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Influence of the Long-Range Coulomb Interaction upon the Energy Spectrum of Infinite Polyenes

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It is shown that the energies of AMO's (E_k) for an arbitrary homonuclear alternating system can be given with the following expression (identical for AMO with α- and β-spin):

$$E_{k\sigma} = \alpha + \tfrac{1}{2}\gamma \pm (\delta^2\gamma^2 + [e_k + \Delta_k(\gamma_{\mu\nu})]^2)^{1/2} \qquad \sigma \in \alpha, \beta$$

where: e_k are the MO energies, obtained by means of the conventional HF method; δ and Δ_k are correlation corrections depending on the one-center (γ), resp. two-center ($\gamma_{\mu\nu}$) coulomb integrals.

By means of the above method, where the interactions between non-adjacent AO's are taken into account, it is shown that the energy gap of an infinite polyene, in the π-electron approximation, is different from zero, regardless of the presence or absence of C—C bond alternation. This means that in adiabatic approximation an infinite atomic chain, satisfying the Born–Karman condition, is not a metal model but a dielectric one.

Key words: Polyenes – band structures of ~ – long-range coulomb interaction on the ~~

1. Introduction

The problem for the nature of the gound state of polyenes is of general interest for the theoretical chemistry. In π-electron approximation the polyenes are a realistic

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model, the study of which gives grounds for drawing conclusions about the energy spectrum of one-dimensional systems in general. The purpose of this work is to investigate the influence of the electron correlation upon the width of the energy gap of infinite polyenes, taking into account the long-range Coulomb interaction. This problem is of special interest, as the width of the gap defines the optical and dielectrical properties of one-dimensional systems. The information about the influence of the electron correlation upon the gap width is very valuable for the study of the structural transitions of these systems.

Different authors [1–6] have treated the problem for the nature of the ground state of polyenes in π-electron approximation, taking into account the electron correlation (see also reviews [7], [8]). However, all these researches were done in the limits of the Hubbard approximation [9], except in some studies [10] where the Coulomb integrals between neighbouring AO's were included in the treatment (see also papers [11], [12]). In the works of Fukutome [13] and of Paldus and Cizek [14] is shown that the long-range Coulomb interaction could play an essential role in obtaining qualitatively and quantitatively correct results.

The influence of the long-range Coulomb interaction upon the energy spectrum of polyenes was treated in the work of Misurkin and Ovchinnikov [15], but the study was done only for the case of ideal geometry, i.e. no bond alternation was taken into account.

The *ab initio* calculations [16] show that the stabile configuration of an infinite all-trans polyene chain (at $T = 0°\mathrm{K}$) with bond alternation is characterised by the following bondlengths: $R_d = 1.343$ Å, $R_s = 1.443$ Å. The calculations were performed with a STO basis: C($8s4p$) H($4s$). These values are in agreement with the ab initio results of Kertesz, Koller and Azman [17].

The ab initio HF-Crystal-Orbital calculations of André and Leroy [18] show that polyenes without bond alternation have lower energy than those with alternation of the bondlengths.

It is not discussed here which structure is more stable – with or without alternation of the bondlengths – because the studies are performed in π-electron approximation. It has only to be noted that in this approximation our calculations show quite a small difference in the ground state energies of the two structures, being of the energy order of the vibrational quanta.

2. Method and Derivation of the Main Relations

In a previous work [19] was shown that if the alternating molecular orbitals (AMO's) are represented as:

$$|k_\alpha\rangle = \sin\theta_k |k\rangle + \cos\theta_k |\bar{k}\rangle$$

$$|k_\beta\rangle = \sin\theta_k |k\rangle - \cos\theta_k |\bar{k}\rangle$$

the AMO energies of an arbitrary alternating system with a singlet ground state is related with the energies $e_k(e_{\bar{k}})$, obtained by means of the conventional

HF-method (LCAO-SCF-MO-PPP), by the following expression:

$$\begin{aligned}
\mathrm{E}_{k\sigma} &= \tfrac{1}{2}(e_k + e_{\bar{k}} + \langle k|\hat{f}^{\sigma}|k\rangle + \langle \bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle) \pm \varepsilon_{k\sigma} \qquad (1)\\
\varepsilon_{k\sigma} &= [\tfrac{1}{4}(\mathrm{e}_k - \mathrm{e}_{\bar{k}} + \langle k|\hat{f}^{\sigma}|k\rangle - \langle \bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle)^2 + \langle k|\hat{f}^{\sigma}|\bar{k}\rangle]^{1/2}\\
&\quad \sigma \in \alpha, \beta\\
\sin 2\theta_k &= \frac{\langle k|\hat{f}^{\sigma}|\bar{k}\rangle}{\varepsilon_{k\sigma}}.
\end{aligned}$$

If we denote by $\hat{F}$ the energy operator in the conventional HF-method ($\hat{F}|k\rangle = \mathrm{e}_k|k\rangle$ and $\hat{F}|\bar{k}\rangle = \mathrm{e}_{\bar{k}}|\bar{k}\rangle$) and by $\hat{F}^{\sigma}$ – the operator for the $\sigma(\sigma \in \alpha, \beta)$ – orbitals in the AMO-method, we can define the operator $\hat{f}$ in the following way:

$$\begin{aligned}
\hat{F}^{\sigma} &= \hat{F} + \hat{f}^{\sigma}\\
\hat{F}^{\sigma}|k_{\sigma}\rangle &= E_{k\sigma}|k_{\sigma}\rangle.
\end{aligned}$$

In the general case the operators $\hat{f}^{\sigma}$ depend on the orbitals $|k_{\alpha}\rangle$ and $|k_{\beta}\rangle$. For homonuclear alternating systems the general expressions for the matrix elements of $\hat{F}^{\sigma}$, derived in the above mentioned paper [19], may be considerably simplified (the AO's $|\mu\rangle$ and $|\nu\rangle$ belong to different subsystems – with a star $|\overset{*}{\mu}\rangle$ and without star $|\mathring{\nu}\rangle$) and can be written down as:

$$\begin{aligned}
\mathrm{F}^{\alpha}_{\mu\mu} &= \langle \mu|\hat{F}^{\alpha}|\mu\rangle = \langle \mu|\hat{F} + \hat{f}^{\sigma}|\mu\rangle = F_{\mu\mu} + \langle \mu|\hat{f}^{\sigma}|\mu\rangle\\
&= \alpha + \tfrac{1}{2}\gamma - \gamma \sum_k \sin 2\theta_k \cdot c^2_{k\mu} = \alpha + \tfrac{1}{2}\gamma - \delta\gamma\\
F^{\beta}_{\mu\mu} &= \alpha + \tfrac{1}{2}\gamma + \delta\gamma\\
F^{\alpha}_{\nu\nu} &= \alpha + \tfrac{1}{2}\gamma + \delta\gamma\\
F^{\beta}_{\nu\nu} &= \alpha + \tfrac{1}{2}\gamma - \delta\gamma\\
F^{\sigma}_{\mu\nu} &= F_{\mu\nu} + 2\gamma_{\mu\nu} \sum_k c_{k\mu}c_{k\nu} \cos^2 \theta_k\\
&= \beta^{\text{core}} - \tfrac{1}{2}p_{\mu\nu}\gamma_{\mu\nu} + \tau_{\mu\nu}\gamma_{\mu\nu}\\
\alpha &= \langle \mu|h(1)^{\text{core}}|\mu\rangle = \langle \nu|h(1)^{\text{core}}|\nu\rangle.
\end{aligned}$$

In the above equations $c_{k\mu(\nu)}$ are the coefficients of the MO's $\gamma_{\mu\nu}$ are the two-center Coulomb integrals, $P_{\mu\nu}$ is the bond order between the μth and the νth AO (the bond order is different from zero only for pairs of AO's belonging to different subsystems, i.e. $P_{\overset{*}{\mu}\overset{*}{\nu}} = P_{\mathring{\mu}\mathring{\nu}} = 0$).

As far as only the resonance integrals $\beta^{\text{core}}_{\mu\nu}$ between neighbouring AO's are taken into account and because $P_{\overset{*}{\mu}\overset{*}{\rho}} = P_{\mathring{\nu}\mathring{\sigma}} = 0$, the matrix elements $F_{\overset{*}{\mu}\overset{*}{\rho}} = F_{\mathring{\nu}\mathring{\sigma}} = 0$.

Corresponding to the above derived expressions, the matrix elements of the operator $\hat{f}^{\sigma}$ in the MO basis $|k\rangle$ and $|\bar{k}\rangle$, and the expressions for the AMO energies have the following form:

$$\langle k|\hat{f}^{\sigma}|k\rangle = 2\sum_{\mu\neq\nu} c_{k\mu}c_{k\nu}\tau_{\mu\nu}\gamma_{\mu\nu}$$

$$\langle \bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle = -\langle k|\hat{f}^{\sigma}|k\rangle$$

$$\langle k|\hat{f}^{\sigma}|\bar{k}\rangle = \delta\gamma$$

$$\begin{aligned} E_{k\sigma} &= \alpha + \tfrac{1}{2}\gamma \pm \left(\delta^2\gamma^2 + \left(e_k + \sum_{\mu\neq\nu} c_{k\mu}c_{k\nu}\tau_{\mu\nu}\gamma_{\mu\nu}\right)^2\right)^{1/2} \\ &= \alpha + \tfrac{1}{2}\gamma \pm (\delta^2\gamma^2 + (|e_k| - Q_k)^2)^{1/2} \\ &= \alpha + \tfrac{1}{2}\gamma \pm (\delta^2\gamma^2 + P_k^2)^{1/2}. \end{aligned} \tag{2}$$

The minus sign "–" refers to the bo g, and the sign plus "+", to the antibonding AMO's. In Hubbard approxi on Eq. (2) turns into:

$$E_{k\sigma} = \alpha + \tfrac{1}{2}\gamma \pm (\delta^2\gamma^2 + e_k^2)^{1/2}. \tag{2a}$$

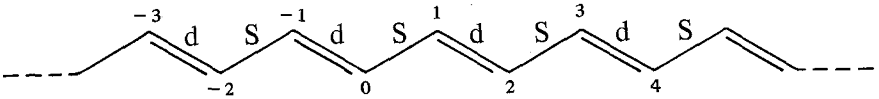
For the correlation corrections we obtain the equations:

$$\delta = \sum_k \sin 2\theta_k = \sum_k \frac{\delta\gamma}{(\delta^2\gamma^2 + P_k^2)^{1/2}} \tag{3}$$

$$\tau_{\mu\nu} = \tfrac{1}{2}p_{\mu\nu} - \sum_k \frac{P_k \cdot C_{k\mu}C_{k\nu}}{(\delta^2\gamma^2 + P_k^2)^{1/2}} \tag{3a}$$

their number, for a definite system, depending on the number of neighbours included in the interaction.

The MO's (Bloch functions) for a cyclic polyene with $4N+2$ AO's could be represented in the following way:



$$|k\rangle = \frac{1}{(4N+2)^{1/2}}\left\{\sum_{-N}^{N} e^{i[\phi_k + (2\mu+1)\omega_k]}|2\mu+1\rangle + \sum_{-N}^{N} e^{-i[\phi_k - 2\mu\omega_k]}|2\mu\rangle\right\}. \tag{4}$$

For the antibonding MO's $|\bar{k}\rangle$ the sign of the sum with even indices is negative

$$\omega_k = \frac{\pi}{2N+1}k, \qquad -N \leq k \leq N$$

$$\phi_k = \operatorname{arctg}\left\{-\left|\frac{\beta_s^{\text{core}} - \beta_d^{\text{core}}}{\beta_s^{\text{core}} + \beta_d^{\text{core}}}\right| \operatorname{tg}\omega_k\right\}.$$

From Eq. (4) we obtain for the bond orders and correlation parameters δ and τ the expressions ($N \to \infty$):

$$\begin{aligned} p_{2s-1} &= p_{1,2s} = p_{0,-(2s-1)} \\ &= 2/\pi \int_0^{\pi/2} \cos[\phi - (2s-1)\omega]\, d\omega \end{aligned}$$

$$p_{2d-1}=p_{0,2d-1}=p_{1,-(2d-1)}$$

$$=2/\pi\int_0^{\pi/2}\cos\left[\phi+(2d-1)\omega\right]d\omega$$

$s, d=1,2,3,\ldots.$

$$\delta=\frac{\delta}{\pi}\int_0^{\pi/2}\frac{d\omega}{(\delta^2\gamma^2+P^2(\omega))^{1/2}} \tag{5}$$

$$\tau_{2d-1}=\tfrac{1}{2}p_{2d-1}-\frac{1}{\pi}\int_0^{\pi/2}\frac{p(\omega)\cos\left[\phi+(2d-1)\omega\right]d\omega}{(\delta^2\gamma^2+P^2(\omega))^{1/2}} \tag{6}$$

$$\tau_{2s-1}-\tfrac{1}{2}p_{2s-1}-\frac{1}{\pi}\int_0^{\pi/2}\frac{p(\omega)\cos\left[\phi-(2s-1)\omega\right]d\omega}{(\delta^2\gamma^2+P^2(\omega))^{1/2}} \tag{7}$$

The number of parameters τ_{2d-1} and τ_{2s-1}, respectively, is determined by the number of the neighbours between which the two-center Coulomb integrals (γ_μ) are taken into account.

The solution of the above coupled Eqs. (5–7) can be found in Appendix I.

In case that the matrix elements of the PPP-Hamilton operator [20],

$$F_{\mu\mu}=\alpha+\tfrac{1}{2}\gamma$$

$$F_{\mu\nu}=\begin{cases}\beta^{\text{core}}-\tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}, & \mu \text{ and } \nu \text{ are neighbouring AO's}\\ -\tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}, & \mu \text{ and } \nu \text{ are non-neighbouring AO's}\end{cases}$$

are calculated by means of the orbitals (4), and only the resonance integrals between neighbouring AO's are taken into account, we obtain the following expressions for the MO energies ($\beta_{s(d)}>0$):

$$\begin{aligned}\mathrm{e}(\omega)&=\sum_{\mu}c_{k\mu}c^{*}_{k\mu}F_{\mu\mu}+\sum_{\mu\neq\nu}c_{k\mu}c^{*}_{k\nu}F_{\mu\nu}\\&=\alpha+\tfrac{1}{2}\gamma+\beta_s^{\text{core}}\cos(\phi-\omega)+\beta_d^{\text{core}}\cos(\phi+\omega)\\&\quad+\tfrac{1}{2}\sum_{d=1}p_{2d-1}\gamma_{2d-1}\cos\left[\phi+(2d-1)\omega\right]\\&\quad+\tfrac{1}{2}\sum_{s=1}p_{2s-1}\gamma_{2s-1}\cos\left[\phi-(2s-1)\omega\right]\\&\quad-\frac{\pi}{2}\leqq\omega\leqq\frac{\pi}{2}.\end{aligned} \tag{8}$$

Including only the first neighbours we obtain:

$$\begin{aligned}\mathrm{e}(\omega)&=(\beta_d^{\text{core}}+\tfrac{1}{2}P_d\gamma_d)\cos(\phi+\omega)+(\beta_s^{\text{core}}+\tfrac{1}{2}P_s\gamma_s)\cos(\phi-\omega)\\&=\beta_d^{\text{eff}}\cos(\phi+\omega)+\beta_s^{\text{eff}}\cos(\phi-\omega)\\&=((\beta_d^{\text{eff}}-\beta_s^{\text{eff}})^2+4\beta_d^{\text{eff}}\beta_s^{\text{eff}}\cos^2\omega)^{1/2}.\end{aligned} \tag{8a}$$

For $P(\omega)$ is obtained, respectively:

$$\begin{aligned} P(\omega) &= |e(\omega)| - Q(\omega) \\ &= |e(\omega)| - \sum_{d=1} \tau_{2d-1}\gamma_{2d-1} \cos[\phi + (2d-1)\omega] \\ &\quad - \sum_{s} \tau_{2s-1}\gamma_{2s-1} \cos[\phi - (2s-1)\omega] \\ &= \beta_d^{\text{core}} \cos(\phi + \omega) + \beta_s^{\text{core}} \cos(\phi - \omega) \\ &\quad + \sum_{d=1} \tau'_{2d-1}\gamma_{2d-1} \cos[\phi + (2d-1)\omega] \\ &\quad + \sum_{s=1} \tau'_{2s-1}\gamma_{2s-1} \cos[\phi - (2s-1)\omega] \end{aligned} \tag{9}$$

where:

$$\tau'_{2d-1} = p_{2d-1} - \tau_{2d-1}$$

$$\tau'_{2s-1} = p_{2s-1} - \tau_{2s-1}.$$

In Hubbard approximation $P(\omega)$ turns to:

$$P(\omega) = \beta_d^{\text{core}} \cos(\phi + \omega) + \beta_s^{\text{core}} \cos(\phi - \omega) \tag{9a}$$

In case that no bond alternation exists ($\beta_s = \beta_d = \beta$, $\gamma_{2s-1} = \gamma_{2d-1}$):

$$P(\omega) = 2\beta \cos\omega + 2 \sum_{P=1} \tau'_{2p-1}\gamma_{2p-1} \cos(2p-1)\omega. \tag{10}$$

In Eq. (8) the summation over s and d, and the summation over p in Eq. (10), respectively, depends on the number of neighbours included in the interaction.

For the width of the energy gap (ΔE_∞) is obtained

$$\Delta E_\infty = 2E(\omega = \pi/2) = 2(\delta^2\gamma^2 + P^2(\pi/2))^{1/2}. \tag{11}$$

In case of ideal geometry ($R_s = R_d$), $P(\pi/2) = 0$ and therefore:

$$\Delta E_\infty = 2\delta\gamma. \tag{12}$$

3. Parametrisation

The calculations are performed using the following approximations for the resonance and the Coulomb integrals: the Coulomb integrals are calculated in two ways. By means of the formula [21]:

$$\gamma_{\mu\nu} = \frac{e^2}{1.328 + tR_{\mu\nu}} = \frac{e^2}{e^2/\gamma + tR_{\mu\nu}} \tag{13}$$

and using formula:

$$\gamma_{\mu\nu} = e^2/rR_{\mu\nu} \tag{14}$$

where the dimensionless parameter t is varied. If $t = 1$, Eq. (13) coincides with the Mataga–Nishimoto approximation [22].

The dependence of the resonance integrals on the bond distance is given by the relation $\beta^{\text{core}} = \beta_0^{\text{core}} \cdot S/S_0$, where S_0 is the overlap integral for the bondlength $R = 1.40$ Å ($Z_C = 3.18$).

An all-trans configuration with valent angles $\measuredangle_{CCC} = 120°$ is chose for the polyenes.

The length of the unit cell $2R_0 = R_s + R_d$, should also be treated as a variable parameter, as there is no information about the geometry of polyenes at $T° = 0°K$.

4. Results and Discussion

The energy gap of the polyenes is in the range 2.2–2.5 eV [11], [23–25].

The value of the resonance integral, corresponding to the Mataga–Nishimoto [22] approximation, is determined for hydrocarbons by means of the PPP-LCI method [26] to be $\beta_0^{\text{core}} = -2.318$ eV. When this parameter is introduced in the calculations, a rather high value for the energy gap is obtained: $\Delta E_\infty = 6.15$ eV($R_0 = 1.40$ Å, for a chain without bond alternation). Too high is also the value $\Delta E_\infty = 6.30$ eV, obtained by means of the parametrisation used in paper [15]: $\beta_0^{\text{core}} = 2.4$ eV, $R_0 = 1.40$ Å, $\gamma = 11.13$ eV. The results presented in the above paper [15] differ materially from ours.

Rather high values for the energy gap ($\Delta E_\infty > 5$ eV) are obtained using the Mataga–Nishimoto approximation for all the possible bondlengths in the range 1.34 Å $\leq R_0 \leq$ 1.48 Å.

It was shown [27] that good results for the energy of electron excitation of alternating hydrocarbons could be obtained by means of the following parametrisation: $\beta_0^{\text{core}} = -2.59$ eV ($R_0 = 1.40$ Å); for the parameter t in Eq. (13) is obtained the value $t = 0.5$. As the optimal value of this parameter is determined

Table 1. Dependence of the energy gap ΔE_∞(eV) on the parameter t (Eq. [13]), on the length of the unit cell ($2R_0 = R_s + R_d$), and on the bond alternation ($R_s = R_0 + r$, $R_d = R_0 - r$). The values for ΔE_∞ obtained with values for r allowing no non-trivial solutions of the Eqs. [5]–[7] ($\delta = 0$, $\tau = 0$) are marked with [a]. The calculations are done with $\beta_0^{\text{core}} = -2.59$ eV

		$t = 1.0$	$t = 0.5$	$t = 0.4$
R_0	r	ΔE_∞	ΔE_∞	ΔE_∞
1.38	0.00	5.15	3.02	2.18
	0.01	5.16	3.06	2.34
	0.02	5.18	3.21	2.97[a]
1.39	0.00	5.28	3.16	2.31
	0.01	5.29	3.19	2.41
	0.02	5.30	3.30	3.30[a]
1.40	0.00	5.40	3.28	2.46
	0.01	5.41	3.32	2.54
	0.02	5.42	3.41	3.30[a]
1.41	0.00	5.53	3.44	2.59
	0.01	5.53	3.47	2.66
	0.02	5.54	3.54	3.30[a]
1.42	0.00	5.66	3.58	2.74
	0.01	5.67	3.60	2.79
	0.02	5.67	3.65	3.30[a]

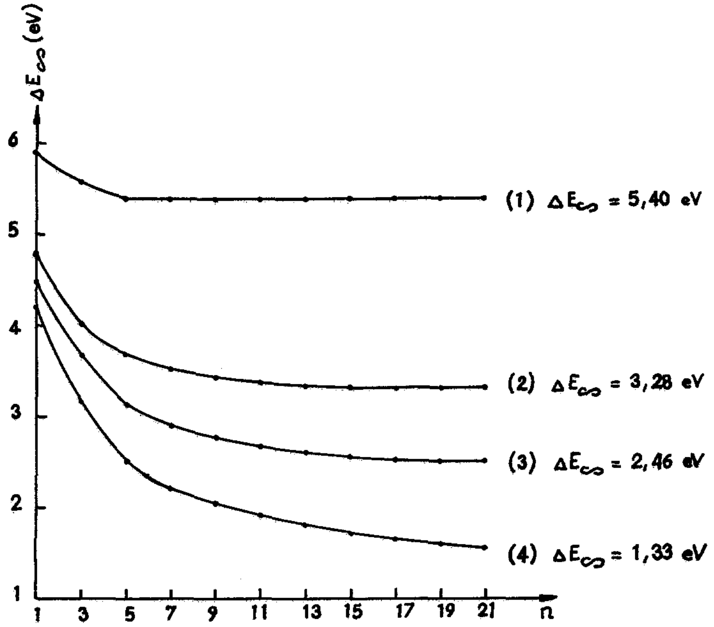


Fig 1. Dependence of the calculated energy gap (Eq. (12); $\gamma = 10.842$ eV; $\beta_0^{\text{core}} = -2.59$ eV) of an infinite polyene without bond alternation on parameter t in Eq. (13) and on the number of neighbours (n), between which the two-center Coulomb integrals are taken into account. (1) $-t = 1.0$; (2) $-t = 0.5$; (3) $-t = 0.4$; (4) $-t = 0.3$. In Hubbard approximation in all cases are obtained the values: $\delta = 0.3934$ and $\Delta E_\infty = 2\delta\gamma = 8.53$ eV.

in the paper [27] for hydrocarbons with small number of π-electrons, in the present work t is a variational parameter. In Table 1 are represented values of the energy gap, calculated with different values of parameter t. It is obvious from this table (see also Fig. 1), that the optimal value of parameter t is $t \simeq 0.4$, when $\beta_0^{\text{core}} = -2.59$ eV.

In Table 2 are represented data for the energy gap, calculated by means of the approximation (14) for the Coulomb integrals.

It is obvious from the both tables that satisfactory values for the energy gap (comparable to the experiment) can be obtained using different sets of parameters.

The problem for the choice of parametrisation in the formalism applied in the present study could be solved through investigation of a greater number of homonuclear systems (such investigations being already in progress), and for uniquely defined geometries.

The result obtained in the present paper is essential in that aspect: in the framework of the applied model and approximations the energy gap of both geometries – with – and without bond alternation – is different from zero. This result might effect significantly the consideration of Peierls's [28] structural transitions of polyenes.

Table 2. Dependence of the energy gap of a polyene without bond alternation ($R_s = R_d = R_0 = 1.40$ Å) on the parameter t in the expression for the two-center coulomb integrals (Eq. (14))

$\gamma_{\mu\nu} = 1/tR_{\mu\nu}$

I: $\gamma = 11.13$ eV, $\beta^{\text{core}} = -2.40$ eV;
II: $\gamma = 10.84$ eV, $\beta^{\text{core}} = -2.59$ eV

I		II	
t	ΔE_∞(eV)	t	ΔE_∞(eV)
1.00	2.50	1.00	1.88
1.32	4.46	1.10	2.46 (2.84[a])
1.62	7.29	1.50	4.35

[a] This value is obtained for $R_s = 1.42$ Å and $R_d = 1.38$ Å.

In Hubbard approximation the condition for existence of a nontrivial solution ($\delta \neq 0$) of Eq. (5) has the form:

$$\pi = \int_0^{\pi/2} \frac{d\omega}{(\delta^2 + (\beta_0/\gamma)^2[(s-d)^2 + 4sd\cos^2\omega])^{1/2}}$$

$$< \frac{\gamma}{\beta_0} \int_0^{\pi/2} \frac{d\omega}{((s-d)^2 + 4sd\cos^2\omega)^{1/2}}$$

or

$$\pi\beta_0/\gamma < \int_0^{\pi/2} \frac{d\omega}{((s-d)^2 + 4sd\cos^2\omega)^{1/2}} = (\beta_0/\gamma)_{\text{crit}}. \tag{15}$$

The critical value $(\beta_0/\gamma)_{\text{crit}}$, beyond which no non-trivial solution ($\delta \neq 0$) of Eq. (5) exists, depends on the bond alternation of the polyene chain, i.e. on the values of $s = \beta_s/\beta_0$ and $d = \beta_d/\beta_0$. In case that $s = d = 1$, tends $(\beta_0/\gamma)_{\text{crit}} \to \infty$, i.e. Eq. (5) possesses non-trivial solutions for any values of the parameters β and γ. For $\beta_0 = 2.59$ eV and $\gamma = 10.842$ eV the ratio $\beta_0/\gamma = 0.2389$. The latter is smaller than the critical value determined by Eq. (15); this is valid for all the values $1 \geq s \geq 0.876$ and $1 \leq d \leq 1.136$, that correspond to the variation of ΔR_0 in the range $0 \leq R_0 \leq 0.08$ Å (at $\Delta R_0 = 0.08$ Å, $(\beta/\gamma)_{\text{crit}} = 0.545$; at the limit $s = 0$, $d = 1$, is $(\beta/\gamma)_{\text{crit}} = 0.5$).

With an increase of the number of neighbours among which the Coulomb interaction is taken into account, the conditions for existence of non-trivial solutions ($\delta \neq 0$, $\gamma \neq 0$) of Eqs. (5)–(7) show stronger dependence on the bond alternation, compared to the Hubbard approximation case. Not every type of alternation, for which non-trivial solution of Eq. (5) in Hubbard approximation exists, allows a non-trivial solution of Eqs. (5)–(7). This, for instance, is obvious in

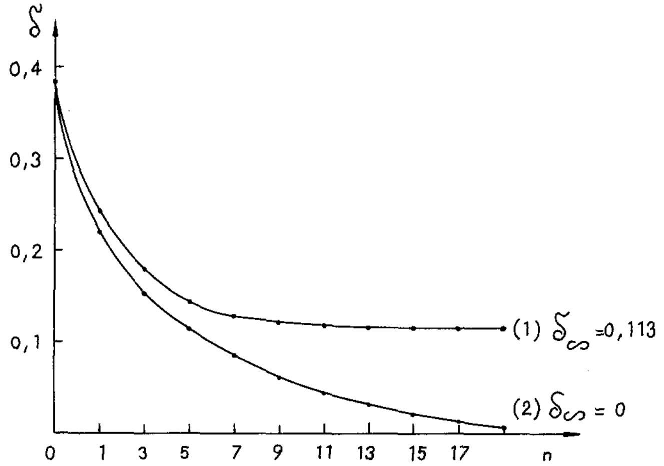


Fig. 2. Dependence of parameter δ on the number of neighbours (n) which are included in the coulomb interaction. (1) polyene with equal bondlengths $R_s = R_d = 1.40$ Å, $t = 0.4$. (2) polyene with bond alternation: $R_s = 1.42$ Å, $R_d = 1.38$ Å, $t = 0.4$. In both cases $\beta_0^{\text{core}} = -2.59$ eV.

Fig. 2, where the dependence of parameter δ on the number of neighbours included in the Coulomb interaction is shown. The greater the number of neighbours included in the interaction, the smaller the values of the parameters δ and τ respectively. In the cases of stronger alternation there exist no non-trivial solutions of Eqs. (5)–(7).

Appendix

The number of equations in the coupled Eqs. (5)–(7) depends on the number of neighbours included in the interaction. In the Hubbard approximation all the quantities τ are equal to zero. If only the first neighbours are taken into account, only τ_s and τ_d are different from zero and the total number of equations is reduced to three. If the second neighbours are also included, five equations are obtained, etc.

Eqs. (5)–(7) can be solved by means of the following iterative procedure: From Eq. (5) δ is determined in Hubbard approximation. With this value δ^0 are calculated all the quantities τ^0_{2s-1} and τ^0_{2d-1} using Eqs. (6) and (7). These values τ^0 determine now a new value δ^1 to obtain new τ^1_{2s-1} and τ^1_{2d-1}. The iterative procedure continues until self-consistence for δ and τ with a chosen precision is achieved.

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