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Semi-Empirical SCF-LCAO Theory with Overlap*

By

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Self-consistent field calculations including the complete overlap matrix have been made to predict the electronic spectra of benzene, napthalene, anthracene and phenanthrene. The results are remarkably similar to those obtained with the neglect of differential overlap.

On a fait des calculs SCF avec la matrice complète des recouvrements afin de prédire les spectres électroniques du benzène, du naphtalène, de l'anthracène et du phénanthrène. Les résultats ressemblent remarquablement à ceux obtenus en négligeant le recouvrement differentiel.

SCF-Rechnungen unter Einschluß der vollständigen Überlappungsmatrix sind zur Bestimmung der Elektronenspektren von Benzol, Naphthalin, Anthracen und Phenanthren unternommen worden. Die Ergebnisse sind den unter Vernachlässigung der differentiellen Überlappung erhaltenen bemerkenswert ähnlich.

There has been in recent years a continuing interest in the interpretation of electronic spectra and structure of aromatic hydrocarbons. To date, however, self-consistent field calculations including estimates of all repulsion and overlap integrals have been carried out only for cyclic systems [2, 14, 35] and for relatively small molecules [29]. To avoid laborious computation, it has been usual to employ the approximation of neglect of differential overlap, characterized by

$$(\mu\nu \mid \varrho\sigma) = \delta_{\mu\nu}\,\delta_{\varrho\sigma} \int\!\!\int \chi_\mu(1)\,\chi_\nu(1)\,\frac{e^2}{r_{12}}\,\chi_\varrho(2)\,\chi_\sigma(2)\,d\tau_1\,d\tau_2$$

$$S_{\mu\nu} = \int \chi_\mu(1)\,\chi_\nu(1)\,d\tau_1 = \delta_{\mu\nu}. \tag{1}$$

Ruedenberg [35a] discusses the approximation and decides that it is valid and effective if the atomic orbitals satisfy Mulliken's approximation [24]

$$\chi_\mu(1)\,\chi_\nu(1) = \frac{1}{2} S_{\mu\nu}\,[\chi_\mu(1)\,\chi_\mu(1) + \chi_\nu(1)\,\chi_\nu(1)] \tag{2}$$

and if the molecular orbitals simultaneously diagonalize the overlap matrix. At this time a more direct check of the approximation seems desirable.

What is being considered is the semi-empirical self consistent field theory of the unsaturation electrons of aromatic hydrocarbons; the theory is that expounded by Pople [32], Pariser and Parr [26], except that the complete overlap matrix and the complete repulsion supermatrix are used at all stages of the calculation. It becomes necessary also to include the effects of penetration of the mobile

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electrons into the σ-electron core. Since no new concepts are introduced such a calculation represents a principally technical advance. At the time of the works quoted [*26*, *33*], a complete SCF calculation presented a computational problem of unreasonable size; advances in computational machinery and programming systems have since reduced the difficulty to the point that calculation of the self-consistent orbitals of a molecule as large as tetracene is neither difficult nor unreasonably costly*.

Large differences between the predictions of the zero overlap procedure and the theory including all overlap and repulsion contributions are not to be expected [*16*, *25*]. The uniform success of the method of PARISER, PARR [*25*, *26*] and POPLE [*33*] for the elucidation of visible and ultraviolet spectra, as well as for the prediction of hyperfine coupling constants in the electron spin resonance spectra of hydrocarbon free radicals make large changes as undesirable as they are unlikely. Comparison of (1) and (2) shows how careful a balance is achieved in the neglect of differential overlap [*16*]. Differences of the core Hamiltonian matrices in the two methods are effectively adjusted for by using the resonance integral for nearest neighbours as an adjustable parameter fitted to an observed spectral interval. Small quantitative differences are to be expected. In particular, in a theory including overlap, the COULSON-RUSHBROOKE theorem [*8*] stating that the π-electron charge density in alternant hydrocarbons is a unit electronic charge in each *2p* atomic orbital is no longer valid. The charge densities will differ in a small but possibly significant way from unity.

That overlap should be neglected in the theory of π-electrons is particularly unfortunate in view of the extremely important role it plays in the elementary theory of bonding in both the LCAO-MO theory [*11*] and the VB theory [*12*]. LYKOS and SCHMEISING [*22*] have pointed out that the eigenvectors of the overlap matrix (maximum-overlap orbitals) closely resemble SCF orbitals for the zero overlap approximation. The overlap matrix and the effective Hamiltonian matrix nearly commute. Each in effect conveys the information of the molecular geometry; both are closely related to the topological matrix [*35c*], as the most important off-diagonal elements correspond to non-vanishing elements of the topological matrix. COULSON and SCHAAD [*19*] have tested the reliability of the zero overlap approximation in non-empirical calculations for the diatomic molecules H_2 and HF and find that it leads to unsatisfactory results. To what degree zero differential overlap is a bona fide approximation for orthogonalized orbitals [*21*] in SCF theory is not yet entirely clear. It seems that the complete inclusion of overlap is a necessary and inevitable step in the effort towards reliable self-consistent field molecular wavefunctions.

The Self-Consistent Field Wavefunction

The theory of the "best" antisymmetrized single-product wavefunction using the core potential of GOEPPERT-MAYER and SKLAR [*17*] and the semi-empirical method of PARISER and PARR is well documented in the literature [*1*, *13*, *15*, *16*, *33*, *34*, *35*]. Included below is such detail as is required to define necessary notation

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* On an IBM 7090, with 32 K memory, the SCF calculation for anthracene takes about 16 minutes. The programme, with its necessary subroutines, has about 4000 machine language instructions. Complete details and programme decks are available on application to the author.

and to indicate departures from the neglect of differential overlap. We restrict ourselves to hydrocarbons with an even number of "active" centres and a like number of atoms.

The π-electron wavefunction chosen is the SLATER determinant of doubly occupied molecular orbitals φ_i; these are linear combinations of carbon $2\,p\pi$ atomic orbitals χ_μ. The number of carbon atoms is $n\left(m = \frac{n}{2}\right)$.

$$\psi_0 = \frac{1}{\sqrt{n!}} \left| (\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_m\alpha)(\varphi_m\beta) \right| \tag{3}$$

$$\varphi_i = \sum_{\mu=1}^{n} \chi_\mu c_{\mu i} \tag{4}$$

The coefficients $c_{\mu i}$ are chosen to minimize the total energy E of the π-electrons.

$$E = \int \cdots \int \psi_0 \, H \, \psi_0 \, d\tau_1 \cdots d\tau_n \tag{5}$$

H is the complete π-electron Hamiltonian

$$H = \sum_{i}^{n} H_i^{\text{core}} + \sum_{i=j}^{n} \frac{1}{r_{ij}} \tag{6}$$

The GOEPPERT-MAYER and SKLAR potential [*17*] has the form

$$H_i^{\text{core}} = -\frac{1}{2}\nabla_i^2 + \sum_{\mu}^{n} U_\mu^+ (i) \tag{7a}$$

where the summation over μ includes all carbon atoms in the molecule and U_μ^+ is the potential of a hypothetical ionized carbon atom which has lost a π-electron.

$$U_\mu^+ (1) = U_\mu^N (1) - \int d\tau_2 \, \chi_\mu^2 (2) \frac{1}{r_{12}} \tag{7b}$$

In this form, the theory neglects electron penetration into the charge cloud surrounding the hydrogen atoms. The relevant penetration integral is about $^1/_2$ electron-volt. The effect is that the carbon atoms without bonded hydrogen are made too electronegative with respect to the other carbons. If overlap is neglected, this does not introduce serious uncertainties, because the charge density at each atomic centre is constrained to unity. In the present paper, it will be necessary to examine the effect of this approximation. Because of the way the potential is defined, it is reasonable that χ should approximately satisfy the characteristic equation

$$\left[-\frac{1}{2}\nabla_1^2 + U^+(1)\right] \chi(1) = W_{2p}\chi(1) \tag{8}$$

W_{2p}, the ionization potential of a π-electron in the trigonal (sp^2p_π) valence state of carbon, has been estimated by MULLIKEN [*24*] to be about -11.28 electron-volts.

The matrix elements $H_{\mu\nu}$ of the core Hamiltonian on the atomic orbital basis may be expressed in terms of the repulsion integrals (1) and the penetration integrals $(\sigma{:}\mu\nu)^\star$. These elements are, on the diagonal,

$$H_{\nu\nu} = W_{2p} - \sum_{\mu \neq \nu} (\mu : \nu\nu) - \sum_{\mu \neq \nu} (\mu\mu \mid \nu\nu) \tag{9a}$$

$\star$ $(\sigma : \mu\nu) = -\int U_\sigma^N (1) \, \chi^\mu (1) \, \chi_\nu (1) \, d\tau_1$

for nearest neighbour atoms,

$$H_{\mu\nu} = S_{\mu\nu} W_{2p} + \beta - \sum_{\substack{\sigma \neq \nu \\ \sigma \neq \mu}} (\mu\nu \mid \sigma\sigma) \tag{9b}$$

and, for the remaining elements,

$$H_{\mu\nu} = S_{\mu\nu} W_{2p} - \sum_{\sigma \neq \nu} (\mu\nu \mid \sigma\sigma). \tag{9c}$$

Three centre penetrations and penetrations between non-adjacent atoms are neglected. In benzene, the integrals (1:23), (1:13) and (1:33) are about 0.03, 0.1 and 0.01 electron volts respectively [*18*, *28*]; these contributions are certainly small compared to other neglected effects. The resonance integral β is retained as an adjustable parameter used to fit the lowest singlet excitation of benzene. Its theoretical value is

$$\beta_{\text{theory}} = -(1{:}12) - (11 \mid 12) \tag{10}$$

where 1 and 2 are adjacent atoms.

The integral approximations employed have been widely discussed. The Coulomb interelectronic repulsions are estimated by the semi-empirical formulae (11) — (13) of PARISER and PARR's second paper [*26*]. The intervals between the excited states in benzene depend only on the repulsion integrals; RUEDENBERG [*35e*] shows that the PARISER-PARR integral values are close to those required to give an exact fit to the observed benzene spectrum when the MULLIKEN approximation is used for the multicentre integrals. The MULLIKEN approximation [*24*] for multi-centre repulsion integrals in LCAO-MO theory has been discussed by RUEDENBERG [*35e*], by PARR and COMPANION [*27*] and in somewhat more detail by HUZINAGA [*18*], who prefers it to the SKLAR-LONDON approximation [*36*] for aromatic 2 pπ-orbitals. More careful estimation of these contributions is difficult and probably unjustified, in view of the semi-empirical estimation of the Coulomb integrals. The overlap matrix has been estimated with hydrogenic 2 *pπ*-orbitals with effective nuclear charge 3.18 [*37*]. Perhaps atomic SCF orbitals might be more appropriate, but we will see that the spectral predictions are insensitive to the inclusion of overlap, and, a fortiori, insensitive to uncertainty in the estimate of overlap. The carbon-carbon bond distance in benzene is 1.397 Å [*5*]; in the polycondensed hydrocarbons all bonds are assumed equal. CRUIKSHANK and SPARKS [*10*] have given a critical survey of measured and theoretical bond lengths

Table 1. *Coulomb and Overlap Integrals*

Internuclear Distance[a]	Coulomb Repulsion[b]	Overlap[c]
0	10.53	—
1.387	7.30	0.25817
2.420	5.46	0.03829
2.794	4.90	0.01740
3.696	3.76	0.00229
4.191	3.34	0.00071
4.839	2.91	0.00015
5.037	2.80	0.00009
5.588	2.58	0.0
6.049	2.38	0.0
6.402	2.25	0.0
7.259	1.98	0.0
7.392	1.95	0.0

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[a] The distances, in Å, are those occurring in phenanthrene and anthracene with the assumption of regular hexagonal rings with side 1.397 Å.

[b] Energy quantities, in this and subsequent tables, are in electron-volts.

[c] Based on STO's, with effective nuclear charge 3.18.

in napthalene, anthracene and related conjugated hydrocarbons. In anthracene the lengths range from 1.369 to 1.437 Å, with estimated standard deviations about 0.005 Å. For simplicity, we have ignored these variations. The corresponding variations in the nearest-neighbour overlap, Coulomb and resonance integrals are ± 0.012, ± 0.07 e. v. and about ± 0.4 e. v. respectively. The changes in the resonance and overlap integrals are not entirely negligible, but will be ignored below nevertheless. The necessary penetration integrals have been estimated using formulae given by RUEDENBERG (See Appendix I for details). β is adjusted to fit the first singlet transition of benzene at 4.9 e. v. Repulsion and penetration integrals appear in Tab. 1.

A general set of equations for the LCAO coefficients has been given by ROOTHAAN [*34*]. To be solved are the eigenvalue equations

$$\underline{F}\,\vec{c}_i = \underline{S}\,\vec{c}_i\,E_i \tag{11a}$$

where $\vec{c}_i$ is the column vector

$$\vec{c}_i = Tr\,(c_{1i}\,c_{2i}\,\cdots\,c_{ni}) \tag{11b}$$

and the effective Hamiltonian matrix $\underline{F}$ has elements

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\sigma}^{n}\sum_{\varrho}^{n} P_{\varrho\sigma}\,[(\mu\nu \mid \varrho\sigma) - \frac{1}{2}\,(\mu\sigma \mid \varrho\nu)] \tag{11c}$$

The COULSON [*6*] charge-density bond-order matrix has elements

$$P_{\mu\nu} = \sum_{i}^{n} g_i\,c_{\mu i}\,c_{\nu i} \tag{11d}$$

and g_i ($= 2$, 1 or 0) is the occupation number of the ith molecular orbital. Where $\underline{C}$ is the matrix whose columns are the orbital vectors c_i, orthonormality of the molecular orbitals requires

$$\underline{C}^{+}\,\underline{S}\,\underline{C} = \underline{I} \tag{12}$$

It is convenient to define

$$\underline{F}' = \underline{F} - W_{2p}\,\underline{S} \tag{13a}$$

so that the eigenvalue equation becomes

$$\underline{F}'\,\vec{c}_i = \underline{S}\,\vec{c}_i\,E_i' \tag{13b}$$

The energies E_i' have as zero reference the value W_{2p}.

Excitation Energies

The ground state wavefunction ψ_0 of energy E_0 is a single determinant of form (3). The excited states $\psi_{i\to k}$ are obtained by promoting an electron from an occupied orbital φ_i to an unoccupied one φ_k and forming either the triplet or the singlet spin state. The matrix elements of the many-electron Hamiltonian (6) between the ground and singly-excited states of a closed-shell molecule with n-electrons are [*33*]

$$\begin{gathered}\langle {}^1\psi_{i\to k} \mid H \mid \psi_0 \rangle = \sqrt{2}\,F_{ik} \\ \langle {}^1\psi_{i\to k} \mid H \mid {}^1\psi_{j\to l} \rangle - \delta_{ij}\,\delta_{kl}\,E_0 = \delta_{ij}\,F_{kl} - \delta_{kl}\,F_{ij} + 2\,(ik \mid lj) - (ij \mid lk) \\ \langle {}^3\psi_{i\to k} \mid H \mid {}^3\psi_{j\to l} \rangle - \delta_{ij}\,\delta_{kl}\,E_0 = \delta_{ij}\,F_{kl} - \delta_{kl}\,F_{ij} - (ij \mid lk)\end{gathered} \tag{14}$$

where F_{ij} is the i-jth element of the effective Hamiltonian operator on the molecular orbital basis.

$$F_{ij} = H_{ij} + \sum_{k=1}^{n/2} [2\,(ij\,|\,kk) - (ik\,|\,kj)] \tag{15}$$

Since the basis orbitals are self-consistent field orbitals, $\underline{F}$ is diagonal and the diagonal elements are the eigenvalues E in (13).

If overlap is neglected and if only the diagonal elements of the complete Hamiltonian matrix are used, the pairing property of orbitals [*32*] leads to an oversimplified interpretation of the spectra. DEWAR and LONGUET-HIGGINS [*15*] introduce interaction between the configurations which are degenerate in HÜCKEL theory. The most important degeneracy persists in SCF theory without overlap, and is that between the excited states $\psi_{m-1\to m+1}$ and $\psi_{m\to m+2}$. When overlap is included, these states are no longer exactly degenerate, but remain nearly degenerate, so that configuration interaction is still necessary. In the Hamiltonian matrix which is diagonalized to give the excitation energies, excitations from the $(m-1)$th and mth molecular orbitals to the $(m+1)$th and $(m+2)$th are included.

Charge Densities and Bond Orders

Ever since the definition of molecular orbital bond-orders by COULSON [*6*] there has been an interest in the properties of these and related quantities of importance in assessing the bond strengths in molecules. RUEDENBERG [*35c*] discusses the mathematical properties of a number of bond-order-like quantities for the case in which the overlap matrix is simply related to the topological matrix and the molecular orbitals are normalized eigenvectors of the topological matrix (essentially HÜCKEL molecular orbitals). He introduces the generalized bond-order-like quantity

$$f_{\mu\nu} = \sum_i g_i\, c_{\mu i}\, c_{\nu i}\, f\,(m_i) \tag{16}$$

where m_i is the ith eigenvalue of the topological matrix. If the complete overlap matrix is used and the orbitals are self-consistent field eigenvectors, the properties outlined by RUEDENBERG are no longer applicable. The topological matrix loses its overwhelming importance and the quantity (16) a measure of its interest. However, it is desirable that a more general definition should reduce to an example of (16) in the case in which RUEDENBERG's limitations apply.

We adopt as the most convenient definition of the bond order between the atoms μ and ν of the ith molecular orbital

$${}_iQ_{\mu\nu} = c_{\mu i} \sum_\sigma c_{\sigma i}\, S_{\sigma\nu} \tag{17}$$

with

$$Q_{\mu\nu} = \sum_i {}_iQ_{\mu\nu}\, g_i$$

for the total bond order. MULLIKEN [*24*] has previously considered this quantity for diatomic molecules. The diagonal elements of $\underline{Q}$ are the "gross atomic populations" [*3*]; ${}_iQ_{\mu\mu}$ is a measure of the fractional charge of the ith molecular orbital belonging to the μth atom

$$\sum_\mu {}_iQ_{\mu\mu} = \sum_{\mu\nu} c_{\mu i}\, S_{\mu\nu}\, c_{\nu i} = 1 \tag{18}$$

The charge density of the ith orbital is exactly one electronic charge and the total charge density is the number of electrons. If the orbitals are eigenvectors of the overlap matrix, $\underset{\sim}{Q}$ reduces to an expression similar to (16), in which $f(m_i)$ is to be replaced by the ith eigenvalue of $\underset{\sim}{S}$, and if $\underset{\sim}{S}$ commutes with the topological matrix we have a RUEDENBERG bond-order-like quantity.

The properties of the off-diagonal elements of $\underset{\sim}{Q}$ are suitable for a bond-order quantity. The simplest application, already considered by MULLIKEN [*24*], is to a homonuclear diatomic molecule, for which it is easily seen that the bond orders for doubly-filled bonding, non-bonding and antibonding orbitals are $+1$, 0 and -1 respectively. For benzene the π-orbitals are determined by symmetry; the distinct elements of $\underset{\sim}{Q}$ are

$$Q_{11} = 1; Q_{12} = \frac{2}{3}; Q_{13} = 0; Q_{14} = -\frac{1}{3} \tag{19}$$

These are just the values of the COULSON bond-order matrix if overlap is neglected. A comparison is intended between bond-orders for SCF wavefunctions when overlap is neglected and when it is included. The results (19) ensure that differences are significant and not artifacts of an ill-chosen definition of the bond-order matrix.

The bond-order matrix $\underset{\sim}{Q}$ is simply related to the COULSON matrix [*6*] and the overlap matrix

$$\underset{\sim}{Q} = \underset{\sim}{P} \cdot \underset{\sim}{S} \tag{20}$$

$\underset{\sim}{P}$ and $\underset{\sim}{S}$ are in general invariant under the transformations of the symmetry group of the SCHRÖDINGER equation. Because the matrix product is noncommutative, $\underset{\sim}{Q}$ as defined above does not have this property. The desirable symmetry may be introduced by redefining $\underset{\sim}{Q}$ [*3*].

$$\underset{\sim}{Q} = \frac{1}{2}(\underset{\sim}{P} \cdot \underset{\sim}{S} + \underset{\sim}{S} \cdot \underset{\sim}{P}) \tag{21}$$

Results

Calculations have been carried out for naphthalene, anthracene and phenanthrene, as well as for benzene. The results are compared with observed spectra in Tab. 2. It is apparent that, for prediction of spectra, the SCF method with zero differential overlap gives results remarkably close to those when overlap is included, and that, in the latter case, it is not important whether or not the hydrogen penetration integrals are included. The appropriate value of the resonance integral β is, of course, different in each case. For benzene, naphthalene and anthracene, there is satisfactory agreement between the calculated and observed energy intervals. These results are in substantial agreement with those of POPLE [*32*] and PARISER [*25*].

The calculations for phenanthrene are less satisfactory. If no configuration interaction is used, the lowest transition is predicted to be polarized perpendicular to the plane of symmetry of the molecule (${}^1L_a$). This statement does not depend upon detailed calculation, but is a simple consequence of the orbital pairing property. When overlap is introduced, the qualitative effect is retained, even though orbital pairing is no longer valid. In naphthalene, but not in anthracene, limited configuration interaction pushes the ${}^1L_b$ level below the ${}^1L_a$ level. For phenanthrene the levels become approximately degenerate. The observed lowest excitation is polarized along the short axis of the molecule [*23*] and therefore is a ${}^1L_b$ band [*31*]. There is some question about the assignment of the observed triplet transition. From an analysis of the vibrational structure in phenanthrene

Table 2

Band[a]	Symmetry	Calculated Energy			Observed Energy
		Zero Overlap	Including Overlap[b]		
		Spectrum of Benzene			
${}^1L_b$	${}^1B_{2u}$	4.90	4.90	4.90	4.9[d]
${}^1L_a$	${}^1B_{1u}$	5.31	5.40	5.39	6.1[d]
${}^1B_{a,\,b}$	${}^1E_{1u}$	6.95	7.11	7.11	6.9[d]
${}^3L_a$	${}^3B_{1u}$	4.01	4.01	4.01	3.7[e]
${}^3B_{a,\,b}$	${}^3E_{1u}$	4.46	4.46	4.45	(4.7)[f]
${}^3L_b$	${}^3B_{2u}$	4.90	4.90	4.90	—
		Spectrum of Naphthalene			
${}^1L_b$	${}^1B_{1u}$	4.43	4.36	4.37	4.1[d]
${}^1L_a$	${}^1B_{2u}$	4.37	4.34	4.35	4.5[d]
${}^1B_b$	${}^1B_{1u}$	6.21	6.25	6.36	5.8[d]
${}^1B_a$	${}^1B_{2u}$	6.59	6.60	6.71	7.4[c]
${}^3L_a$	${}^3B_{2u}$	3.11	3.05	3.05	2.6[g]
${}^3B_b$	${}^3B_{1u}$	4.15	4.08	3.94	—
${}^3L_b$	${}^3B_{1u}$	4.43	4.38	4.63	—
${}^3B_a$	${}^3B_{2u}$	4.90	4.81	4.93	—
		Spectrum of Anthracene			
${}^1L_a$	${}^1B_{2u}$	3.60	3.56	3.58	3.3[c]
${}^1L_b$	${}^1B_{1u}$	4.16	4.08	4.05	[3.5][c]
${}^1B_b$	${}^1B_{1u}$	5.64	5.61	5.82	4.8[c]
${}^1B_a$	${}^1B_{2u}$	6.67	6.60	6.78	6.7[c]
${}^3L_a$	${}^3B_{2u}$	2.23	2.19	2.20	1.8[g]
${}^3B_b$	${}^3B_{1u}$	3.98	3.89	3.65	—
${}^3L_b$	${}^3B_{1u}$	4.16	4.08	4.50	—
${}^3B_a$	${}^3B_{2u}$	5.39	5.25	5.44	—
		Spectrum of Phenanthrene			
${}^1L_b$	${}^1A_1$	4.36	4.32	4.36	3.6[h]
${}^1L_a$	${}^1B_1$	4.32	4.29	4.33	4.1[c]
${}^1B_b$	${}^1B_1$	5.60	5.52	5.62	4.9[c]
${}^1B_a$	${}^1A_1$	5.74	5.69	5.78	6.6[c]
${}^3L_a$	${}^3B_1$	3.33	3.29	3.33	2.7[g]
${}^3B_a$	${}^3A_1$	4.03	3.97	4.00	—
${}^3B_b$	${}^3B_1$	4.33	4.22	4.32	—
${}^3L_b$	${}^3A_1$	4.36	4.29	4.39	—

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[a] Ref. 32. Platt's L_a, L_b, B_a and B_b correspond respectively to Clar's p, α, β and β'.

[b] Hydrogen penetrations ignored and included, respectively.

[c] Ref. 20.

[d] E. Miller Layton, Jr.: J. mol. Spectr. **5**, 181 (1960).

[e] D. R. Kearns: J. chem. Physics **36**, 1608 (1962).

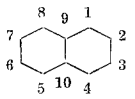
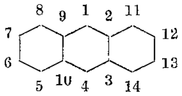
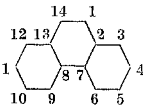
[f] J. R. Platt: J. mol. Spectr. **9**, 288 (1962).

[g] D. F. Evans: J. chem. Soc. **1957**, 1351.

[h] Ref. 30.

and phenanthrene-d-10, Pesteil et al. [*30*] conclude that the triplet belongs to the same (spatial) transition as the singlet at 28900 cm^{-1} (3.6 e. v.). The triplet should therefore be polarized along the long axis of the molecule. This assignment is at odds with that of CLAR and ZANDER [4] based on correlation of singlets and triplets in a series of condensed aromatic hydrocarbons. Since the ^1L_b transition is quite weak [20] (f = 0.003), it seems that the spin-forbidden ^3L_b transition might be too weak to observe; on the other hand, the ^1L_a transition is relatively intense (f = 0.18). The calculations predict that the lowest triplet is polarized along the long axis (^3L_a) and that the next lowest triplet is 0.7 e. v. removed. In the table we have adopted this assignment.

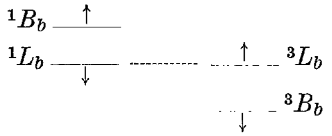
Table 3. *Charge Densities and Bond Orders*

Molecule		Zero Overlap	No Hydrogen Penetrations	With Hydrogen Penetrations
	Q_{11}	1.0	0.9760	0.9963
	Q_{22}	1.0	0.9968	1.0002
	Q_{99}	1.0	1.0544	1.0069
	Q_{12}	0.7486	0.7487	0.7498
	Q_{23}	0.5798	0.5799	0.5788
	Q_{19}	0.5316	0.5306	0.5306
	$Q_{9,10}$	0.5551	0.5560	0.5577
	Q_{11}	1.0	0.9378	0.9929
	Q_{22}	1.0	1.0570	1.0084
	Q_{55}	1.0	0.9768	0.9946
	Q_{66}	1.0	0.9973	1.0006
	Q_{12}	0.6124	0.6105	0.6121
	Q_{23}	0.5109	0.5127	0.5139
	Q_{56}	0.7709	0.7719	0.7733
	Q_{67}	0.5517	0.5504	0.5492
	Q_{89}	0.4968	0.4957	0.4947
	Q_{11}	1.0	0.9770	0.9957
	Q_{22}	1.0	1.0454	1.0047
	Q_{33}	1.0	0.9779	0.9989
	Q_{44}	1.0	0.9944	0.9995
	Q_{55}	1.0	0.9971	1.0005
	Q_{66}	1.0	0.9714	0.9962
	Q_{77}	1.0	1.0368	1.0045
	Q_{12}	0.4658	0.4554	0.4564
	Q_{23}	0.5710	0.5715	0.5704
	Q_{34}	0.7180	0.7182	0.7201
	Q_{45}	0.6141	0.6140	0.6120
	Q_{56}	0.7140	0.7150	0.7167
	Q_{67}	0.5811	0.5799	0.5789
	Q_{78}	0.4272	0.4175	0.4205
	Q_{27}	0.5748	0.5826	0.5832
	$Q_{1,14}$	0.8105	0.8178	0.8184

For the excitations $m \rightarrow (m+2)$ and $(m-1) \rightarrow (m+1)$, associated with PLATT's [31] states L_b and B_b, a Hamiltonian matrix

$$\begin{pmatrix} E_{11} & E_{12} \\ E_{12} & E_{22} \end{pmatrix}$$

is encountered; its eigenvalues are $1/2\,(E_{11} + \mathrm{E}_{22}) \pm [(E_{11} - E_{22})^2 + 4\,E_{12}{}^2]^{1/2}$. For the singlet excitations, E_{12} is positive, so that the lower state is ^1L_b; for the triplets, however, E_{12} is negative and the upper state is ^3L_b. With zero differential overlap $E_{11} = E_{22}$ and, as well, degeneracy is predicted between ^1L_b and ^3L_b [25]. When overlap is included, it is found that the quantities $1/2\,(E_{11} + E_{22})$ and E_{12} suffer only minor changes (for the triplet as well as the singlet), but E_{11} and E_{22} are no longer equal. The calculated splitting of L_b and B_b is increased, as the sketch illustrates, so that the ^3L_b level is anomalously more energetic than the ^1L_b level. Interaction with



nearby higher configurations is expected to reverse the shift of the triplet level; the singlet will not be so strongly affected since the higher singlets are further removed (above ^1B_b).

In Tab. 3 appear the charge densities and bond-orders calculated with neglect of overlap, with overlap but neglected hydrogen penetrations, and, finally, with overlap and hydrogen penetrations included. The bond orders are remarkably insensitive to the approximation employed — the largest difference is 2%. More sensitive are the charge densities (diagonal elements of $\underline{Q}$). For zero overlap these are constrained to unity. If overlap is included but hydrogen penetration ignored, the atoms at joints of the molecular topological diagram are relatively electronegative and charge shift is predicted. When hydrogen penetrations are included the charges all become nearly unity, showing that the charge shift is an artifact of the neglect of hydrogen penetrations. With the present choice of core penetration integrals slight shifts to joint atoms occur, but these should not be regarded significant. JULG and PULLMAN [19] have examined the effect of introduction of hydrogen penetrations into the core potential. In estimating diagonal elements of the core Hamiltonian they neglect carbon penetrations as well as hydrogen penetrations. For primary, secondary and tertiary carbons in methylcyclopropene, fulvene and heptafulvene, the sum of the carbon and hydrogen penetrations is practically constant (2.34 e. v.). The neglect of carbon penetration integrals may be considered equivalent to inclusion of hydrogen penetration in the skeletal potential W_{2p} [26].

Discussion

The present results confirm the remarkable success of the approximation of zero differential overlap. Both the spectral predictions and the calculated bond-order matrix are insensitive to the inclusion of atomic orbital overlaps. These statements may be traced to the overwhelming importance of the topology of the molecule; geometrical considerations play only a secondary role. RUEDENBERG [35a] has detailed the division of the energy contributions into short-range and long-range forces — the short-range forces are intimately related to molecular topology. The bond order matrices are quite similar to those derived with simple MO theory [7], so similar that the simple theory relating mobile bond-order to bond length may be applied without change. The approximate linear relationship between bond-order and bond-length devised by CRUIKSHANK [10]

$$r_{\mu\nu} = 1.57 - 0.267\, Q_{\mu\nu} \qquad (22)$$

may be applied with unmitigated success to the present data.

If carbon penetrations are included, it is necessary also to include hydrogen penetrations. Otherwise carbon atoms without bonded hydrogens are considered relatively too electronegative, and the predicted charge distribution is distorted. The estimated bond-orders, however, are insensitive to the exclusion of hydrogen penetrations. So also are the spectral predictions, because of the manner in which β as an empirical quantity compensates for errors.

It is to be expected that inclusion of overlap will cause as little modification in SCF calculations for non-alternant molecules and for free radicals as for the simple hydrocarbons presented above. Extensive calculations to confirm this expectation are being undertaken.

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Appendix I — Penetration Integrals

RUEDENBERG [*35d*] has given formulae for the integrals of the core Hamiltonian in which the carbon atoms are neutral. It is assumed that a carbon atom may be represented as a nucleus of electronic charge 4 (the K-shell electrons are assumed to completely screen two units of charge), surrounded by the charge cloud of a single $2s$-electron and three orthogonal $2p$-electrons. The electron charge cloud is equivalent to the tetrahedral sp^3 configuration. SLATER orbitals are adopted for the "static" electrons, as was done for the "active" $2p\pi$-orbital It is assumed that the effective nuclear charge for all "static" orbitals is the same.

The value $Z = 3.18$ is adopted as the effective nuclear charge for the "static" as well as the "active" orbitals. RUEDENBERG discusses the choice of a different set of screening parameters based on minimization of the π-electron energy and simultaneous adjustment of the core screening to reproduce the electron affinity of carbon. The core orbitals he requires are much more diffuse than those used here, and the related penetration integrals much larger than those previously employed [*18*, *28*]. The energy minimization depends upon the difference of two large quantities; neglect of σ-π-interaction implies imperfectly understood errors. Further, it is more usual that atomic orbitals appropriate in LCAO theory are contracted, not expanded, from free atom orbitals. Under these circumstances we feel justified in reverting to the ad hoc adoption of the ZENER-SLATER screening constant [*37*].

The hydrogen atom is assumed a proton partially screened by a $1s$ electron with effective nuclear charge 1.0 in the series of calculations in which hydrogen penetrations are included. The *C-H* bond length is 1.08 Å [*5*].

The necessary penetration integrals are $(1:22) = 0.708$ e.v.
$(\mathrm{h}:11) = 0.607$ e.v.
$(1:12) = 1.685$ e.v.

If overlap is neglected, penetration integrals are unnecessary [*19*] and the value $\beta = -2.39$ e.v. provides the fit to the lowest excitation of benzene. If hydrogen penetrations are neglected, the appropriate value of β is -4.48_8 e.v., and if they are included, it is -4.64 e. v. The "theoretical" value of β is, from (10), -3.99 e. v. The agreement is quite satisfactory, suggesting that it may be unnecessary to introduce β as an empirical parameter. In Tab. 2, the predicted spectra tend to be slightly more blue than the observed, except in the base of benzene, so that a reduced estimate of β would not introduce large discrepancies.

Appendix II

π-electron SCF machine programmes have been described by a number of authors. The only feature of the present programme that is unusual is the storage and referencing of the repulsion supermatrix. The element $(\mu\nu \mid \varrho\sigma)$ is not distinct from $(\mu\nu \mid \sigma\varrho)$ or $(\varrho\sigma \mid \mu\nu)$ — these symmetries must be exploited if memory capabilities are to be used to the best advantage. Together they constitute a saving of about $85^0/_0$ of the storage necessary for the repulsions referenced simply as four-dimensional arrays. The algorithm assigning an index *i* to an element of the supermatrix is: —

(*i*) Order μ, ν so that $\mu > \nu$

(*ii*) $I = \nu + \frac{1}{2} \mu (\mu - 1)$

(*iii*) Repeat (*i*) and (*ii*) for ϱ, σ assigning an index J.

(*iv*) Repeat (*i*) and (*ii*) for I, J assigning the index i.

It is readily seen that there is a 1-to-1 correspondence between the indices *i* and distinct elements of the repulsion supermatrix.

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