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A Perturbational Molecular Orbital Method for the Absorption Spectra of Aromatic Compounds

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ABSTRACT

Core potentials required for self-consistent field (scf) molecular orbital calculations of the spectra of π-electron systems can be expressed by functions of the Slater nuclear charge and the apparent core charge. The core potentials of a perturbed π-electron system are reasonably evaluated using these functions. A novel first order perturbation method is suggested to analyze spectral change by small variations of the core. The spectra of aza and azonia aromatic compounds can be estimated by this perturbation method. The spectra of azobenzene, anthraquinone and its diimine are discussed on the basis of the spectra of their corresponding hydrocarbons. An unusual effect on the spectrum of azulene by a methyl substituent can be successfully explained by the first order perturbation method.

1 INTRODUCTION

Approximate molecular orbital theory has been widely used to understand the electronic spectra of aromatic compounds.[1] The most convenient method, the self-consistent field (scf) procedure, is by nature semi-empirical in order to avoid difficulties of the *ab initio* evaluations of many energy integrals.[2,3] Although the method has ambiguity in evaluation of the energy integrals, such as atomic integrals of core potential and electron repulsion, it can be simply applied to large molecules such as dyes. It has also the advantage of the possibility of modification of these integrals to match the potential field on a molecule.

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The evaluation of these atomic integrals requires estimates of ionization potentials, electron affinities, Slater effective nuclear charges (z) and core charges. The simultaneous estimations of these parameters are, however, not easy. In this paper it is shown that these atomic integrals can be expressed as a function of the Slater nuclear charges (z_r) and apparent core charges (Ω_r).

The perturbational effect on the electronic spectra of a π-electron system by a small variation of the core is also discussed.

2 THEORY

2.1 Some assumptions in the approximate molecular orbital theory

The following assumptions are made in the usual approximate molecular orbital method:

1. The molecular orbital Φ_i can be written as a linear combination of the Slater atomic orbitals (χ_r).

$$\Phi_i = \sum_r c_{ri}\chi_r \tag{1}$$

2. The π-approximation is adopted, because a planar molecule is assumed. Therefore the summation in eqn (1) can be made only over the p-orbitals of each atom.
3. The zero-differential overlap approximation is assumed.

On the basis of these assumptions the Roothaan equations for the LCAO coefficients simplify to eqn (2):

$$\sum_s F_{rs}c_{ri} = \varepsilon_i c_{ri} \tag{2}$$

where the elements of the Fock matrix (F_{rs}) are given by eqns (3) and (4):

$$F_{rr} = W_{rr} - 1/2q_r c_r + \sum_{r\neq s} (q_s - Q_s)\gamma_{rs} \tag{3}$$

$$F_{rs} = W_{rs} - 1/2p_{rs}\gamma_{rs} \tag{4}$$

In eqns (3) and (4), q_r, p_{rs}, γ_{rr} and γ_{rs} are the π-electron density on the core r, the mobile bond order between the cores r and s, the electron repulsion on the core r and that between cores r and s, respectively.

2.2 Approximation of the core integrals

The core integral W_{rr} is the negative value of the valence state ionization potential of the atom (r). The core integral W_{rs} is approximately obtained by eqn (5), in which S_{rs} denotes the overlap integral between cores r and s, and the value of K is taken to be 0·4314.

$$W_{rs} = K\, S_{rs}(W_{rr} + W_{ss}) \tag{5}$$

The electron repulsion γ_{rs} is given by the Nishimoto–Mataga equation (eqn (6)), where e denotes the electron charge

$$\gamma_{rs} = e^2/(R_{rs} + d_{rs}) \tag{6}$$

In eqn (6), R_{rs} is the distance between cores r and s, and

$$d_{rr} = e^2/\gamma_{rr} \tag{7}$$

$$d_{rs} = 2d_{rr}d_{ss}/(d_{rr} + d_{ss}) \tag{8}$$

In the conventional calculation of the approximate molecular orbital theory some values of these parameters are suggested, but values somewhat different from these are required in the case of molecules in which the cores are affected by substituents or by hydrogen bonding. Using the conventional values of carbon, nitrogen and oxygen, the core integrals W_{rr} and the electron repulsion γ_{rr} can be expressed as a respective function of the Slater nuclear charge (z_r) and the apparent core charge (Ω_r), as in eqns (9) and (10). Their coefficients are determined by the least squares method, where the apparent core charge (Ω_r) is assumed to be equal to the electron number of the neutral atoms. These values of the perturbed potential of the core are then easily estimated by evaluations only of the values of z_r and Ω_r.

$$W_{rr} = -\exp(0{\cdot}342\, z_r + 0{\cdot}555\, \Omega_r + 0{\cdot}758) \tag{9}$$

$$\gamma_{rr} = \exp(0{\cdot}154\, z_r + 0{\cdot}250\, \Omega_r + 1{\cdot}166) \tag{10}$$

Values calculated using eqns (9) and (10) are compared with conventional values in Table 1, with good agreement (the correlation factors for W_{rr} and γ_{rr} are 0·998 and 0·972, respectively).

TABLE 1

Conventional and Calculated Values of W_{rr} and γ_{rr}

Core	*z*	Ω	$-W_{rr}$ *(eV)*		γ_{rr} *(eV)*	
			Conventional	*Calculated*	*Conventional*	*Calculated*
—C=	3·25	1	11·30	11·16	11·17	11·13
—N=	3·90	1	14·12	14·12	12·34	12·34
—$\ddot{\mathrm{N}}$—	4·25	2	27·73	28·59	16·72	16·63
O=	4·55	1	17·64	17·70	13·64	15·23
—$\ddot{\mathrm{O}}$—	4·9	2	34·63	33·90	18·49	18·60

2.3 Perturbational change of energy of the excited state by a small variation of the core potentials

The transition energy ($\Delta E(i-k)$) from the ith molecular orbital to the kth can be written as:

$$\Delta E(i-k) = H_k - H_i + \sum_j (2J_{jk} - K_{jk}) - \sum_j (2J_{ji} - K_{ji}) - J_{ik} + 2K_{ik} \tag{11}$$

where the molecular integrals H_i, J_{jk} and K_{jk} are

$$H_i = \sum_r (c_{ri})^2 I_{rr} + 2 \sum_{s>r} (c_{ri})(c_{si}) W_{rs} \tag{12.1}$$

$$J_{jk} = \sum_{r,s} (c_{rj})^2 (c_{sk})^2 \gamma_{rs} \tag{12.2}$$

$$K_{jk} = \sum_{r,s} (c_{rj})(c_{sj})(c_{rk})(c_{sk}) \gamma_{rs} \tag{12.3}$$

$$I_{rr} = W_{rr} - \sum_{s \neq r} \gamma_{rs} Q_s \tag{12.4}$$

The energy difference between the ground state and the Lth excited state can be written as eqn (13), after the configuration interaction procedure.

$$\Delta E_L = \sum_{i-k} (C_{i-k,L})^2 \, \Delta E(i-k) + 2 \sum_{\substack{i-k \\ j-l}} (C_{i-k,L})(C_{j-l,L}) H_{i-k,j-l} \tag{13}$$

where the wave function (Ψ_L) of the Lth excited state is developed by the wave functions (Φ_{i-k}) corresponding to the electron configuration of the transition from the ith molecular orbital to the kth molecular orbital.

$$\Psi_L = \sum_{i-k} C_{i-k,L} \Phi_{i-k} \tag{14}$$

The molecular integrals $H_{i-k,j-l}$ in eqn (13) are given by eqn (15).

$$H_{i-k,j-l} = \sum_{r,s} (2C_{rj} C_{sl} C_{sk} C_{ri} - C_{sj} C_{ri} C_{rk} C_{sl}) \, \gamma_{rs} \tag{15}$$

The first order perturbational energy can be developed by variations of the z_r and Ω_r values (eqn (16)).

$$\delta(\Delta E_L) = \sum_r (\Delta E_L)'_{zr} (\Delta z_r) + \sum_r (\Delta E_L)'_{\Omega r} (\Delta \Omega_r) + \sum_r (\Delta E_L)''_{z\Omega r} (\Delta z_r)(\Delta \Omega_r) \tag{16}$$

where $(\Delta E_L)'_{zr}$ and $(\Delta E_L)'_{\Omega r}$ are the partial derivatives of ΔE_L with respect to z_r and Ω_r, respectively, and $(\Delta E_L)''_{z\Omega r}$ is the secondary partial derivative.

When only one of z_r or Ω_r is changed, the third term in eqn (16) is absent and eqn (16) can then be rewritten as eqn (16'), in which the respective coefficients of the first order term are denoted by $z_{\text{sens}}(r, L)$ and $Q_{\text{sens}}(r, L)$ as the respective sensitivities of ΔE_L.

$$\delta(\Delta E_L) = \sum z_{\text{sens}}(r, L)(\Delta z_r) \quad \text{or} \quad \sum Q_{\text{sens}}(r, L)(\Delta \Omega_r) \tag{16'}$$

These sensitivities are obtained by partially differentiating eqn (13) with respect to z_r and Ω_r, respectively, assuming all constant developing coefficients.

$$\begin{aligned} z_{\text{sens}}(r, L) = {} & \sum_{i\text{-}k} (C_{i\text{-}k,L})^2(\Delta E(i-k))'_{zr} \\ & + 2\sum_{\substack{i\text{-}k \\ j\text{-}l}} (C_{i\text{-}k,L})(C_{j\text{-}l,L})(H_{i\text{-}k,j\text{-}l})'_{zr} \end{aligned} \tag{17.1}$$

$$\begin{aligned} Q_{\text{sens}}(r, L) = {} & \sum_{i\text{-}k} (C_{i\text{-}k,L})^2(\Delta E(i-k))'_{zr} \\ & + 2\sum_{\substack{i\text{-}k \\ j\text{-}l}} (C_{i\text{-}k,L})(C_{j\text{-}l,L})(H_{i\text{-}k,j\text{-}l})'_{\Omega r} \end{aligned} \tag{17.2}$$

The partial derivatives $(\Delta E(i-k))'_{zr}$ and $(\Delta E(i-k))'_{\Omega r}$ are composed by the differential coefficients of the atomic integrals and their differential coefficients are obtained from eqns (9) and (10) as follows:

$$(W_{rr})'_{zr} = 0{\cdot}342\ W_{rr} \tag{18.1}$$

$$(W_{rr})'_{\Omega r} = 0{\cdot}555\ W_{rr} \tag{18.2}$$

$$(\gamma_{rr})'_{zr} = 0{\cdot}154\ \gamma_{rr} \tag{18.3}$$

$$(\gamma_{rr})'_{\Omega r} = 0{\cdot}250\ \gamma_{rr} \tag{18.4}$$

The differential coefficients of W_{rs} and γ_{rs} are expressed in terms of those of W_{rr} and γ_{rr}, respectively, by eqns (18.5)–(18.8).

$$(W_{rs})'_{zr} = \{W_{rs}/(W_{rr} + W_{ss})\}(W_{rr})'_{zr} + (W_{rs}/S_{rs})(S_{rs})'_{zr} \tag{18.5}$$

$$(W_{rs})'_{\Omega r} = \{W_{rs}/(W_{rr} + W_{ss})\}(W_{rr})'_{\Omega r} \tag{18.6}$$

$$(\gamma_{rs})'_{zr} = G(s, r)(\gamma_{rr})'_{zr} \tag{18.7}$$

$$(\gamma_{rs})'_{\Omega r} = G(s, r)(\gamma_{rr})'_{\Omega r} \tag{18.8}$$

where $G(s, r) = 2[(\gamma_{rs}/\gamma_{rr})\{d_{ss}/(d_{rr} + d_{ss})\}]^2$.

To evaluate the differential coefficient of the overlap integrals between carbon (s) and heteroatom (r) in eqn (18.5), the value of S_{rs} is expressed by an exponential function of the distance (R_{rs}) and the value of z_r. The coefficients in eqn (19) were determined by the least squares method; the regression was excellent (correlation factor = 1·000).*

$$S_{rs} = \exp\,(-0{\cdot}3107\ R_{rs}z_r + 0{\cdot}0453\ z_r - 0{\cdot}7236\ R_{rs} + 0{\cdot}8701) \qquad (19)$$

Using the above differential coefficients, the partial derivatives $(\Delta E_{i-k})'_{zr}$ and $(\Delta E_{i-k})'_{\Omega r}$ are given by the following equations:

$$(\Delta E_{i-k})'_{zr} = \Lambda(r, i, k)(W_{rr})'_{zr} + \Gamma(r, i, k)(\gamma_{rr})'_{zr} + 2\sum_{s\neq r}(c_{rk}c_{sk} - c_{ri}c_{si})(W_{rs}/S_{rs})(S_{rs})'_{zr} \qquad (20.1)$$

$$(\Delta E_{i-k})'_{\Omega r} = \Lambda(r, i, k)(W_{rr})'_{\Omega r} + \Gamma(r, i, k)(\gamma_{rr})'_{\Omega r} - \sum_{s\neq r}(c_{sk}^2 - c_{si}^2)\gamma_{rs} \qquad (20.2)$$

where

$$\Lambda(r, i, k) = c_{rk}^2 - c_{ri}^2 + 2\sum_{s\neq r}[(c_{rk}c_{sk} - c_{ri}c_{si})W_{rs}/(W_{rr} + W_{ss})] \qquad (21.1)$$

$$\begin{aligned}\Gamma(r, i, k) = {} & (q_r - Q_r)\sum_{s\neq r}(c_{sk}^2 - c_{si}^2)G(s, r) \\ & + (c_{rk}^2 - c_{ri}^2)\sum_{s\neq r}(q_s - Q_s)G(s, r) - \sum_{s\neq r}\{p_{rs}(c_{rk}c_{sk} - c_{ri}c_{si})G(s, r)\} \\ & + 0{\cdot}5q_r(c_{rk}^2 - c_{ri}^2) + c_{rk}^2c_{ri}^2 \\ & - \sum_{s\neq r}(c_{ri}^2c_{sk}^2 + c_{rk}^2c_{si}^2 - 4c_{ri}c_{si}c_{rk}c_{sk})G(s, r) \qquad (21.2)\end{aligned}$$

3 APPLICATION OF PERTURBATION THEORY TO ELECTRONIC SPECTRA OF AROMATIC COMPOUNDS

3.1 Molecular orbital calculations

The molecular orbital calculations were carried out by the conventional PPP method,[3,4] coupled with the variable β and configuration interaction procedures. For simplicity, the wave function Ψ_L in eqn (14) was developed only by the wave functions of the one electron transferred configuration (Φ_{i-k}), having energy differences less than 7 eV from the configuration

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* The values of S_{rs} between any atoms can be expressed by eqn (19')

$$S_{rs} = \exp\,[(-0{\cdot}1112R_{rs} + 0{\cdot}1339)z_rz_s + (0{\cdot}0449R_{rs} - 0{\cdot}3759)(z_r + z_s) - 0{\cdot}8627R_{rs} + 2{\cdot}0631 \qquad (19')$$

When the atom (s) is carbon ($z = 3{\cdot}25$), eqn (19') is rewritten as (19'') which is very similar to eqn (19).

$$S_{rs} = \exp\,(-0{\cdot}3165R_{rs}z_r + 0{\cdot}0593z_r - 0{\cdot}7168R_{rs} + 0{\cdot}8414) \qquad (19'')$$

of the least energy. All atomic integrals were estimated by given z and Ω values of the π-core. The sensitivities, $z_{\text{sens}}(r, L)$ and $Q_{\text{sens}}(r, L)$, were calculated by eqns (17.1) and (17.2).

3.2 Shift of electronic spectra by replacements of carbon with heteroatom

Aromatic hydrocarbons can be regarded as the 'mother' compounds of corresponding heteroaromatic compounds. Mataga[4] discussed the electronic spectra of quinoline, isoquinoline and acridine by application of a perturbation theory based on scf theory including configuration interaction. However, the use of the sensitivities suggested in this paper has a wider application.

Benzene is the carbocyclic analogue of pyridine, naphthalene that of both quinoline and isoquinoline, and anthracene that of acridine. The energy differences resultant from the perturbation were calculated by eqn (16'), using only the sensitivity $z_{\text{sens}}(r, L)$ calculated by eqn (17.1), since the nitrogen core has the same Ω value as the carbon core. The values of $z_{\text{sens}}(r, L)$ and $\delta(\Delta E_L)$ of the mother hydrocarbons are listed in Table 2, where Δz is taken to be 0·65.

TABLE 2

Sensitivities and Perturbed Energies of the Excited State of the Aza Aromatics

Hydrocarbon	r	L	$z_{\text{sens}}(r, L)$	$\delta(\Delta E_L)$ *(eV)*	ΔE_L *(eV)*[a]		*Observed (eV)*
					Perturbation	*Calculation*	
Benzene	1	1	−0·309	−0·201	4·693	4·660	4·95
		2	−0·255	−0·166	6·035	6·003	
		3	−0·273	−0·178	6·847	6·850	
		4	−0·291	−0·189	6·836	6·977	
Naphthalene	1	1	−0·114	−0·074	4·079	4·035	3·98
		2	−0·147	−0·095	4·556	4·396	
		3	−0·196	−0·127	5·630	5·469	
		4	−0·113	−0·073	5·697	5·776	
	2	1	−0·158	−0·103	4·051	3·981	3·91
		2	−0·091	−0·059	4·593	4·586	
		3	−0·191	−0·124	5·633	5·550	
		4	−0·155	−0·101	5·669	5·647	
Anthracene	9	1	−0·110	−0·072	3·615	3·557	3·57
		2	−0·093	−0·060	3·667	3·623	
		3	−0·092	−0·060	4·841	4·421	
		4	−0·082	−0·058	4·891	5·023	

[a] Values calculated using z = 3·90 and Q = 1·0.

The approximate values calculated by the perturbation theory agreed fairly well with both calculations by the PPP method and with experimental observations (Table 2). The negative sign of z_{sens} indicates a bathochromic shift resulting from replacement of a carbon core with nitrogen. The absolute values of $z_{\text{sens}}(r, L)$ can be arranged in decreasing order as follows:

benzene > naphthalene > anthracene

The electronic spectra of aromatic systems containing a nitrogen atom will then become more similar to those of their mother hydrocarbons with increasing annelation of the aromatic ring.

The perturbation by eqn (16') cannot be directly applied to the β band at 180 nm in benzene, since it arises from the doubly degenerate states (E_3 and E_4). After CI treatment the wave functions of these excited states are written as follows:

$$\Psi_3 = 0{\cdot}7071(\Phi_{2\text{-}5} + \Phi_{3\text{-}4}) \tag{22.1}$$

$$\Psi_4 = 0{\cdot}7071(\Phi_{2\text{-}4} - \Phi_{3\text{-}5}) \tag{22.2}$$

Using these wave functions, the energies of the system perturbed at the core (r) are given by solving eqn (23)

$$(\Delta E_3 + \delta(\Delta E_3) - E)(\Delta E_4 + \delta(\Delta E_4) - E) - (\delta H')^2 = 0 \tag{23}$$

where $\delta\Delta E_k$ is the first order perturbation of ΔE_k given by eqn (16') and $\delta H'$ is expressed by eqn (24)

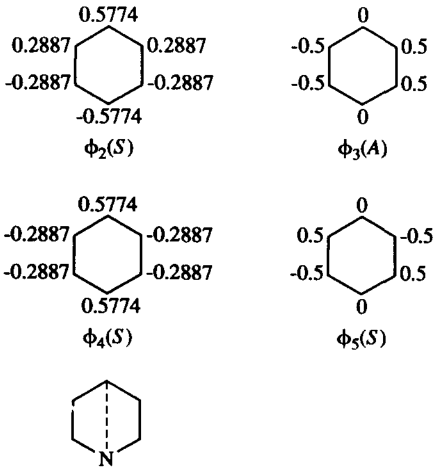
$$\delta H' = 0{\cdot}5(\delta H_{2\text{-}4,2\text{-}5} - \delta H_{3\text{-}4,3\text{-}5} + \delta H_{2\text{-}4,3\text{-}4} - \delta H_{2\text{-}5,3\text{-}5}) \tag{24}$$

$$\delta H_{i\text{-}k,j\text{-}l} = \sum{}' (2C_{rj}C_{sl}C_{sk}C_{ri} - C_{sj}C_{ri}C_{rk}C_{sl})\delta\gamma_{rs} \tag{25}$$

If $\delta H'$ is eliminated, the perturbed energies are equal to those given by eqn (16'). The molecular orbitals of benzene are shown in Fig. 1. When the perturbed core is selected at the 1- or 4-positions, it is very apparent that all values of $\delta H_{i\text{-}k,j\text{-}l}$ in eqn (24) are eliminated. The perturbation equation (eqn (16')) can then be simply applied, even to those doubly degenerate excited states, using the perturbed system **[I]** for pyridine.

Replacement of a bridgehead carbon in polycyclic aromatic hydrocarbons with nitrogen gives the corresponding azonia derivatives, such as the bicyclic quinolizinium (**II**) and the tricyclic benzo[*b*]quinolizinium (**III**), benzo[*a*]quinolizinium (**IV**) and benzo[*c*]quinolizinium (**V**) moieties (Fig. 2).

The transition energy of the daughter system ($z + \Delta z$, $\Omega + \Delta\Omega$) can be estimated by eqn (16), because azonia nitrogen has different z- and Ω-values from those of carbon. However, calculation of the third term in eqn (16) is somewhat tedious. This difficulty can be solved by using the foster mother (z, $\Omega + \Delta\Omega$) as an alternative to the mother system.



[I]

Fig. 1. The molecular orbitals of benzene. *S* and *A* denote symmetry and antisymmetry respectively, about the C_2 symmetry axis shown by the dotted line.

The transition energies of the azonia daughter systems, estimated from the foster mother systems in place of the mother system, are compared with both the molecular orbital calculations and the observed value (Table 3).

The spectrum of *trans*-azobenzene was estimated from the spectrum of *trans*-stilbene (Fig. 3). The first band of stilbene is observed near 190 nm with the vibrational sub-bands. The first band of azobenzene, appearing near 320 nm, is very similar to that of stilbene, but its sub-band is less defined.[1]

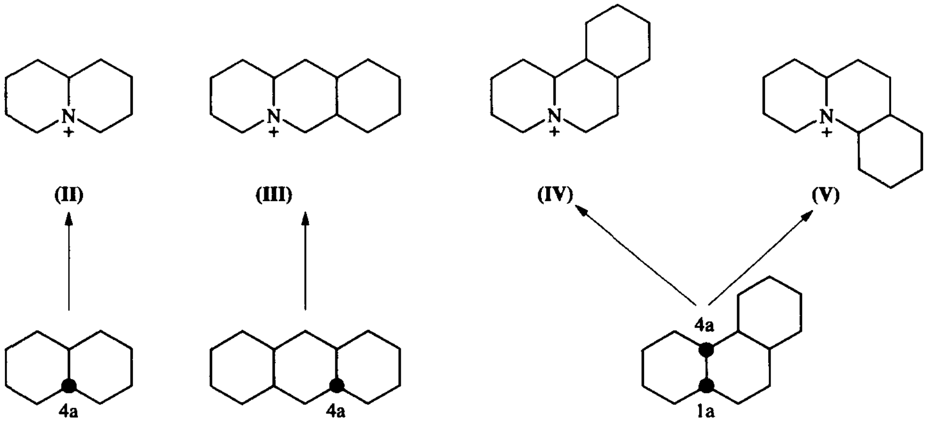


Fig. 2. Bicyclic and tricyclic azonia aromatic compounds.

TABLE 3
Sensitivities at the Bridgehead Position of the Mother Hydrocarbons and the Excited State Energies of Azonia Aromatic Daughters

Aromatic hydrocarbon		*Perturbed mother system*			*Daughter system*		
	Transition energy[a]	*r*	*Transition energy*[b]	z_{sens}	*Transition energy*[c]		
					(A)	*(B)*	*(C)*[d]
Naphthalene	33·50	4a	34·02	−5·276	30·06	30·14	30·98
Anthracene	29·74	4a	29·59	−0·944	28·88	26·73	25·09
Phenanthrene	31·56	1a	29·59	−1·936	28·14	28·60	28·23
		4a	31·37	−2·493	29·50	28·10	27·43

[a] In units of 10^3 cm^{-1}, calculated using $z = 3{\cdot}25$ and $\Omega = 1{\cdot}0$.
[b] In units of 10^3 cm^{-1}, calculated using $z = 3{\cdot}25$ and $\Omega = 1{\cdot}7$.
[c] In units of 10^3 cm^{-1}, calculated using $z = 4{\cdot}0$ and $\Omega = 1{\cdot}7$.
[d] (A) Estimation, (B) calculation by molecular orbital method and (C) observed values.

As shown in Table 4, both the estimated and the calculated first $\pi\pi^*$-transitions of azobenzene are at considerably longer wavelengths compared with the observed value. This difference is caused by assuming a longer length (1·4 Å) of the central double bond (1·25 Å) compared with that (1·4 Å) of azobenzene (1·25 Å).[5] The shortening of the central double bond leads to a decrease in the HOMO energy and an increase in the LUMO energy, since the central double bond is bonding in the HOMO, but antibonding in the LUMO. Since the lowest excited states of both stilbene and azobenzene are composed mainly of the transition from HOMO to LUMO, the first absorption band is shifted to shorter wavelength (larger wave number) by the shortening of the central double bond. However, the bond length of 1·25 Å, observed in the central double bond of azobenzene, is inadequate for the molecular orbital calculation, because the calculated first band is a forbidden (doublet) transition, contrary to the observation that it is allowed. A central double bond length of 1·3 Å was therefore tentatively assumed for the perturbational and the molecular orbital calculations.

In a case of replacement of two cores of the mother system, the second order terms with respect to the two cores must be added to eqn (16′). If

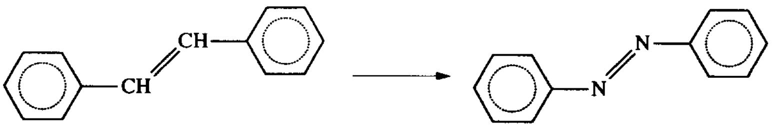


Fig. 3. *trans*-Stilbene and *trans*-azobenzene.

TABLE 4
Spectra of Perturbed Stilbene and Azobenzene (nm)

	t-Stilbene		*Azobenzene*			
	Calculated	*(obs)*	*Estimate (1)*	*Estimate (2)*[b]	*Calculated*	*(obs)*
I[a]	297	(295)	344	—	365	—
II[a]	273	—	274	313	327	324

[a] I: The length of the central double bond is 1·4 Å; II: the length of the central double bond is 1·3 Å.

[b] Estimates (1) and (2) are the results starting from stilbene and benzylidene aniline, respectively.

perturbations only by the z-value are considered, the second order terms can be expressed as follows:

$$\sum (C_{i-k,L})^2(\Delta E(i-k))''_{z,r,s}(\Delta z_r)(\Delta z_s) \tag{26}$$

where $(\Delta E(i-k))''_{z,r,s}$ is the secondary partial derivative of $\Delta E(i-k)$ with respect to z_r and z_s. This secondary partial derivative of $\Delta E(i-k)$ can be easily shown to be a function of both W_{rs} and of $p_{rs}\gamma_{rs}$. The value of W_{rs} may not vanish and that of $p_{rs}\gamma_{rs}$ may not be so small as to be ignored, only if the perturbed cores r and s are adjacent to each other. As shown in Table 4, the first order estimation of the wavelength of azobenzene from stilbene using a central double bond of 1·3 Å is about 50 nm

TABLE 5
Perturbation of the First Absorption Band of Stilbene[a]

Stilbene (C=C, 1·3 Å)	*First order perturbation*[b]		*Second order perturbation*
	First order term[b]	*Second order term*[c]	
4·536 [273 nm]	−0·082	−0·110	−0·450
Total	Estimated result		
−0·642 [318 nm]	3·894		

[a] $\Delta z_r = \Delta z_s = 0{\cdot}65$, $\Delta\Omega_r = \Delta\Omega_s = 0$. Transition energies are given in eV; cores r and s are those of the central double bond.

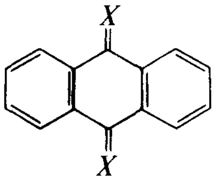
[b] Calculated by eqn (16).

[c] Calculated by eqn (26).

shorter than the value calculated using the molecular orbital method. This may be caused by a considerable contribution of the second term, because of the replacement of two adjacent carbon cores with nitrogen. However, the second term (−0·11) calculated using the secondary partial derivative of $\Delta E(i - k)$ was not large enough to explain the shortcoming of the first order estimation. On the other hand, the second order perturbation was calculated to be −0·450 eV. As listed in Table 5, the first order perturbation, in conjunction with the second order one, satisfactorily estimates the absorption band of azobenzene. The significant contribution of the second order perturbation arises from the adjacent perturbed cores of the central double bond in C_2 symmetry.

Another estimation of the absorption band of azobenzene was made starting from benzylidene aniline; this compound leads to azobenzene by a single replacement of a carbon core with nitrogen. As shown by estimate (2) in Table 4, the result (313 nm) approximates to the molecular orbital calculation (327 nm).

The π-electron systems of anthraquinone (**VIII**) and its diimine (**VII**) correspond to a hydrocarbon, namely anthraquinonedimethane (**VI**), having double bonds of distance 1·2 Å in its quinonoid part.



VI: $X = CH_2$, $z = 3{\cdot}25$
VII: $X = NH$, $z = 3{\cdot}90$
VIII: $X = O$, $z = 4{\cdot}55$

Since the two perturbed cores are not adjacent in system **VI**, both of the second order terms with respect to the cores and the second order perturbation can be neglected. The first order perturbation (eqn (16')) will thus give a good estimate of the absorption bands of systems **VII** and **VIII**. The values of z of the core (X) in systems **VI-VIII** are shown above.

The excited states can be classified by D_2 symmetry; the (SS) state is symmetrical around both the C_x and C_y axes, but the (AA) state is antisymmetrical around both axes. The transitions from the ground state to these states are forbidden. The (SA) state is symmetrical around the C_x axis, but antisymmetrical around the C_y axis, while the (AS) state has a reverse symmetry. The transitions from the ground state to these excited states are allowed, the former being the x band and the latter the y band. The results of the first order perturbation treatment for system **VI** are shown in Table 6. The perturbational shifts using the changing z value of the core X are in fair agreement with the molecular orbital calculations, except that the transition to the (AA) state exhibits a very much larger shift than that estimated by eqn (16') which can be explained as follows (Table 6).

TABLE 6
Perturbation in System **VI**

System	*z(X)*	*SS*		*SA*		*AS*		*AA*	
		mo	*est*	*mo*	*est*	*mo*	*est*	*mo*	*est*[a]
VI	3·25	36·5	—	37·2	—	40·5	—	42·8	—
Order		(1)		(2)		(3)		(4)[b]	
VII	3·9	35·6	35·0	35·7	35·9	39·3	38·3	38·2	41·3
Order		(1)		(2)		(4)		(3)	
Observed (Ref. 7)		[f]		37·6		40·8		[f][c]	
VIII	4·55	33·2	33·4	31·9	34·6	36·9	36·1	31·4	39·8
Order		(3)		(2)		(4)		(1)	
Observed (Ref. 7)		[f]		30·3		36·8		[f]	

[a] 'mo' and 'est' denote calculations by the molecular orbital method and estimations by the first order perturbation, respectively.
[b] The order of the level is shown in parentheses. The estimated energies, on the basis of the presumed **II** (z = 3·45), are shown in square brackets.
[c] Forbidden absorption.

As shown by Fig. 4, the energies of $E_4(AA)$ (5·30 eV) and $E_5(AA)$ (5·60 eV) of system **VI** are close to each other. Their wave functions, $\Psi_4(AA)$ and $\Psi_5(AA)$, are developed by transitions having (AA) symmetry.

$$\Psi_4(AA) = 0{\cdot}6733\,(\Phi_{8\text{-}11} + \Phi_{6\text{-}9}) + 0{\cdot}1999\,(\Phi_{7\text{-}12} + \Phi_{5\text{-}10}) + 0{\cdot}0265\,(\Phi_{4\text{-}11} - \Phi_{6\text{-}13}) - 0{\cdot}0777\,(\Phi_{2\text{-}9} - \Phi_{8\text{-}15}) \quad (27.1)$$

$$\Psi_5(AA) = 0{\cdot}6931\,(\Phi_{8\text{-}11} - \Phi_{6\text{-}9}) + 0{\cdot}0342\,(\Phi_{7\text{-}12} - \Phi_{5\text{-}10}) + 0{\cdot}1100\,(\Phi_{4\text{-}11} + \Phi_{6\text{-}13}) - 0{\cdot}0797\,(\Phi_{2\text{-}9} + \Phi_{8\text{-}15}) \quad (27.2)$$

These can be mixed, even with small variations of the z value of the core X, because of their proximity. This mixing of the wave functions alters $\Psi_4(AA)$ to a wave function having a larger value of $\Phi_{6\text{-}9}$, with a larger negative z_{sens} value (−0·601). Then, z_{sens} of $\Psi_4(AA)$ becomes a larger negative value than that of the mother system **VI**, even with small variations of z of the core X (Table 7).

TABLE 7
Variation of the Weight of $\Phi_{6\text{-}9}$ and z_{sens} with Change of the z Value of Core X

z	*3·25*	*3·45*	*3·65*	*3·85*
Weight (%) of $\Phi_{6\text{-}9}$	45·3	81·3	90·9	93·2
z_{sens} (10^3 cm^{-1})	−1·186	−4·122	−5·268	−5·750v

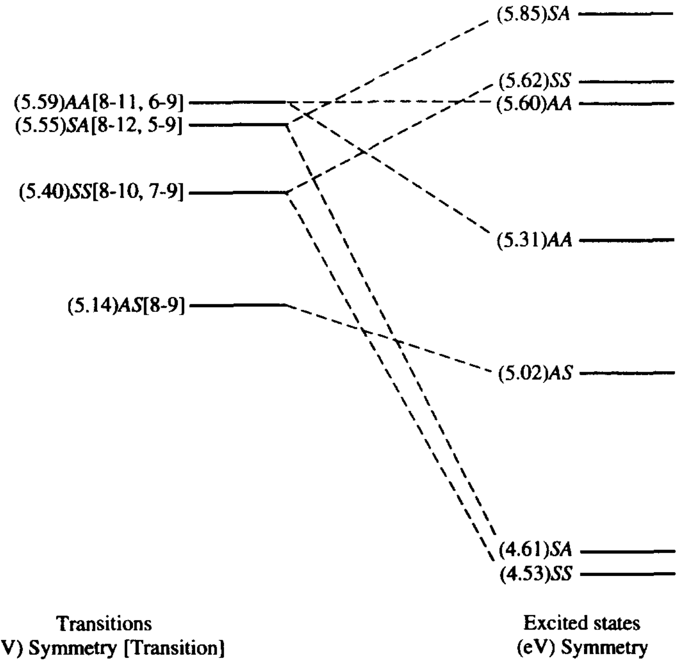


Fig. 4. Levels of the Transitions and of the Excited States of System VI.

The other wave functions, $\Psi_1(SS)$ and $\Psi_2(SA)$, also can mix with $\Psi_6(SS)$ and $\Psi_7(SA)$, respectively, by variation of the z value of the core X. However, they are so far apart that the degree of their mixing is small.

3.3 Perturbation by attachment of a methyl group on the aromatic ring

The electron density on the carbon core increases by attachment of a methyl group having an electron donating inductive effect. According to the Slater rule, one electron increase in the density of the atom results in a 0·35 decrease in the nuclear charge (z) by increasing electron repulsion. This implies that the decrease in z, in combination with the methyl group, should be less than 0·35, because of a fractional increase in the electron density on the carbon atom. Absolute z_{sens} values of alternate aromatic hydrocarbons and their aza and azonia homologs are calculated to be less than 5×10^3 cm^{-1}. The presence of a methyl group in these compounds will thus shift their first absorption band by less than 1×10^3 cm^{-1}; this conclusion is in good accord with the experimental observations (Table 8).

In contrast to the case of alternate aromatic hydrocarbons, a notable shift in the electronic spectra of azulene has been observed by introduction

TABLE 8
Shifts of Absorption Maxima due to Presence of a Methyl Group

Pyridine			Quinoline		
Position	z_{sens} *(10^3 cm^{-1})*	*Shift*[a] *(10^3 cm^{-1})*	*Position*	z_{sens} *(10^3 cm^{-1})*	*Shift*[a] *(10^3 cm^{-1})*
2	−2·21	−0·7	2	−2·448	−0·2
3	0·25	−0·9	3	−0·33	−0·5
4	−5·14	0·3	4	−3·80	0
			6	0·18	−0·4
			7	−0·73	−0·1

[a] Ref. 6.

of a methyl group (Table 9). This is due to the large absolute values of z_{sens} of the carbon core in a nonalternate aromatic system.

Introduction of a methyl group at position (r) evokes the change of energy of the first excited state as expressed in first order approximation in eqn (28).

$$\delta(\Delta E_1) = z_{sens}(r, 1)\, \Delta z \qquad (28)$$

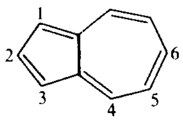
Since Δz has a negative sign, substitution at a position having a positive z_{sens} will decrease the wave number and vice versa. As shown in Table 9 this expectation agrees with the experimental results. When σ_0 and σ denote the wave numbers of azulene and substituted azulene, respectively, eqn (28) can be rewritten by:

$$\sigma = \sigma_0 + (\Delta z) z_{sens}(r, 1) \qquad (29)$$

An approximate linear relationship exists between the observed wave number and $z_{sens}(r, 1)$ (correlation coefficient = −0·91). The least squares

TABLE 9
Absorption Bands of Methyl-Substituted Azulenes

Position	z_{sens} *(r, 1) (10^3 cm^{-1})*	*Wave number* *(σ)*[a] *(10^3 cm^{-1})*
1	4·114	13·55
2	−2·646	14·88
4	−4·921	14·73
5	1·347	13·97
6	−7·220	14·82
non	--	14·35



[a] Ref. 8.

method shows that the slope and the intercept of the line are $-0{\cdot}116$ and $14{\cdot}2 \times 10^3$ cm^{-1}, respectively. These results seem to be reasonable, since the intercept is close to the wave number ($14{\cdot}3 \times 10^3$ cm^{-1}) of unsubstituted azulene. The value of Δz is thus evaluated to be about $-0{\cdot}12$, on the basis of the value of the slope.

As the summary, the core potentials of a perturbed π-system can be reasonably evaluated by use of the functions of the Slater nuclear charge (z) and the apparent core charge (Ω). The first order perturbation method suggested in this paper is shown to be a promising method for the evaluation of the absorption spectra of a perturbed π-system, but the secondary partial derivatives and the second order perturbations need to be included where the two perturbed cores are adjacent in C_2 (or D_2) symmetry, such as in stilbene. The first order perturbation was successfully applied to an understanding of the absorption spectra of the aza and azonia aromatic systems, azobenzene, anthraquinone homologs and the methyl-substituted azulene. The perturbation method suggested in this paper can be more widely applied to many other systems, including dyes and to intra- and intermolecular hydrogen bonding systems. These applications will be discussed in a subsequent paper.

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