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Relationes

Perturbation Theory for Excited States of Molecules. III

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The configuration interaction perturbation theory and the single configuration perturbation theory developed in Paper I is applied to the problem of chemical reactivity for conjugated hydrocarbon molecules. Various related hetromolecules are also considered. It is found that the pattern of reactivity for excited states is much the same as for the ground state.

1. Introduction

When a reagent is brought up to a reactive position in a conjugated system the energy of the molecule changes. This change in energy provides an index of chemical reactivity. A full discussion of chemical reactivity with regard to Huckel molecular orbital theory has been given by Coulson and Longuet-Higgins [1]. They point out that the change in energy due to the approach of the reagent may arise from three causes:

(1) polarization of the non bonding and sigma electrons;
(2) steric effects;
(3) changes in the energy of the mobile π-electrons.

In this paper a comparison is made of the changes in energy due to the approach of a reagent for the ground state and excited states of a number of conjugated molecules. To treat the excited states the CIPT and SCPT methods, which were developed in Paper I, are used. The perturbed orbitals are obtained by coupled Hartree-Fock perturbation theory and may be expressed in terms of a complete set of functions (v_i). In all cases the calculations will be restricted to π-electron type calculations using the Pariser, Parr, Pople approximations, [2], so that the complete set is truncated and the matrix elements with respect to the truncated set $\{\omega_r\}$ are:

$$\langle \omega_r | h(1) | \omega_s \rangle = - \sum_{t \neq s}^{n} \gamma_{rt} \delta_{rs} + \beta_{rs}$$

$$\left\langle \omega_r \omega_s \left| \frac{1}{r_{12}} \right| \omega_t \omega_u \right\rangle = \gamma_{rs} \delta_{rt} \delta_{su}$$

$\beta_{rs} = -2.39$ eV if r and s are neighbouring atoms else 0

where the Hamiltonian for the conjugated molecule is of the form:

$$\mathscr{H} = \sum_{i=1}^{n} h(i) + \sum_{i<j}^{n} \frac{1}{r_{ij}}$$

and there is one function ω_r corresponding to each carbon atom of the conjugated system. These approximations lead to certain simplifications in the possible causes of the change of energy. Causes (1) and (2) listed above are essentially due to changes in the σ core or $\sigma - \pi$ interactions and consequently the change in energy due to these causes will be neglected in a π-electron calculation. Thus the assumptions made in this paper will be essentially the same assumptions as those made by Coulson and Longuet-Higgins who conclude that cause (3) is the principle factor in the reactivation energy.

2. Indices of Reactivity

The index of reactivity commonly used [1, 3] is the point charge index. This theory assumes that the change in total π-electron energy when a reagent approaches an atom of a conjugated system arises mainly from the induced charge at that atom. So that the change in energy when a test charge is brought close to the atom is taken to be the index of chemical reactivity at that atom. We may consider the change in π-electron energy, δE, when a test charge $\delta\alpha_r$ is brought close to an atom r by expanding in a Taylor series:

$$\delta E = \frac{\partial E}{\partial \alpha_r}\delta\alpha_r + \tfrac{1}{2}\frac{\partial^2 E}{\partial \alpha_r^2}\delta\alpha_r^2 + \cdots . \tag{1}$$

The quantities $\frac{\partial E}{\partial \alpha_r}$ and $\frac{1}{2}\frac{\partial^2 E}{\partial \alpha_r^2}$ may be obtained as first and second order energies of a perturbation using CIPT or SCPT where the perturbation matrix z_{ij} is given by:

$$z_{ij} = \langle \omega_i | z(1) | \omega_j \rangle = \delta_{ir}\delta_{jr} . \tag{2}$$

This type of perturbation will be refered to as a point perturbation. With this perturbation $\frac{\partial E}{\partial \alpha_r}$ is an approximation to the charge on the r^{th} atom of the conjugated system [3] and will be denoted by q_r. The quantities $\frac{\partial^2 E}{\partial \alpha_r^2}$ are called the atom-atom polarizabilities and will be denoted by π_{rr}.

Basically there are two types of reagent, cationoid and anionoid, reagents. One difference is that the former bear a net positive charge whereas the latter bear a net negative charge. Thus one would expect the approach of a cationoid reagent to lead to a decrease in the induced charge $\delta\alpha_r$ and the approach of a anionoid reagent to lead to a increase in $\delta\alpha_r$. One would therefore expect examining the first term of the Taylor series (1) that the cationoid reaction would be favoured by high values of q_r and anionoid reactions by low values of q_r.

The molecules considered in this paper are alternant hydrocarbons and it is well known that the charge densities at each atom, within the Pariser, Parr, Pople approximations, are unity [4]. The charge densities predicted by Hartree-Fock theory and by any combination of determinants formed from Hartree-Fock orbitals are also unity; consequently the simple picture of reactivity where the magnitude of the charge is examined is unsatisfactory. Thus it is necessary to examine π_{rr} as an index of reactivity to distinguish between the atoms of the conjugated system. In these cases for negative π_{rr} the larger the absolute value of π_{rr} the more reactive the site.

Table 1

Molecule	Atom	E(SCPT)		E(CIPT)		E(GS)
		Singlet	Triplet	Singlet	Triplet	
Diphenyl	1	−0.0589	−0.0029	−0.0609	−0.0444	−0.0554
	6	−0.1034	−0.0672	−0.1327	−0.0531	−0.0617
	5	−0.0670	−0.0543	−0.0783	−0.0521	−0.0593
	4	−0.0634	−0.0485	−0.0664	−0.0488	−0.0602
Napthalene	1	−0.0536	−0.0526	−0.0756	−0.0510	−0.0546
	2	−0.0857	−0.0446	−0.0670	−0.0468	−0.0622
	3	−0.0891	−0.0616	−0.0753	−0.0545	−0.0595
Anthracene	1	−0.0591	−0.0547	−0.0638	−0.0535	−0.0544
	2	−0.0818	−0.0515	−0.0830	−0.0579	−0.0625
	3	−0.0712	−0.0609	−0.0860	−0.0585	−0.0596
	10	−0.0763	−0.0470	−0.0765	−0.0429	−0.0676
Benzene						
$d=2.8$ Å	1	−0.00027	−0.00024	−0.00031	−0.00022	−0.00030
$d=1.4$ Å	1	−0.00427	−0.00408	−0.00466	−0.00369	−0.00453
$d=0$ (point perturbation)	1	−0.05636	−0.05402	−0.05516	−0.05169	−0.05931

In Table 1 we give the second order energies E_r^2 $(=\frac{1}{2}\pi_{rr})$ for the first singlet and first triplet states of benzene, napthalene, anthracene, and diphenyl. These are compared with E_r^2 for the ground state of these molecules. In most cases the values of π_{rr} for the various states are similar. In almost all cases SCPT and CIPT predict the same measure reactivity however there is one ambiguous case namely atom 1 of the first excited triplet of diphenyl. This may be due to the assumption made that diphenyl is planar which is known to be a poor approximation.

McWeeny, [3], has suggested a refinement or the usual index used for chemical reactivity. A reagent pictured as a test charge is not realistic and in principle the reagent causes a perturbation of the molecule that is in no sense confined to one atom. McWeeny suggests that one should take the second order energy of a perturbation by a point charge located at a distance "*d*" directly above a carbon atom. In Table 1 second order energies for such perturbations of benzene are listed where "*d*" is taken to one or two bond lenths above a carbon atom. It is clear that qualitatively the pattern of reactivity remains the same for both point perturbation and this second measure. However point perturbation predicts that the reactivity of the ground state is greater than the first singlet excited state when CIPT is used whereas the second measure predicts the reverse.

3. Reactivity for Heteromolecules

We may also define the quantities $\pi_{r,s}$ where

$$\pi_{r,s} = \frac{\partial q_r}{\partial \alpha_s} = \frac{\partial^2 E}{\partial \alpha_s \, \partial \alpha_r} = \frac{\partial q_s}{\partial \alpha_r} = \pi_{s,r} \, . \tag{3}$$

These may be used to discuss the reactivity of heteromolecules. Consider the change in charge at atom s due to a substituent at atom r. We may express the relationship as follows:

$$\delta q_s = \pi_{s,r} \, \delta \alpha_r \, . \tag{4}$$

Consequently if we know $\pi_{s,r}$ we may determine the charge density at any atom of a monosubstituted molecule. The substituent at atom r will affect the charges at the various atoms in different ways so that we may revert to the charge at an atom as the index of reactivity. The charge at any atom s of a substituted molecule is given by

$$q_s \text{ (Substituted)} = 1 + \delta q_s \, . \tag{5}$$

The inductive parameter of the substitution is $\delta \alpha_r$ and its value will depend on the type of substitutions.

If we consider one electron perturbations where the perturbation matrix is of the form

$$z_{ij} = \delta_{ir} \delta_{jr} + \delta_{is} \delta_{js} \tag{6}$$

for some r, s $r \neq s$, the first and second order perturbation energies will be estimates of $\delta E'$ and δE^2 where

$$\delta E^1 = \frac{\partial E}{\partial \alpha_r} \delta \alpha_r + \frac{\partial E}{\partial \alpha_s} \delta \alpha_s \tag{7}$$

Table 2

Substituent	Triplet or Singlet	Atom	q (substituted) CIPT
Nitrogen (parameter -2.17 eV)	S	1	1.24
	S	2	0.98
	S	3	0.90
	S	4	0.98
	T	1	1.22
	T	2	0.91
	T	3	0.95
	T	4	0.08
Methyl (parameter 0.52 eV)	S	1	0.94
	S	2	1.02
	S	3	1.01
	S	4	1.01
	T	1	0.95
	T	2	1.02
	T	3	1.01
	T	4	0.98

and

$$\delta E^2 = \tfrac{1}{2}\left(\frac{\partial^2 E}{\partial \alpha_r^2}\,\delta\alpha_r^2 + \frac{2\partial^2 E}{\partial\alpha_r\,\partial\alpha_s}\,\delta\alpha_s\,\delta\alpha_r + \frac{\partial^2 E}{\partial\alpha_s}\,\delta\alpha_s^2\right). \tag{8}$$

Thus a knowledge of $\pi_{r,r}$ for all atoms of the system will enable $\pi_{r,s}$ to be calculated perturbatively. In Table 2 q_r (substituted) is listed for a number of monosubstituted benzenes (each substituted at atom 1). The inductive parameters were taken from Table 11 in the review article by Amos and Hall [6].

4. Conclusion

We must await experimental evidence for an evaluation of the usefulness of this procedures described in this paper. It may turn out that the earlier assumptions made are invalid. In particular it may be argued that the changes in geometry of a molecule in its excited state are important so that changes in energy due to (2) cannot be neglected. It is well known that the sigma core is not the same for the ground and excited states of even the most simple conjugated systems but it is unlikely that this will affect the relatively crude methods of finding an index of reactivity outlined here.

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