A Semi-empirical Approach to the SCF Molecular Orbitals

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Introduction

The semi-empirical ASMO method recently proposed by Pariser and Parr⁽¹⁾ presents a way to calculate the transition energies and oscillator strengths of a variety of π-electron systems without much labour, in such a quantitative conformity with experiments as is rarely found in this kind of calculation. One of the essential points of their method is to alter the values of Coulomb repulsion integrals over atomic orbitals by introducing semi-empirical elements on a similar ground as in the method of "atoms in molecules" of Moffit⁽²⁾. The reasonable nature of such revision of integral values is illustrated by

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1) R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

2) W. Moffit, *Proc. Roy. Soc.*, **A210**, 245 (1951).

the improvements in the results of their calculations. Nothing is known, however, of the improvements in the form of MO's which might be brought about by introducing the revised integrals, and one has to be content with the naive Hückel method or to resort to the elaborate, laborious, self-consistent field method of Roothaan[3].

In this preparatory note, a trial is given to incorporate the Pariser and Parr's semi-empirical method into the iterative procedure of Roothaan in order to reflect their reasonable revision of the integral values on the form of molecular orbitals. In the course of this calculation, the author found that Pople's treatment of unsaturated hydrocarbon[4] was based on a similar idea, but there, the Coulomb repulsion integrals were approximated by the Coulomb energy between two point charges instead of the charged sphere model of Pariser and Parr, and the details were somewhat different from the present treatment.

Modification of Roothaan's SCF Equation

A molecular orbital (ϕ_i) of a π-electron system is expressed as a linear combination of atomic orbitals (χ_p),

$$\phi_i=\sum_p c_{ip}\chi_p.$$

The coefficients c_{ip} are determined by a homogeneous set of equations derived by Roothaan.

$$\sum_q c_{ip}(L_{pq}-S_{pq}\varepsilon_i=0,$$

$$L_{pq}=G_{pq}+I_{pq},$$

$$G_{pq}=\sum_i^{occ}[2J_{i,pq}-K_{i,pq}],$$

$$\begin{aligned}I_{pq}&=\int\chi_p(\nu)H_{core}\chi_q(\nu)d\tau_\nu\\&=\int\chi_p(\nu)[T(\nu)+\sum_r U_r(\nu)]\chi_q(\nu)d\tau_\nu\,.\end{aligned}$$

$U_r(\nu)$ is the potential on the electron ν due to the atom r stripped of its π-electron. $J_{i,pq}$ and $K_{i,pq}$ are defined as follows:

$$\begin{aligned}J_{i,pq}&=\iint\phi^*_i(\mu)\phi_i(\mu)[e^2/r_{\mu\nu}]\\&\qquad\chi^*_p(\nu)\chi_q(\nu)d\tau_\nu\,d\tau_\mu,\\K_{i,pq}&=\iint\phi_i^*(\mu)\phi_i(\nu)[e^2/r_{\mu\nu}]\\&\qquad\chi^*_q(\mu)\chi_q(\nu)d\tau_\mu d\tau_\nu\,.\end{aligned}$$

The simplifying assumptions of Pariser and Parr such as; 1) zero differential overlap, $\chi_p\chi_q=0$, 2) neglect of non-neighbour core integral I_{pq}, are taken into account here, so that $J_{i,pq}$ and $K_{i,pq}$ are rewritten in terms only of atomic Coulomb repulsion integrals as follows,

$$\begin{aligned}J_{i,pq}&=0,\ p\neq q,\\J_{i,pp}&=\sum_q c^2_{iq}\int\chi^*_q(\mu)\chi_q(\mu)[e^2/r_{\mu\nu}]\chi^*_p(\nu)\chi_p(\nu)d\tau_\mu d\tau_\nu=\sum_q c^2_{iq}(qq\,|\,pp)\\&=c^2_{ip}\,(pp\,|\,pp)+\sum_{q\neq p}c^2_{iq}(qq\,|\,pp),\\K_{i,pq}&=c_{ip}c_{iq}\,(pp\,|\,qq).\end{aligned}$$

Similarly, the core integrals reduce to two integrals:

$$\begin{aligned}I_{pq}&=\alpha_p, && p=q,\\&=\beta_{pq}, && p\neq q,\text{ atom } p \text{ being linked directly to atom } q,\\&=0, && \text{otherwise.}\end{aligned}$$

Thus the expression for the quantity L_{pq} is replaced by

$$\begin{aligned}L_{pp}&=\alpha_p+\sum_i 2c^2_{ip}(pp\,|\,pp)+\sum_i\sum_{q\neq p}2c^2_{iq}(pp\,|\,qq)\\&\quad-\sum_i c^2_{ip}\,(pp\,|\,pp)\\&=\alpha_p+\frac{1}{2}Q_p(pp\,|\,pp)+\sum_{q\neq p}Q_q(qq\,|\,pp),\\L_{pq}&=\beta_{pq}-\sum_i c_{ip}c_{iq}(pp\,|\,qq)\\&=\beta_{pq}-\frac{1}{2}P_{pq}(pp\,|\,qq),\quad p\neq q.\end{aligned}$$

Here Q_p is the π-electron density on p-atom and P_{pq} reduces to the mobile bond order, if atoms p and q are the neighbouring atoms, but if not, it has not any definite physical meaning. In addition to these simplifications, the following assumptions are made in this paper in dealing with the core integrals α_p and β_{pq}.

1) The Coulomb integral α_p can be approximated as the valence state ionization potential (W_{2p}) of a $2p$ electron on a free atom, less the sum only of the Coulomb repulsion integrals $(pp\,|\,qq)$, summation being carried out over all the other atoms q involved in the π-electron system. This neglect of Coulomb penetration integrals is found to reduce the labour without having a significant influence on the good numerical performance of Pariser and Parr's original work. 2) The resonance integral β_{pq} which as in ref. 1, is one of the empirical parameters and is carried from molecule to molecule, is assumed, apart from Pariser and Parr, to be proportional to the inverse sixth-power of the bond distance r_{pq} and the proportionality constants are so chosen as to reproduce the observed first transition energy of a particular molecule as closely as possible. As the reference molecule, ethylene, formaldehyde and pyrazine

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[3] C.C.J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); R. G. Parr and R.S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

[4] J.A. Pople, *Trans. Farad. Soc.*, **49**, 1375 (1953).

are chosen for the bond C=C, C=O and C=N, respectively. In ref. 1, it is postulated that β_{pq} can be expressed as, $\beta_{pq}=a\exp(-br_{pq})$. Two experimental data being needed to fix the parameters a and b, it is not easy to extend it to other cases than C=C bonds. Whether or not the inverse sixth-power equation is appropriate will be tested by applying it to a variety of compounds and by comparing the results with observations. Taking these assumptions into account, the matrix element L_{pp} can be written down as,

$$\begin{aligned} L_{pp}=W_{2p}+\frac{1}{2}Q_p(pp\,|\,pp) \\ +\sum_{q\neq p}(Q_q-1)(qq\,|\,pp). \end{aligned}$$

If we put, $Q_p=Q_q=1$, then L_{pp} becomes a constant. As L_{pp} in the present treatment plays an analogous role to the Coulomb integral in the simple molecular orbital method, the constant L_{pp} will bring about a uniform distribution of π-electrons as in the alternant hydrocarbons treated by the simple molecular orbital method. For non-alternant hydrocarbons and hetero-molecules, Q_p, $Q_q\neq1$ and L_{pp} depends in a complicated manner on the geometrical configuration of the molecule, that is L_{pp} is a function not only of the charge density of p-atom and q-atoms. In Wheland and Mann's iterative method, the Coulomb integral on an atom p is dependent only on Q_p[5]. The above mentioned functional relation, however, is a more satisfactory one and is in harmony with the Coulson and Longuet-Higgins' theory[6], where the charge density on an atom and the Coulomb integral of other atoms are connected to each other by their mutual polarizability (π_{pq}).

Roothaan's iterative procedure to find the self-consistent set of c_{ip}'s is then followed, making at each step a guess at a better set of c_{ip} values to attain a rapid convergence. The symmetry coordinates are fully made use of in order to reduce the order of secular equations. Of the molecules calculated in this paper, ethylene and benzene have geometrical symmetry sufficient for finding the self-consistent set of c_{ip}'s only through the symmetry requirements, and so the iteration is unnecessary.

Numerical Values of the Basic Quantities

Following Pariser and Parr, the Coulomb repulsion integrals $(pp\,|\,qq)$ are computed by making use of their uniformly charged sphere model for bond distances longer than 2.80 Å and proper quadratic extrapolation formulae are used for bonds shorter than 2.80 Å. The resonance integral β_{pq} is computed as mentioned above from the formula, $\beta_{pq}=k/r^6_{pq}$, k being the proportionality constant, to which numerical values -17.464, -13.983 and -8.8086 are assigned for C=C, C=N and C=O bond, respectively. In Fig. 1 are shown the geometricals and designations for the calculated eight molecules. Except for s-triazine, geometricals are all based on the experimental data.

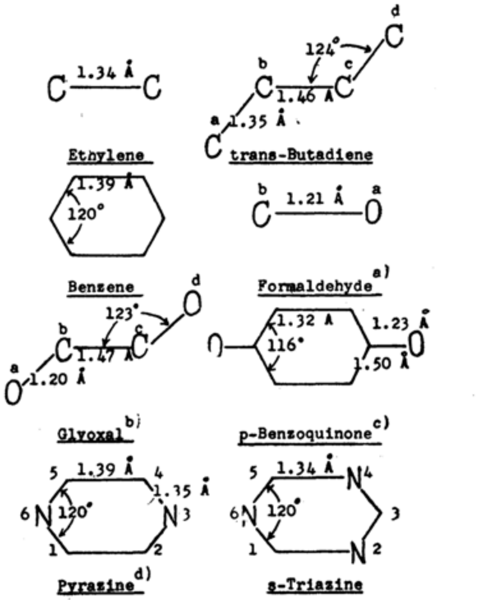

Fig. 1. Geometricals and designations of the calculated molecules.

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a) D. P. Stevenson, J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2508 (1939).

b) J. E. LuValle and V. Schomaker, ibid., **61**, 3520 (1939).

c) S.M. Swingle, ibid., **76**, 1409 (1954).

d) V. Schomaker and L. Pauling, ibid., **61**, 1769 (1939).

Results of Calculation

After the iterative processes have come to convergence, the electronic transition energies are calculated by use of the following formula, no configuration interaction being allowed for, except in the symmetry degenerate cases of benzene and s-triazine.

$$\left.\begin{matrix} E_{Vij} \\ E_{Tij} \end{matrix}\right\}-E_N=(\epsilon_j-\epsilon_i)-(J_{ij}-K_{ij})\pm K_{ij}.$$

Here, E_N, E_V and E_T designate the energy of the ground, excited singlet and excited triplet configuration, respectively, electronic excitation being from orbital i to j. J and K are the Coulomb repulsion and exchange

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[5] G.W. Wheland and D.E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

[6] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39; **A192**, 16 (1947).

repulsion integrals in terms of molecular orbitals.

$$J_{ij}=\iint\phi^*_i(\mu)\phi_i(\mu)[e^2/r]\phi^*_j(\nu)\phi_j(\nu)d\tau_\mu d\tau_\nu\ ,$$
$$K_{ij}=\iint\phi^*_i(\mu)\phi^*_j(\mu)[e^2/r]\phi_i(\nu)\phi_j(\nu)d\tau_\mu d\tau_\nu\ .$$

The calculated results are compared in Tables I-III with the observed values and with those by Pariser and Parr.

TABLE I

CALCULATED TRANSITION ENERGIES VS. EXPERIMENTAL VALUES OF HYDROCARBONS

Molecule	State	Calculated energy above the ground state (ev)		Obs.*) (ev)
		This paper	Pariser-Parr	
Ethylene	$^1B_{1u}$	(7.60)	(7.60)	7.60
	$^3B_{1u}$	4.47	4.5	3.1—5.6
trans-Butadiene	^1B_u	6.19	6.21	6.0
	^1A_g	7.72	7.87	7.2(?)
	^3B_u	4.10	3.92	—
	^3A_g	6.17	4.61	—
Benzene	$^1B_{2u}$	4.96	4.9	4.9
	$^1B_{1u}$	5.37	5.3	6.0
	$^1E_{1u}$	7.01	7.0	7.0
	$^3B_{1u}$	3.62	4.0	3.8
	$^3E_{1u}$	4.52	4.45	—
	$^3B_{2u}$	4.96	4.9	—

*) See ref. 1 and those cited there.

It can be seen there that, in spite of the neglect of the Coulomb penetration integrals, the calculated values agree well with those observed, almost to the same extent as do the Pariser and Parr's values. It must, also, be noted that these agreements are obtained without taking account of the configuration interactions, except in benzene and triazine. This may be accepted as a good reason for neglecting the Coulomb penetration integrals and for the availability of the simple inverse sixth-power formula to compute β_{pq}, at least in hydrocarbons.

TABLE II

CALCULATED TRANSITION ENERGIES VS. EXPERIMENTAL VALUES FOR PYRAZINE AND S-TRIAZINE

Molecule	State	Calculated energy above the ground state (ev)		Obs. (ev)
		This paper	Pariser-Parr	
Pyrazine	$^1B_{3u}$	4.74	4.71	4.77
	$^3B_{3u}$	3.03	3.85	3.35
s-Triazine	$^1A'_2$, $^3A'_2$	5.43	5.29	5.62*)
	$^1A'_1$	6.17	—	—
	$^1E'_1$	7.41	—	—
	$^3A'_1$	4.97	4.26	—

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* R.C. Hirt, F. Halverson and R.G. Schmitt, *J. Chem. Phys.*, 22, 1148 (1954).

The calculation of *s*-triazine is based on the assumed bond length shown in Fig. 1, because it was non-existent. A slightly shorter C=N bond distance (1.34 Å) than in pyrazine is presumed for *s*-triazine, taking into account that the C=N bond in cyanuric triazide is shorter than 1.35 Å. As shown in Table II, the calculated result for N→V transition in *s*-triazine is improved, compared with Pariser-Parr's value. Recently it is reported that the existence of this molecule was shown by Grundmann and Kreutzberger. The experimental data of ultraviolet and infrared absorption spectra are published, and the detailed x-ray analysis is reported in progress, by which the present calculation might be revised so as to allow for the experimentally determined bond lengths.

TABLE III

CALCULATED TRANSITION ENERGIES VS. EXPERIMENTAL VALUES FOR OXYGEN CONTAINING MOLECULES

Molecule	State	Calculated energy above the ground state (ev)	Obs. (ev)
Formaldehyde*)	$^1A_1$	7.80	7.95
	$^3A_1$	4.49	—
Glyoxal	^1B_u	7.47	7.51**)
	^3B_u	5.09	—
p-Benzoquinone	$^1B_{2u}$	6.08	5.21***)
	$^3B_{2u}$	4.37	—

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* Slight differences in calculated results between the present and the previous communication (This Bulletin, 27, 565 (1954).) are due to the different bond lengths adopted.

** Estimated value; see the previous communication (This Bulletin, loc. cit.)

*** G. Scheibe et al., *Ber.*, 59, 2617 (1926).

A comment on the calculated results of *p*-benzoquinone will be given in Sec. V.

The self-consistent molecular orbitals finally obtained are tabulated in Tables IV-V. Unfortunately, none of the molecules treated in this paper has definite dipole moment and there seems to be no means of crucial test for the quality of the molecular orbitals obtained. A few points are still to be noted. 1) The bond lengths r_{ab} and r_{bc} of *trans*-butadiene calculated from the theoretical bond orders through the bond order-bond length relation of Coulson are 1.35 Å and 1.49 Å, while the assumed values are 1.35 Å and 1.46 Å, respectively, a situation satisfactorily self-consistent. For other molecules containing hetero-atoms, the existence of excess charge prevents one from setting up a simple relation between bond orders and bond lengths. However, the bond length r_{12} of pyrazine, where the net positive charge on carbon atoms is comparatively small, the computed and assumed (experimental) bond lengths are in complete agreement, 1.39 Å.

2) The π-electron density on nitrogen atoms of pyrazine is computed by the simple molecular orbital method using the set of correction parameter for nitrogen atom which was found by Lowdin[7] to result in satisfactory agreements between the computed and observed values of dipole moment in diazines. It is 1.155 in units of electronic charge, while the present method gives only a little higher value, 1. 238.

These together with the fact that the present method applied to fulvene[8], yields the value of dipole moment in satisfactory agreement with the estimated value, might be helpful for judging the quality of the molecular orbitals obtained here.

TABLE IV

SELF-CONSISTENT MOLECULAR ORBITALS*)

Molecule	ε (ev)	Molecular Orbital	
trans-Butadiene	-2.480	$\phi_1=0.4397\ (\chi_a+\chi_d)+0.5538\ (\chi_b+\chi_c)$	$q_a=1$
	-0.296	$\phi_2=0.5538\ (\chi_a-\chi_d)+0.4397\ (\chi_b-\chi_c)$	$q_b=1$
	10.826	$\phi_3=0.5538\ (\chi_a+\chi_d)-0.4397\ (\chi_b+\chi_c)$	$p_{ab}=0.974$
	13.010	$\phi_4=0.4397\ (\chi_a-\chi_d)-0.5538\ (\chi_b-\chi_c)$	$p_{bc}=0.227$
Formaldehyde	-3.701	$\phi_1=0.5472\ \chi_a+0.8370\ \chi_b$	$q_a=1.401$
	10.916	$\phi_2=0.8370\ \chi_a-0.5472\ \chi_b,\ q_b=0.599$	$p_{ab}=0.916$
Glyoxal	-5.140	$\phi_1=0.5541\ (\chi_a+\chi_d)+0.4393\ (\chi_b+\chi_c)$	$q_a=1.384$
	-3.853	$\phi_2=0.6205\ (\chi_a-\chi_d)+0.3390\ (\chi_b-\chi_c)$	$q_b=0.616$
	9.202	$\phi_3=0.4393\ (\chi_a+\chi_d)-0.5541\ (\chi_b+\chi_c)$	$p_{ab}=0.908$
	11.847	$\phi_4=0.3390\ (\chi_a-\chi_d)-0.6205\ (\chi_b-\chi_c)$	$p_{bc}=0.156$

*) q: π-electron density in units of e; p: mobile bond order

TABLE V

SELF-CONSISTENT MOLECULAR ORBITALS

Molecule	ε (ev)	Molecular Orbital	
Pyrazine	-4.507	$\phi_1=0.3646\ (\chi_1+\chi_2+\chi_4+\chi_5)+0.4838\ (\chi_3+\chi_6)$	$q_1=0.881$
	-2.107	$\phi_2=0.2397\ (\chi_1-\chi_2-\chi_4+\chi_5)-0.6205\ (\chi_3-\chi_6)$	$q_3=1.238$
	-0.316	$\phi_3=0.5000\ (\chi_1+\chi_2-\chi_4-\chi_5)$	$p_{12}=0.651$
	9.572	$\phi_4=0.3421\ (\chi_1+\chi_2+\chi_4+\chi_5)-0.5157\ (\chi_3+\chi_6)$	$p_{23}=0.650$
	11.013	$\phi_5=0.5000\ (\chi_1-\chi_2+\chi_4-\chi_5)$	
	13.506	$\phi_6=0.4388\ (\chi_1-\chi_2-\chi_4+\chi_5)+0.3390\ (\chi_3-\chi_6)$	
s-Triazine	-4.965	$\phi_1=0.3569\ (\chi_1+\chi_3+\chi_5)+0.4538\ (\chi_2+\chi_4+\chi_1)$	$q_1=0.620$
	-1.940	$\phi_2=0.2138\ (\chi_1-2\chi_3+\chi_5)-0.3478\ (\chi_2+\chi_4-2\chi_6)$	$q_2=1.380$
	-1.940	$\phi_3=0.3703\ (\chi_1-\chi_5)\quad+0.6024\ (\chi_2-\chi_4)$	$p_{12}=0.621$
	10.402	$\phi_4=0.6024\ (\chi_1-\chi_5)\quad-0.3703\ (\chi_2-\chi_4)$	
	10.402	$\phi_5=0.3478\ (\chi_1-2\chi_3+\chi_5)+0.2138\ (\chi_2+\chi_4-2\chi_6)$	
	13.448	$\phi_6=0.4538\ (\chi_1+\chi_3+\chi_5)-0.3569\ (\chi_2+\chi_4+\chi_6)$	

Criticism of the Assumption-1

Now it seems necessary to make a remark on the validity of assumption-1, made in sec. II. According to the approximation of zero-differential overlap adopted throughout the present calculation, the Coulomb integral (α_p) of an electron in the potential field due to the atomic cores in a molecule is expressed in terms of the Coulomb repulsion integrals as well as of the Coulomb penetration integrals as follows:

$$\alpha_p = W_{2p} - \sum_q [(pp\,|\,qq) + (q:\,pp)]\,,$$

Of the integrals in this equation, the Coulomb penetration integrals $(q:\,pp)$ can not be computed easily, in cases where the atoms p and q are of different species. As, in addition, the order of magnitude of $(q:\,pp)$ is supposed to be relatively small, they are left out, as a first approximation, in the calculations in the preceding sections. In order to see how much the results would be affected by this simplification, *trans*-butadiene is treated by use of the Coulomb integrals computed without leaving out the Coulomb penetration integrals. Instead of computing $(q:\,pp)$ exactly, corrections are made for L's by subtracting 1.0 and 1.5 ev, respectively, from the L_{pp}(atom p being a methylene carbon)

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[7] P.O. Lowdin, *J. Chem. Phys.*, **19**, 1323 (1951).

[8] H. Kon, to be published soon.

[9] R.G. Parr and B.L. Crawford, Jr., *J. Chem. Phys.*, **16**, 1049 (1948).

and L_{qq} (atom q being a methine carbon). This manner of correction comes from the following consideration: The values of Coulomb penetration integrals ($p: qq$), where atom p and q are both carbon, can be obtained through the formula derived by Parr and Crawford9) using the Slater type atomic orbitals. They are 0.91 and 0.58 ev for the interatomic distances 1.35 Å and 1.46 Å, respectively. The methylene carbon atoms in butadiene have one formal double bond (1.35 Å), while the methine carbons have one formal single (1.46 Å) and double bond. Assuming the contributions from the other atoms than those linked together directly to be small, the corrections to be made for L's of a methylene and methine carbon atoms are 0.91 and 1.49 ev, respectively, which are rounded to 1.0 and 1.50 ev as given above. This correction, though it is only approximate because of ignoring the effect of the hydrogen atom and the non-neighbouring carbon atoms, would be sufficient for the qualitative purpose.

TABLE VI

COMPARISON OF CALCULATED RESULTS WITH AND WITHOUT CORRECTION

	Correction	
	with	without
Orbital energy (ev)	− 2.730	− 2.480
	− 0.434	− 0.296
	10.689	10.826
	12.777	13.010
Excit. energy (ev)		
^1B_u	6.20	6.19
^3B_u	4.10	4.10
Coeff. of AO		
c_{1a}	0.4258	0.4397
c_{2a}	0.5645	0.5538
π-elec. density		
q_a	0.953	1.000
q_b	1.046	1.000
Bond order		
p_{ab}	0.972	0.974
p_{bc}	0.228	0.227

The calculated results of transition energy, coefficients of AO, π-electron densities and mobile bond orders, with and without correction are compared in Table VI. As can be seen there, the overall alteration brought about by introducing the correction is a minor one. And though the orbital energies are changed a little after correction, the transition energies are almost unchanged. The same holds for the relation between the AO coefficients and the bond orders derived from the former.

Conspicuous among the results may be the fact that the uniformity of π-electron distribution in butadiene (or, the hydrocarbons in general), which is assured in the Hückel method is broken down by the correction. At any rate the results in Table VI, together with the good agreements between the calculated and the observed transition energies show that one can safely dispense with Coulomb penetration integrals at least in computing the transition energies of hydrocarbons (and those hetero-molecules where the perturbation due to the hetero-atoms are not so serious), and that the wave functions so obtained would be fairly good approximations to the best possible ones.

The numerical agreement between the computed and experimental transition energy of p-benzoquinone is shown to be inferior to other cases. (Table III) The situation may probably be improved by making such a correction as mentioned above, especially for the tertiary carbon atoms (p) where, owing to the adjacent electronegative oxygen atoms, the amount to be subtracted from L_{pp} is considered too great to be ignored. It can also be understood from the similar point of view that the π-electron densities on nitrogen atoms listed in Table V appear a little higher than desirable.

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