

INTERACTION OF SIGMA AND PI ELECTRONS IN THE FREE-ELECTRON MODEL. IV. EXCITATION ENERGIES IN LINEAR COMPOUNDS

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The rigorous electron-electron and electron-core integrals of the one-dimensional free-electron model are applied to calculations of the lowest excitation energies in polyenes and symmetrical cyanine dyes. In order to obtain the convergent results, each one-electron excitation energy has been approximated by one-half of that for the two-electron excitation and any molecular core has been assumed as equal to a set of equidistant point charges distributed along a straight line.

1. Introduction

The purpose of this paper is to apply the rigorous integrals of Part III [1] to the calculation of the electron excitation energies in polyenes and symmetrical cyanine dyes. From the point of view of this rigorous approach, the present calculations on the electron-electron interaction represent the revision of [2]–[4]. These former results can be considered as valid in a non-rigorous, or “oversimplified”, FE scheme at $R \rightarrow 0$; see the Appendix of Part III. Moreover, in the case of the purely $\pi-\pi$ interaction, the integrals of [3] and [4] have to be multiplied by $2/3$, because, at $R \rightarrow 0$, the $\pi-\pi$ integrals are equal both to those for the $\sigma-\sigma$ interaction and to those obtained with a constant electron density on the cross-section of the potential box.

No significant errors have been made in the previous calculation of the electron-core integrals and the numerical results of [4] hold at this point; for $R \rightarrow 0$ they apply equally to electrons σ and π .

2. The formulae

Let us take into account only π electrons and assume the radius R of the potential box tending to zero. In the most part of cases we investigate the excitations in which one electron is raised between two levels:

$$\frac{n_e}{2} \rightarrow \frac{n_e}{2} + 1, \quad (1)$$

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where n_e is the (even) number of π electrons in a molecule. Let the FE path length L and the bond length be the same as in [2] – [4]. Each excitation energy is contributed by: (a) the kinetic energy,

$$\Delta E_{\text{kin}} = \frac{(n_2)^2 - (n_1)^2}{8mL^2} \hbar^2 \quad (2)$$

where n_1 and n_2 are respectively the indices of the ground and excited one-electron FE levels; (b) the electron-electron interaction energy, ΔE_{ee} , which is referred to the difference between the closed-shell ground state and the centre of gravity of the excited singlet and triplet; the excited states are produced again by the one-electron transition $n_1 \rightarrow n_2$. Following Section 3 of Part III, ΔE_{ee} is approximated by one-half of expression (14) of that paper; the summation with respect to i runs over all double-occupied one-electron levels of the ground state except n_1 , *i. e.*

$$1 \leq i < n_1 \quad \text{and} \quad n_1 < i \leq \frac{n_e}{2}; \quad (3)$$

(in most cases $n_1 = \frac{n_e}{2}$; see Eq. (1). According to Part II [5] and Part III we have

$$\lim_{R \rightarrow 0} (J_{n_2 i} - J_{n_1 i}) = e^2 L^{-1} \lim_{R \rightarrow 0} (I_{2n_2, 2i} - I_{2n_2, 0} - I_{2n_1, 2i} + I_{2n_1, 0}); \quad (4)$$

$$\begin{aligned} \lim_{R \rightarrow 0} (J_{n_2 n_2} - J_{n_1 n_1}) &= e^2 L^{-1} \lim_{R \rightarrow 0} (-2I_{2n_2, 0} + 2I_{2n_1, 0} + I_{2n_2, 2n_2} - I_{2n_1, 2n_1}) = \\ &= e^2 L^{-1} [\lim_{R \rightarrow 0} (-2I_{2n_2, 0} + 2I_{2n_1, 0}) - \ln n_2 + \ln n_1 - \\ &\quad - (2n_2 \pi)^{-1} \text{Si}(2n_2 \pi) + (2n_1 \pi)^{-1} \text{Si}(2n_1 \pi)]; \end{aligned} \quad (5)$$

$$\begin{aligned} &\lim_{R \rightarrow 0} (K_{n_2 i} - K_{n_1 i}) = \\ &= e^2 L^{-1} \lim_{R \rightarrow 0} (I_{n_2+i, n_2+i} + I_{n_2-i, n_2-i} - I_{n_1+i, n_1+i} - I_{n_1-i, n_1-i}) + \\ &\quad + e^2 L^{-1} \lim_{R \rightarrow 0} (-2I_{n_2+i, n_2-i} + 2I_{n_1+i, n_1-i}) \end{aligned} \quad (6)$$

where

$$\begin{aligned} &\lim_{R \rightarrow 0} (J_{n_2 \pm i, n_2 \pm i} - J_{n_1 \pm i, n_1 \pm i}) = \\ &= -\ln |n_2 \pm i| + \ln |n_1 \pm i| - \\ &\quad - [(n_2 \pm i)\pi]^{-1} \text{Si}[(n_2 \pm i)\pi] + [(n_1 \pm i)\pi]^{-1} \text{Si}[(n_1 \pm i)\pi]. \end{aligned} \quad (7)$$

Owing to Eq. (3) of Part III, all $\lim_{R \rightarrow 0} I_{s,t}$ with $s \neq t$ (the indices s and t are integers or zero) can be calculated from Eq. (1) of Part III. Let us note that owing to symmetry properties of the Si function, the relation holds

$$\lim_{R \rightarrow 0} I_{s,t} = \lim_{R \rightarrow 0} I_{-s,t} = \lim_{R \rightarrow 0} I_{s,-t} = \lim_{R \rightarrow 0} I_{-s,-t}. \quad (8)$$

The last component to the excitation energy, (c), is that of the electron-core interaction

$$\begin{aligned} \Delta E_{e \text{ core}} = & \frac{Ze^2}{L} \sum_{j=1}^{j=q} \left\{ \text{Si} \left(\frac{2\pi n_2}{L} a_j \right) - \text{Si} \left[\frac{2\pi n_2}{L} (L - a_j) \right] \right\} \sin \left(\frac{2\pi n_2}{L} a_j \right) - \\ & - \frac{Ze^2}{L} \sum_{j=1}^{j=q} \left\{ \text{Si} \left(\frac{2\pi n_1}{L} a_j \right) - \text{Si} \left[\frac{2\pi n_1}{L} (L - a_j) \right] \right\} \sin \left(\frac{2\pi n_1}{L} a_j \right) + \\ & + \frac{Ze^2}{L} \sum_{j=1}^{j=q} \left\{ \text{Ci} \left(\frac{2\pi n_2}{L} a_j \right) + \text{Ci} \left[\frac{2\pi n_2}{L} (L - a_j) \right] \right\} \cos \left(\frac{2\pi n_2}{L} a_j \right) - \\ & - \frac{Ze^2}{L} \sum_{j=1}^{j=q} \left\{ \text{Ci} \left(\frac{2\pi n_1}{L} a_j \right) + \text{Ci} \left[\frac{2\pi n_1}{L} (L - a_j) \right] \right\} \cos \left(\frac{2\pi n_1}{L} a_j \right) + \\ & + \frac{2Ze^2}{L} \ln(n_2) - \frac{2Ze^2}{L} \ln(n_1). \end{aligned} \quad (9)$$

In the last row of (9) the relation

$$\begin{aligned} \sum_{j=1}^{j=q} \cos \left(\frac{2\pi n}{L} a_j \right) &= \sum_{j=1}^{j=q} \cos \left(\frac{2\pi n j}{q+1} \right) = \\ &= \frac{1}{2} \sin(2\pi n) \text{ctg} \left(\frac{\pi n}{q+1} \right) - \cos^2 \pi n = -1 \end{aligned} \quad (10)$$

has been used for $n = n_1$ and $n = n_2$. Eqs (9) and (10) hold unless n_1 , or n_2 , is a multiple of $q+1$. The summations in (9) and (10) run over the number q of all equidistant atomic centres.

The symbol Ze is the nuclear charge. In most cases it is assumed equal to $+1e$ which makes the π -electron system electrically neutral. However, a strong screening of an electron-core interaction by the remaining electrons can be assumed, too. The effect has been discussed in [4], and the corresponding screened Z have been also introduced to the Tables. In comparison with [4], no additional difficulties occur in the treatment of the configurational interaction for the electron-core operator. The corresponding matrix elements are equal to those of [4].

3. Calculations

Tables I and II presents the pattern of the electron states respectively for ethylene and butadiene. The energy of the ground state is put equal to zero. In the case of butadiene, the excitations between diverse pairs of the one-electron levels have been taken into account. Usually the results are much closer to experiment when the term $\Delta E_{e \text{ core}}$ is omitted.

TABLE I
Energy levels (excitation energies) of ethylene (in eV); $R \rightarrow 0$. The ground state energy is put equal to zero.
No configurational interaction has been taken into account

State	Simple FE method (Eq. (2))	ASFEMO method					"Exact" LCAO method [6]	Experiment
		ΔE_{kin} (Eq. (2))	ΔE_{ee} (Eqs (4) - (7))	$\Delta E_{e \text{ core}}$ (Eq. (9))	total ΔE ; $Z = 1$	total ΔE ; $Z = \frac{1}{2}$		
1	0	0	0	0	0	0	0	0
average ^a of V_{12} and T_{12}	6.88	6.88	-1.80	5.80Z	10.88	7.98	6.0	6.1-6.2 ^c
2 ^b	13.76	13.76	-3.60	11.59Z	21.75	15.95	12.5	~ 9.5 ^d

^a This state corresponds to the one-electron excitation from $n_1 = 1$ to $n_2 = 2$.

^b This state corresponds to the two-electron excitation from $n_1 = 1$ to $n_2 = 2$.

^c This is the arithmetical mean of singlet (7.6 eV; see *e. g.* [7]) and triplet (4.6 eV [8]; 4.8 eV [9]).

^d See [10].

TABLE II
Energy levels of butadiene (in eV); $R \rightarrow 0$. The ground state energy is put equal to zero.
No configurational interaction has been taken into account

State	Simple FE method	ASFEMO method					"Exact" LCAO method [11]	Experiment
		ΔE_{kin} (Eq. (2))	ΔE_{ee} (Eqs (4) - (7))	$\Delta E_{e \text{ core}}$ (Eq. (9))	total ΔE ; $Z = 1$	total ΔE ; $Z = \frac{1}{4}$		
V_0	0	0	0	0	0	0	0	0
average of ^a V_{23} and T_{23}	3.84	3.84	0.82	2.00Z	6.66	5.16	2.33	4.6 ^b
average of ^a V_{13} and T_{13}	6.14	6.14	-1.12	6.06Z	11.08	6.54	5.46	5.6 ^c
average of ^a V_{24} and T_{24}	9.21	9.21	1.74	3.32Z	14.27	11.78	5.41	—
average of ^a V_{14} and T_{14}	11.52	11.52	-0.52	7.38Z	18.38	12.85	9.39	—

^a The average of states V_{ab} and T_{ab} corresponds to the one-electron excitation from $n_1 = a$ to $n_2 = b$.

^b This is the arithmetical mean of singlet 6.0 eV [7] and triplet 3.2 eV [8].

^c This figure is the arithmetical mean of singlet 7.2 eV [7] and triplet 3.9 eV [8].

TABLE III

Electron-electron interaction and locations of absorption maxima in polyenes. Excitation energies (ΔE) in eV; wavelengths (λ) of absorption maxima in Å

Polyene	Number of FE (n_e)	Simple FE method			ASFEMO method				Experimental λ
		ΔE	λ	$\Delta\lambda$	$(\Delta E_{\text{kin}} = \Delta E \text{ of the simple FE method})$				
					ΔE_{ee}	total ΔE ($\Delta E_{\text{kin}} + \Delta E_{\text{ee}}$)	λ	$\Delta\lambda$	
Hexatriene	6	2.74	4520		1.43	4.17	2970		2600 [12]
Octatetraene	8	2.13	5810	1290	1.48	3.61	3430	460	3020 [12]
Axerophthene	10	1.74	7105	1295	1.47	3.21	3855	425	3460 [12]
Anhydro-Vitamin A	12	1.48	8395	1290	1.40	2.87	4310		3690 [12]
	14	1.28	9685	1295	1.33	2.61	4740	430	3995 [13]
	16	1.13	10980	1290	1.26	2.39	5180	440	4090 [13]
	18	1.01	12270	1290	1.20	2.21	5605	425	4160 [13]
	20	0.91	13560	1290	1.14	2.06	6030	425	4230 [13]
	22	0.83	14855	1295	1.09	1.92	6445	415	4510 [12]
β -Carotene	24	0.77	16145	1290	1.04	1.81	6860		4750 [12]
Dehydro	26	0.71	17435	1295	1.00	1.71	7265	405	—
β -Carotene	28	0.66	18730	1295	0.95	1.62	7675	410	—

TABLE IV

Nuclear charge effect on the electron excitation energies in polyenes; $\Delta E_{\text{tot}} = \Delta E_{\text{kin}} + \Delta E_{\text{ee}} + \Delta E_{e \text{ core}}$. All ΔE in eV; λ in Å

n_e	$\Delta E_{e \text{ core}}$	$\Delta E_{\text{tot}}; Z = 1$	λ	$\Delta\lambda$
4	2.00 Z	6.66	1860	
6	1.01 Z	5.18	2395	535
8	0.62 Z	4.23	2930	535
10	0.42 Z	3.63	3415	485
12	0.29 Z	3.16	3920	505

Table III gives the excitation energies and the corresponding wavelengths for polyenes. We have put $\lambda = 12395/(\Delta E)$, where λ is expressed in angstroms, and ΔE — in electronvolts. Only excitations between the levels represented by Eq. (1) have been considered.

We see that the vinylene shift, $\Delta\lambda$, of the simple FE model is reduced to less than one half of its value by the electron-electron interaction. At the same time $\Delta\lambda$ slightly decreases with the increase of the chain length. The insertion of the electron-core interaction (Table IV) makes $\Delta\lambda$ somewhat larger. The behaviour of λ and $\Delta\lambda$ for symmetrical cyanine dyes (Table V and VI) is of a similar nature. Let us note that for polyenes the interaction

TABLE V

Electron-electron interaction and locations of the lowest absorption maxima in symmetrical cyanine dyes. Excitation energies (ΔE) in eV; wavelengths (λ) of absorption maxima in Å; number of positive centres in the chain: q

Number of FE (n_e)	Simple FE method			ASFEMO method				Experiment [14], [15] λ
	ΔE	λ	$\Delta\lambda$	$(\Delta E_{kin} = \Delta E \text{ of the simple FE method})$				
				ΔE_{ee}	total ΔE ($\Delta E_{kin} + \Delta E_{ee}$)	λ	$\Delta\lambda$	
(i) case of a larger number of FE: $n_e = q+1$								
4	6.00	2065		1.03	7.03	1765		2200
6	3.73	3325	1260	1.67	5.40	2295	530	3090
8	2.70	4590	1265	1.67	4.37	2835	540	4090
10	2.11	5875	1285	1.62	3.73	3325	490	5100
12	1.73	7150	1275	1.51	3.24	3825	500	
14	1.47	8440	1290	1.43	2.90	4275	450	
16	1.27	9720	1280	1.34	2.61	4750	475	
18	1.13	11010	1290	1.27	2.40	5165	415	
20	1.01	12300	1290	1.20	2.21	5610	445	
(ii) case of a smaller number of FE: $n_e = q-1$								
2	3.60	3445		-1.30	2.30	5390		2200
4	2.67	4640	1195	0.69	3.36	3690	-1700	3090
6	2.10	5900	1260	1.25	3.35	3700	10	4090
8	1.73	7165	1265	1.33	3.06	4050	350	5100

TABLE VI

Nuclear charge effect on the electron excitation energies in symmetrical cyanine dyes; $\Delta E_{tot} = \Delta E_{kin} + \Delta E_{ee} + \Delta E_{ecore}$. All ΔE in eV; wavelengths λ of absorption maxima in Å; the number of positive centres in the chain: q

Number of FE (n_e)	ΔE_{ecore}	$\Delta E_{tot}; Z=1$	λ	$\Delta\lambda$	$\Delta E_{tot}; Z = \frac{2}{q}$		λ	$\Delta\lambda$
(i) case of a larger number of FE: $n_e = q+1$								
4	2.36 Z	9.39	1320		8.60		1440	
6	1.12 Z	6.52	1900	580	5.85		2120	680
8	0.59 Z	4.96	2500	600	4.54		2730	610
10	0.44 Z	4.17	2970	470	3.83		3240	510
(ii) case of a smaller number of FE: $n_e = q-1$								
2	4.62 Z	6.92	1790		5.38		2305	
4	1.78 Z	5.14	2410	620	4.07		3045	740
6	0.93 Z	4.28	2895	485	3.62		3430	385
8	0.57 Z	3.63	3415	520	3.19		3890	460

effects make the theoretical λ apparently closer to experiment than are the λ of the simple FE model.

The effect of the revised integrals of Part III on the topics considered in [3] will be examined elsewhere.

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