Theoret. Chim. Acta (Berl.) 36, 1 – 10 (1974)

Perturbation Theory for Excited States of Molecules

5. Polarizabilities of Singlet and Triplet Excited States of Conjugated Molecules

B. L. Burrows
Department of Mathematics, The Polytechnic, Stafford

A. T. Amos
Department of Mathematics, The University, Nottingham

Received May 28, 1974

Components of the electric polarizability tensor are calculated for the three lowest singlet and three lowest triplet excited states of a number of conjugated molecules. The method used is the configuration interaction perturbation theory described in the first two papers of this series. A simpler method based on Hückel theory is examined and found to be unsatisfactory.

Key words: Electric polarizability tensor – Polarizability tensor, electric, components of ~

1. Introduction

Lately there have been a number of papers concerned with the calculation of excited-state polarizabilities of conjugated molecules [1–5]. These have all dealt only with pi electrons and in some cases Hückel theory has been used and in others the Pariser-Parr-Pople scheme has been adopted. A recent study of the polarizabilities of the singlet and triplet excited states of ethylene [1] has emphasized the importance of correlation effects which suggests that the most satisfactory procedure for the calculation of excited-state polarizabilities is one based on multi-configurational interaction wave functions which include doubly-excited configurations.

The configuration interaction method which we have described and used previously [2, 6] does have this desirable property and, therefore, we have felt it worthwhile to extend our calculations to states other than the strongly-excited singlet p state. Up to now practically all attention has been focussed on this one state and it seems more than time to obtain some information concerning the other low-lying excited states and to consider triplet states as well as singlets.

Given that the multi-configuration method can be used to compute satisfactory values for excited-state polarizabilities, an obvious question to arise is whether a simpler method would do as well. For it is undeniable that the multi-configuration method is very time consuming and, as the size of molecule increases, so do the difficulties of applying the method. Therefore, if, as seems likely, more and more experimental values become available with the consequent need for more theoretical calculations, a simpler method would be very welcome. In the third section of this note we investigate the simplest of all simple methods – the Hückel method. Our conclusion is that while it works quite well for the strongly-excited *p* singlet state of the polyacenes it is not so satisfactory for the other singlet states or for the triplets.

2. Configuration-Interaction Polarizability Calculations

Using the configuration-interaction method (C.I.P.T.) described in Ref. [6] we have computed the polarizability components of the three lowest singlet excited states and the three lowest triplet excited states of the first three molecules in the polyacene series and of benzene, phenanthrene, azulene, butadiene and hexatriene. The results are given in Table 1. For comparison we also give the ground-state results for the same molecules, computed with the same parameter values. Earlier we published polarizability components for the *p* singlet states of some of the molecules considered here [2]; there are minor changes due to differences between parameters and numerical round off. These are not significant except in the case of naphthalene where the old results are in error and should be replaced by the ones given here.

We should emphasize that the calculation uses mono-excited configurations built up from the perturbed molecular orbitals and, thus, relative to the unperturbed orbitals will, in fact, include doubly excited configurations the importance of which has been stressed by Tyutyulkov and Kanev [1]. In principle C.I.P.T. uses all mono-excited configurations (and further configurations would neces-

Table 1. Polarizability components and the average polarizabilities of the ground state, the lowest three singlet states and the lowest three triplet states of a number of molecules. Only the contribution from the pi electrons is given and this will be zero when the field is perpendicular to the plane. Units are 10^{-25} cm^3. Also given is the excitation energy of the excited states in cm^{-1}. For butadiene and hexatriene the long axis is taken to be that joining carbon atoms 1 and 3

Molecule	State	Excitation Energy	Polarizability Long axis	Short axis	Average
Benzene	Ground state	—	62	62	41
	Singlets	39,273	65	65	43
		46,627	83	83	55
		56,160	82	82	54
	Triplets	26,651	45	45	30
		34,869	75	75	50
		34,869	77	77	52
Naphthalene	Ground state	—	152	100	84
	Singlets	33,555	193	96	96
		36,207	358	146	168
		45,481	133	138	90
	Triplets	18,737	147	100	82
		28,419	111	115	75
		30,305	212	92	101

Table 1 (continued)

Molecule	State	Excitation Energy	Polarizability		
			Long axis	Short axis	Average
Anthracene	Ground state	—	272	149	140
	Singlets	29,446	761	182	314
		31,258	397	136	178
		38,102	546	197	248
	Triplets	12,781	278	131	136
		23,886	257	159	138
		29,088	413	132	182
Tetracene	Ground state	—	417	206	207
	Singlets	25,553	1281	219	500
		32,253	671	195	285
		33,145	834	230	354
	Triplets	13,117	299	158	152
		19,768	338	204	181
		28,399	−26	216	63
Phenanthrene	Ground state	—	244	145	129
	Singlets	31,998	368	167	178
		35,023	483	231	238
		40,449	252	142	131
	Triplets	20,263	181	152	111
		27,574	259	218	159
		29,104	303	132	145
Azulene	Ground state	—	198	110	103
	Singlets	16,013	154	103	86
		26,492	212	131	114
		35,699	201	110	104
	Triplets	13,186	207	132	113
		15,327	157	89	82
		20,645	211	115	109
Trans Butadiene	Ground state	—	93	16	36
	Singlets	41,799	240	19	86
		54,082	−6	12	2
		55,857	95	15	37
	Triplets	13,925	78	6	28
		54,082	42	9	17
		54,562	490	18	169
Hexatriene	Ground state	—	208	26	78
	Singlets	34,548	524	28	184
		46,075	1	22	8
		50,314	506	30	179
	Triplets	9,808	195	13	69
		21,740	163	16	60
		30,608	119	18	46

Table 2. The long-axis component of the pi electron contribution to the polarizability of the first singlet excited state of tetracene computed with 2, 9, 16, 25, and 36 configurations

Number of Configurations	α_L for 1*st* excited singlet (B_{2u})
2	1179
9	993
16	1095
25	1281
36	1364

sitate a change in the ground-state function for consistency) but in the present calculations for anthracene, phenanthrene and tetracene a limited form of C.I.P.T. was used and only 25 configurations were included. Previous calculations for the *p* singlet of anthracene and phenanthrene using all 49 mono-excited configurations are in good agreement with the results in this paper which leads us to think that it is a reasonable approximation. However, in Table 2 the long-axis component of the pi electron contribution to the polarizability of tetracene for the first singlet excited state is given using various forms of limited C.I.P.T. These results are disturbing since they show that it is necessary to use a large number of configurations to get reliable estimates of the polarizability components. Thus limited C.I.P.T. should be used with caution. It is probably safest to increase the number of configurations used in the limited C.I.P.T. until the results obtained become reasonably consistent and settle on one value.

For the record the values of the Pariser-Parr-Pople parameters used in the calculation are as follows:

For a pi electron basis $\{\omega_r\}$

$$\left\langle \omega_r\omega_s \left| \frac{1}{r_{12}} \right| \omega_u\omega_v \right\rangle = \gamma_{rs}\delta_{ru}\delta_{sv}$$

where

$$\gamma_{rs} = 11\ \text{eV} \quad \text{if} \quad r = s$$
$$= 7.1\ \text{eV}$$

if *r* and *s* are neighbours and otherwise is calculated using an electrostatic model where the pi orbital is represented by $\frac{1}{2}$ unit charge 0.82 Å above and below the carbon atom.

$$\langle \omega_r | h_{\text{core}} | \omega_s \rangle = -\sum_{k \neq r} \gamma_{kr}, \quad r = s$$
$$= -2.39\ \text{eV}, \quad r \text{ and } s \text{ neighbours}$$
$$= 0, \quad \text{otherwise}.$$

It should be understood that the figures given in Table 1 refer only to the contribution to the polarizabilities from the pi electrons. They have to be supplemented by contributions from the sigma electrons to give the total polarizabilities. The sigma contributions are usually and quite properly obtained by using bond polarizability values for the CH and CC bonds. Both empirical and theoretical values of these are available but since, in our view, these available values are quite old and need revision, we have not thought it worthwhile to give the sigma contributions.

It is generally assumed that the sigma contribution is the same for the ground and excited states. If this is so, or nearly so, the significant quantity will be the difference between the ground and excited state polarizabilities.

When these differences are examined it will be seen that they fall into an obvious pattern. For the polyacenes, the lowest singlet is the *p* state in the Clar classification (for naphthalene, however, the *p* state is second lowest) and this state has a much higher polarizability than the ground state.

The second lowest state is the α state (the lowest state for naphthalene) and this differs relatively little from the ground state. Notice that any changes occur because of the change in the long-axis component of the polarizability; the short-axis component remains much more constant. As might be expected the phenanthrene results lie between those of naphthalene and anthracene. Surprisingly the azulene polarizabilities do not resemble those of naphthalene at all and it is interesting to see that the lowest excited state actually has a smaller polarizability than the ground state.

The triplet states of these molecules show very much less variation in polarizability than the singlet states and differ only slightly from the ground state. The third lowest triplet of tetracene is the exception but this is nearly degenerate with the fourth lowest which, in fact, has polarizability values more in line with the others given in the table.

The polyene results in no way resemble those of the ring systems and it is argueable that the method we have adopted is not a very satisfactory one for these molecules. Therefore the results should be treated with caution. However they do show what would be expected intuitively, namely the very small short-axis[1] component which remains more or less the same in ground and excited states. The long-axis component is much more variable being generally large although for the second excited state it becomes near to zero or actually negative.

3. Hückel Theory

We now wish to examine whether simple Hückel theory can be used to obtain theoretical values of excited-state polarizabilities. Suppose we consider an alternant hydrocarbon with $2n$ pi-electrons. Let us denote the orbital energies of the occupied orbitals by $E_1, E_2, E_3 \ldots E_n$ in order of decreasing energies. If these are calculated by the Hückel method they will be given by

$$E_k = \tilde{\alpha} + \varepsilon_k \beta$$

---

[1] Note that the short and long axes do not necessarily exactly coincide with the principal axes of the polarizability tensor in the case of the polyenes. For the other molecules they will on symmetry grounds.

where $\tilde{\alpha}^2$ and β are the Hückel parameters and ε_k is a dimensionless parameter. The total ground-state energy will be

$$E = 2 \sum_{k=1}^{n} E_k .$$

If the molecule is perturbed by an electric field of magnitude λ the E_k will change. Provided the field-potential is taken to be zero at the centre of molecular charge, for alternant hydrocarbons the first-order term will be zero so that

$$E_k = \tilde{\alpha} + \varepsilon_k \beta + \lambda^2 \varepsilon_k'' \gamma$$

where γ is a parameter which depends on the units chosen to represent the potential of the electric field.

Consequently the second order change in E will be $E'' = 2\gamma \sum_{k=1}^{n} \varepsilon_k''$ so that the polarizability is given by

$$\alpha = -4\gamma \sum_{k=1}^{n} \varepsilon_k'' .$$

The circumstances of most calculations are such that γ will be in units of $c^2 d^2 \beta^{-1}$ where d is the average CC bond length, usually taken to be 1.4 Å. Our interpretation of this β is that it should equal the average nearest-neighbour element in the SCF Pariser-Parr-Pople Hamiltonian for the molecule under consideration. This means that β lies between -5.0 and -4.5 eV. If this order of magnitude value is adopted for β and the above equation for α is used then there is quite satisfactory agreement between Hückel and SCF polarizabilities for the ground state.

To examine excited states we need the orbital energies of the virtual orbitals which we denote by $E_{\bar{1}}$, $E_{\bar{2}}, \ldots E_{\bar{n}}$ in order of increasing energy. For alternant hydrocarbons the energies of the virtual orbitals and occupied are related by pairing theorems [7, 8] so that

$$E_{\bar{k}} = \tilde{\alpha} - \varepsilon_k \beta$$

and, when an electric field is applied,

$$E_{\bar{k}} = \tilde{\alpha} - \varepsilon_k \beta - \lambda^2 \varepsilon_k'' \gamma .$$

Consider now an excited state obtained by an excitation from an occupied orbital ϕ_l to a virtual orbital $\phi_{\bar{m}}$. The total energy will be

$$E = 2 \sum_{k=1}^{n} E_k + E_{\bar{m}} - E_l$$

so that the polarizability is given by

$$\alpha = -2\gamma \left[2 \sum_{k=1}^{n} \varepsilon_k'' - \varepsilon_m'' - \varepsilon_l'' \right],$$

---

[2] The tilda is just to distinguish it from the polarizability α.

or the change in polarizability $\Delta\alpha(l\to\bar{m})$ relative to the ground state by

$$\Delta\alpha(l\to\bar{m})=2\gamma(\varepsilon''_l+\varepsilon''_m)\,. \tag{1}$$

Of course this is a very approximate result indeed, since it totally ignores the proper treatment of exchange and the fact that there are degeneracies between the states $l\to\bar{m}$ and $m\to\bar{l}$.

For naphthalene we obtain the following values of the ε''_i:—Electric field in long-axis direction: $\varepsilon''_1=-0.8536$ $\varepsilon''_2=-2.0000$. Electric field in short-axis direction: $\varepsilon''_1=-0.1727$ $\varepsilon''_2=0.1250$. Equation (1) then implies that for the lowest state (the α state), $\Delta\alpha(\text{long axis})\approx 300.10^{-25}\,\text{cm}^3$ and $\Delta\alpha(\text{short axis})\approx 5.10^{-25}\,\text{cm}^3$. For the p state $\Delta\alpha(\text{long axis})\approx 200.10^{-25}\,\text{cm}^3$ and $\Delta\alpha(\text{short axis})\approx 40.10^{-25}\,\text{cm}^3$. The results for the p state are satisfactory but for the α-state they are completely wrong.

For butadiene we find the following values for the ε''_i:—Electric field in long-axis direction: $\varepsilon''_1=-0.0556$ $\varepsilon''_2=0.6006$. Electric field in short-axis direction: $\varepsilon''_1=0.0596$ $\varepsilon''_2=0.0193$. Equation (1) implies, therefore, that for the lowest state $\Delta\alpha(\text{long axis})\approx 10.10^{-25}\,\text{cm}^3$, $\Delta\alpha(\text{short axis})\approx -10.10^{-25}\,\text{cm}^3$, and for the second lowest $\Delta\alpha(\text{long axis})\approx -60.10^{-25}\,\text{cm}^3$, and $\Delta\alpha(\text{short axis})\approx -8.10^{-25}\,\text{cm}^3$. Clearly these do not at all correspond to the configuration-interaction results.

The above assumes that the Hückel theory results are applicable to singlet excited states but, of course, since the two-electron terms in the Hamiltonian are not properly treated the results should be applicable to the triplet states as well. Obviously these Hückel results correspond to the configuration-interaction results even less well for the triplet states than for the singlets.

Our conclusion is, therefore, that Hückel theory cannot be applied to the calculation of excited-state polarizabilities with any confidence. We might add that we have attempted to make more satisfactory calculations using Hückel orbitals by including Coulomb and exchange integrals and treating any degeneracies in a proper manner but while this does give rather better results than the crude Hückel formula they are still unsatisfactory.

Needless to say this disappointing conclusion does not apply to ground-state polarizabilities where Hückel calculations give very satisfactory results. And we also must recognize that for the p-singlet states of ring molecules the Hückel values seem to be in agreement with the more accurate calculations (see naphthalene above and Table 3 of Ref. [2]) but this agreement cannot be regarded as anything but fortuitous.

4. Comparison between Theoretical and Experimental Values

By making electro-optical absorption experiments, Liptay *et al.* [9] were able to estimate certain components of the polarizability tensors in the ground and first excited singlet state of some aromatic hydrocarbons and some tetraphenyl polyenes. For anthracene and tetracene they were able to determine the short-axis component and the average polarizabilities. To facilitate comparison with our theoretical results it is convenient to consider the experimental values for the differences between the ground and p excited state since this avoids having to include sigma terms. The changes in the average polarizabilities are of the order of 160.10^{-25} cm^3 for anthracene and 260.10^{-25} cm^3 for tetracene although the experimental error may be sufficient to change the second figure by as much as ± 2. Nevertheless there is quite clearly good agreement between the theoretical and experimental values. The changes in the short-axis components are 60 ± 40.10^{-25} cm^3 for anthracene and 150 ± 60.10^{-25} cm^3 for tetracene. These are not in good agreement with the theoretical values although the situation is rather confused by the large experimental uncertainties.

The experimental results obtained by Liptay *et al.* for the tetraphenyl polyenes are not directly comparable with our theoretical results for the polyenes since the phenyl group will considerably enhance the polarizability and in any case we do not consider our results for the polyenes to be particularly satisfactory. However, Liptay *et al.* do find enormous increases in the long-axis components in going from the ground to first excited state and these increases become more pronounced as the chain length increases. Relatively speaking the short-axis components change much less. These general features are mimicked by our polyene calculations although we emphasize that the numerical values are an order of magnitude smaller.

By observing the Stark effect on molecules held in a polystyrene matrix, Barnett, Kurzmack, and Malley [10] have obtained values for the change $\Delta(\frac{1}{2}\alpha_x + \alpha_y + \alpha_z)$ (x is the short-axis direction) between the ground and first excited state in anthracene and tetracene. Their experimental values are 36 Å^3 and 62 Å^3 while the theoretical ones from Table 1 are 50 Å^3 and 87 Å^3 so that the agreement is only qualitative.

Varma and Oosterhoff [11] have experimentally determined the change in the average polarizability of tetracene while Meyling and Wiersma [12] have obtained the change in the long-axis component for the same molecule in both cases between the ground and first excited state. These two results are 42.5 Å^3 which is rather larger than our theoretical value and 4.5 Å^3 which differs considerably from both the theoretical values and other experimental ones.

Very recently Mathies and Albrecht [13] have obtained experimental values for the average polarizabilities and the short-axis components of the polarizability tensor for the α excited states of benzene and naphthalene and the p excited states of naphthalene and anthracene. For the p states their results in Å^3 relative to the ground-state values are $\Delta\alpha = 9.7$, $\Delta\alpha_s = 9.5$ for naphthalene and $\Delta\alpha = 17$, $\Delta\alpha_s = 8$ for anthracene. The $\Delta\alpha$ values agree well with the theoretical ones but the $\Delta\alpha_s$ experimental and theoretical results differ by a factor of two. For the α states the experimental results are $\Delta\alpha = 1.2$, $\Delta\alpha_s = 1.8$ for benzene and $\Delta\alpha = 1.9$, $\Delta\alpha_s = -0.1$ for naphthalene. These agree with our theoretical results in the case of naphthalene but not in the case of benzene. We should add that our theoretical values differ considerably from those obtained by Mathies and Albrecht for the α states.

Recently Barker, Noe, and Marchetti [14] have measured the change in the long-axis component of the polarizability of azulene in going from the ground state to the first excited state. The value they obtain is -35.10^{-25} cm^3 which is in fair agreement with the theoretical value of -44.10^{-25} cm^3. What is particularly pleasing, of course, is that both theory and experiment agree that the first excited state has a smaller polarizability than the ground state.

Table 3. Solvent shifts and polarizability changes

Molecule	Excited state	$\Delta\nu$[16][a]	$\Delta\alpha$[b]
Naphthalene	α	275	12
	p	900	84
Anthracene	p	865	84
Tetracene	p	855	231
Phenanthrene	α	200	49
	p	1010	109

[a] In cm^{-1} to nearest 5 cm^{-1}.
[b] In units of 10^{-25} cm^3.

On the assumption that the dispersion force between two molecules can be approximated by the London formula which relates it to the polarizabilities of the molecules, it should be possible to use data on solvent-shift effects to find estimates of the difference of the polarizability of a solute molecule in its ground and excited state. We have recently pointed out the considerable uncertainty of the polarizability values obtained in this way [15] but now that we have more theoretical values it is perhaps worthwhile to reconsider this point.

The relationship between the solvent shift $\Delta\nu$ and polarizability change $\Delta\alpha$ when all minor terms are neglected takes the form

$$\Delta\nu = \frac{C}{f}\Delta\alpha \tag{2}$$

where C is a constant which depends on the solvent and f depends on the size of the solute molecule, so that f is roughly proportional to the number of benzene rings in the solute molecule. In Table 3 we give values of $\Delta\nu$ measured by Robertson *et al.* [16] for various different excitation energies of a number of aromatics in the solvent *n*-pentane. It seems to us quite clear that no relationship of the form (2) can relate these values of $\Delta\nu$ and $\Delta\alpha$. This we believe is due to the inadequacy of the London approximation and, hence, of Eq. (2) rather than any error in the theoretical values of $\Delta\alpha$.

References

1. Tyutyulkov, N. N., Kanev, I. M.: Compt. Rend. Bulg. Acad. Sci. **26**, 919 (1973)
2. Amos, A. T., Burrows, B. L.: Theoret. Chim. Acta (Berl.) **23**, 327 (1972)
3. Trsic, M., Uzhinov, B. M., Matzke, P.: Mol. Phys. **18**, 851 (1970)
4. Matzke, P., Chacon, O., Sanhueza, E., Trsic, M.: Int. J. Quantum Chem. **4**, 407 (1972)
5. Espinoza, Ll., Trsic, M., Sanhueza, E.: Chem. Phys. Letters **22**, 154 (1973)
6. Amos, A. T., Burrows, B. L.: Theoret. Chim. Acta (Berl.) **22**, 283 (1971)
7. Koutecky, J.: J. Chem. Phys. **44**, 3702 (1966)
8. Amos, A. T.: Theoret. Chim. Acta (Berl.) **7**, 20 (1967)
9. Liptay, W., Walz, G., Baumann, W., Schlosser, H.-J., Deckers, H., Detzer, N.: Z. Naturforsch. **26**a, 2020 (1971)

10. Kurzmack, M.A., Malley, M.M.: Chem. Phys. Letters **21**, 385 (1973); Barnett, G.P., Kurzmack, M.A., Malley, M.M.: Chem. Phys. Letters **23**, 237 (1973)
11. Varma, C.A.G.O., Oosterhoff, L.J.: Chem. Phys. Letters **8**, 1 (1971)
12. Meyling, J.H., Wiersma, D.A.: Chem. Phys. Letters **20**, 383 (1973)
13. Mathies, R., Albrecht, A.C.: J. Chem. Phys. **60**, 2500 (1974)
14. Barker, J.W., Noe, L.J., Marchetti, A.P.: J. Chem. Phys. **59**, 1304 (1973)
15. Amos, A.T., Burrows, B.L.: Theoret. Chim. Acta (Berl.) **29**, 139 (1973)
16. Robertson, W.W., Weigang, O.E., Matsen, F.A.: J. Mol. Spectry. **1**, 1 (1959)

Dr. A. T. Amos
Department of Mathematics
The University of Nottingham
University Park
Nottingham NG7 2RD, England