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Additional information on J. Chem. Phys.

and no effects on the pressure in the apparatus due to the evolution of a gas have been observed.

Kusch and Mann[7] have reported the apparent evolution of free iodine in the formation of a molecular beam of lithium iodide. The effect is identified by an objectionable chemical reaction between the iron oven and the iodine. Whether or not this effect is related to the present series of phenomena is uncertain.

Nernst,[8] using the air displacement method of V. Meyer, found the molecular weight of sodium chloride vapor at 1970°C and atmospheric pressure to be about 59. This indicates that the vapor consisted predominantly of monomers. The experiment was, however, performed with sodium chloride in the vapor phase only, whereas the present experiments were carried out essentially in sodium chloride vapor, which, while not necessarily in equilibrium with the liquid phase, was not independent of that phase.

Zimm and Mayer[9] measured the vapor pressure of

potassium chloride over its *crystals*, not that of its molten salt, and calculated the entropy of the vapor. Comparison of the experimental value with the entropy of a gaseous mixture of KCl and $(KCl)_2$ allowed the authors to estimate the extent of association in the vapor. It was found that at 800°K less than 2 percent, probably less than 0.3 percent, of the molecules have associated to form dimers.

The extent of the formation of complex molecules for halides other than those studied in this work is unknown. It is clear that any interpretation of the kind of unresolved spectra observed in the molecular beam *magnetic* resonance method must take into account the possibility of contributions to the spectrum by molecules which are not the assumed monomers.

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[7] P. Kusch and A. K. Mann, Phys. Rev. **76**, 707 (1949).
[8] W. Nernst, Nachr. Kön. Ges. Wiss. Göttingen, Math.-physik. Kl. 75 (1904).
[9] B. H. Zimm and J. E. Mayer, J. Chem. Phys. **12**, 362 (1944).

A Semi-Empirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules. I.*†

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A semi-empirical theory is outlined which is designed for the correlation and prediction of the wavelengths and intensities of the first main visible or ultraviolet absorption bands and other properties of complex unsaturated molecules, and preliminary application of the theory is made to ethylene and benzene.

The theory is formulated in the language of the purely theoretical method of antisymmetrized products of molecular orbitals (in LCAO approximation), including configuration interaction, but departs from this theory in several essential respects. First, atomic orbital integrals involving the core Hamiltonian are expressed in terms of quantities which may be regarded as semi-empirical. Second, an approximation of zero differential overlap is employed, and an optional uniformly charged sphere representation of atomic π-orbitals is introduced, which greatly simplify the evaluation of electronic repulsion integrals and make applications to complex molecules containing heteroatoms relatively simple. Finally, although the theory starts from the π-electron approximation, in which the unsaturation electrons are treated apart from the rest,

provision is included for the adjustment of the σ-electrons to the π-electron distribution in a way which does not complicate the mathematics.

Electronic energy levels in the theory are expressed in terms of ionization potentials of atoms, resonance integrals of bonds, Coulomb repulsion integrals between two π-electrons on the same atom and between two π-electrons on different atoms, and penetration integrals between π-electrons and neutral atoms. Preliminary applications to ethylene and benzene in which only the carbon-carbon resonance integral is treated as an empirical quantity show that the theory can reproduce the results of the purely theoretical method with very little labor. The reasonableness of considering all of the above quantities as semi-empirical is pointed out, however, and it is through a detailed examination and exploitation of this in the second paper of this series that correction for the inadequacies of the π-electron approximation is made and improved agreement with experiment is attained.

1. PREFACE

THIS paper is the first of a series presenting a new semi-empirical theory of the electronic spectra and structure of unsaturated molecules. Papers I and II

present the main elements of the theory with primitive examples; later papers will emphasize applications to various molecules and series of molecules. The theory is primarily designed for the prediction of wavelength and intensity of the main visible or near ultraviolet electronic absorption bands of unsaturated organic molecules, but such topics as resonance energy, electron

density, bond order, and dipole moment will receive some attention, and applications to certain saturated and certain inorganic molecules will also be considered.

The theory starts from the so-called π-electron approximation in which the unsaturation, or π, electrons of a molecule are treated apart from the rest, the latter being manifest only in the effective "core" in the field of which the former move. Wave functions for various states of the π-electrons are built from $2p$ atomic orbitals on the individual atoms, and energies of the various states are computed in a prescribed manner. The theory combines the advantages of the conventional semi-empirical LCAO MO method with the advantages of the conventional purely theoretical method of antisymmetrized products of molecular orbitals (in LCAO approximation), including configuration interaction.

The degree to which the semi-empirical LCAO MO method[1] can successfully correlate organic spectra has been examined by several authors.[2] The method is useful, but consideration of configuration interaction is essential for ultimate understanding of band positions and intensities. Configuration interaction is not quantitatively provided for in the conventional method, however, and furthermore, the method does not take proper cognizance of electronic interaction—it makes no distinction between singlet and multiplet states, for example. The present theory may be regarded as a quantitative prescription for inclusion of configuration interaction effects in a semi-empirical LCAO MO theory from which internal inconsistencies have been removed.

The method of antisymmetrized products of molecular orbitals (in LCAO approximation), including configuration interaction, as developed by Goeppert-Mayer and Sklar,[3] Craig,[4] and Roothaan,[5] and as discussed in detail by Mulliken,[6,7] provides a proper theoretical framework for a consistent theory. In its purely theoretical form this method is impractical, however; it lacks the empirical element which one must expect in a genuinely useful theory, and its mathematics is unwieldy—benzene is the most complex molecule on which the method has been fully tested,[8] and the organic chemist may reasonably expect more! The present theory incorporates an empirical element into the antisymmetrized product method. This by itself would not yield a wieldy method, but through the exploitation of a certain approximate property of atomic $2p$ orbitals in molecules a sweeping

simplification of the mathematics is achieved which makes applications to complex molecules feasible.

2. THE TOTAL ENERGY OF AN ELECTRONIC STATE

For a molecule containing n π-electrons moving in the field of a core (in C_6H_6, for example, there are 6 π-electrons in the field of a $C_6H_6{}^{+6}$ core), the Hamiltonian operator will be expressed in the form[3]

$$H = H_{core} + \tfrac{1}{2}\sum_{ij}(e^2/r_{ij}),\qquad(1)$$

where e^2/r_{ij} is the electrostatic repulsion between π-electrons i and j, and

$$H_{core} = \sum_i H_{core}(i),\qquad(2)$$

where $H_{core}(i)$ is the kinetic energy operator for electron i plus its potential energy operator in the field of the core:

$$H_{core}(i) = T(i) + U_{core}(i).\qquad(3)$$

Other than π-electrons are evinced only through the terms $U_{core}(i)$. This is the so-called π-electron approximation.

Wave functions for the n-electron system will be constructed from normalized antisymmetrized product functions of the type

$$\Phi_\Lambda = \frac{1}{\sqrt{n!}}\begin{vmatrix}(\phi_1\alpha)^1 & (\phi_1\beta)^1 & (\phi_2\alpha)^1 & \cdots \\ (\phi_1\alpha)^2 & (\phi_1\beta)^2 & (\phi_2\alpha)^2 & \cdots \\ (\phi_1\alpha)^3 & (\phi_1\beta)^3 & (\phi_2\alpha)^3 & \cdots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix},\qquad(4)$$

where Λ is a running index characterizing the assignment of electrons to particular *molecular orbitals* ϕ_i with spin functions α or β; i.e., Λ is an index indicating the *spin-orbital configuration*.[6] The molecular orbitals (MO) ϕ_i will further be taken to be orthonormal linear combinations of atomic orbitals (AO) χ_p on the several nuclei:

$$\phi_i = \sum_p C_{ip}\chi_p.\qquad(5)$$

This is the familiar LCAO *approximation*.

The expectation value for the energy of Φ_Λ, $\int\Phi_\Lambda{}^*H\Phi_\Lambda dv$, is given by the formula:[6]

$$E_\Lambda = \sum_i I_i + \tfrac{1}{2}\sum_{ij}(J_{ij} - K_{ij}')$$

(sums over occupied MO's in Φ_Λ), (6)

where

$$I_i = \int \phi_i{}^*(1)H_{core}(1)\phi_i(1)dv\qquad(7)$$

[1] See, for example, Mulliken, Rieke, and Brown, J. Am. Chem. Soc. **63**, 41 (1941), and R. S. Mulliken and C. A. Rieke, J. Am. Chem. Soc. **63**, 1770 (1941), where the semi-empirical LCAO MO method is described and applied in detail to the phenomenon of hyperconjugation.
[2] See, for example, J. R. Platt, J. Chem. Phys. **18**, 1168 (1950).
[3] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).
[4] D. P. Craig, Proc. Roy. Soc. (London) **200**, 474 (1950).
[5] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).
[6] R. S. Mulliken, J. chim. phys. **46**, 497 (1949).
[7] R. S. Mulliken, J. chim. phys. **46**, 695 (1949).
[8] Parr, Craig, and Ross, J. Chem. Phys. **18**, 1561 (1950).

is the *core energy* for the MO ϕ_i,

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2)(e^2/r_{12})\phi_i(1)\phi_j(2)dv \qquad (8)$$

is the *Coulomb integral* between MO's ϕ_i and ϕ_j, and

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2)(e^2/r_{12})\phi_j(1)\phi_i(2)dv \qquad (9)$$

is the *exchange integral* between ϕ_i and ϕ_j, with $K_{ij}' = K_{ij}$ if ϕ_i and ϕ_j have the same spins in Φ_A, $K_{ij}' = 0$ if ϕ_i and ϕ_j have different spins in Φ_A.

Now a single Φ_A may or may not be a good approximation to the total π-electron wave function Ψ_S for an actual electronic state S of the system. In cases for which a single Φ_A suffices, energies may be computed directly from Eq. (6); in cases for which a combination of several Φ_A is needed, a *configuration interaction* calculation needs to be performed by carrying out a linear variational calculation with the Φ_A as starting functions; i.e., by writing

$$\Psi_S = A_1\Phi_1 + A_2\Phi_2 + \cdots, \qquad (10)$$

determining the energy by solution of a *secular equation*

$$|H_{mn} - S_{mn}E| = 0, \qquad (11)$$

and determining the coefficients A_m by solution of the simultaneous equations

$$\sum_m A_m[H_{mn} - S_{mn}E] = 0, \quad n = 1, 2, \cdots. \qquad (12)$$

The matrix elements,

$$S_{mn} = \int \Phi_m^*\Phi_n dv \qquad (13)$$

and

$$H_{mn} = \int \Phi_m^*\mathbf{H}\Phi_n dv, \qquad (14)$$

required for this calculation are readily derived; in particular, the H_{mn} always turns out to be expressible in terms of integrals which are generalizations of those appearing in Eqs. (7)-(9); namely, *core integrals*,

$$I_{ij} = \int \phi_i^*(1)\mathbf{H}_{core}(1)\phi_j(1)dv, \qquad (15)$$

and *electronic repulsion integrals*,

$$(ij|kl) = \int \phi_i^*(1)\phi_k^*(2)(e^2/r_{12})\phi_j(1)\phi_l(2)dv. \qquad (16)$$

Once one has chosen starting MO's and decided on the extent of configuration interaction to be taken into account, the determination of electronic energy levels is reduced to the problem of computing core integrals and electronic repulsion integrals. Methods for handling these two types of integrals are described in Secs. 3 and 4. The more subtle problems of choosing the initial MO's and deciding on the extent of configuration interaction are also considered in Sec. 3.

3. CORE INTEGRALS

Since according to Eqs. (5) and (15),

$$I_{ij} = \sum_p \sum_q C_{ip}^* C_{jq} H_{pq}^{core}, \qquad (17)$$

where

$$H_{pq}^{core} = \int \chi_p^*(1)\mathbf{H}_{core}(1)\chi_q(1)dv, \qquad (18)$$

it is sufficient for determination of the core integrals to know the LCAO coefficients C_{ip} and the AO matrix elements H_{pq}^{core}.

To determine the C_{ip}, one *might* set up a semi-empirical procedure of the conventional form,[1,9] using the linear variational method with some effective one-electron Hamiltonian operator $\mathbf{H}_{eff}(1)$ equal either to $\mathbf{H}_{core}(1)$ or to a self-consistent operator $\mathbf{F}(1) = \mathbf{H}_{core}(1) + \mathbf{G}(1)$, where $\mathbf{G}$ includes in the proper way[5] the effect of the other π-electrons on electron 1. One would then obtain simultaneous equations for the coefficients and for one-electron orbital energies of the form

$$\sum_p C_{ip}[H_{pq}^{eff} - S_{pq}e] = 0$$

and

$$|H_{pq}^{eff} - S_{pq}e| = 0, \quad \text{respectively.}$$

If $\mathbf{H}_{eff} = \mathbf{H}_{core}$ were used, the roots of the secular equation would be the diagonal elements $I_i \equiv I_{ii}$, and the off-diagonal I_{ij} would be zero; if $\mathbf{H}_{eff} = \mathbf{F}$ were used, the roots of the secular equation (for a closed-shell ground state) would be the self-consistent field energies.[5] In the former case one could proceed immediately to the use of the formulation of Sec. 2 for determination of total electronic energies, but one would have to be prepared to include a large amount of configuration interaction in order to compensate for the inadequacies of the MO's employed. The MO's used in the self-consistent case would be better, but one would be inextricably tied to a difficult and tedious iterative computational scheme.[10]

The point of view advocated here will be intermediate. Configuration interaction, sufficiently invoked, can correct in effect any error made in the choice of the LCAO coefficients. For this reason, any coefficients C_{ip} may be employed. One may therefore choose the coefficients arbitrarily, subject to the orthonormalization conditions. The closer the chosen MO's are to the

[9] R. G. Parr, J. Chem. Phys. **19**, 799 (1951).
[10] See, for example, R. G. Parr and R. S. Mulliken, J. Chem. Phys. **18**, 1338 (1950), where a self-consistent LCAO MO calculation on butadiene is carried out.

"best" or self-consistent field LCAO MO's, the less configuration interaction will have to be invoked. However, large deviations from self-consistent LCAO MO's brought on by ignorance or dictated by convenience may always be compensated through configuration interaction.

A procedure for obtaining the $H_{pq}{}^{\text{core}}$ will now be outlined. Let

$$\alpha_p \equiv H_{pp}{}^{\text{core}} = \int \chi_p{}^*(1)\mathbf{H}_{\text{core}}(1)\chi_p(1)dv \qquad (19)$$

and[11]

$$\beta_{pq} \equiv H_{pq}{}^{\text{core}} = \int \chi_p{}^*(1)\mathbf{H}_{\text{core}}(1)\chi_q(1)dv \qquad (20)$$

and assume tentatively that

$$\beta_{pq}=0 \text{ when } p \text{ and } q \text{ are non-neighbors.} \qquad (21)$$

The *resonance integrals* β_{pq} may be shown by theoretical elucidation of H_{core} to depend on the type and length of the bond pq and the atoms p and q, but not sensibly on neighboring bonds or atoms.[12] Accordingly, they may be naturally carried from molecule to molecule and will be treated as basic empirical quantities.

The *Coulomb integrals* α_p, on the other hand, will depend on the bonding to atom p and the neighbors of atom p, and therefore are not appropriate for carry-over from molecule to molecule. They are better expressed in terms of more basic quantities, as follows: According to the argument of Goeppert-Mayer and Sklar,[3] the core Hamiltonian of Eq. (3) may be written as

$$\mathbf{H}_{\text{core}}(1) = \mathbf{T}(1)+\mathbf{U}_p(1)+\sum_{q \neq p}\mathbf{U}_q(1)+\sum_r \mathbf{U}_r{}^*(1), \qquad (22)$$

where the atoms q are charged in the core (e.g., a carbon atom in benzene) and the atoms r are uncharged in the core (e.g., a hydrogen atom in benzene), and where the asterisk connotes a potential which is due to a *neutral* atom. Further,

$$\mathbf{U}_q(1) = \mathbf{U}_q{}^*(1) - \int \chi_q{}^*(2)\chi_q(2)(e^2/r_{12})dv_2. \qquad (23)$$

If, therefore, the AO's χ_p are atomic eigenfunctions in the sense that

$$[\mathbf{T}(1)+\mathbf{U}_p(1)]\chi_p(1)=W_p\chi_p(1), \qquad (24)$$

where W_p is an appropriate *atomic valence state ioniza-*

tion potential, then Eqs. (19) and (22)–(24) yield

$$\alpha_p = W_p - \sum_{q \neq p}[(pp|qq)+(q:pp)]-\sum_r (r:pp), \qquad (25)$$

where $(pp|qq)$ is the *Coulomb repulsion integral* between χ_p and χ_q [compare Eq. (16)] and $(q:pp)$ and $(r:pp)$ are *Coulomb penetration integrals* between χ_p and *neutral* atoms q and r:

$$(q:pp) = -\int \mathbf{U}_q{}^*(1)\chi_p{}^*(1)\chi_p(1)dv. \qquad (26)$$

Equation (25) will be taken as the fundamental formula for determination of the atomic Coulomb integrals α_p from the empirical atomic ionization potentials W_1.

4. ELECTRONIC REPULSION INTEGRALS

The electronic repulsion integrals of Eq. (16) are of the form

$$(ij|kl) = \int \Omega_{ij}(1)(1/r_{12})\Omega_{kl}(2)dv, \qquad (27)$$

with $\Omega_{ij}(1)=e\phi_i{}^*(1)\phi_j(1)$ and $\Omega_{kl}(2)=e\phi_k{}^*(2)\phi_l(2)$, and can be interpreted as classical electrostatic repulsions between the charge distribution Ω_{ij} and Ω_{kl}. To obtain approximate values for these integrals, one may make the assumption of *formal neglect of differential overlap*,

$$\chi_p{}^*\chi_q \equiv 0 \quad \text{for} \quad p \neq q, \qquad (28)$$

and employ ϕ_i which are orthonormalized accordingly;[12] i.e., make

$$\sum_p C_{ip}{}^*C_{jp} = \delta_{ij}. \qquad (29)$$

One then obtains

$(ij|kl) = $ linear combination of integrals over atomic orbitals of the form $(pp|qq)$. (30)

The problem is thus reduced to the evaluation of a relatively small number of integrals over atomic orbitals, all of them being Coulomb repulsion integrals.

Formulas or tables for the integrals $(pp|qq)$ may be found in the literature.[14] Alternatively, the *uniformly charged sphere approximation* may be employed,[15,16] in

[11] Equation (20) is the *formal* definition of β_{pq} with which one works in conjunction with the formal neglect of overlap of Eq. (28). For theoretical purposes, β_{pq} is better thought of as defined by

$$\beta_{pq} = H_{pq}{}^{\text{core}} - (S_{pq}/2)(H_{pp}{}^{\text{core}}+H_{qq}{}^{\text{core}}), \qquad (20a)$$

which takes more realistic account of the overlap integral

$$S_{pq} = \int \chi_p{}^*(1)\chi_q(1)dv. \quad \text{(See references 1 and 6.)}$$

[12] This may be shown to be true when β_{pq} is defined as in reference 11.

[13] One does not have to *orthogonalize* subject to formal neglect of differential overlap, but this appears to be the most natural and consistent procedure.

[14] Formulas for Coulomb repulsion integrals $(pp|qq)$, for Slater $2p\pi$ AO's, both for $Z_p=Z_q$ and $Z_p \neq Z_q$, are given by C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951). Numerical values for $Z_p \neq Z_q$ are not available in the literature, except for a few special cases. Numerical values for $Z_p = Z_q$ have been given by several authors; the best table now available is that of H. J. Kopineck, Z. Naturforsh. **5a**, 420 (1950).

[15] The uniformly charged sphere approximation seems to have been employed first by G. E. Kimball, who investigated such an approximation for $1s$ orbitals. See G. F. Neumark, Ph.D. thesis, Columbia University, 1951.

[16] For a preliminary discussion of the uniformly charged sphere approximation for $2p\pi$ orbitals, see R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).

TABLE I. Electronic repulsion integrals in ethylene (ev).

Integral	Exact value[a]	Approximate value[b]
J_{11}	13.08 ⎫	
J_{22}	13.44 ⎬	13.09 or 13.58
J_{12}	13.01 ⎭	
K_{12}	4.16	3.84 or 4.50

[a] Reference 18. These values are for Slater $2p\pi$ AO's with effective charge $Z=3.18$.
[b] Values in first column are calculated neglecting differential overlap; values in second column are calculated using uniformly charged sphere approximation. See text and reference 19.

which each $\chi_p{}^*\chi_p e$ is replaced by a pair of tangent uniformly charged nonconducting spheres of *diameter*

$$R_p = (4.597/Z_p) \times 10^{-8} \text{ cm,}^{17} \qquad (31)$$

where Z_p is the Slater effective nuclear charge for the $2p\pi$ atomic orbital χ_p, and the integrals $(pp|qq)$ are computed by means of classical electrostatic theory. A pronounced advantage of the uniformly charged sphere model is the relative ease with which heteroatoms may be handled.

5. PRIMITIVE APPLICATIONS TO ETHYLENE AND BENZENE

Tables I–IV give the results of application of the method outlined in Secs. 2–4 to ethylene and benzene. Results obtained by the much more tedious non-empirical antisymmetrized product method using Slater $2p\pi$ AO's are also displayed in the tables.[8,18] The two methods agree within the limits of precision in the nonempirical method. Agreement with experiment is another matter, which will be discussed briefly in Sec. 6 and in detail in paper II of this series.

The two π-electron LCAO MO's in ethylene are determined by symmetry. Neglecting overlap, they are

$$\left.\begin{array}{l} \phi_1 = \dfrac{1}{\sqrt{2}}(\chi_1 + \chi_2) \\[2mm] \phi_2 = \dfrac{1}{\sqrt{2}}(\chi_1 - \chi_2) \end{array}\right\}, \qquad (32)$$

where χ_1 and χ_2 are $2p\pi$ AO's on carbons 1 and 2. The electronic repulsion integrals, when differential overlap

is neglected, are therefore given by the simple formulas

$$\left.\begin{array}{l} 2J_{11} = 2J_{22} = 2J_{12} = (11|11) + (11|22) \\[2mm] 2K_{12} = (11|11) - (11|22) \end{array}\right\}. \qquad (33)$$

Table I gives purely theoretical values for these integrals,[18] values computed from Eq. (33) using exact values for the atomic Coulomb integrals $(11|11)$ and $(11|22)$, and values computed from Eq. (33) using uniformly charged sphere values for $(11|11)$ and $(11|22)$.[19]

Table II gives purely theoretical values for the π-electron energy levels of ethylene, values computed ignoring differential overlap, and values computed using the uniformly charged sphere approximation, a value of β being employed in the last two calculations which will make the "states" 1 and 2 have the same splitting as in the first calculation. Here states 1 and 2 arise from assignment of two electrons to the MO's ϕ_1 and ϕ_2, respectively. State N is the result of mixing states 1 and 2

TABLE II. Electronic energy levels of ethylene (ev).

State	Exact LCAO MO energy[a]	Approximate energy[b]	
$1(^1A_{1g})$	0.0	0.0	0.0
$2(^1A_{1g})$	12.5	12.5	12.5
$T(^3B_{1u})$	1.8	2.4	1.8
$V(^1B_{1u})$	10.2	10.1	10.8
Mean of T and V	6.0	6.2	6.2
$N(^1A_{1g})$	−1.3	−1.1	−1.4

[a] Reference 18. These values are for Slater $2p\pi$ AO's with effective charge $Z=3.18$.
[b] Values in first column are calculated neglecting differential overlap; values in second column are calculated using uniformly charged sphere approximation. See text and reference 19. $\beta = -3.125$ ev has been employed in each case.

to give the best approximation to the ground state obtainable from the AO's χ_1 and χ_2. States T and V are the triplet and singlet states arising from assignment of one electron to ϕ_1 and one electron to ϕ_2. The formulas for the energies of these various states have been given elsewhere,[18] and so will not be given here. The quantity α enters all the energies in the same additive way (note that the two carbon atoms in ethylene are equivalent) and, therefore, cancels when excitation energies are computed.

Neglecting overlap, the six π-electron LCAO MO's in benzene, as determined by symmetry, are[3]

$$\phi_l = \frac{1}{\sqrt{6}} \sum_{p=1}^{6} \omega^{lp} \chi_p, \quad l = 0, \pm 1, \pm 2, 3; \qquad (34)$$

---

[17] This value for the diameter forces the integral $(pp|pp)$ to be in agreement with the value computed for Slater $2p\pi$ AO's, $(pp|pp)$ $=0.1957\ (e^2/a_0)Z_p$. (See, for example, R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys. 16, 1049 (1948).) For the uniformly charged sphere model, with $\chi_p{}^2 e$ replaced by two tangent uniformly charged spheres each of diameter R_p and carrying charge $e/2$, since the repulsive potential between one such sphere and itself is from classical electrostatics $(12/5R_p)$ for unit charge, $(pp|pp) = (e/2)^2 |2(12/5R_p) + 2(1/R_p)| = (17/10)\ (e^2/R_p)$. Hence, equating the two expressions for $(pp|pp)$, $R_p = (17/10)$ $(a_0/0.1957Z_p) = (4.597/Z_p) \times 10^{-8}$ cm.
[18] R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys. 16, 526 (1948).

[19] If one inserts the usual $Z_c = 3.18$ in Eq. (31), one finds $R_c = 1.45$A, which would cause spheres on neighboring carbon atoms to overlap in ethylene and benzene. The electrostatics can be handled in this case (see reference 15), but it is simpler and in more natural accord with Eq. (28) to contract the spheres enough that neighboring spheres are just tangent, which procedure has been used in computing Tables I–IV and which corresponds to $Z_c = 3.40$ in ethylene and $Z_c = 3.30$ in benzene.

where $\omega = \exp(2\pi i/6)$ and χ_p is the $2p\pi$ AO on carbon p. Without the formal neglect of differential overlap there are thirty different electronic repulsion integrals in benzene, the values of which cluster in four distinct groups.[20] With the assumption of formal neglect of differential overlap there are only four distinct integrals; namely,

$$
\left.
\begin{aligned}
6J_{00} = 6J_{01} &= \text{etc.} = (11|11) + 2(11|22) \\
&\quad + 2(11|33) + (11|44) \\
6K_{01} = 6K_{12} &= \text{etc.} = (11|11) + (11|22) \\
&\quad - (11|33) - (11|44) \\
6K_{02} = 6K_{13} &= \text{etc.} = (11|11) - (11|22) \\
&\quad - (11|33) + (11|44) \\
6K_{03} = 6K_{1-2} &= \text{etc.} = (11|11) - 2(11|22) \\
&\quad + 2(11|33) - (11|44)
\end{aligned}
\right\}. \quad (35)
$$

TABLE III. Electronic repulsion integrals in benzene (ev).

Integral	Exact value[a]	Approximate value[b]
J_{00} group	8.627, 8.522, 8.495, 8.554, 8.474, 8.517, 8.623. 8.648, 8.787, 8.872; average 8.61	8.56
K_{01} group	2.584, 2.674, 2.867, 2.601, 2.633, 2.772; average 2.69	2.66
K_{02} group	1.304, 1.453, 1.338, 1.367, 1.328, 1.299, 1.302, 1.375, 1.344, 1.362; average 1.35	1.35
K_{03} group	0.934, 1.074, 1.007, 0.993 average 1.00	1.03

[a] Reference 8. These values are for Slater $2p\pi$ AO's with effective charge $Z = 3.18$.
[b] Calculated using uniformly charged sphere approximation. See text and reference 19.

In Table III purely theoretical values for these integrals[8] are compared with values computed from Eq. (35) and the uniformly charged sphere approximation.[21]

Table IV gives purely theoretical values for the π-electron energy levels of benzene[8] and values computed using the uniformly charged sphere approximation and a value of β chosen to make the energies of the first excited singlet state equal in the two calculations. Here interaction[22] has been taken into account between

[20] See reference 8, especially footnote 9.
[21] Exact (reference 8) values for the atomic Coulomb integrals are $(11|11) = 16.93$, $(11|22) = 9.03$, $(11|33) = 5.67$, $(11|44) = 4.97$ ev; uniformly charged sphere approximation values (see footnote 19) are $(11|11) = 17.61$, $(11|22) = 8.84$, $(11|33) = 5.58$, $(11|44) = 4.90$ ev.
[22] This interaction can be handled by group theory, but this is a specialized technique not applicable to unsymmetrical molecules. Rather it appears preferable to handle the interaction by the configuration interaction technique of Sec. 2, which is completely general.

TABLE IV. Electronic energy levels of benzene (ev).

State	Exact LCAO MO energy[a]	Approximate energy[b]
$^1A_{1g}$	0.0	0.0
$^1B_{2u}$	5.9	5.9
$^1B_{1u}$	7.3	7.3
$^1E_{1u}$	9.8	9.9
$^3B_{2u}$	5.8	5.9
$^3B_{1u}$	3.1	3.2
$^3E_{1u}$	4.4	4.5

[a] Reference 8. These values are Slater $2p\pi$ AO's with effective charge $Z = 3.18$.
[b] Calculated using uniformly charged sphere approximation. with $\beta = -2.790$ ev. See text and reference 19.

all configurations which arise from excitation of an electron from an MO ϕ_1 or ϕ_{-1} to an MO ϕ_2 or ϕ_{-2}. Formulas for the energies again may be found elsewhere,[3] and α again does not enter the excitation energies.

6. DISCUSSION

These results show that the present semi-empirical theory is capable of duplicating the results of the nonempirical antisymmetrized product method in cases where the latter has been applied, and with such a large reduction in labor that applications are now made possible to much more complex molecules than have heretofore been treated by an antisymmetrized product method.

How about agreement with experiment, however? Although the experimental data themselves are not unambiguously understood, even in ethylene and benzene, enough is known to make one realize that the nonempirical method is not entirely satisfactory. The present theory, admittedly being semi-empirical, has a flexibility not inherent in the nonempirical method. The possibility of exploiting this flexibility will be investigated in the next paper of this series.

Quantities which enter the expressions for the electronic energy levels of a molecule in the present theory are of four types: (1) atomic ionization potentials, W_p; (2) bond resonance integrals, β_{pq}; (3) Coulomb repulsion integrals, $(pp|qq)$; (4) Coulomb penetration integrals, $(q:pp)$. In the preliminary calculations of Sec. 5 above, only the first two of these types were regarded as empirical. One might well ask whether empirical adjustment of the last two would also be worth while. In the next paper such an adjustment will indeed be carried out, and there will emerge both an improved fit of the theory with experiment and a natural correction for the inadequacies of the π-electron approximation.