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Self-Consistent Perturbation Theory for Conjugated Molecules

IV. First Order Changes in Orbital Energies, Correlation with Ionization Potentials and Polarographic Reduction and Oxidation Potentials of Heteromolecules

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The first order changes in the orbital energies of a number of hydrocarbons due to perturbations at particular atoms are given. These are useful for discussing ionization potentials, polarographic reduction and oxidation potentials, and electron affinities of heteromolecules.

Die Änderungen erster Ordnung von Einelektronenenergien bei Störung an bestimmten Atomen werden für eine Reihe von Kohlenwasserstoffen angegeben. Sie erweisen sich als brauchbar für die Diskussion von Ionisationspotentialen, polarographischen Oxydations- und Reduktionspotentialen und Elektronenaffinitäten von Heteromolekülen.

Les variations au premier ordre des énergies des orbitales, sous l'influence de perturbations sur des atomes déterminés, sont données pour un certain numbre d'hydrocarbures. Elles sont utiles pour la discussion des potentiels d'ionisation, des potentiels d'oxydation et de réduction polarographiques et des affinités électroniques des molécules hétéroatomiques.

In paper I [*1*] of this series a self-consistent perturbation theory for conjugated molecules was developed. This theory is particularly suitable for calculating changes in certain quantities due to the effect of a perturbation consisting of one electron terms. Among other quantities the perturbation will change the orbital energies. In terms of the perturbation parameter λ we have that the orbital energy E_i will be given by

$$E_i = E_i^0 + \lambda E_i' \tag{1}$$

to first order, so that E_i' is the first order correction to the unperturbed orbital energy E_i^0.

As an example of this Tab. 1 shows the unperturbed π orbital energy levels E_i^0 for the naphthalene molecule and the first order corrections due to a perturbation of $z_{rr} = \lambda\beta$ ($\beta = -4.78$ eV) at the 1 position. The unit of energy is β and the E_i^0

Table 1. *Zero-order orbital energies in naphthalene and first order corrections due to substitution at position 1*

i	E_i^0	E_i'	i	E_i^0	E_i'
1	1.9824	0.0806	6	−0.9029	0.1833
2	1.5816	0.0879	7	−1.1209	0.0003
3	1.3668	0.1408	8	−1.3668	0.1408
4	1.1209	0.0003	9	−1.5816	0.0879
5	0.9029	0.1833	10	−1.9824	0.0806

are given relative to the diagonal elements of the SCF Hamiltonian i.e. the quantity usually denoted by α in Hückel theory. Because of the pairing property of alternants this ensures that the E_i^0 satisfy the relation

$$E_{2n-i+1}^0 = -E_i^0 \tag{2}$$

where $2n$ is the number of carbon atoms. Another consequence of the pairing property is that the first order corrections E_i' satisfy

$$E_{2n-i+1}' = E_i' \tag{3}$$

and this is confirmed by the values in Tab. 1. Note that the negative sign in Eq. (2) does not appear in Eq. (3) so that there is no longer a pairing between the orbital energies of the perturbed system i.e. $E_{2n-i+1} \neq -E_i$.

The most important of the orbital energy levels are those of the highest occupied and lowest unoccupied orbitals since the former is related to the ionization potential (Koopman's theorem) and polarographic oxidation potential while the latter can be used to find the electron affinity and polarographic reduction potential of the molecule (see, for example, [7]). These, in turn, determine the electron acceptor and donator properties of the molecule and their importance has been recently emphasized by the PULLMANS [5]. Since there are so few experimental

Table 2. *Values of E_n^0 and E_n' in units of β for substitution at various positions in certain hydrocarbons*

Molecule	E_n^0	Position of Substitution	E_n'
Butadiene	0.9645	1	0.4036
		2	0.0964
Hexatriene	0.8201	1	0.3215
		2	0.0082
		3	0.1703
Naphthalene	0.9029	1	0.1833
		2	0.0951
Anthracene	0.7507	1	0.0943
		2	0.0862
		9	0.2046
Phenanthrene	0.8785	1	0.1178
		2	0.0351
		3	0.1403
		4	0.0588
		9	0.1614
Biphenyl	0.9546	2	0.0748
		3	0.0462
		4	0.1869
Azulene (lowest unoccupied orbital)	−0.7137	1	0.0671
		2	0.1462
		4	0.1883
		5	−0.0059
		6	0.2720
Azulene (highest occupied orbital)	0.7630	1	0.2700
		2	−0.0100
		4	0.0405
		5	0.1492
		6	0.0580

values available it is more than usually important to have reliable calculations. In Tab. 2, therefore, we give the values of the first order corrections E'_n to the energy of the lowest occupied orbital for substitution at various positions in the molecules discussed in paper I. These will be useful for considering the changes in ionization potentials and polarographic oxidation potentials when an heteroatom is introduced into the parent hydrocarbon. To find the total potentials the zero-order E^0_n are needed also and so these, too, are included in the table. For the nonalternant azulene the corresponding values of E^0_{n+1} and E'_{n+1} required to compute electron affinities and polarographic reduction potentials are also to be found in Tab. 2 but for the alternants the E^0_{n+1} and E'_{n+1} can be found from the E^0_n and E'_n by using Eqs. (2) and (3).

Table 3. *First order corrections to the orbital energies for substitution in benzene*

Position of Substitution	E'_n [a]	E'_n [a]
1	.0111	.3223
1 and 4	.0222	.6446
1 and 3; 1 and 2	.1778	.4890
1, 2 and 3; 1, 3 and 5	.5001	.5001
1, 2 and 5	.2304	.7696

The energies are in units of β. $E^0_n = 1.1740$

[a] When λ is positive the values in the first column are to be used and when λ is negative those in the second column.

The quantities in Tab. 2 refer to single substitution. For multiple substitution in the molecules in that table the new E'_n will be the sum of the individual E'_n's for the single substitutions. For benzene, however, this will not be the case since the degeneracy among the zero-order orbitals means that different combinations of these must be taken depending on the positions of the substituents. In addition, this degeneracy means that two values of E'_i must be given, one to be used when the perturbation parameter λ is positive and the other when it is negative. The first order changes needed to discuss substitutions in benzene are given in Tab. 3.

It is not the intention here to make an elaborate comparison between theory and experiment and, indeed, there is very little experimental information on heteromolecules available for such a comparison. In a few cases, however, there is a reasonable amount of accurate experimental data in the literature which can be used to check the values in Tab. 2 and 3. For example, TURNER [*8*] has given a series of experimental ionization potentials for methyl and aza substituted benzenes found using photoelectron spectroscopy and these are given in Tab. 4. The differences, $\Delta I = I - I_{\text{benzene}}$, between the ionization potentials of the heterocyclics and benzene should equal $-\lambda E'_n$. For aza substitution we have taken $\lambda = 0.36$ i.e. the value deduced in paper III [*2*] and for methyl substitution we have used $\lambda = -0.22$ which is the average of the values obtained in the same

Table 4. *Experimental Ionization Potentials of Substituted Benzenes and Theoretical Estimates of Changes from the Benzene Value*

Methyl Substitution				Aza Substitution			
Molecule	I_{exp}	ΔI_{exp}	ΔI_{theor}	Molecule	I_{exp}	ΔI_{exp}	ΔI_{theor}
toluene	8.84	−0.41	−0.34	pyridine	9.28	0.03	0.02
o-xylene	8.56	−0.69	−0.51	pyridazine	8.91	−0.34	0.31
m-xylene	8.55	−0.70	−0.51	pyrimidine	9.47	0.22	0.31
p-xylene	8.44	−0.81	−0.68	pyrazine	9.27	0.02	0.04

The units are eV. $\Delta I = I - I_{\text{benzene}}$ with $I_{\text{benzene}} = 9.25$ eV.

paper. The computed ΔI obtained in this way are also shown in Tab. 4. Apart from pyridazine where the experimental value seems out of line with those of the other heterocyclics the agreement is satisfactory. The maximum error is of the order of 2% of the total ionization potential which is certainly less than the error involved in using Koopman's theorem. Note that the electron-impact data of OMURA, BABA and HIGASI [4] predicts the ionization potentials of pyrimidine and pyridazine to be almost the same in agreement with the theoretical estimate and in disagreement with the experimental data quoted in Tab. 4.

Table 5. *Half-Wave Oxidation Potentials of Methyl Substituted Hydrocarbons*

Molecule	$\Delta\varepsilon$	E'_n
Toluene	0.32	0.32
m-xylene	0.39	0.49
o-xylene	0.41	0.49
p-xylene	0.53	0.64
1, 3, 5 trimethylbenzene	0.50	0.50
1 methylnaphthalene	0.11	0.18
2 methylnaphthalene	0.09	0.10
2, 3 dimethylnaphthalene	0.19	0.19
2, 6 dimethylnaphthalene	0.18	0.19
9 methylanthracene	0.13	0.20
9, 10 dimethylanthracene	0.22	0.41

$\Delta\varepsilon = \varepsilon - \bar{\varepsilon}$ where $\bar{\varepsilon}$ is the half-wave potential of the heteromolecule and ε that of the parent hydrocarbon. Experimental values taken from [6].

Polarographic oxidation potentials should also be proportional to E_n so that the change in the oxidation potential of a substituted hydrocarbon from the value for the parent hydrocarbon should be proportional to E'_n. This is tested in Tab. 5 where it can be seen that the theoretical and experimental values for the change in half wave potentials agree reasonably well. The constant of proportionality between the theoretical and experimental values will give the inductive parameter z_{rr} for methyl substitution and this suggests that λ is approximately -0.2 in agreement with the average value obtained in paper III.

Polarographic reduction potentials can be related to the energy of the lowest unoccupied orbital. For a good discussion see the book by STREITWIESER [7]. STREITWIESER has used Hückel perturbation theory to correlate the change in the half-wave reduction potentials of methyl substituted azulenes from the value for

Table 6. *Half-Wave Reduction Potentials of Methyl Substituted Azulenes*

Molecule	Change in Half-Wave Potential in eV		
	Experimental	Calculated (Hückel)	Calculated (SCF)
1-Methylazulene	−0.06	−0.00	−0.04
2-Methylazulene	−0.12	−0.05	−0.08
4-Methylazulene	−0.08	−0.11	−0.10
5-Methylazulene	−0.01	−0.05	0.00
6-Methylazulene	−0.08	−0.13	−0.14
1, 2-Dimethylazulene	−0.14	−0.07	−0.11
1, 3-Dimethylazulene	−0.10	−0.00	−0.07
1, 4-Dimethylazulene	−0.12	−0.13	−0.13
1, 8-Dimethylazulene	−0.10	−0.13	−0.13
4, 7-Dimethylazulene	−0.08	−0.11	−0.10
4, 8-Dimethylazulene	−0.12	−0.21	−0.20

The experimental values are taken from Ref. [3] and the Hückel values from Tab. 7.2 of Ref. [7].

azulene with the change in the orbital energy. His results and the experimental ones obtained by CHOPARD-DIT-JEAN and HEILBRONNER [3] are shown in Tab. 6. Using the self-consistent values given in Tab. 2 we have made a similar calculation taking for the perturbation parameter $\lambda = -0.11$ which is smaller than that used in Tab. 4 and 5. The smaller value does, however, lead to better agreement with experiment and STREITWIESER's Hückel values. While the agreement with experiment is not perfect the overall pattern of results is predicted quite well and the maximum differences between theory and experiment amounts only to about 5% of the total half-wave potential.

The figures in Tab. 4, 5 and 6 give reasonable cause to believe that the self-consistent perturbation theory can be used to compute ionization potentials and polarographic reduction and oxidation potentials as accurately for substituted hydrocarbons as for the parent hydrocarbons. There seems to be no reason why the same should not be true of calculations of electron affinities although there are no experimental values available to test this belief.

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