

A Comparative Study of SCFMO Calculations on Alternant and Nonalternant Hydrocarbons

J. E. BLOOR and B. R. GILSON*

Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia 22901

N. BREARLEY

Physics Department, British Columbia Research Council, Vancouver 8, Canada

Received March 21, 1967

A form of the semiempirical self-consistent-field LCAO- π -MO method in which allowance is made for bond length-bond order correlation is presented. The results of calculations of excited state energies calculated according to this method are compared with those calculated by several other methods. The comparison indicates that the method here described can successfully predict the spectra of various classes of conjugated hydrocarbons with a consistent set of parameters. It is shown that the success of the Hückel LCAO procedure in predicting the p -band transition energy is principally due to three factors: the relative unimportance of configuration interaction, the invariance of the SCF electron-interaction terms for various hydrocarbons, and the proportionality of the Hückel energy number to the corresponding term in the SCF theory.

Mittels einer semiempirischen SCF-LCAO- π -MO-Methode mit Bindungslängen-Bindungsordnungs-Korrelation werden eine größere Anzahl konjugierter Moleküle berechnet. Die Ergebnisse werden mit denen verschiedener anderer Methoden verglichen. Unsere Methode sagt unter Verwendung eines konsistenten Parametersatzes die Spektren unterschiedlicher Klassen von Molekülen gut voraus. Drei Faktoren verursachen den Erfolg der Hückel-Methode bei der Berechnung der p -Banden: geringe Bedeutung der Konfigurationen-Wechselwirkung, Ähnlichkeit der SCF-Elektronenwechselwirkungsglieder für verschiedene Kohlenwasserstoffe, Proportionalität von Hückelzahl und dem entsprechenden Glied in der SCF-Theorie.

Une variante de la méthode SCF MO LCAO semi-empirique pour les électrons π , tenant compte d'une corrélation entre la longueur et l'indice de liaison, est présentée. Les résultats obtenus par cette méthode pour les énergies des états excités sont comparés γ ceux calculés par plusieurs autres méthodes. La comparaison indique que la méthode décrite peut prédire avec succès les spectres de différentes classes d'hydrocarbures conjugués en utilisant un ensemble de paramètres cohérents. On montre que le succès de la méthode de Hückel dans la prédiction de l'énergie de transition de la bande p est principalement du γ trois facteurs: la non importance relative de l'interaction de configuration, l'invariance des termes d'interaction électronique SCF pour des hydrocarbures variés, et la proportionnalité du nombre énergétique de Hückel au terme correspondant dans la théorie SCF.

Introduction

The semiempirical self-consistent-field molecular-orbital (SCFMO) method, frequently referred to as the P.P.P. method after its originators PARISER and PARR [1] and POPLE [2], has been very successfully applied to predictions of electronic transitions of aromatic hydrocarbons and of conjugated polyenes for which it is

* NASA Research Trainee 1966.

possible to assume a fixed geometry. However, relatively few SCF calculations have been performed on compounds which contain both aromatic rings and double bonds, and for nonalternant hydrocarbons for which the exact geometry is unknown. There have also been very few systematic SCFMO studies in which the parameters for one class of compounds are carried over into another class, although this type of study has been performed by KOUTECKÝ and his collaborators [3] for the antisymmetrized-molecular-orbital configuration-interaction (ASMO CI) method, in which Hückel molecular orbitals (HMO's) are used as a basis set in the configuration interaction rather than SCF MO's. We present here a systematic study in which we have applied one SCFMO procedure to four different classes of molecules:

1. Polycyclic aromatic hydrocarbons,
2. Conjugated polyolefins,
3. Alternant hydrocarbons containing both vinyl groups and aromatic rings,
4. Nonalternant hydrocarbons.

The method used is a modification of standard procedures in which the only experimental data used are values taken from valence-state tables and an initial idealized geometry of the molecule. The bond lengths, and consequently the resonance integrals, are allowed to vary with bond order until self-consistency is reached; however, nonbonded distances are kept constant for simplicity in computation. No attempt has been made to take σ -bond changes explicitly into consideration.

We have also made a comparative study between our method and three other SCFMO methods which have recently been suggested. To make this study as complete as possible, we have also carried out new calculations using these methods as described in the literature.

Methods

In order to provide a more thorough comparison of our proposed method with those used by others and to establish more clearly the limitations, if any, of the different methods, we have carried out calculations on a few specially chosen molecules using the following calculational procedures:

1. Our variable-resonance-integral method: The one-center repulsion integral γ_{11} for carbon was calculated using the I - A approximation, using HINZE and JAFFÉ's [4] values for I (the valence-state ionization potential) and A (the valence-state electron affinity). The two-center integrals were then calculated by the Nishimoto-Mataga (NM) method [5] widely used previously by ourselves and by many others. A set of coordinates using idealized bond distances and angles was initially used to calculate the two-center repulsion integrals. Only the nearest-neighbor two-center integrals were then allowed to change, using a bond distance calculated theoretically from the bond order by the relationship

$$r_{pq} = 1.517 - 0.18 p_{pq} . \quad (1)$$

Resonance integrals were included only between nearest neighbors, consistent with the zero-differential-overlap (ZDO) approximation. These resonance integrals were calculated at each iteration using a Mulliken magic formula [6] expansion:

$$\beta_{pq} = \frac{-(I_p + I_q)}{2} \frac{S_{pq}}{1 + S_{pq}} . \quad (2)$$

The overlap integrals S_{pq} were evaluated at each iteration, using the bond distances calculated from (1) and a standard expression for Slater-type $2p\pi$ atomic orbitals with an effective charge of 3.18 [7]. In trial calculations on molecules which might be expected to exhibit bond alternation, e.g. butadiene and heptfulvene, it was found not to matter whether we started with an initial set of bond distances which were all equal or with a model of alternating single and double bonds; the calculation in both cases converged into models possessing strong bond alternation. As will be discussed in detail elsewhere [8] the bond distances predicted by this method corresponded very closely to those calculated by the method recently developed by DEWAR et al. [9, 10] specifically for predicting groundstate properties.

2. The variable- β method of NISHIMOTO and FORSTER [11, 12, 13]: This method is very close to that used by ourselves but differs from it in the important point that an additional empirical parameter is introduced in the dependence of the resonance integral on bond order, and that this parameter is claimed to vary from molecule to molecule or, at least, from class to class.

3. The method proposed by FISCHER-HJALMARS [14] and applied by SKANCKE [15, 16] to several aromatic hydrocarbons: The method differs from ours only in the particular way in which the parameters are calculated: i.e., atomic spectroscopic data are used directly to calculate the repulsion integrals rather than valence-state ionization potentials, and a different expression is used for the dependence of the resonance integral on distance: for carbon-carbon bonds

$$\beta_{ij} = -S_{ij}[k_1(\gamma_{ii} + \gamma_{jj}) + k_2\gamma_{ij}]. \quad (3)$$

The constants k_1 and k_2 are obtained by fixing β for ethylene and benzene so that the spectra are fitted. This method seemed quite promising, and we therefore used it for a number of molecules for which SKANCKE did not carry out calculations. These are compared with our data in Tab. 2.

4. The "Improved LCAO π -electron method" suggested by ADAMS and MILLER [17]: In this method, Löwdin-orthogonalized AO's [18] are used as the basis set for the MO's, and penetration integrals are included. The method as used in Ref. [17] does not allow for changes in geometry during the calculation. We have carried out calculations using this method for naphthalene and fulvene and have come to somewhat different conclusions than the originators of the method. For example, ADAMS and MILLER [19] neglected all the core matrix elements over Löwdin orbitals (H_{pq}^λ) for distances greater than 2.8 Å. We, on the other hand, found that the H_{pq}^λ matrix elements did not fall off in value as the distance r_{pq} is increased and also that many of the elements became positive in sign. As a result we found that the effect of including these matrix elements could be considerable. We also found that the magnitude of this effect was very sensitive to the precise manner in which the core elements over atomic orbitals (H_{pq}^0) were calculated. When ADAMS and MILLER's procedure was followed for fulvene we found that inclusion of non-nearest neighbor H_{pq}^λ matrix elements had considerable effect. The difference between a calculation including all non-nearest neighbor H_{pq}^λ values and not including them was 2.7 kK for the first singlet transition and 3.76 kK for the second. Since, therefore, one of the principal features of the "improved

method," i.e. neglect of non-nearest neighbor H_{pq}^1 values, is not justifiable, except perhaps in special cases, we decided not to carry out further calculations using this method.

Results of Comparative Study

A comparison of the tabulated results of NISHIMOTO and FORSTER [11, 12, 13] with our own (Tab. 1) indicates that, despite the larger number of empirically-chosen parameters, method 2 gives results not significantly different from those of our method 1. The latter method has therefore the advantage that no parameter values are required for new calculations that cannot directly be adopted from other molecular calculations, whereas in method 2 the empirical parameter denoted A_0 in Ref. [11] depends on the number of rings in a manner that cannot be easily extrapolated to new cases. It may be, however, that this extra parameter becomes necessary when heteroatoms are introduced.

The method of FISCHER-HJALMARS (method 3) tends to give transition energies which are quite high, compared with both the experimental transition energies and those calculated by the other methods described. However, a plot of the band frequencies calculated by this method against the experimental frequencies is fairly linear, although the slope is somewhat larger than unity.

Table 1. Comparison of results of methods 1 and 2

Molecule	Transition Symmetry	Method 1		Method 2		Expt.	
		ν (kK)	f	ν (kK)	f	ν (kK)	f
Naphthalene	${}^1B_{1u}$	32.45	0	32.54	0	32.03	0.002 (x)
	${}^1B_{2u}$	36.43	0.204 (y)	35.65	0.200 (y)	36.39	0.18 (y)
	${}^1B_{1u}$	45.69	1.949 (x)	45.04	1.960 (x)	45.42	1.70 (x)
	${}^1B_{2u}$	49.63	0.615 (y)	49.00	0.579 (y)	52.52	0.21
Anthracene	${}^1B_{2u}$	28.86	0.274 (y)	28.10	0.317 (y)	26.95	0.10
	${}^1B_{1u}$	40.07	2.745 (x)	38.98	2.522 (x)	38.97	2.28
	${}^1B_{2u}$	47.61	0.087 (y)	47.20	0.221 (y)	45.26	0.28
Phenanthrene	1A_1	30.21	0	29.28	0	30.25	0.003 (y)
	1B_1	34.56	0.311 (x)	33.53	0.322 (x)	34.13	0.18 (x)
	1B_1	40.60	1.541 (x)	39.71	1.486 (x)	39.62	1.09
		41.31	0.572 (y)	40.16	0.540 (y)		
	1A_1	45.77	0.303 (y)	44.35	0.330 (y)	47.04	0.6
		49.58	0.263 (x)	48.01	0.265 (x)		
Pyrene	${}^1B_{1u}$	27.99	0	27.99	0	26.94	0.002
	${}^1B_{2u}$	29.72	0.701 (x)	28.68	0.680 (x)	29.84	0.47
	${}^1B_{1u}$	39.03	0.956 (y)	37.93	0.948 (y)	36.70	0.47
	${}^1B_{2u}$	43.36	1.616 (x)	42.00	1.468 (x)	41.54	1.00
Azulene	1B_1	15.80	0.024 (y)	15.47	0.0221 (y)	15.8	0.045
	1A_1	27.60	0.006 (x)	27.19	0.005 (x)	29.5	0.08
	1B_1	34.55	0.115 (y)	34.06	0.117 (y)	36.1	
	1A_1	37.64	1.819 (x)	37.24	1.818 (x)	36.47	1.10
	1B_1	44.99	0.421 (y)	44.37	0.443 (y)	42.3	0.38

Table 2. Comparison of results of methods 1 and 3

Molecule	Method 1		Method 3		Expt.	
	ν (kK)	f	ν (kK)	f	ν (kK)	f
Butadiene ^a	44.86	0.984	51.10	1.037	46.05	
	53.18	0	63.71	0		
	64.49	0	64.65	0		
Hexatriene ^a	36.37	1.365	44.82	1.384	37.34	
	44.97	0	58.08	0		
	52.92	0	58.29	0		
	52.95	0	63.23	0		
	63.85	0.024	64.11	0.073		
Naphthalene ^b	32.45	0	35.04	0	32.03	0.002
	36.43	0.204	38.16	0.05	36.39	0.18
	45.69	1.949	51.76	2.14	45.42	1.70
	49.63	0.615	53.78	0.87	52.52	0.20
	62.55	0.943	—	—	59.80	0.6
Anthracene ^b	28.86	0.274	29.72	0	26.95	0.10
	29.31	0	30.99	0.2		
	40.07	2.745	44.71	0.001	38.97	2.28
	47.61	0.087	45.27	3.23	45.26	0.28
	48.40	0.297	49.77	0.54		
	49.06	0	64.04	1.18		
Phenanthrene ^b	30.21	0	32.40	0	30.25	0.003
	34.56	0.311	35.18	0.46	34.13	0.18
	40.60	1.541	44.56	0.0005	39.62	1.09
	41.31	0.572	47.55	1.49		
	45.77	0.303	50.45	1.01	47.04	0.6
	49.58	0.263	55.71	0.18		
Perylene ^b	25.12	0.882	32.30	0.76	23.05	0.33
	29.57	0	46.77	1.37	39.60	0.44
	40.86	1.631	47.21	1.20	40.86	
	46.38	0	50.24	0.93	48.50	2.17
	47.47	0.928	54.74	0.14		
	48.04	0	56.86	2.02		
	48.88	0	59.78	1.07		
Biphenylene ^b	26.71	0	37.10	0	25.47	($\epsilon_{\max} = 250$)
	32.01	0	47.98	1.94	28.2	($\epsilon_{\max} = 10^4$)
	38.10	0	—	—		
	41.40	2.015	(46.76)	0.08 ^c)	40.25	($\epsilon_{\max} = 10^5$)
Fulvene ^a	24.57	0.034	34.11	0.065	27.6	0.012
	39.10	0.631	46.16	0.675	41.3	0.32
	53.13	0.325	60.57	0.430		
Heptafulvene ^a	21.58	0.040	31.76	0.053	23.45	0.02
	32.93	0.440	42.75	0.518	35.85	0.3
	46.55	0.095	53.78	0.017	47.00	

^a New Values we have calculated using method 3.

^b Values calculated by method 3 and reported in Ref. [15] and [16].

^c Only other transition reported in Ref. [15] with this symmetry. Low f value indicates it does not actually correspond to this transition.

The fourth method, that of ADAMS and MILLER, gives results for polycyclic alternant hydrocarbons that are distinctly inferior to those of methods 1 and 2. For the conjugated polyenes, however, the results are close to those of all the other methods. The variety of the compounds treated by ADAMS and MILLER [17] was too small to assess the performance of the method in general. It appeared at first that their method had the great advantage that triplet levels were predicted in good agreement with experiment, but closer investigation shows that the real source of this lay in using very limited CI [19]. This effect of CI is known to be very great for triplet states when NM repulsion integrals are used, as was done by ADAMS and MILLER.

As a result of this comparative study, it was decided to continue with our own method (method 1), since (a) the extra empirical parameter introduced by NISHIMOTO and FORSTER appeared to lead to no improvement, (b) the method of FISCHER-HJALMARS produced poorer agreement for the excited states (and ionization potentials [8]), and (c) the "improved method" of ADAMS and MILLER [17] does not appear to give any real improvement and is in its present published form unjustifiable.

Analysis of Results

A plot of the results of our calculations on singlet energies against the corresponding experimental results is given in Fig. 1. This graph includes experimental data, wherever possible, on the first three transitions (empirically known as α , p

Table 3. Results of Calculations on Large Polycyclic Systems

Molecule	Assignment	ν (calc.), kK	f	ν (exp.) ^a , kK
Tetracene	B_{3u}	23.798	0.293	23.8
	B_{2u}	26.572	0	
	B_{2u}	36.004	3.331	36.0
	B_{3u}	39.096	0	
	B_{3u}	39.437	0.050	
Pentacene	B_{3u}	20.580	0.337	19.6
	B_{2u}	25.549	0	
	B_{2u}	33.867	5.726	32.3
	B_{3u}	35.545	0.136	
Triphenylene ^b	A_1	31.808	0	29.3
	A_2	34.654	0	35.0
	E	36.165	0	
	E	39.527	1.697	38.5
	E	43.414	0.045	
Coronene ^b	B_{2u}	26.120	0	25.3
	B_{1u}	29.178	0	29.8
	E_{1u}	35.190	2.113	32.8
	E_{1u}	44.277	0.002	

^a Based on spectra in FRIEDEL, R. A., and M. ORCHIN: Ultraviolet spectra of aromatic compounds. New York: John Wiley and Sons, Inc. 1951.

^b Calculations performed by P. N. SCHATZ and associates, using our Method 1.

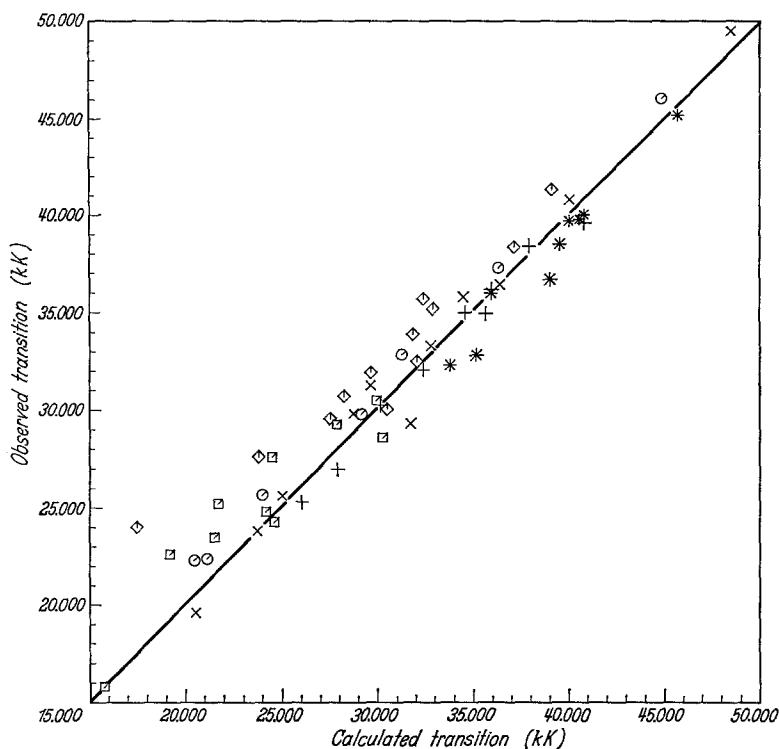


Fig. 1. Comparison between calculated and observed spectra of hydrocarbons.
 × + * Polycyclic alternant hydrocarbons, ◇ □ Nonalternants, ○ Polyenes

and β type transitions) of twelve polycyclic hydrocarbons (class 1), the first two transitions for twelve nonalternants (class 4), the first transition of six polyenes (class 2) and the first transition of styrene and the first observed transition of stilbene (class 3). The actual calculated values are summarized in Tabs. 1—7. There is some scatter about the line for perfect agreement between experiment and theory, but considering the diversity of the structures of the molecules under consideration and the wide range of transition energies (35.0 kK) the agreement between theory and experiment is satisfactory.

Comparison of our results with the extensive ASMOCI calculations of HUMMEL and RUEDENBERG [20] shows that our method compares very favorably with their TBX method in which experimental bond distances are utilized in calculating the matrix elements of the CI matrix. The chief failure of our method is pyrene (Tab. 1). For this molecule, however, crystallographic measurements [21] reveal a bond distance for the bond joining the 4—5 positions (standard Chemical Abstracts nomenclature) that is shorter ($r_{45} = 1.32 \text{ \AA}$) than the ethylene double bond. The unknown factors responsible for this abnormally short bond distance may be responsible for the discrepancy between the calculated and experimental results.

Although the grouping about a common line is much closer for the different classes than the corresponding plot using HMO data [3], there is still a considerable scatter, which may, however, be reduced for individual classes by considering

them separately. For classes 1 and 3 there is a regression line very close to the perfect line, i.e.,

$$\nu_{\text{obs}} = 0.997 \nu_{\text{calc}} - 0.197 \text{ kK} .$$

For class 2 the regression line is

$$\nu_{\text{obs}} = 0.980 \nu_{\text{calc}} + 1.953 \text{ kK} ,$$

while for class 4 molecules (omitting the first fulvalene transition) the regression line is

$$\nu_{\text{obs}} = 0.973 \nu_{\text{calc}} + 2.328 \text{ kK} .$$

This shows that for nonalternants and polyenes the calculated frequencies are too low even without any corrections for solvent effects. Thus we must conclude that in our SCFMO method the different classes give different regression lines, although these lines are very much closer together than in the HMO method. In order to carry out a more thorough investigation, it is necessary to have more complete experimental data, particularly for nonalternants. The existence of these separate lines does, however, seem to be a definite limitation of the method presented here which we have failed to rectify.

Phenyl Ethylenes

The series benzene, ethylene, styrene, stilbene is an excellent family of molecules for testing theoretical procedures, since, once the parameters have been adjusted in order to fit benzene and ethylene, no further adjustment should be necessary to predict the effect of a vinyl or styryl group on the benzene spectrum. Nevertheless, no previous SCFMO study of the full series appears to have been made, although several calculations on stilbene have been reported [22, 23].

We have carried out calculations on this series using three methods: our method (method 1), the Fischer-Hjalmars method (method 3), and Beveridge and Jaffé's [22] method. The results are summarized in Tab. 4. These results for stilbene show that, whereas all these methods predict a strong transition polarized along the major axis, at about the same frequency and in reasonable agreement with experiment, only method 1 predicts correctly the amount of shift of the p band of benzene on substitution by a vinyl and by a styryl group. This is partly because of the poor prediction by both the other methods of the frequency of the benzene p band; i.e., the Fischer-Hjalmars method predicts it 4.2 kK low and the Beveridge and Jaffé method 6.4 kK low. However, the predicted shift from styrene to stilbene is also lower, by these methods, than observed, especially in the case of Fischer-Hjalmars' method, which predicts a red shift of only 2.5 kK, which is less than half of that observed. The performance of method 1 compared to the other two methods for this series is further justification for our preference for this method.

The results of the calculation on stilbene using method 1 differ from those of BEVERIDGE and JAFFÉ [22] in the order of the second and third allowed transitions. These authors assign the band observed at 223 $m\mu$ (44.8 kK) to the long-axis-polarized transition [${}^1H^+({}^1B_{3u}) \leftarrow {}^1A_g$] and they assign a band at 200 $m\mu$ (50 kK) to a principally short-axis-polarized transition [${}^1G^+({}^1B_{2u}) \leftarrow {}^1A_g$]. In our calculation, however, the relative energies of these two transitions are reversed (Tab. 4).

Table 4. Comparison of Phenyl Ethylenes

Molecule	Method 1			Method 3			BEVERIDGE-JAFFÉ			Exp. ν (kK)
	ν (kK)	f	Pol. ^a	ν (kK)	f	Pol. ^a	ν (kK)	f	Pol. ^a	
Ethylene	62.67			62.13			57.41			61.54
Benzene	37.97	0		39.37	0		39.62	0		38.40
	48.44	0		45.26	0		43.56	0		49.5
	55.10	1.167		59.51	1.260		57.06	1.210		55.87
Styrene	35.75	0		37.84	0		38.02	0		34.97
	40.09	0.641	15.8°	39.87	0.082	24.9°	38.09	0.301	21.8°	40.82
	48.86	0.449	101.5°	49.14	0.090	159.0°	48.79	0.689	4.7°	
	50.87	0.649	28.7°	56.06	0		53.46	0.976	69.2°	
	51.19	0		56.21	0.967	50.5°				
Stilbene	32.85	1.192	14.6°	37.35	0.826	13.2°	33.78	0.571	13.9°	34.01
	39.51	0		37.94	0		37.59	0		
	39.61	0		37.96	0		37.73	0		
	46.01	0		43.08	0		41.15	0		
	46.59	0.784	88.4°	47.25	0.661	4.85°	45.66	0.558	1.7°	44.84
	51.57	1.089	179.8°	53.94	0		51.02	0		49.75
	52.40	0		54.27	0		51.81	0		
	60.61	0		55.33	1.337	71.9°	52.08	0.831	70.0°	

^a Polarizations are given for styrene and stilbene as angles measured from an axis parallel to the bond attached to the benzene ring. In the case of stilbene, short-axis-polarization implies $\alpha = 90^\circ$, long-axis, $\alpha = 0^\circ$ or 180° .

Conclusive assignment of the two observed bands can only be obtained from polarization measurements on single crystals such as those reported by ANEX on azobenzene [24]. However, a study of substitution effects on the positions para to the ethylenic bond in stilbene offers some tentative evidence in favor of our assignment.

An examination of the wave functions of the excited states reveals that the ${}^1B_{3u}$ transition is built up of configurations which can be described as one-electron excitations involving wave functions nearly completely localized in the benzene rings, with near-nodes on the vinyl-substituted carbon atoms and para to them (in our calculation, $\psi_5, \psi_6, \psi_9, \psi_{10}$ in order of ascending energy). The ${}^1B_{2u}$ transition, on the other hand, is built up mainly of two configurations, one of which involves the highest occupied MO (ψ_7) and also ψ_9 , while the other involves the lowest unoccupied MO (ψ_8) and also ψ_6 . The orbitals ψ_7 and ψ_8 contain a considerable amount of the ethylenic wave function mixed into them, and do not have nodes para to this group. To a first approximation, therefore, one would expect the ${}^1B_{3u} \leftarrow {}^1A_g$ transition to be relatively uninfluenced by substitution in the para positions, but the ${}^1B_{2u} \leftarrow {}^1A_g$ transition would be changed in a similar way to the strong first transition (mainly ψ_7^8), but the shifts should not be as large as for this transition. Spectral curves for para-aminostilbene, para-(N,N-dimethylamino)stilbene, and para-methoxystilbene [25] show that the 46-kK band is in fact moved toward lower frequencies by the substituents in the order ($\text{Me}_2\text{N} > \text{NH}_2 > \text{MeO}$). The curves do not extend far enough to give the behavior of the 50-kK band. However, measurements made by BROCKLEHURST [26] on stilbene, *p*-nitrostilbene, and *p*-nitro-*p'*-(N,N-dimethylamino)stilbene in ethanol clearly show (Tab. 5) that the effect of the substituents in both these compounds is to move the 44-kK band of stilbene to lower frequencies (by 2.2 kK for the NO_2 group and by 10 kK for the disubstituted stilbene) and increase its intensity, whereas in all three compounds there is an almost identical transition at 47.6 kK which

Table 5. *Experimental Spectra of Stilbene Derivatives*

Compound	Observed Bands in kK				
	ν_3	ν_2	$\Delta\nu_2^c$	ν_1	$\Delta\nu_1^c$
Stilbene ^a	ca. 48 (Infl.)	43.9	(0)	34.2	(0)
<i>p</i> -nitrostilbene ^a	47.6	41.7	2.2	29.0	5.2
<i>p</i> -nitro- <i>p</i> ¹ -dimethylaminostilbene ^d	47.1	33.6	10.3	23.5	10.7
Stilbene ^b	49.3	43.7	(0)	33.8	(0)
<i>p</i> -methoxystilbene ^b	?	43.5	0.2	32.5	1.3
<i>p</i> -aminostilbene ^b	?	42.7	1.0	30.5	3.3
<i>p</i> -dimethylaminostilbene ^b	ca. 49	42.0	1.7	29.0	4.8

^a Measured by P. BROCKLEHURST in C₂H₅OH on an Optika automatic recording instrument.

^b Taken from spectral curves reported by BEALE and ROE, Ref. [23].

^c $\Delta\nu$ is the frequency shift relative to stilbene.

appears unchanged by substitution. On the basis of these experimental results, we are led to *tentatively* assign the substituent-influenced transition to the ${}^1B_{2u} \leftarrow {}^1A_g$ (short-axis-polarized) and the other to the ${}^1B_{3u} \leftarrow {}^1A_g$ transition, in agreement both with our calculation by method 1 and the calculation of PERKAMPUS [23], and contrary to the assignment suggested by BEVERIDGE and JAFFÉ [22].

Conjugated Polyolefins

Although there has been published a great deal of work on polyenes using HMO's [27, 28, 29, 30], there has not, until recently, been any report of a systematic study of the spectra of long-chain polyenes by the PPP MO method. Recently, however, FORSTER [13] has reported calculations on the energy of the first transi-

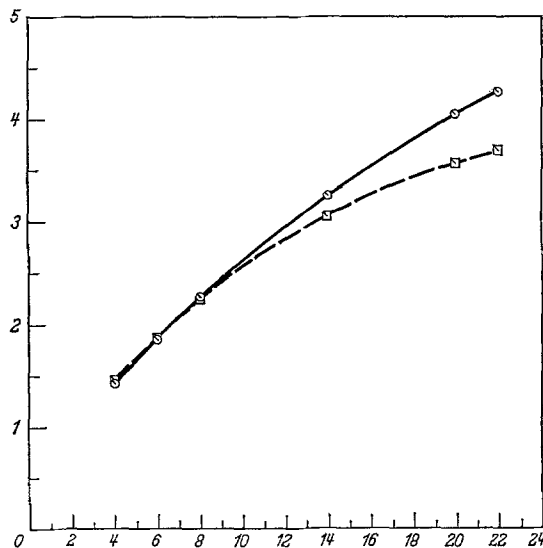


Fig. 2. Dependence of transition moments of principal transition on length of carbon chain for polyenes. □ : before CI, ○ : after CI

tion, using his variable- β method. ADAMS and MILLER have also applied their "improved LCAO-MO-SCF method" to a number of polyenes. These authors, however, did not report oscillator-strength values, and the latter workers did not give values for the overtone band frequencies. Calculations on the spectra of

Table 6. *Polyene Spectra*

Number of Carbon Atoms	¹ B-Band		¹ C-Band		¹ D-Band		¹ F-Band	
	$\nu(\text{calc})$	f	$\nu(\text{calc})$	$\nu(\text{exp})$	$\nu(\text{calc})$	f	$\nu(\text{calc})$	f
4	44.86	0.984	53.18		64.49	0	76.27	0.331
6	36.37	1.365	52.92		63.85	0.024	67.46	0.378
8	31.31	1.744	47.99	47.10	56.06	0.132	59.04	0.210
14	24.07	2.753	37.75		42.44	0.329	45.67	0.110
20	21.13	3.737	32.87	33.6 ^a	35.39	0.477	39.44	0.119
22	20.50	4.042	31.87	30.8 ^a	33.69	0.516	38.10	0.122

^a Corrected value based on Carotenoid with allowance for substitution.

^b Carotenoid.

polyenes have also been made by a resonance-force model [31, 32] and a "molecules-in-molecules" method [33, 34]. These latter two models tend to minimize the amount of delocalization, whereas in the LCAO MO methods there is considerable delocalization. PARKHURST and ANEX [35] have made a comparison of the results

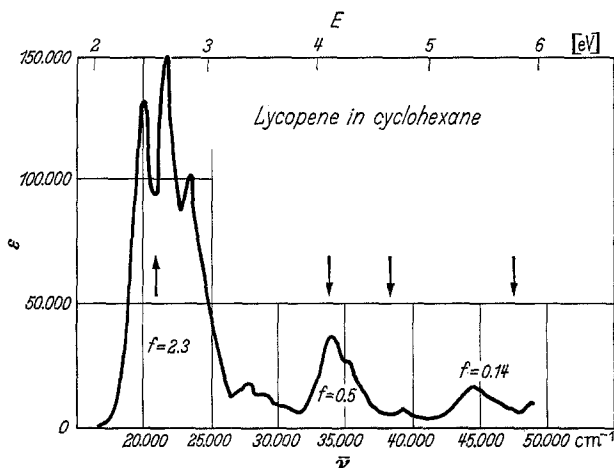


Fig. 3. Comparison of experimental spectrum of lycopene with allowed transitions calculated for C_{22} -polyene

of these theories with experimental data and concluded that the HMO theory does not explain the overtone bands found in the spectra of polyenes and cannot be used to simultaneously predict the correct linear relationship between intensity and chain length and also the correct decrease in transition energy with chain length. In order to see whether our PPP-SCF-MO model rectifies these deficiencies in the simpler HMO method, we have carried out calculations on a number of polyenes of differing chain length. The data in Tab. 6 show immediately that the correct fall-off with chain length for the first transition is obtained. The plot of transition moment versus number of double bonds, analogous to the one in Ref. [35], is shown both before and after CI in Fig. 2. This graph demonstrates clearly that the departure from linearity of the simple HMO model with alternating double and single bonds is due to the failure to include the effects of CI. Even the limited amount of CI which we have included, allowing only for single excitations from each occupied to each virtual orbital, has such a large effect on the longer polyenes that the plot becomes approximately linear. The results for the polyene of 11 double bonds are compared with an experimental spectrum [34] of lycopene in Fig. 3. Comparison of this figure with the similar figures given by MURRELL [36] and by MERZ et al. [34] shows that the SCFMO theory is just as capable as the "molecules-in-molecules" type model in calculating overtones.

Nonalternant Hydrocarbons

The only previous extensive study, using CI, of the spectra of nonalternant hydrocarbons is the work of KOUTECKÝ et al. [37], who used Hückel MO's calculated with the use of a constant resonance integral for all the bonds and the NM method for calculating repulsion integrals. Their calculations are compared with ours and with other work in Tab. 7. The calculations of NAKAJIMA and KATAGIRI [38] were carried out using HMO's but no CI. In our variable- β calculation for fulvene, we find that configuration interaction lowered the first transition by

Table 7. *Calculations on Nonalternants*

Molecule	This work		KOUTECKÝ		NAKAJIMA		Exp.
	ν	f	ν	f	ν	f	
Fulvene	24.57	0.034	15.12	0.002	26.79	0.049	27.6 ^a (log ε = 2.40)
	39.10	0.631	35.34	0.528	42.20	0.92	41.3 ^a (4.15)
	53.13	0.325	51.92	0.235			
	57.61	0.278	55.55	0.001			
Heptafulvene	21.58	0.040	13.57	0.019	22.75	0.057	23.45 ^b (log ε = 2.5)
	32.93	0.440	30.95	0.751	36.55	0.89	35.85 ^b (4.0)
	46.55	0.095	44.58	0			47.00 ^b (4.8)
	47.32	1.297	47.05	1.658			
	49.62	0	48.03	0.281			
50.89	0.073						
6-Vinylfulvene	21.76	0.020					25.2 ^c (log ε = 2.3)
	31.89	1.192					33.9 ^c (4.5)
	43.55	0.008					
	49.27	0.273					
	49.98	0.108					
8-Vinyl-heptafulvene	18.58	0.014					22.6 ^{d,e} (log ε = 2.7)
	19.21	0.023					30.7 ^d (4.70)
	28.31	1.028					
	40.56	0.109					
	42.18	0.600					
	43.31	0.127					
47.70	0.014						
1,2-Benzofulvene	27.96	0.110	22.58	0.070			29.24 ^f (log ε = 3.22)
	32.17	0.150	31.23	0.282			32.47 ^f (3.80)
	40.01	0.878	39.70	0.907			38.31 ^f (4.4)
	42.74	0.009	41.32	0.231			
	43.97	0.190	44.28	0.187			
	50.76	0.102					
Dibenzofulvene	30.33	0.110	27.14	0.070			28.57 ^f (log ε = 2.6)
	32.44	0.172	32.64	0.285			35.71 ^f (4.26; f = 0.33)
	34.35	0.003	33.71	0.015			39.06 ^f (4.77)
	39.45	0.543	39.50	0.510			40.50 ^f (4.53)
	41.43	0.792	41.14	0.865			43.5 ^f (4.73)
	44.36	0.868					
44.84	0.216						
3,4-Benzo-heptafulvene	25.09	0.026	20.99	0.022			30.5 ^g (log ε = 3.14)
	30.00	0.327	29.49	0.234			33.78 ^g
	37.20	1.147	38.74	0.695			35.6 ^g } (3.97)
	37.93	0	39.92	0.112			36.9 ^g
	39.53	0.039	41.59	1.080			38.3 ^g (4.30)
	41.58	0.588					40.8 ^g (4.07)
						42.2 ^g (3.97)	
Azulene	15.80	0.024	13.46	0.011			15.80 ^h (f = 0.009)
	27.60	0.006	25.50	0.007			29.50 ^h (0.08)
	34.55	0.115	33.91	0.178			36.10 ^h

Table 7. (continued)

Molecule	This work		KOUTECKÝ		NAKAJIMA		Exp.
	ν	f	ν	f	ν	f	
Azulene	37.64	1.819	34.81	1.540			36.47 ^h (1.10)
	44.99	0.421	45.65	0.603			42.30 ^h (0.38)
	47.32	0.005					
Acenaphthylene ^a	24.66	0.019					24.27 ⁱ (log ϵ = 2.19)
	30.57	0.155					30.03 ⁱ (3.69)
	31.22	0.275					31.05 ⁱ (4.01)
	38.86	0					37.73 ⁱ (3.48)
	44.14	1.296					43.48 ⁱ (4.72)
	47.66	0.012					
	47.98	0					
Fulvalene	17.14	0			16.45	0	? tail ^j
	17.50	0.015			17.18	0.03	24.0 ^j
	29.71	1.201			29.53	1.2	31.9 ^j (f = 0.4)
	42.70	0					
	48.80	0					
Sesquifulvalene	19.96	0.010			20.41	1.02	
	20.58	0.029			22.51	0.05	
	24.24	1.087			24.45	0.02	24.8 ^j (f = 0.47)
	26.54	0.005					
	39.50	0.312					
	41.77	0.010					
	42.32	0.026					
Heptafulvalene	15.05	0			14.03	0	? tail ^j
	15.42	0.013			14.52	0.02	27.6 (f = 0.38)
	23.85	1.285			22.51	1.1	
	37.55	0					
	38.56	0					
	40.92	0					
	41.87	0.279					

^a SCHALTEGGER, H., M. NEUENSCHWANDER, and D. MEUCHE: *Helv. chim. Acta* **48**, 955 (1965).

^b DOERING, W. VON E., and D. W. WILEY: *Tetrahedron* **11**, 183 (1960).

^c NEUENSCHWANDER, M., D. MEUCHE, and H. SCHALTEGGER: *Helv. chim. Acta* **46**, 1760 (1963).

^d BERTELLI, D. J.: *J. Amer. chem. Soc.* **86**, 3329 (1964).

^e Very broad band.

^f PULLMAN, A., et al.: *Bull. Soc. chim. France* **1951**, 702.

^g BERTELLI, D. J.: *J. Amer. chem. Soc.* **87**, 3719 (1965).

^h HEILBRONNER, E.: In *Non-benzenoid aromatic compounds*, ed. D. GINSBURG. New York: Interscience Publishers, Inc. 1959.

ⁱ Organic electronic spectral data. New York: Interscience Publishers, Inc. 1960.

^j Reported in NAKAJIMA, T., and S. KATAGIRI: *Molecular Physics* **7**, 149 (1963).

^k In a recent study of a cenaphthylene [HEILBRONNER, E., J. MICHL, J. P. WEBER, and R. ZAHRADNÍK: *Theoret. chim. Acta* **6**, 141 (1966)], SCF calculations were reported in which the positions of the second and third transitions were the reverse of those given here, although the parameters used were very similar, except for the use of a constant β . Experimental evidence for their assignment is also given.

0.07 eV, from 3.112 to 3.046 eV, and the second one from 5.10 to 4.84 eV. This demonstrates that Nakajima's apparently successful result is due to his neglect of the effects of CI, although it is now generally recognized that we must include CI, at least among degenerate or near-degenerate states, to obtain a realistic interpretation of the first few transition of conjugated hydrocarbons. In general, our calculations agree very well with those of KOUTECKÝ. As predicted by KOUTECKÝ [37], the allowance for bond alternation greatly improves the fit between theory and experiment for the first transition. For example, our variable- β method predicts the first transition in azulene, fulvene, and heptafulvene to be higher, respectively by 2.3, 9.5, and 8.0 kK than the corresponding transitions calculated in Ref. [37].

Relationship to Hückel Calculations

The HMO theory has been very successful [39] even though it ascribes electronic transition energies to a simple difference of energy values E_{ik} .

$$E_{ik} = (K_k^H - K_i^H) \beta$$

(where K_k^H and K_i^H are the Hückel numbers, defined by

$$K_i^H = \sum_p \sum_q C_{ip}^H C_{iq}^H, \text{ the sum over all bonded atoms } p, q)$$

This success has prompted many attempts at explanation in terms of the formalism of sophisticated methods which include the electron-electron interaction terms [40, 41, 42, 43]. The great majority of these studies have attempted to interpret the success of HMO theory in predicting one-electron properties in terms of an effective Hamiltonian which includes implicitly the electron-repulsion terms. On the other hand, in an extensive study by the ASMOCI method, using Hückel MO's, of the p -band transition energies of all types of hydrocarbons, KOUTECKÝ et al. [3, 37, 44] recognized the significance of the different values for repulsion-energy terms for different classes of hydrocarbons and suggested that the success of the HMO estimates of the p -band transition energies was due to the constancy of the terms involving repulsion integrals within each class. We independently [45] came to the same conclusion based on our earlier SCF calculations on alternant hydrocarbons. In our previous study, we suggested that the electron-repulsion terms are not included in the Hückel effective Hamiltonian at all, but that the success of the HMO theory depended on two factors: the constancy of the electron-repulsion terms, and the similarity between the Hückel number K_i^H and the corresponding quantity in SCF theory K_i^{SCF} . In Ref. [45], the definition was made:

$$K_i^{\text{SCF}} = \sum_p \sum_q C_{ip}^{\text{SCF}} C_{iq}^{\text{SCF}} ;$$

however, since in the current study β is not a constant, it is more meaningful to define:

$$K_i^{\text{SCF}} = \sum_p \sum_q C_{ip}^{\text{SCF}} C_{iq}^{\text{SCF}} \beta_{pq} .$$

When our previous study was carried out, we had very limited computing facilities and it was only possible to give support for this theory by analysis of data for a few polycyclic aromatic hydrocarbons. We have now extended this analysis to our calculations of p -band type transitions for all the compounds of Tab. 8.

The p -band transition energy neglecting CI may be written as

$$E_{ik} = (K_k^{\text{SCF}} - K_i^{\text{SCF}}) + \frac{1}{2} \sum_{p \neq q} [(C_{ip} C_{iq} - C_{kp} C_{kq}) P_{pq} \gamma_{pq}] + 2K_{ik} - J_{ik}.$$

In Tab. 8 we have tabulated values of K_i^{SCF} for the highest occupied MO, and also the electron-repulsion terms, defined as Δ :

$$\Delta = 2K_{ik} - J_{ik} + \frac{1}{2} \sum_{p \neq q} [(C_{ip} C_{ik} - C_{kp} C_{kq}) P_{pq} \gamma_{pq}]$$

(as in Tab. 3, Ref. [45]).

For the alternant hydrocarbons, we find a fairly constant ratio of K_i^{SCF}/K_i^H and a fairly constant value for the repulsion energy term of 1.7 ± 0.3 eV; the only significant exception being biphenylene. For the polyenes, the repulsion-energy term falls off with increase in the number of atoms, leveling off at a value slightly over 1.8 eV.

For the nonalternant hydrocarbons, there is again a roughly constant repulsion-energy term; however, it is considerably lower than that for alternants; azulene is here the most significant exception, as might be expected, since azulene is considerably off the regression lines found in previous attempts to relate Hückel constants to p -band transition energies [39]. The graph in Fig. 4 demonstrates visually how good the actual relationship between the K_i^{SCF} 's and the observed p -band

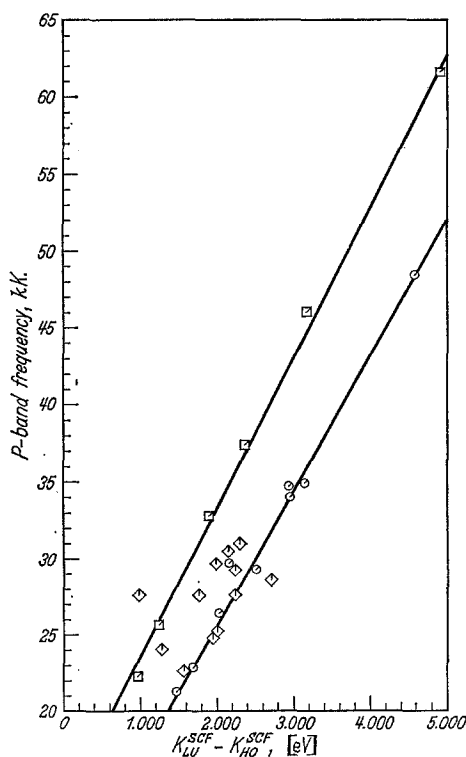


Fig. 4. Comparison of observed transition frequencies with calculated values of $K_{LU}^{\text{SCF}} - K_{HO}^{\text{SCF}}$.
 □ Polyenes, ◇ Nonalternant Hydrocarbons, ○ Cyclic Alternant Hydrocarbons

Table 8. Comparison between Hückel and SCF Calculations

Molecule	$K_{\text{HO}}^{\text{H}}/\beta$	$K_{\text{HO}}^{\text{SCF}}$	$K_{\text{HO}}^{\text{SCF}}/K_{\text{HO}}^{\text{H}}$	$K_{\text{LU}}^{\text{H}}/\beta$	$K_{\text{LU}}^{\text{SCF}}$	$K_{\text{LU}}^{\text{SCF}}/K_{\text{LU}}^{\text{H}}$	$E_{\text{H}}^{\text{calc.}}$	$E(p)^{\text{calc.}}$	Δ
Benzene	+1.0000	-2.2901	-2.2901				5.8597	4.7074	1.2795
Naphthalene	+0.6180	-1.4748	-2.3863				4.6867	4.5161	1.7371
Anthracene	+0.4121	-1.0157	-2.4522				3.7231	3.5783	1.6917
Phenanthrene	+0.6052	-1.4846	-2.4530				4.4690	4.2848	1.4998
Tetracene	+0.2950	-0.7375	-2.5004				3.1117	2.9505	1.6366
Triphenylene	+0.6840	-1.5810	-2.3113				4.5665	3.9436	1.4044
Pyrene	+0.4450	-1.0813	-2.4296				3.8529	3.6852	1.6904
Perylene	+0.3473	-0.8533	-2.4569				3.1914	3.1138	1.4848
Coronene	+0.5392	-1.2576	-2.3323				3.8771	3.2383	1.3620
Biphenylene	+0.4450	-1.1542	-2.5986				3.3196	3.3116 ^a	1.0111
Styrene	+0.6622	-1.6304	-2.4623				5.0419	4.9710	1.7811
Stilbene	+0.5043	-1.2523	-2.4832				4.0793	4.0731 ^a	1.5748
Butadiene	+0.6180	-1.5960	-2.5823				5.5880	5.5615	2.3961
Hexatriene	+0.4450	-1.1879	-2.6692				4.5382	4.5088	2.1626
Octatetraene	+0.3473	-0.9534	-2.7451				3.9250	3.8820	2.0183
Tetradecaheptaene	+0.2091	-0.6235	-2.9826				3.1050	2.9838	1.8579
Eicosaecene	+0.1495	-0.4829	-3.2308				2.8154	2.6202	1.8497
Docosahendeacene	+0.1365	-0.4532	-3.3204				2.7694	2.5416	1.8631
Fulvene	+0.6180	-1.5554	-2.5167	-0.2541	+0.6987	-2.7497	3.1130	3.0461	0.8588
Heptafulvene	+0.2163	-0.6130	-2.8340	-0.4450	+1.1600	-2.6064	2.7490	2.6758	0.9761
6-vinylfulvene	+0.6180	-1.5488	-2.5059	-0.1628	+0.4632	-2.8458	2.7788	2.6976	0.7669
8-vinylheptafulvene	+0.1455	-0.4279	-2.9414	-0.4450	+1.1527	-2.5901	2.4592	2.3827	0.8785
1,2-Benzofulvene	+0.5855	-1.3377	-2.2847	-0.3399	+0.9003	-2.6487	3.7886	3.4662	1.5507
Dibenzofulvene	+0.6387	-1.6373	-2.5633	-0.4301	+1.0831	-2.5181	3.9079	3.7603	1.1876
3,4-Benzohexafulvene	+0.2936	-0.7994	-2.7224	-0.5509	+1.3542	-2.4582	4.1100	3.7198	1.9564
Azulene	+0.4773	-1.0949	-2.2940	-0.4004	+0.8930	-2.2304	2.1535	1.9593	0.1656
Acenaphthylene	+0.6375	-1.5593	-2.4459	-0.2846	+0.7976	-2.5915	3.3385	3.0579	1.0416
Fulvalene	+0.6180	-1.5612	-2.5280	+0.2541	-0.2763	-1.0872	2.1846	2.1244	0.8997
Sesquifulvalene	+0.5702	-1.0831	-1.8995	-0.4450	+0.8712	-1.9576	3.1780	3.0052	1.2237
Heptafulvalene	-0.1826	+0.1654	-0.9055	-0.4450	+1.1580	-2.6021	1.9134	1.8659	0.9207

^a Very limited CI calculation.

transition energies is. The values in cols. 4 and 7 of Tab. 8 demonstrate the close relationship between K_i^H and K_i^{SCF} for the highest occupied MO and the lowest unoccupied MO, respectively. The existence of these relationships, combined with the fact that all deviations from normality on the plot of Fig. 4 can all be explained by the existence of a nontypical value of Δ , confirm fully the suggestion [44, 45] that the success of HMO theory in predicting p -band transition energies should not be regarded as due to the use of an effective Hamiltonian that includes an average value for the electron-repulsion-energy terms, but rather to the fact that the repulsion-energy terms are, for a given class of molecules, approximately constant. It should be noted that although the K_i^H and K_i^{SCF} values are similar, the atomic orbital coefficients from which they are calculated often greatly, and for non-alternant molecules the charge densities calculated by the HMO and SCFMO methods can differ considerably. It should also be noted that with the SCF treatment the alternant and nonalternant hydrocarbons are on two parallel lines separated by 2.3 kK, a situation that does not obtain with HMO calculations [3, 37]. The nonalternants tend to scatter around the line for the alternants, rather than determining a separate line.

The relationship between ground-state properties as calculated by our SCFMO method, by the HMO method, and by the method of DEWAR [9, 10] which is only useful for ground-state properties will be treated in a subsequent paper.

Acknowledgements. Thanks are due to the Computing Center of the University of Virginia for a generous grant of time on a Burroughs 5500 computer, to Dr. FISCHER-HJALMARS for helpful encouragement. Part of this work was supported by an NSF Institutional Grant to the University of Virginia. We also are grateful to Dr. HEILBRONNER for a copy of his absorption spectrum of lycopene.

References

1. PARISER, R., and R. G. PARR: *J. chem. Physics* **21**, 446, 767 (1953).
2. POPLÉ, J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
3. KOUTECKÝ, J., J. PALDUS, and R. ZAHRADNÍK: *J. chem. Physics* **36**, 3129 (1962).
4. HINZE, J., and H. H. JAFFÉ: *J. Amer. chem. Soc.* **84**, 540 (1962).
5. NISHIMOTO, K., u. N. MATAGA: *Z. physik. Chem. (Frankfurt)* **12**, 335 (1957).
6. MULLIKEN, R. S.: *J. Chim. physique* **46**, 497 (1949).
7. ZENER, C.: *Phys. Rev.* **36**, 51 (1930).
8. BLOOR, J. E., and B. R. GILSON: Unpublished work.
9. CHUNG, A. L. H., and M. J. S. DEWAR: *J. chem. Physics* **42**, 756 (1965).
10. DEWAR, M. J. S., and G. J. GLEICHER: *J. Amer. chem. Soc.* **87**, 685 (1965).
11. NISHIMOTO, K., u. L. S. FORSTER: *Theoret. chim. Acta* **3**, 407 (1965).
12. — — *Theoret. chim. Acta* **4**, 155 (1965).
13. FORSTER, L. S.: *Theoret. chim. Acta* **5**, 81 (1966).
14. FISCHER-HJALMARS, I.: *Arkiv Fysik* **21**, 123 (1962).
15. SKANCKE, P. N.: *Acta chem. Scand.* **18**, 1671 (1964).
16. — *Acta chem. Scand.* **19**, 401 (1965).
17. ADAMS, O. W., and R. L. MILLER: *J. Amer. chem. Soc.* **88**, 404 (1966).
18. LÖWDIN, P. O.: *J. chem. Physics* **18**, 365 (1950).
19. ADAMS, O. W.: Private communication.
20. HUMMEL, R. L., and K. RUEDENBERG: *J. physio. Chem.* **66**, 2334 (1962).
21. CAMERON, A., and J. TROTTER: *Acta cryst.* **18**, 636 (1965).
22. BEVERIDGE, D. L., and H. H. JAFFÉ: *J. Amer. chem. Soc.* **87**, 5340 (1965).
23. PERKAMPUS, H. H.: *Theoret. chim. Acta* **1**, 226 (1963); **6**, 45 (1966).
24. ANEX, B. G.: Symposium, Columbus, Ohio (1964).

25. BEALE, R. N., and E. M. F. ROE: *J. Physique Radium* **15**, 595 (1954).
26. BROCKLEHURST, P.: Private communication.
27. OOSHIMA, Y.: *J. physic. Soc. Japan* **12**, 1246 (1957).
28. LONGUET-HIGGINS, H. C., and L. SALEM: *Proc. Roy. Soc. (London) A* **251**, 172 (1959).
29. SALEM, L.: *Proc. Cambridge phil Soc.* **57**, 353 (1961).
30. — Molecular orbital theory of conjugated systems. New York: W. A. Benjamin, Inc. 1966.
31. SIMPSON, W. T.: *J. Amer. chem. Soc.* **73**, 5363 (1951).
32. — *J. Amer. chem. Soc.* **77**, 6164 (1955).
33. POPLÉ, J. A., and S. H. WALMSEY: *Trans. Faraday Soc.* **58**, 441 (1962).
34. MERZ, J. H., P. A. STRAUB, and E. HEILBRONNER: *Chimia (Aarau)* **19**, 302 (1965).
35. PARKHURST, L. J., and B. G. ANEX: *J. chem. Physics* **45**, 862 (1966).
36. MURRELL, J. N.: *The theory of the electronic spectra of organic molecules*, p. 155. London: Methuen & Co. Ltd. 1963.
37. KOUTECKÝ, J., P. HOCHMAN, and J. MICHEL: *J. chem. Physics* **40**, 2439 (1964).
38. NAKAJIMA, T., and S. KATAGIRI: *Molecular Physics* **7**, 149 (1964).
39. STREITWIESER, A.: *Molecular orbital theory for organic chemists*, Chapter 8. New York: John Wiley and Sons 1961.
40. McWEENY, R.: *Molecular orbitals in chemistry, physics, and biology*, p. 305, edited by LÖWDIN, P. O., and B. PULLMAN. New York: Academic Press Inc. 1964.
41. I'HAYA, Y.: *Advances in quantum chemistry*, Vol. I, p. 203ff, edited by LÖWDIN, P. O. New York: Academic Press 1964.
42. FISCHER-HJALMARS, I.: *Molecular orbitals in chemistry, physics, and biology*, p. 361, edited by LÖWDIN, P. O., and B. PULLMAN. New York: Academic Press 1964.
43. — *Theoret. chim. Acta* **4**, 332 (1966).
44. KOUTECKÝ, J.: *Modern quantum chemistry, Part I*, p. 171, edited by SINANOĞLU, O. New York: Academic Press 1965.
45. BLOOR, J. E., and N. BREARLEY: *Canad. J. Chem.* **43**, 1761 (1965).

Prof. Dr. JOHN E. BLOOR
Cobb Chemical Laboratory
University of Virginia
Charlottesville, Virginia 22901, USA