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Perturbation Theory for Excited States of Molecules

2. Electric Polarizabilities

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Components of the electric polarizability tensor are calculated for a number of conjugated hydrocarbons. The methods of calculation used were the configuration interaction perturbation theory and the single configuration perturbation theory introduced in paper 1. The results obtained are compared with experiment and with Hückel calculations. It is found that there is some ambiguity in the experimental evidence. The $\sigma-\pi$ separability approximations are discussed and the relationship between Hückel theory and the single configuration method is examined.

Die Komponenten des elektrischen Polarisierbarkeitstensor werden für eine Anzahl konjugierter Moleküle mittels a) einer CI-Störungstheorie und b) einer auf einer einzelnen Konfiguration basierenden Störungstheorie berechnet. Die Resultate werden sowohl mit denen der Hückeltheorie als auch mit dem Experiment verglichen, wobei der letztere Vergleich nicht ganz eindeutig ist. Die $\sigma-\pi$-Separabilität wird diskutiert und die Relation zwischen der Hückeltheorie und der durchgeführten Störungsrechnung untersucht.

Les composantes du tenseur de polarisabilité électrique sont calculées pour un certain nombre d'hydrocarbures conjugés. Les méthodes de calcul utilisées ont été celles présentées dans l'article 1: théorie des perturbations multi ou mono configurationnelles. Les résultats obtenus sont comparés à l'expérience et aux calculs par la méthode de Hückel. Une certaine ambiguité se dégage des faits expérimentaux. Les approximations de séparabilité $\sigma-\pi$ sont discutées et l'on examine la relation entre la théorie de Hückel et la méthode mono configurationnelle.

1. Introduction

When a constant external electric field acts on a molecule the potential energy changes by $eX\Sigma x_i$ where X is the field strength and x_i the co-ordinate of the i-th electron measured from some arbitrary origin in the direction of the field. The change in energy to first order is μX where μ is the component of the dipole moment of the molecule in the field direction. In addition there is a second order effect which is quadratic in the components of the field. The coefficients α_{ij} multiplying these components transform as a second order tensor – the electric polarizability tensor. These remarks apply equally to the molecule if it is in an excited state as when it is in its ground state although the components α_{ij} will, of course, differ in the two states. Naturally the great bulk of experimental information available is for the ground state polarizabilities although experimental results are beginning to become available for the average polarizabilities of molecules in their lowest excited states.

Trsic, Uzhinov and Matzke have recently published semi-empirical calculations of excited state polarizabilities for a number of conjugated hydrocarbons [1]. However their calculations were based on Hückel theory which is not entirely satisfactory for excited states. For this reason we have thought it worth while to repeat some of these calculations using the perturbation methods developed in the first paper of this series [2]. Our calculations give only the π electron contributions to the polarizabilities so in order to make comparisons with experiment it is necessary to estimate the sigma contributions. This problem is discussed in Section 2 of the paper.

In Paper 1 we pointed out that there were several possible types of wave functions which could be used for the excited states and we developed perturbation expansions based on two of them. Since they are necessarily approximate we have thought it important to show that, nevertheless, both do give results which are independent of the origin of the co-ordinates in the potential term since otherwise any results would be entirely spurious.

We have obtained values for the average polarizabilities of several molecules in their lowest singlet state using both types of excited state wave functions and we compare these results with those of Trsic *et al.* who used the Hückel method. We also discuss the relation between the Hückel method and the single configuration method devised in Paper 1. Finally we compare the theoretical results with those experimental results which are available but find that the discrepancies are such that further experimental information is required to clarify the situation.

2. σ and π Contributions to the Polarizability

Even for the ground state of conjugated molecules the full inclusion of σ effects into a polarizability calculation has so far not been attempted. Instead, and to some extent this is to be prefered, there have been a number of papers which have shown that to within a certain degree of approximation the sigma contribution to the polarizability can be regarded as the sum of bond and atomic contributions [3, 4]. Moreover, it seems a well founded empirical fact that these local contributions are more or less invariant and so numerical values in one molecule can be transferred to another. We now wish to show that to some extent the same is true for excited states.

To be explicit, consider the ground state Hartree-Fock wave function for a conjugated molecule, i.e.

$$\Psi_0 = |\chi_1^0\alpha\chi_1^0\beta \ldots \chi_n^0\alpha\chi_n^0\beta u_1^0\alpha u_1^0\beta \ldots u_m^0\alpha u_m^0\beta| \tag{1}$$

where we assume that there are n σ-orbitals $\chi_1 \ldots \chi_n$ and m occupied π orbitals $u_1 \ldots u_m$. As is well known the σ orbitals can be well localized to form CC and CH bond and Carbon core orbitals and we assume this has been done. The π orbitals cannot, of course, be localized to the same extent. Instead they can be written as a linear sum of l (say) $2p_z$ type atomic orbitals $\{\omega_r\}$ localized about the carbon atoms, i.e.

$$u_i^0 = \sum_{r=1}^{l} a_{ir}^0 \omega_r . \tag{2}$$

The number, l, of these atomic orbitals will equal the number of carbon atoms in the molecule and for the cases we are considering $l = 2m$. Because of this there will be m virtual π orbitals which can be used to form excited states. Thus, corresponding to the configuration interaction wave function in Paper 1 we have

$$\Psi^s = \sum_I c_I S(q, p) \Psi_0 \tag{3}$$

where p and q are summed over the π orbitals only. In other words we are assuming the same sigma core for the excited states as for the ground state. This is known not to be absolutely correct but any errors arising from this can probably be allowed for by an empirical choice of σ parameters.

The effect of all this can be seen by examining Eqs. (21) and (22) of Paper 1. There will be σ effects incorporated into the $\boldsymbol{H}^{s1}$ matrix but these will only occur along the diagonal and have the same value for each configuration. Thus, in view of Eq. (20), they exactly cancel in (22) and have no effect on the $\{c_I^1\}$. Also because of the orthogonality condition in (23) there will be no σ contributions to the first term in E^2 (Eq. 21) and so the complete σ contribution to E^2, and hence to the polarizability, will arise solely from $\boldsymbol{H}^{s2}$ and is easily seen to be just $E_G^2(\sigma)$, i.e. the same as the σ contribution to the ground state. We now appeal to the papers cited earlier which have shown this contribution is the sum of local contributions arising from the change in the localized orbitals $\{\chi_i^0\}$ due to the electric field.

Now let us turn to the first order change in the π orbitals. It has been shown in Ref. [5] that this can be expressed approximately as

$$u_i^1 = \Sigma\, a_{ir}^1 \omega_r + \Sigma\, a_{ir}^0 \omega_r^1\,, \tag{4}$$

i.e. a part consisting of a change in the orbital coefficients and a part which arises from a change of the atomic basis orbitals in the presence of the field. For the ground state the latter gives rise to a contribution to the polarizability which approximately equals $l\alpha_{2_{p_z}}$ where $\alpha_{2_{p_z}}$ is the polarizability of a $2p_z$ basis orbital.

As far as excited states are concerned the change in the basis orbitals will affect $\boldsymbol{H}^s$ in three ways:

(i) through contributions to the exchange and Coulomb integrals,
(ii) through the change in the orbital energies,
(iii) through the change in E_G.

The third of these is easiest to deal with since, by exactly the same arguments as we used earlier for sigma contributions, it follows that this leads to the same increase in the excited state polarizability i.e. $l\alpha_{2_{p_z}}$ as in the ground state polarizability. The first effect i.e. the contributions to exchange and Coulomb integrals, depends on integrals like $[\omega_r^0\omega_s^0|\omega_t^0\omega_u^1]$, $[\omega_r^0\omega_s^1|\omega_t^0\omega_n^1]$ etc., i.e. two electron integrals involving the unperturbed and perturbed basis functions. It is entirely within the spirit of π-electron theory to ignore these since they are essentially $\sigma-\pi$ interaction integrals. In exactly the same way, since $\varepsilon_i^1 = \langle u_i^0|F^1|u_i^0\rangle$, and $\varepsilon_i^2 = \langle u_i^0|F^2|u_i^0\rangle + \langle u_i^0|F^1|u_i^1\rangle$, it follows that the second contribution depends on the same type of integrals as the first and thus, for the same reasons may be neglected.

Hence we can conclude that the σ orbitals and local π basis orbitals give the same contribution to the excited state as to the ground state. To remove these terms from our calculation we can therefore write

$$\alpha_{\text{excited state}} - \alpha_{\text{ground state}} = \alpha_{\text{e.s.}}^{\pi} - \alpha_{\text{g.s.}}^{\pi} \tag{5}$$

where α^{π} is the non-local π contribution. This latter may be computed by assuming that (4) may be replaced by

$$u_i^1 = \Sigma\, a_{ir}^1 \omega_r \tag{6}$$

and proceeding with the same type of calculation as in Paper 1.

3. Invariance of Polarizability with Origin

If we now consider the π contribution separately we see that the matrix elements of the perturbation become

$$z_{rs} = eX \int \omega_r x \omega_s d\tau$$

in the notation of Paper 1 [2]. Since the atomic orbitals are localized z_{rs} vanishes unless $r = s$ when the integral reduces to the x component of atom r. On physical grounds, it follows that the polarizability components should be independent of origin and, of course, a complete and accurate calculation would lead to an origin-independent result. Since however we are using approximate methods it behoves us to show that as a result of the approximations we do not get results which depend on the choice of origin. To do this consider a change of origin

$$\bar{x}_r = x_r - x\,. \tag{7}$$

If we consider the coupled Hartree-Fock perturbation equations (equations 4–9 of paper [2]) it is easy to see that the new first order orbital energies are related to the old energies by the relation

$$\bar{\varepsilon}_i^1 = \varepsilon_i^1 - x\,. \tag{8}$$

From this relation it follows that:

$$\bar{\varepsilon}_i^1 - \bar{F}^1 = \varepsilon_i^1 - F^1\,, \tag{9}$$

$$\bar{\varepsilon}_i^1 - \bar{\varepsilon}_j^1 = \varepsilon_i^1 - \varepsilon_j^1\,, \quad \text{for all } i,j\,. \tag{10}$$

$$\bar{\varepsilon}_i^2 = \varepsilon_i^2\,, \tag{11}$$

$$\bar{u}_i^1 = u_i^1\,, \tag{12}$$

and

$$\bar{u}_i^2 = u_i^2\,. \tag{13}$$

where in each case the bar denotes "after change of origin".

If we now examine the matrices H_{IJ}^1 and H_{IJ}^2 defined in equations 14–18 of Paper 1 we see that the only changes due to transfer of origin occur in the diagonal elements and are respectively the changes in the first and second order ground state energies ΔE_G^1 and ΔE_G^2.

Now

$$E_G^2 + \Delta E_G^2 = \sum_{\substack{\text{occ}\\ i}} \langle \bar{u}_i^0 | \bar{z} | \bar{u}_i^1 \rangle\,. \tag{14}$$

Therefore

$$\Delta E_G^2 = - \sum_{\substack{\text{occ}\\ i}} \langle u_i^0 | u_i^1 \rangle x = 0\,. \tag{15}$$

Thus the change in polarizability for the excited state due to the change of origin is given by

$$\Delta E = \Delta E_G^1 \sum_{IJ} C_I^0 C_I^1 \tag{16}$$

which is zero by virtue of the normalisation conditions for $\{C_I\}$.

We may therefore conclude that the polarizabilities calculated by this perturbation method are invariant with respect to a change of origin.

4. Comparison with Hückel Type Calculations

The purpose of this section is to relate our single configuration method to the Hückel type calculations described by Trsic, Uzhinov and Matzke. To do this we use their notation so that we consider a $2n$ π electron system with the lowest excited singlet state being represented by the singly excited configuration $S(n+1, n)\Psi_0$.

A simple re-arrangement of formula (9) of Trsic *et al.* shows that the Hückel result for the polarizability in the z-direction is

$$\alpha_{\text{e.s.}}^\pi = \alpha_G^\pi + 2 \sum_{k \neq n} \frac{|\langle u_k^0 | z | u_n^0 \rangle|^2}{e_n - e_k} + 2 \sum_{l \neq n+1} \frac{|\langle u_l^0 | z | u_{n+1}^0 \rangle|^2}{e_l - e_{n+1}} \tag{17}$$

where $\{e_k\}$ are the Hückel orbital energies. The corresponding single configuration result is

$$\alpha_{\text{e.s.}}^\pi = \alpha_G^\pi + 2\varepsilon_n^2 - 2\varepsilon_{n+1}^2 + C \tag{18}$$

where C represents the contribution from the Coulomb and exchange terms. Since

$$\varepsilon_i^2 = \langle u_i^0 | F^2 | u_i^0 \rangle + \langle u_i^0 | F^1 | u_i^1 \rangle \tag{19}$$

and because

$$u_i^1 = \sum_{j \neq i} \frac{\langle u_i^0 | F^1 | u_j^0 \rangle}{\varepsilon_i^0 - \varepsilon_j^0} u_j^0 \tag{20}$$

it follows that (17) is equivalent to

$$\begin{aligned} \alpha_{\text{e.s.}}^\pi = \alpha_G^\pi &+ 2 \sum_{k \neq n} \frac{|\langle u_n^0 | F^1 | u_k^0 \rangle|^2}{\varepsilon_n^0 - \varepsilon_k^0} - 2 \sum_{l \neq n+1} \frac{|\langle u_{n+1}^0 | F^1 | u_l^0 \rangle|}{\varepsilon_{n+1}^0 - \varepsilon_l^0} \\ &+ 2\langle u_n^0 | F^2 | u_n^0 \rangle - 2\langle u_{n+1}^0 | F^2 | u_{n+1}^0 \rangle + C . \end{aligned} \tag{21}$$

Thus the first three terms have the same form as the Hückel result except that the operator z in the matrix elements is replaced by the self-consistent first order term F^1. This is very similar to what is found in ground state calculations where again, the self-consistent and Hückel formulas have the same form except that where, in the latter case, the operator z occurs, in the former case it must be replaced by the operator F^1. For excited states, however, we see that there are extra terms which occur in the single configuration method which are not to be seen in the Hückel results. These are the terms arising from F^2 and from the Coulomb and exchange integrals.

Table 1

Perturbation at atom	E^2 Hückel P.T.	E^2 S.C.P.T.	E^2 C.I.P.T.
1	−0.066	−0.064	−0.070
2	−0.095	−0.113	−0.120

The second order perturbation energy of trans butadiene computed by three methods and with the perturbation restricted to a single atom (cf., Paper 1 [2]).

In order to examine how well the Hückel and single configuration interaction results agree we have essentially repeated the calculations of Paper 1 and computed second order energies for the first excited singlet state of *trans*-butadiene. The perturbations were of the same type as in Paper 1 where the perturbations are confined to one atom so that the E_2 represent, in effect, excited state atom-atom polarizabilities.

The results of using the single configuration, configuration interaction and Hückel methods are given in Table 1. The Hückel results appear to correspond closely to the single configuration results. This correspondence is reinforced, as we shall see in the next section, when we compare Hückel and single configuration electric polarizabilities.

5. Results and Discussion

In Table 2 we give the π contribution to the electric polarizability components for the long and short axes of a number of conjugated molecules calculated by configuration interaction and single configuration methods. All of the molecules were assumed planar, even diphenyl although this is a very bad approximation. The values of the β and γ integrals used are as follows:

$$\beta_{ij} = \begin{cases} -\sum\limits_{k} \gamma_{ik} + \gamma_{ii} & \text{if } i = j\,, \\ -2.39 \text{ eV} & \text{if } i \text{ and } j \text{ are neighbours}\,, \\ 0 & \text{otherwise}\,, \end{cases}$$

$$\gamma_{ij} = \begin{cases} 11 \text{ eV} & \text{if } i = j\,, \\ 7.1 \text{ eV} & \text{if } i \text{ and } j \text{ are neighbours}\,. \end{cases}$$

The remaining γ integrals were computed on the assumption of a classical electrostatic model representing the charge distribution in a π orbital by $\frac{1}{2}$ unit charge 0.82 Å above and below the carbon nucleus. The CC bond length were all taken to be 1.4 Å and all the angles 120°, as is generally done for ground state calculations. Although it is true that molecular geometry changes in the excited state and, therefore, should give rise to slightly different values of the integrals we believe that to attempt to include these effects would be grossly over elaborate in view of the relative crudity of the basic $\sigma - \pi$ model.

For the purpose of comparison with the Hückel results of Trsic *et al.*, in Table 3 we give the average π polarizabilities $\bar{\alpha} = \frac{1}{3}(\alpha_x + \alpha_y)$. The results computed

Table 2

Molecule	CI		S.C.	
	α_L	α_S	α_L	α_S
Anthracene	756.8	179.8	692.8	168.3
Azulene	153.9	103.2	152.2	99.4
Diphenyl	339.5	112.4	341.8	122.2
Phenanthrene	353.6	166.3	582.5	224.5
Naphthalene	311.4	127.5	350.5	139.9
Benzene	64.85	64.85	—	—
trans-Butadiene	238.5	18.76	194.50	18.70
cis-Butadiene	152.5	44.96	142.08	44.96

π contributions to the diagonal elements of the polarizability tensor computed by the two methods of Paper 1. [Units of 10^{-25} cm^3. L and S refer to the long and short axes of the molecule. For the butadienes the long axis is taken to be that joining atoms 2 and 4 for *trans* and 2 and 3 for *cis*.]

Table 3

Molecule	C.I.P.T.	S.C.P.T.	Hückel
Anthracene	312.21	287.05	279.6
Azulene	85.7	83.87	114.7
Diphenyl	150.64	154.67	385.2
Phenanthrene	173.3	269.0	338.7
Naphthalene	146.3	163.5	147.4
Benzene	43.23	—	—
cis-Butadiene	65.82	62.34	—
trans-Butadiene	85.75	71.07	—

π contribution to the average polarizability in the lowest singlet excited state computed by three different methods [units are 10^{-25} cm^3 for columns 1 and 2 and $e^2d^2\beta^{-1}$ for column 3. For conversion factor for column 3 see text]. For naphthalene the state is the second lowest (B_{2u}) state.

in this paper are in units of 10^{-25} cm^3 but the Trsic results are in units of $e^2d^2\beta^{-1}$ where d is the average CC bond lenth and β is the Hückel β for the excited state. It is a little difficult to say exactly what these values ought to be, but, roughly speaking, and in view of the ground state values given in the same paper, a fairly sensible conversion factor to 10^{-25} cm^3 would be ~ 100.

With this conversion factor we see that the agreement between the Hückel and single configuration values is not too bad as we might have expected from the butadiene results in the previous section. The exceptions to this are azulene, which is a non-alternant and where Hückel and self-consistent treatments often differ, and diphenyl which we have treated as planar whereas Trsic *et al.* have, more correctly, allowed for the twisting about the centre bond.

On the other hand, if we compare the single configuration values with what are presumably the more accurate configuration interaction ones the situation is less satisfactory. In some cases the two differ only marginally whereas in others e.g. naphthalene and phenanthrene, there is relatively more change. We can find no pattern in these differences and, it may be recalled, we were confronted with a

Table 4

Molecule	$\Delta\alpha$ theoretical		$\Delta\alpha$ experimental
	S.C.P.T.	C.I.P.T.	
Benzene	—	2.16	105.7
Naphthalene	79.5	62.3	171.2
Anthracene	146.7	171.9	425.6
Phenanthrene	140.0	44.3	186
Azulene	18.8	17	21

Comparison of theoretical and experimental values of $\Delta\alpha$, the difference between the ground and excited state average polarizability [units of 10^{-25} cm^3].

similar situation for the butadiene atom-atom polarizabilities in Paper 1. As we pointed out then, it seems that the only safe procedure is to compute values using the configuration interaction method.

Finally, let us compare the theoretical values with the experimental ones. To do this we must first include σ contributions. In view of the results obtained in Section 2 i.e. that the σ contributions are approximately the same in the ground and excited states, it seems that the most satisfactory comparison is between theoretical and experimental values of $\Delta\alpha = \bar{\alpha}_e - \bar{\alpha}_g$, i.e. the difference between the average polarizability in the ground and excited states, since the theoretical value is just the difference between the π values. The values of $\Delta\alpha$ are given in Table 4, the theoretical values of $\bar{\alpha}_g(\pi)$ being taken from Ref. [5] (since no diphenyl ground state values was computed there we have omitted it from the table) and the experimental values from Ref. [1].

It can be seen immediately that there is no agreement between theory and experiment, in most cases the experimental values being enormously larger than the theoretical ones. It is just possible that different σ effects between ground and excited state could explain these differences but, since one would expect these to be more or less the same for anthracene as for phenanthracene and for azulene as for naphthalene, this seems unlikely.

The experimental results we have quoted are based on Abe's theory [6] which relates polarizabilities of the ground and excited states to solvent – shift effects and his equations are known to lead to large values of the excited state polarizabilities. In anthracene, for example, the excited state polarizability is predicted by this method to be almost three times that of the ground state! An alternative method of obtaining α values from solvent – shift data is due to Suppan [7]. It seems to be believed that Suppan's approach would give excited state polarizabilities quite close to those of the ground state which would fit our theoretical values for benzene, naphthalene and azulene but not for the larger molecules. However, so far as we know, the only estimated value of α obtained in this way for the molecules we have considered is the value of $\Delta\alpha = 20$ for naphthalene which certainly agrees with the order of magnitude of our best calculation. It would clearly be helpful to have more experimental information on this topic since until the experimentalists agree we are at a loss to say whether or not our perturbation methods are adequate to compute excited state properties.

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