oxystearic acid exemplifies this) of the center of unsaturation also occur in both systems. On the other hand, however, elaidinization and decarboxylation appear to be uniquely characteristic of direct $\gamma$ radiolysis, and it may therefore prove possible on the basis of these distinctive features (particularly the former, since decarboxylatable free fatty acids occur rarely in living organisms) to evaluate the relative quantitative importance of direct and indirect effects of ionizing radiation on lipids *in vivo*.

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# The Effect of Including Non-Nearest Neighbor $\beta$ Terms in Pariser–Parr–Pople Type Self-Consistent Molecular Orbital Calculations on $\pi$-Electron Systems

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**Abstract:** A systematic study of the effect of inclusion of all $\beta_{ij}$ terms in semiempirical $\pi$-electron calculations has been made. The two principal effects are the occurrence of charge separation in alternate hydrocarbons similar to that obtained when using orthogonalized orbitals, and a change in the spacing of higher energy levels in polyenes.

Most calculations which use the Pariser and Parr[1] and Pople[2] self-consistent molecular orbital (SCMO) approach take as a basic assumption that all non-nearest neighbor $\beta$ terms may be neglected. Fischer-Hjalmars pointed out the necessity of including non-nearest neighbor $\beta$ terms in Hückel-type calculations in order for the approximations employed to be consistent.[3] The purpose of this report is to examine critically the effect of inclusion of all $\beta$ terms in the secular determinant for molecules in the polyene–polyacene series. The properties examined will be charge distribution, spectral transitions, and ionization potentials. While some work has been done including non-nearest neighbor $\beta$ terms, such as Hoffman's[4] extended Hückel theory (which is not a self-consistent field method), Allinger's[5] configuration interaction work, and Orloff and Fitts' modified Hückel scheme,[6] no one has yet done a systematic survey on the effect of this inclusion.

## Method

The calculations were performed on either an IBM 1620 digital computer with disk pack or an IBM 7040. The program is written in Fortran and is constructed so as to give the operator many variations in operations with only minor changes in the input parameters. One of the basic sets of information needed is the geometry of the molecule in question. The bond lengths and bond angles for the compounds studied were obtained from the Chemical Society tables.[7] The geometries of the higher polyenes were assumed to be similar to hexatriene with the same bond-length alternation. All internuclear separations are automatically calculated by the program.

The valence-state data for carbon was from the work of Hinze and Jaffé.[8] These values are $-11.16$ ev for the valence-state ionization potential and 0.03 ev for the electron affinity. These yield a semiempirical value[1] of 11.13 ev for the one-center, two-electron repulsion integral.

Two approximations were tried for evaluating the two-center repulsion integrals. These were a Pariser and Parr[1] type parabolic interpolation, at distances less than 5 A with a $1/r$ dependence at greater distances, and the Mataga[9] formula (eq 1, in au).

$$\gamma_{ij} = \frac{1}{R_{ij} + \dfrac{2}{\gamma_{ii} + \gamma_{jj}}} \tag{1}$$

The use of the Mataga approximation has given better spectral agreement than the Pariser and Parr approximation; therefore, they were used for the reported results.

One of the main difficulties encountered in the inclusion of all $\beta$ terms is that of finding a suitable function to express the more distant interactions correctly. After testing several approximations, including methods where $\beta$ was proportional to overlap and methods where it was a simple exponential, it was decided to use a function of the form of eq 2. In this equation, $S$ is the

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[1] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

[2] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[3] I. Fischer-Hjalmars, *Advan. Quantum Chem.*, **2**, 25 (1965).

[4] R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

[5] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Am. Chem. Soc.*, **87**, 3430 (1965). This work has been extended to use SCMO wave functions: N. L. Allinger, private communication.

[6] M. K. Orloff and D. D. Fitts, *J. Am. Chem. Soc.*, **85**, 3721 (1963).

[7] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Publication 11, The Chemical Society, London, 1958; Publication 18, 1965.

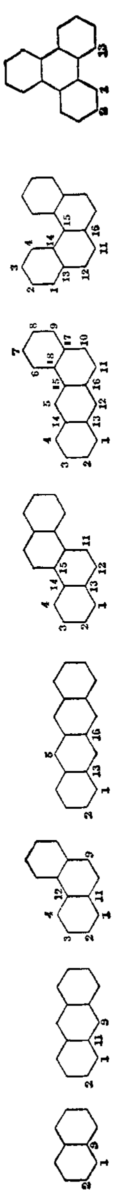
[8] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[9] K. Nishimoto and N. Mataga, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

Table I. Charge Densities for the Aromatic Hydrocarbons[a]

| | $q_1$ | $q_2$ | $q_3$ | $q_4$ | $q_5$ | $q_6$ | $q_7$ | $q_8$ | $q_9$ | $q_{10}$ | $q_{11}$ | $q_{12}$ | $q_{13}$ | $q_{14}$ | $q_{15}$ | $q_{16}$ | $q_{17}$ | $q_{18}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 1.006 | 1.003 | | | | | | | 0.983 | | | | | | | | | |
| Anthracene | 1.007 | 1.003 | | | | | | | 1.014 | | 0.983 | | | | | | | |
| Phenanthrene | 1.013 | 1.000 | 1.003 | 1.007 | | | | | 1.008 | | 0.980 | 0.991 | | | | | | |
| Naphthacene | 1.005 | 1.006 | | | 1.019 | | | | | | | | 0.979 | | | 0.981 | | |
| Chrysene | 1.009 | 1.000 | 1.003 | 1.009 | | | | | | | 1.008 | 1.008 | 0.984 | 0.989 | 0.993 | | | |
| 1,2-Benzanthracene | 1.006 | 1.009 | 1.005 | 1.004 | 1.022 | 1.010 | 1.004 | 1.003 | 1.005 | 1.005 | 1.006 | 1.017 | 0.960 | 0.979 | 0.986 | 0.987 | 0.987 | 0.985 |
| 3,4-Benzophenanthrene | 1.003 | 1.003 | 1.002 | 1.013 | | | | | | | 1.007 | 1.007 | 0.986 | 0.990 | 0.994 | 0.987 | | |
| Triphenylene | 1.009 | 1.002 | | | | | | | | | | | 0.989 | | | | | |

[a] Numbering system:



$$\beta_{ij} = \frac{(2 - S_{ij})S_{ij}}{2 - S_{ij}^2}(H_{ii}H_{jj})^{1/2} \quad (2)$$

overlap integral, and $H_{ii}$ and $H_{jj}$ are taken as the valence-state ionization potentials of the atoms in question. This form is related to the original proposal by Mulliken[10] of $\beta$ proportional to overlap. The overlap intergral is approximated by a function of the type shown in 3, where $A$, $B$, and $C$ are constants having the values of 3.503, 1.1526, and −0.7946, respectively.

$$S_{ij} = A(0.5Z_{\text{eff}}R_{ij})^B e^{CZ_{\text{eff}}R_{ij}} \quad (3)$$

This formula was obtained by empirically fitting the constants against a number of theoretically calculated overlap integrals, both for homoatomic and heteroatomic cases. Although the theoretical formula for the homoatomic case is no more complex than this, that for the heteroatomic case is considerably more complex. Thus, eq 3 was used to conserve machine-storage and computing time. $Z_{\text{eff}}$ for carbon was taken as 3.18 for the calculation of overlap. It should be emphasized that this $\beta$ function is not to be considered as the optimum function to use in all calculations. It is merely a convenient form for the present work which gives $\beta$ terms of a reasonable magnitude.

The use of a $\beta$ function of this type has led to charge separation in the molecules considered similar to that obtained by Adams and Miller[11] using orthogonalized orbitals and the same valence-state and integrals data, and also to the results obtained from the extended Hückel method.[4] The spectral properties and ionization potentials of the molecule are in reasonable agreement with experiment without any calibration of spectral parameters.

The spectra of the molecules under consideration were calculated by a configuration interaction (CI) method using singly excited configurations resulting from the three highest occupied orbitals and the three lowest unoccupied orbitals. This procedure yields the first nine energy states above the ground state for both singlet and triplet configurations. The limited amount of CI used was dictated by the limited storage and speed of the 1620 computer.

## Results and Discussion

It was found in this study that inclusion of all $\beta$ terms leads to significant charge separation in systems where the charge was not dictated by symmetry. These results are shown in Tables I and II. This was not observed for the alternant hydrocarbons when non-nearest neighbor $\beta$'s were omitted. The charge distribution is near that reported by Adams and Miller.[11] The distribution in polyenes is such that $\pi$-electron density piles up on the terminal carbon at the expense of the next inner carbon. The central carbons of the longer polyenes are almost neutral with a slight alternation of charge occurring. This higher electron density on the terminal carbons is experimentally verified by the nmr work of Hobgood and Goldstein[12] on butadiene. Their studies show that the terminal hydrogens experience a greater shielding than the internal hydro-

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(10) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

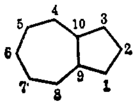
(11) O. W. Adams and R. L. Miller, *ibid.*, **88**, 404 (1966).

(12) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, **12**, 76 (1964).

Table II. Charge Densities for the Polyenes H(CH═CH)$_n$H

| $n$ | $q_1$ | $q_2$ | $q_3$ | $q_4$ | $q_5$ | $q_6$ | $q_7$ | $q_8$ | $q_9$ | $q_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.00 | | | | | | | | | |
| 2 | 1.020 | 0.980 | | | | | | | | |
| 3 | 1.024 | 0.980 | 0.996 | | | | | | | |
| 4 | 1.025 | 0.980 | 0.999 | 0.996 | | | | | | |
| 5 | 1.026 | 0.980 | 1.000 | 0.995 | 0.998 | | | | | |
| 6 | 1.026 | 0.980 | 1.001 | 0.995 | 1.000 | 0.998 | | | | |
| 7 | 1.026 | 0.980 | 1.001 | 0.995 | 1.000 | 0.998 | 0.999 | | | |
| 8 | 1.027 | 0.980 | 1.002 | 0.995 | 1.001 | 0.998 | 1.000 | 0.999 | | |
| 9 | 1.027 | 0.980 | 1.002 | 0.995 | 1.001 | 0.998 | 1.000 | 0.999 | 1.000 | |
| 10 | 1.027 | 0.980 | 1.002 | 0.995 | 1.001 | 0.998 | 1.000 | 0.999 | 1.000 | 0.999 |

Table III. Charge Distributions of Azulene by Several Methods



| | | | | | This work | |
|---|---|---|---|---|---|---|
| Position | Nonempirical SCF[a] | Hoffmann's extended Hückel[b] | Pariser-Parr[c] | VESCF[d] | Non-nearest $\beta$ terms neglected | All $\beta$ terms used |
| 2 | +0.003 | −0.011 | +0.021 | −0.004 | −0.005 | +0.025 |
| 1,3 | −0.049 | −0.175 | −0.096 | −0.061 | −0.089 | −0.087 |
| 9,10 | −0.042 | +0.025 | −0.013 | −0.009 | −0.015 | +0.006 |
| 4,8 | +0.092 | +0.109 | +0.121 | +0.063 | +0.091 | +0.065 |
| 5,7 | −0.034 | −0.002 | −0.049 | −0.009 | −0.016 | −0.019 |
| 6 | +0.062 | +0.103 | +0.052 | −0.039 | +0.064 | +0.047 |

[a] A. Julg, *J. Chim. Phys.*, **52**, 377 (1955). [b] Reference 4. [c] R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956). [d] Variable electronegativity self-consistent field: R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **13**, 38 (1960).

gens. This greater shielding reflects a higher electron density at the terminal position.

The charge buildup in naphthalene and the other condensed ring systems is at the $\alpha$ and $\beta$ positions at the expense of the bridge positions. This is again similar to the distribution reported by Adams and Miller,[11] but the magnitude of separation is smaller in this work.

Azulene, a nonalternant hydrocarbon, was the only molecule studied for which charge separation appeared for both inclusion and noninclusion of non-nearest neighbor $\beta$ terms. The charge separation for both calculations, along with the results of previous calculations on azulene, are shown in Table III. Both sets of results are consistent with the other reported values except at the 9 and 10 positions. The calculations using all $\beta$ terms give a positive charge at this bridge position similar to that obtained for the bridge positions of the polyacenes. All of the previous calculations except the extended Hückel method, which also includes all $\beta$ terms, gave a negative density at this point. The $C^{13}$ nmr work of Lauterbur implies that these positions should indeed bear a positive charge.[13] It is interesting to note that the recent calculations by Bloor,[14] in which he retained only the nearest neighbor $\beta$'s and allowed no variation of $\beta$ with bond length, gave results almost identical with the present work with only nearest neighbor $\beta$'s, for both charge densities and relative bond orders.

The first three singlet transitions, the first triplet transitions, and the ionization potentials for the polyenes and polycyclic aromatics are shown in Tables IV and V. For all the polyenes except ethylene, the spectral agreement is fair. The calculated first singlet

Table IV. Electronic Transition and Ionization Potential Results for the Polyenes H(CH═CH)$_n$H (ev)[a]

| $n$ | | IP | $^1\Delta E_1$ | $^1\Delta E_2$ | $^1\Delta E_3$ | $^3\Delta E_1$ |
|---|---|---|---|---|---|---|
| 1 | NN $\beta$ only | 11.16 | 8.50 | | | 2.84 |
| | All $\beta$ terms | 11.16 | 8.50 | | | 2.84 |
| | Experimental[b] | 10.62 | 7.60 | | | 3.12[c] |
| 2 | NN $\beta$ only | 9.00 | 6.06 | 7.31 | 8.72 | 1.87 |
| | All $\beta$ terms | 9.54 | 6.02 | 6.98 | 9.04 | 1.84 |
| | Experimental | 9.07 | 5.71 | | | |
| 3 | NN $\beta$ only | 9.25 | 4.90 | 6.19 | 7.20 | 1.41 |
| | All $\beta$ terms | 8.76 | 4.86 | 5.97 | 6.80 | 1.38 |
| | Experimental | 8.26 | 4.63 | | | |
| 4 | NN $\beta$ only | 8.88 | 4.26 | 5.49 | 6.25 | 1.44 |
| | All $\beta$ terms | 8.33 | 4.22 | 5.32 | 6.32 | 1.41 |
| | Experimental | 7.8 | 4.08 | | | |
| 5 | NN $\beta$ only | 8.65 | 3.83 | 5.03 | 5.57 | 1.42 |
| | All $\beta$ terms | 8.05 | 3.80 | 4.89 | 5.61 | 1.39 |
| | Experimental | | 3.71 | | | |
| 6 | NN $\beta$ only | 8.48 | 3.54 | 4.72 | 5.06 | 1.42 |
| | All $\beta$ terms | 7.86 | 3.50 | 4.60 | 5.10 | 1.39 |
| | Experimental | | 3.41 | | | |
| 7 | NN $\beta$ only | 8.36 | 3.32 | 4.50 | 4.68 | 1.43 |
| | All $\beta$ terms | 7.72 | 3.29 | 4.38 | 4.72 | 1.40 |
| | Experimental | | 3.18 | | | |
| 8 | NN $\beta$ only | 8.27 | 3.16 | 4.35 | 4.37 | 1.45 |
| | All $\beta$ terms | 7.61 | 3.13 | 4.20 | 4.44 | 1.42 |
| | Experimental | | 3.02 | | | |
| 9 | NN $\beta$ only | 8.20 | 3.04 | 4.13 | 4.24 | 1.47 |
| | All $\beta$ terms | 7.53 | 3.01 | 4.03 | 4.27 | 1.45 |
| | Experimental | | | | | |
| 10 | NN $\beta$ only | 8.14 | 2.94 | 3.93 | 4.16 | 1.50 |
| | All $\beta$ terms | 7.47 | 2.92 | 3.87 | 4.16 | 1.48 |
| | Experimental | | 2.77 | | | |

[a] IP = ionization potential, NN = nearest neighbor. [b] Unless otherwise noted, spectral data are from H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962. Ionization potentials are from W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A185**, 182 (1946), for the olefins and M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959), for the aromatics. [c] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

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(13) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).
(14) J. E. Bloor, *Can. J. Chem.*, **43**, 3026 (1965).

**Table V.** Electronic Transition and Ionization Potential Results for the Aromatic Hydrocarbons (ev)[a]

| Compound | IP | $^1\Delta E_1$ | $^1\Delta E_2$ | $^1\Delta E_3$ | $^3\Delta E_1$ |
|---|---|---|---|---|---|
| Benzene | | | | | |
| NN $\beta$ Only | 10.55 | 5.31 | 6.60 | 7.43 | 2.92 |
| All $\beta$ terms | 9.97 | 4.93 | 6.23 | 7.06 | 2.59 |
| Experimental[b] | 9.52 | 4.91 | 6.19 | 7.02 | 3.68[c] |
| Naphthalene | | | | | |
| NN $\beta$ only | 9.56 | 4.72 | 5.12 | 6.24 | 2.81 |
| All $\beta$ terms | 8.83 | 4.33 | 4.82 | 5.89 | 2.53 |
| Experimental | 8.26 | 3.97 | 4.33 | 5.61 | 2.64[c] |
| Anthracene | | | | | |
| NN $\beta$ only | 8.90 | 4.12 | 4.28 | 5.50 | 2.23 |
| All $\beta$ terms | 8.08 | 3.85 | 3.86 | 4.95 | 2.02 |
| Experimental | 7.55 | | | 4.88 | 1.84[d] |
| Phenanthrene | | | | | |
| NN $\beta$ only | 9.23 | 4.34 | 4.58 | 5.58 | 2.75 |
| All $\beta$ terms | 8.43 | 3.97 | 4.28 | 5.14 | 2.48 |
| Experimental | 8.03 | 3.62 | 4.23 | 4.94 | 2.70[e] |
| Naphthacene | | | | | |
| NN $\beta$ only | 8.32 | 3.26 | 3.84 | 4.44 | 1.48 |
| All $\beta$ terms | 7.55 | 3.02 | 3.44 | 4.08 | 1.32 |
| Experimental | 7.00[f] | 2.63[g] | | 4.60[g] | 1.27[h] |
| Chrysene | | | | | |
| NN $\beta$ only | 9.05 | 4.31 | 4.38 | 5.47 | 2.82 |
| All $\beta$ terms | 8.24 | 4.00 | 4.05 | 4.96 | 2.57 |
| Experimental | 7.80[f] | 3.44[g] | 4.12[g] | 4.71[g] | 2.45[i] |
| 1,2-Benzanthracene | | | | | |
| NN $\beta$ only | 8.83 | 3.96 | 4.03 | 4.81 | 2.34 |
| All $\beta$ terms | 8.04 | 3.60 | 3.73 | 4.50 | 2.12 |
| Experimental | 7.57[f] | 3.22[g] | 3.68[g] | 4.35[g] | 2.05[i] |
| 3,4-Benzophenanthrene | | | | | |
| NN $\beta$ only | 9.17 | 4.24 | 4.51 | 5.09 | 2.98 |
| All $\beta$ terms | 8.36 | 3.87 | 4.17 | 4.74 | 2.68 |
| Experimental | 7.86[f] | 3.81[g] | 4.07[g] | 4.76[g] | 2.48[j] |
| Triphenylene | | | | | |
| NN $\beta$ only | 9.34 | 4.39 | 4.70 | 5.36 | 3.39 |
| All $\beta$ terms | 8.55 | 4.01 | 4.32 | 4.94 | 3.00 |
| Experimental | 8.0[f] | 4.11[g] | 4.45[g] | 4.91[g] | 2.89[e] |

[a] IP = ionization potential, NN = nearest neighbor. [b] See footnote *b*, Table IV. [c] See footnote *c*, Table IV. [d] D. P. Craig and I. Ross, *J. Chem. Soc.*, 1589 (1954). [e] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [f] G. Briegleb, *Angew. Chem., Intern. Ed. Engl.*, **3**, 617 (1964). These values are estimations based on charge-transfer spectral data. [g] E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press Inc., New York, N. Y., 1964. The values reported here are the maximum of the first band and the energy average for the higher bands. This method of estimation was chosen because of a good deal of overlapping of the higher energy bands. This overlap would tend to obscure the position of the true maximum. [h] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964). [i] D. S. McClure, *ibid.*, **17**, 905 (1949). [j] E. Clar and D. G. Steward, *J. Am. Chem. Soc.*, **74**, 6236 (1952).

appears to be independent of whether or not the non-neighbor $\beta$'s are included. The higher transitions are much more dependent on these terms, but the dependence decreases as the chain length increases. For five or more double bonds the third transition, as calculated by the two methods, agrees as well as the first. The second transition, however, is dependent upon the method to at least nine double bonds.

No such trends are noticeable in the aromatic spectral results. The agreement with experiment, however, is somewhat better with the inclusion of all $\beta$ terms. The results for benzene are excellent for the singlet states. The triplet is, however, too low. For the higher members, the triplet agreements are almost fortuitously good.

The calculated ionization potentials for all of the molecules are consistently about 0.5 ev too high. This could easily be overcome by using different valence-state data, by decreasing the magnitude of the $\beta$ integral, or by including appropriate empirically determined neutral atom pentetration integrals in the calculations.

The spectral results for azulene are listed in Table VI. The first six transitions are known in this case. Again, inclusion of all $\beta$ terms gives considerable improvement. The triplet energies for azulene are as yet not known. It is interesting to note that in the case of azulene the results of calculations using orthogonalized atomic orbitals are considerably poorer than the present results.[15]

**Table VI.** Electronic Transitions and Ionization Potential for Azulene

| State | Exptl value (ev) | All $\beta$ terms (ev) | NN $\beta$ only (ev) |
|---|---|---|---|
| $^1E_1$ | 2.14 | 2.17 | 2.46 |
| $^1E_2$ | 3.68 | 3.63 | 3.92 |
| $^1E_3$ | ~4.3 | 4.74 | 4.93 |
| $^1E_4$ | 4.88 | 5.14 | 5.20 |
| $^1E_5$ | ~5.3 | 5.95 | 6.42 |
| $^1E_6$ | ~6.6 | 6.69 | 7.08 |
| IP | 7.4 | 7.85 | 8.73 |

## Conclusion

It was found that inclusion of all $\beta$ terms in SCMO calculations leads to significant charge separation in alternant hydrocarbons in the series studied. No charge separation is expected in SCMO calculations which neglect non-nearest neighbor $\beta$ terms.[16,17] It was also found that this inclusion can yield significant changes in the energy levels and energy level spacings of the compounds studied.

**Acknowledgments.** The authors express their appreciation to the L.S.U.N.O. Computer Center (supported in part by N.S.F. Grant No. GP 2964) and the L.S.U. Baton Rouge Computer Center for generous provision of computer time. They also thank Dr. O. W. Adams of Abbott Laboratories for making available his SCMO program from which the present program evolved. Financial support for this work was partially provided by the Cancer Association of Greater New Orleans.

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(15) O. W. Adams, private communication.

(16) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

(17) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).