Early quantum chemistry of polyenes. Useful stimulus in research on conducting polymers

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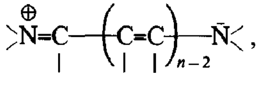
Early quantum-chemical modeling of polyenes is compared with modern developments. An inconsistency in modern treatments not present in early models is tolerated and interpreted by modern authors as an indication of a general failure of single-electron approaches (the discrepancy between the measured value of the elastic force constant of the molecular skeleton and the fitted value). In contrast, we find the discrepancy to be due to a specific defect of the used SSH model. Single-electron approaches, in the view of modern authors, fail in explaining excited-state properties (in particular the low lying 2 ^1A_g state in polyenes). However, the feature results unambiguously from an early single-electron-coupling model.

Early quantum chemistry has an aspect which should be relevant to modern research. Being exposed to a world of unexplained facts, researchers were driven to attempt to understand these facts on the basis of quantum-mechanical models that were as simple as possible but sufficiently detailed to embrace the main experimental features. An important problem in inventing models then was to extract physical features that are essential in understanding the experimental facts while neglecting others.

In present day quantum chemistry of polyenes [1] rigidity of the basic formalism is emphasized more than the aspect of understanding experimental facts, and the formalism is strongly altered to allow comparison with experiment, tolerating adjustable parameters and inconsistencies. Standard models are applied and critical assumptions usually not questioned anymore. Reviving the worries of the early days and bringing up unsettled questions should be useful in modern conjugated polymer research.

In the late 1940s the color of organic dyes was puzzling. A simple empirical relationship was known for cyanine dyes (100 nm shift of absorption band each time when increasing the chain length by a -CH=CH- unit). The strong difference between the absorption of cyanines and polyenes was unexpected. It had been assumed [2] that long polyenes as well as cyanines have uniform bond lengths along the chain. A theoretical treatment explaining the basic difference between the spectroscopic properties of cyanine dyes and polyenes was needed to understand the color of organic dyes.

To approach this problem a given π electron was viewed as moving along the chain of a cyanine dye,



$$\overset{\oplus}{>N}{=}\underset{|}{C}{-}\left(\underset{|}{C}{=}\underset{|}{C}\right)_{n-2}{-}\bar{N}<,$$

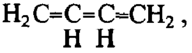
as if it were solely in the Coulomb field of the presently closest C(+) or N(++) respectively, all other π electrons, by their high mobility, shielding the charges of the residual C(+) in the chain. For simplicity, the variation of the potential along the chain was neglected, i.e. it was assumed that the wavefunction of the π electron can be considered as the product of a function of the coordinates perpendicular to the chain which is the same for all π electrons and a function of the coordinate s along the chain (length L) which is a sine wave with nodes at both ends and 0, 1, 2, ... nodes between. The $2n$ π electrons occupy the n lowest free-electron molecular orbitals and the optical excitation energy (transition of the electron from the highest occupied to the next orbital) is given by

$$\Delta E=\frac{h^2}{8mL^2}(2n+1)\approx A/n\,,$$

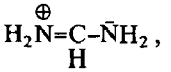
$$\text{with}\,A=\frac{h^2}{16ma^2}=9.57\ \text{eV}\,. \tag{1}$$

L is the chain length, $a=1.4$ Å the bond length, m the mass of the electron and h Planck's constant. Agreement with experiment showed that this simple model leads to a rationalization of the color of cyanine dyes [3]. The model was refined by using a more realistic potential $V(x, y, z)$ constructed from Slater potentials of C (and N) atoms and more sophisticated atomic potentials, assuming for all CC bonds the same length, the experimental bond length in benzene. The agreement between predicted and observed positions and intensities of absorption bands stayed unchanged, supporting the simple free-electron model approach. Digital computers did not exist at that time and a room-filling analog computer to solve the Schrödinger equation in these quite complex molecular model potentials was developed [4].

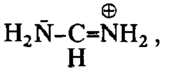
But how to understand the difference between the absorption of polyenes $H\!\left(CH{=}CH\right)_nH$ and cyanine dyes? The simplest cases, butadiene and amidinium ion,



$$H_2C{=}\underset{H}{C}{=}\underset{H}{C}{=}CH_2\,,$$



$$H_2\overset{\oplus}{N}{=}\underset{H}{C}{-}\bar{N}H_2\,,$$



$$H_2\bar{N}{-}\underset{H}{C}{=}\overset{\oplus}{N}H_2\,,$$

were considered using the free-electron model approximation [5]. The four π electrons present in both cases occupy the two lowest levels. The charge density (sum of sine-squares) has a minimum between two equal maxima (symbolized by the single bond between the two double bonds in butadiene and the two equal bonds (resonance hybrid) in the amidinium ion). The σ-bonded elastic molecular lattice of charged C (and N) atoms in the Coulomb field of the π-electron cloud is compressed since the nuclei are attracted by the π-electron cloud in between.

Each σ bond is shortened according to the electron density in the bond. This decreases the potential of the π electrons within the bond, and this again increases the π-electron density. The additional π-electron accumulation in the short bonds causes a further shortening until an equilibrium situation is reached between Coulomb attraction of nuclei and π electrons and elastic repulsion of the compressed σ bonds.

Based on the experimental values of the CC single bond length and the elastic force constant of the CC single bond, this consideration leads to bond lengths in butadiene which are in reasonable agreement with the experimental values, but the treatment is not unambiguous (sp^3 instead of sp^2 hybridization in σ-bond orbitals, and deviation from Hooke's law at high compression). For that reason a somewhat different approach to elucidate the geometry of long polyenes was used.

Starting with the hypothesis that the above consideration on the compression of the σ-bonded lattice by the π-electron cloud would result in an alternation between single and double bonds of a polyene essentially independent of the chain length, the expression

$$\Delta E=\frac{h^2}{8mL^2}(2n+1)+V_0(1-\tfrac{1}{2}n)\,, \tag{2}$$

with $V_0=2$ eV was obtained [6]. The position of the absorption maxima and the oscillator strength of the absorption bands were found to be in agreement with experiment. Thus, the pertinent problem was: can we theoretically substantiate the hypothesis of bond alternation independent of chain length? More specifically: given the bond lengths in butadiene (which were known), what are the bond lengths in a long polyene (which were unknown)?

The program to answer this question, avoiding the above-mentioned ambiguity, was clear: bond length and π-electron density in the middle of the bond are related. Thus we must construct the potential $V(x,$

y, z) for butadiene with the experimental bond lengths (say, by using atomic Slater potentials) and compute the electron density distribution in the ground state by solving the Schrödinger equation. Then the long polyene must be treated in the same manner, assuming the same alternation of bond distances. The hypothesis that the bond alternation is independent of the chain lengths is correct only if the calculated density in each "single" bond is the same as in the "single" bond of butadiene and if the same holds for the "double" bonds, i.e. if self-consistency is reached between assumed bond lengths and bond lengths resulting from the calculated π-electron densities. This turned out to be the case [7].

An even simpler way [7] to get an unambiguous justification of the hypothesis on which eq. (2) is based was obtained by replacing the actual potential by a simple model potential (sine-wave potential with amplitude fitted to the experimental position of the absorption maximum of the long polyene). Again, the same π-electron density alternation of "single" bonds and "double" bonds in the long polyene and in butadiene was observed. The straightforwardness and simplicity of the two approaches should be seen.

A generalization to compute the bond lengths of arbitrary π-electron systems was obtained by calculating a function relating bond length and density in the middle of a bond. The bond lengths in a given π-electron system were then obtained by first assuming any reasonable bond lengths and varying the bond lengths until self-consistency for each bond was reached, i.e. agreement of density obtained by solving the Schrödinger equation and density corresponding to the assumed bond length.

The method used in several levels of sophistication [8] can be illustrated for the logically simplest extension of the free electron model, the step potential model [9,10]. The potential $V(s)$ is assumed to be constant in each bond and given by an averaged Coulomb energy of the electron in the middle of the bond in the effective nuclear charge of the adjacent C atoms. This was achieved in ref. [9] by fitting with the more sophisticated earlier treatment. To fix the potential step V_i in a more transparent way leading to essentially the same result, we consider the electron as being in a Slater atomic orbital and the potential is then averaged over the plane perpendicular to the bond and crossing the bond in its middle; the two adjacent C atoms are considered as point charges of $Z_{\mathrm{Slater}}-1$ atomic units where $Z_{\mathrm{Slater}}=3.25$ for C; the other atoms are assumed to be shielded by the residual π electrons. This gives for bond i (bond length d_i)

$$V_i/\mathrm{eV}=39[(d_i/a)-1]-24[(d_i/a)-1]^2 . \qquad (3)$$

To take care of the coupling of the π electrons to the elastic lattice the bond lengths of butadiene and benzene are used as experimentally given parameters and the following relation between calculated density $\rho(s)$ in the middle of bond i (ρ_i) and bond length d_i is obtained:

$$\rho_i a=1-10.2[(d_i/a)-1]+35[(d_i/a)-1]^2 . \qquad (4)$$

This formalism (as well as the more sophisticated early approaches) gives the bond lengths of π-electron systems in good agreement with experiment. It should be emphasized that all consequences from (3) and (4) follow unambiguously, e.g. equal bonds in benzene and Hückel annulenes up to the 14-annulene, bond length alternation in all other annulenes and polyenes [9].

It is of interest to compare this approach with the popular SSH model [11] which is based on the Hamiltonian

$$H=\sum_i \tfrac{1}{2}K_x(u_i-u_{i+1})^2 -2\sum_i [t_0+(u_i-u_{i+1})\alpha]P_{i,i+1} . \qquad (5)$$

The first term is the elastic energy of the lattice resulting from the compression of the σ bonds (u_i is the deviation of atom i from its reference configuration), and the second term is the electronic energy ($p_{i,i+1}$ is the bond order operator). t_0, K_x and α are adjustable parameters.

The value used for K_x to obtain a band gap in agreement with experience is $K_x=\frac{3}{4}K$ and $K=23$–28 eV/Å^2 [11,12], and the measured value is $K(\exp)=47.5$ eV/Å^2 [1]. If the measured K value were used the calculated band gap would be 1/40 of the measured gap, showing the seriousness of the inconsistency of the model. The discrepancy is assumed by modern authors [1] to be an indication of the failure of single-particle models. A comparison of the SSH model with the step potential model suggests a different reason.

We consider the change in the π-electron potential by proceeding from the reference configuration (bond lengths a) to a configuration with alternating bond lengths (deviation $d_i - a$ alternating between $+\Delta$ and $-\Delta$).

In the step potential model the potential (eq. (3))

$$V_i/\mathrm{eV} = 39\Delta/a - 24(\Delta/a)^2 \tag{6}$$

alternately increases and decreases by $39\Delta/a$ (first term in (6)), and in addition, the average potential drops by $24(\Delta/a)^2$ (second term in (6)). This latter effect is neglected in the SSH model (second term in (5)). Taking it into account, we have to add the electronic term $-24(\Delta/a^2)$ eV to the elastic energy

$$\tfrac{1}{2}K_x(u_i - u_{i+1})^2 = \tfrac{1}{2}K\Delta^2,$$

$$\tfrac{1}{2}K\Delta^2 = \tfrac{1}{2}K(\exp)\Delta^2 - (24\ \mathrm{eV})(\Delta/a)^2 \tag{7}$$

and with $K(\exp) = 47.5\ \mathrm{eV/Å^2}$ we obtain $K = 23\ \mathrm{eV/Å^2}$; this is in agreement with the adjusted value $K = 23$–$28\ \mathrm{eV/Å^2}$. The discrepancy is removed. Thus, the first term in (5) is not the elastic energy of the σ-bonded lattice, but the sum of this elastic energy and of a hitherto neglected π-electronic contribution due to the overproportional increase of the Coulomb attraction towards the adjacent nuclei.

The quantitative treatment of this effect (e.g. using Slater orbitals in deriving (3) or considering $d_i - a$ (in analogy to the SSH approach) to alter between $+\Delta$ and $-\Delta$) is not free from ambiguity. For that reason we have purposely avoided this ambiguity in the early work, as mentioned above, by using the π-electron-density–bond-length relation to treat the coupling of the π electrons with the lattice.

In summary, we find that the discrepancy in K mentioned in ref. [1] is not due to a failure of single-electron approaches. It does not diminish the value of the SSH model [11] and of the step potential model [9,10], which leads to essentially the same results as the SSH model without the need for fitted parameters K_x, α and t_0 and without being restricted to electron hole symmetry.

It has become a dogma that the single-electron approach used in the early models fails in describing the spectra of π-electron systems [13]. In polyenes with $n \geqslant 4$, the $2\,^1\mathrm{A_g}$ state was observed below the $1\,^1\mathrm{B_u}$ state [14] and this has induced setting up this dogma. However, as we show in the following, the dogma is not justified. The observation can be rationalized by using an early single-electron-coupling model [15–17]. A given π electron is considered to be in the time-dependent field of the incident light and in the time-dependent Coulomb field of the clouds of the other π electrons (non-linear optical properties were recently treated in the single-electron approach by taking the field-dependent distribution of the residual π electrons into account [18]).

We use the free-electron model in its simplest form to grasp the essence of the effect considered in ref. [14] (for more refined treatments see ref. [19]). The wavefunctions are sine functions, and the transition energies are obtained by a perturbation treatment using the potential given by eq. (3) with $d_i = 1.34$ and 1.46 Å for a double bond and a single bond. For the transitions $n \to n+1$ (ΔE_1), $n-1 \to n+1$ (ΔE_2) and $n \to n+2$ (ΔE_3) this gives (if the perturbation integral is approximated by a sum of atomic contributions)

$$\Delta E_1 = A(n+\tfrac{1}{2})/n^2 + V_0, \quad \Delta E_2 = A(2/n)\,,$$

$$\Delta E_3 = A2(n+1)/n^2 + V_0\,, \tag{8}$$

with $A = 9.57$ eV (eq. (1)), $V_0 = 39\ \mathrm{eV}(1.46/1.40 - 1) = 1.67$ eV (eq. (3)). The transitions 2 and 3 are coupled leading to transition energies [15]:

$$\Delta E_2^{\mathrm{corr}} = [a - b(1+\eta^2)^{1/2}]^{1/2}\,;$$

$$\Delta E_3^{\mathrm{corr}} = [a + b(1+\eta^2)^{1/2}]^{1/2}\,, \tag{9}$$

with $2a = (\Delta E_2)^2 + (\Delta E_3)^2$, $2b = (\Delta E_3)^2 - (\Delta E_2)^2$,

$$\eta = (4/b)(\Delta E_2 \Delta E_3)^{1/2} \times \langle n-1, n+1 | g | n, n+2 \rangle\,. \tag{10}$$

The coupling element $\langle n-1,\ n+1 | g | n,\ n+2 \rangle$ is evaluated by replacing an integral by a sum of atomic contributions:

$$\langle n-1, n+1 | g | n, n+2 \rangle = \sum_{i=1}^{2n} \sum_{j=1}^{2n} \Psi_{n-1}(i) \Psi_{n+1}(i) \times g(i,j) \Psi_n(j) \Psi_{n+2}(j)\,, \tag{11}$$

with

$$\Psi_\nu(i) = n^{-1/2} \sin[(\pi\nu/2n)(i-\tfrac{1}{2})]\,. \tag{12}$$

The Coulomb repulsion $g(i,j)$ between the electron

Table 1
Polyenes with n double bonds. Coupling element and transition energies from eqs. (8)–(12). Experimental values (from ref. [14]) in parenthesis

n	$\langle n-1, n+1 \vert g \vert n, n+2\rangle$ (eV)	ΔE_1 (eV)	$\Delta E_2^{\mathrm{corr}}$ (eV)	$\Delta E_3^{\mathrm{corr}}$ (eV)
2	1.50	7.65 (5.91)	7.94	16.90
3	0.73	5.39 (4.93)	5.73	10.56
4	0.71	4.36 (4.40)	4.00 (3.97)	8.09
5	0.63	3.78 (4.02)	3.09 (3.48)	6.66 (5.4)
6	0.56	3.40 (3.65)	2.52 (2.91)	5.73 (5.12)

engaged in transition 2 (located in atom i) and the electron engaged in transition 3 (located in atom j) is assumed to be $U=8$ eV for $i=j$ and $V_1=\frac{1}{2}U=4$ eV for $j=i\pm 1$, and 0 otherwise (these values are in the range recommended in the modern literature [1].

The values of $\langle n-1,\ n+1 \vert g \vert n,\ n+2\rangle$ and $\Delta E_1(1\,^1\mathrm{B_u})$, $\Delta E_2^{\mathrm{corr}}(2\,^1\mathrm{A_g})$, $\Delta E_3^{\mathrm{corr}}(3\,^1\mathrm{A_g})$ are given in table 1 and compared with experimental data. The agreement shows that the early single-electron-coupling model is sufficiently accurate to grasp the effect.

Modern authors [1] may not know the early work explaining bond lengths alternation in polyenes and spectroscopic features of π-electron systems. They undervalue the power of single-electron treatments. It may be helpful to revive some old attempts where great care was given to avoid ambiguity. The problem in the modern approach (to bypass difficulties by tolerating inconsistencies and parameter fits) should be seen. The step potential model should be seen as a useful alternative to the SSH model. By its conceptual simplicity it focuses on what is essential in interpreting experimental data.

References

[1] D. Baeriswyl, D.K. Campbell and S. Mazumdar, in: Conjugated Conducting Polymers, ed. H.G. Kiess (Springer, Berlin, 1992).

[2] J.E. Lennard-Jones, Proc. Roy. Soc. London A 158 (1937) 280;
C.A. Coulson, Proc. Roy. Soc. London A 169 (1939) 413; J. Chem. Phys. 7 (1939) 1069;
R.S. Mulliken, J. Chem. Phys. 7 (1939) 364.

[3] H. Kuhn, Helv. Chim. Acta 31 (1948) 1441.

[4] H. Kuhn, Chimia 9 (1955) 237; J. Chem. Phys. 25 (1956) 293; Angew. Chem. 71 (1959) 93;
H. Kuhn, W. Huber, G. Handschig, H. Martin, F. Schäfer and F. Bär, J. Chem. Phys. 32 (1960) 467;
F. Bär, W. Huber, G. Handschig, H. Martin and H. Kuhn, J. Chem. Phys. 32 (1960) 470.

[5] H. Kuhn, Chimia 4 (1950) 203.

[6] H. Kuhn, J. Chem. Phys. 17 (1949) 1198.

[7] H. Kuhn, W. Huber and F. Bär, in: Calcul des fonctions d'onde moléculaire, éditions du centre national de la recherche scientifique, 13 Quai Anatole-France, Paris 1958, Colloque International 1957, pp. 179–201.

[8] H.D. Försterling, W. Huber and H. Kuhn, Intern. J. Quantum Chem. 1 (1967) 225.

[9] C. Kuhn, Phys. Rev. B 40 (1989) 7776.

[10] C. Kuhn and W.F. van Gunsteren, Phys. Rev. B, submitted for publication.

[11] W.P. Su, J.R. Schrieffer and A.H. Heeger, Phys. Rev. B 22 (1980) 2099; B 28 (1983) 1138.

[12] S.R. Phillpot, D. Baeriswyl, A.R. Bishop and P.S. Lomdahl, Phys. Rev. B 35 (1987) 7533.

[13] R. Silbey, in: Conjugated polymeric materials: opportunities in electronics, optoèlectronics and molecular electronics, eds. J.L. Bredas and R.R. Chance (Kluwer, Dordrecht, 1990) p. 4.

[14] B.S. Hudson, B.E. Kohler and K. Schulten, in: Excited states, ed. E.C. Lim (Academic Press, New York, 1982) pp. 1–95; K. Schulten, I. Ohmine and M. Karplus, J. Chem. Phys. 64 (1976) 4422.

[15] H. Kuhn and W. Huber, Helv. Chim. Acta 33 (1959) 363.

[16] W. Huber, G. Simon and H. Kuhn, Z. Naturforsch. 17a (1962) 99.

[17] H.D. Försterling and H. Kuhn, Intern. J. Quantum Chem. 2 (1968) 413.

[18] C. Kuhn, Synth. Metals 41–43 (1991) 3681; in: Electronic properties of polymers, eds. H. Kuzmany, M. Mehring and S. Roth, Springer Series in Solid State Sciences, Vol. 107 (Springer, Berlin, 1992).

[19] C. Kuhn, Synth. Metals, submitted for publication.