^2 \frac{e^2}{R_{12}} |\psi_j(2)|^2 d\tau_1 d\tau_2$$

$$K_{ij} = \iint \psi_i^*(1)\psi_i(2) \frac{e^2}{R_{12}} \psi_j^*(2)\psi_j(1) d\tau_1 d\tau_2$$

These integrals take into account the mutual repulsions of the electrons. The repulsions lead to interactions between the several excited configurations of the molecule and thereby modify the MO π -electronic energy levels. The evaluation of these integrals by semiempirical techniques is discussed by Pople.²² The evaluation of J_{ij} and K_{ij} for oxazole is discussed elsewhere.^{15,16}

Although in section III we limited the application of our method to the ground state properties of molecules, such a restriction is not necessary. The energy of the $\pi \rightarrow \pi^*$ transitions may be calculated from eq. 6 using the energy levels and wave functions obtained from a constructed Hamiltonian as well as those obtained from an SCF Hamiltonian. As an example, we list in Table XVI the transition energies for oxazole as calculated from the constructed and SCF¹⁶ Hamiltonians; the agreement is excellent. Since the Hückel approximation neglects all electronic repulsion terms, the quantitative results for the $\pi \rightarrow \pi^*$ spectral transitions as calculated from the Hückel Hamiltonian for oxazole are not meaningful and consequently are not presented.

TABLE XVI
ELECTRONIC SPECTRAL TRANSITION ENERGIES (IN E.V.) FOR
OXAZOLE

Transition	Constructed	SCF ^a	Transition	Constructed	SCF ^a
¹ E ₃ → ₄	6.3	6.2	³ E ₃ → ₄	3.6	3.6
¹ E ₂ → ₄	6.5	6.6	³ E ₂ → ₄	4.8	4.9
¹ E ₃ → ₅	6.9	6.8	³ E ₃ → ₅	5.6	5.2
¹ E ₂ → ₅	7.5	7.5	³ E ₂ → ₅	5.4	5.6

^a M. K. Orloff and D. D. Fitts, *Tetrahedron*, in press.

V. Discussion

In section III we presented a sufficient number of illustrations to demonstrate the validity of our method. As with the Hückel method, the ultimate justification for our procedure is that it gives reliable results. The philosophy underlying this experimental justification of theoretical methods has been eloquently discussed by Kim and Hameka.²³

(22) J. A. Pople, *Proc. Phys. Soc. (London)*, **A68**, 81 (1955).

(23) H. Kim and H. F. Hameka, *J. Am. Chem. Soc.*, **85**, 1398 (1963).

Furthermore, we have shown that our method retains the simplicity of a Hückel MO treatment in that it involves neither the explicit calculation of Hamiltonian matrix elements nor the computational difficulties associated with SCF techniques. However, the constructed Hamiltonian implicitly considers electronic repulsion terms and a self-consistent field since all of its matrix elements are determined from SCF Hamiltonians.

An important consideration in our method occurs when more than one framework molecule is used in a construction. In such cases there must be an "internal consistency" amongst the several framework Hamiltonians. That is, the SCF-MO calculations that are performed to obtain the framework Hamiltonians must use uniform parameters and the same approximations. The resulting constructed Hamiltonian then approximates the actual SCF Hamiltonian which would have been obtained by a complete SCF calculation using the same parameters and the same approximations.

In order to ensure that the constructed Hamiltonian closely approximates the SCF Hamiltonian, it is important to make a judicious selection for the framework molecule(s). From a small number of framework molecules, one may formulate the constructed Hamiltonians for numerous compounds. For example, the availability of framework Hamiltonians for furan, imidazole, pyridine, and indole alone would permit the direct formulation of constructed Hamiltonians for several hundred molecules. Thus, quasi-SCF calculations may be readily performed on large organic molecules. This procedure might be particularly useful in theoretical studies on molecules of biological interest.

Our method is also useful in carrying out MO calculations on a related series of molecules. Here, one needs only to perform a single SCF-MO calculation. From the resulting SCF Hamiltonian one may formulate the constructed Hamiltonians for all the other molecules in the series.

Finally, inasmuch as the constructed Hamiltonian is a better approximation to the SCF Hamiltonian than is the Hückel Hamiltonian, the wave functions associated with the constructed Hamiltonian are a good choice of starting orbitals to utilize in a complete SCF-MO calculation. Once again employing oxazole as an example, one iteration in an SCF calculation brings the constructed Hamiltonian matrix elements in Table I to within at least 0.05 Hückel unit of the SCF Hamiltonian matrix elements, while three iterations bring them to within 0.02 Hückel unit. Therefore, for those who prefer the greater reliability of a complete SCF-MO calculation, a constructed Hamiltonian may be used to define starting orbitals, which rapidly converge to the self-consistent molecular orbitals.