ELSEVIER

Synthetic Metals 68 (1995) 173–181

SYNTHETIC METALS

Considerations on correlation effects in π-electron systems

Christoph Kuhn [a], Hans Kuhn [b]

[a] *Laboratoire Leon Brillouin, Centre d'Etudes de Saclay, Bâtiment 563, F-91191 Gif-sur-Yvette Cedex, France*
[b] *Max-Planck-Institut für biophysikalische Chemie, Postfach 2841, D-37018 Göttingen, Germany*

Received 4 July 1994; accepted 21 July 1994

Abstract

Conventional models use antisymmetrized configurations of molecular orbitals (MOs) expressed as linear combinations of atomic orbitals (LCAOs) to describe correlation effects. In the free electron (FE) model and beyond the antisymmetry condition is neglected. This leads to a strong simplification and to physical transparency in describing correlation effects by electron repulsion without losing the essence, determining spectroscopic properties. Examples are studied where the correlation effects in the ground state and in the excited state are not very different (strong absorption band in dyes and polyenes) and examples where this is not the case (first absorption band in porphyrin, which is diminished in intensity to a tenth by electron correlation, transition into the 2^1Ag state in polyenes, which is shifted below the 1^1Bu state by electron correlation). The appropriate evaluation of the electron repulsion integral is crucial in quantitative approaches. The evaluation procedures in the FE approach and in conventional models are critically considered. The nearly free electron (NFE) model approach (numerical solution of 1D Schrödinger equations for appropriate model potentials and straightforward numerical evaluation of interaction integrals) avoids difficulties in using and overstressing perturbation theory.

Keywords: Correlation; π-Electron systems; Free electron model; Dyes; Polyenes

1. Introduction

It is frequently stated that the single-electron approach used in early models, such as the free electron (FE) model and its refinements, fails in describing spectra of π-electron systems since it does not consider correlation effects [1]. It should be emphasized that the FE model takes care of interdependence of electron motion, but in a way that is different to conventional models. The antisymmetry condition of the total electronic wave function is neglected in treating electronic correlation [2]. This simplification leads to a description which is sufficiently accurate for practical purposes. By avoiding adjustable parameters the model is physically transparent and useful in interpreting experimental data. We demonstrate in some examples how electronic correlation is considered and how the results compare with experimental data.

2. The π-electron systems in their ground state

In single-electron models the many-body π-electron Hamiltonian is simplified to a Hamiltonian of independent electrons moving in orbitals to be described as solutions of the 3D Schrödinger equation of an electron in a potential $V(x,y,z)$ associated with the lattice sites. These orbitals have nodes in the layer plane (orthogonality with the σ-electrons). $V(x,y,z)$ is constructed from atomic contributions [3,4]. With the particular postulates defining $V(x,y,z)$ the correlation of electrons in the ground state is indirectly considered: it is assumed that $V(x,y,z)$ is the sum of the Slater potentials of the two adjacent charged lattice sites. The contributions of all other sites are neglected: their charges are considered to be shielded by the residual π-electrons while next-neighbour sites are unshielded. In this way it takes care of the interdependence of the electron under consideration with all other electrons. The motion of this electron is considered to be correlated with the motions of the other electrons.

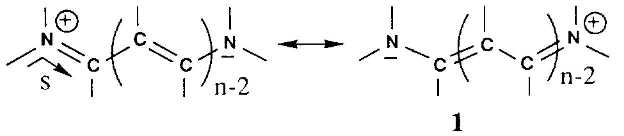
The Schrödinger equations for such potentials $V(x,y,z)$ have been solved in some typical cases [3,4]. It was shown that a considerable simplification in the shape of this potential still leads to a reasonable description of unbranched π-electron systems. The wave functions can be written as the product of a function $\Psi_\nu(s)$ of

0379-6779/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0379-6779(94)02282-4

the coordinate s along the zigzag line connecting the atoms in the chain and a function of the coordinates perpendicular to the chain which is identical for all solutions of physical interest. The functions $\Psi_\nu(s)$ are solutions of the 1D Schrödinger equation in the potential $V(s)$ where $V(s)$ is the average of $V(x,y,z)$ taken over the coordinates perpendicular to s. $V(s)$ again has been systematically simplified in order to investigate what is crucial to describe the relevant properties of π-electrons [3,4]. In the case of a chain with bonds fixed to equal bond lengths, the most radical simplification, $V(s)$ = constant along the chain, still leads to a reasonable description of the wave functions of an electron in the potential $V(x,y,z)$ if the electron wave is assumed to extend by about one bond length beyond the centres of the sites at the chain ends (length $L=a\ (Z+1)$, bond length $a=1.40$ Å, number of sites Z). In this case $\Psi_\nu(s)$ is simply a sine function:

$$\Psi_\nu(s)=\left(\frac{2}{L}\right)^{1/2}\sin\left(\pi\frac{s}{L}\nu\right)\qquad \nu=1,\,2,\,3\,\ldots \qquad (1)$$

As shown below this simplification is appropriate in the case of a cyanine dye with resonating structures:



1

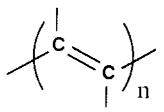
where $L=2an$. The $N=2n$ π-electrons occupy the $N/2=n$ orbitals of lowest energy.

This simple model [5] (the FE model) can easily be refined by solving the Schrödinger equation for the given potential $V(s)$ which has troughs at each atom in the chain, but this does not change the wave functions essentially [6]. The troughs can easily be taken into account to check this statement. However, in the case of unequal bond lengths a refinement is important in describing orbital wave functions and energies [3,4,6]. $V(s)$ is lower in short bonds because the adjacent nuclei, on average, are closer to the electron; the Coulomb attraction is larger. We assume, for simplicity, that the potential is constant along a given bond, its value being given by the value of $V(s)$ in the middle of the bond. Numerical evaluation gives the following relation between potential V_i in bond i and bond length d_i [7]:

$$\frac{V_i}{eV}=39\left(\frac{d_i}{a}-1\right)-24\left(\frac{d_i}{a}-1\right)^2 \qquad (2)$$

This model, the step-potential model [6], is the logically simplest extension of the FE model. It describes this generalized situation sufficiently accurately for the present purposes, and it can easily be refined if desired for its justification. The exact wave functions for a stepwise constant potential are easily obtained by numerical evaluation.

The step-potential model allows us, in an easy way, to calculate the bond lengths in π-electron systems. Bond lengths and π-electron density in a bond are related: the π-electron cloud attracts the nuclei. Thus, assuming first a σ-bonded molecular skeleton with uniform bond length a, the skeleton is elastically deformed in the field of the π-electron cloud and the cloud is deformed in the changed potential. The process is repeated until self-consistency between bond length and π-electron density is reached in each bond. This consideration leads to bond alternation in polyenes:



2

($d_i=1.34$ and 1.46 Å for a double bond and a single bond, respectively), while the bond lengths in a cyanine dye are essentially equal. Assuming equal bond lengths in polyenes when starting the search for self-consistency, the total π-electron density is accumulated in bonds 1–2, 3–4, ..., causing an instability leading to bond alternation. In cyanine dyes, however, the density accumulations are at atoms 1, 3, 5, ..., and not in bonds (Fig. 1). The step-potential model leads to equal bond lengths in benzene and Hückel annulenes up to the 14-annulene and bond alternation in all other annulenes and to the expectation that cyanines, with increasing chain length, change from equal bond lengths to alternating bonds and a soliton-like region of equal bonds in their centre [6].

Extensions of the model are required for considering heteroatoms included in the π-electron system. By adding a potential trough at the site of the heteroatom it takes care of the difference in electronegativity be-

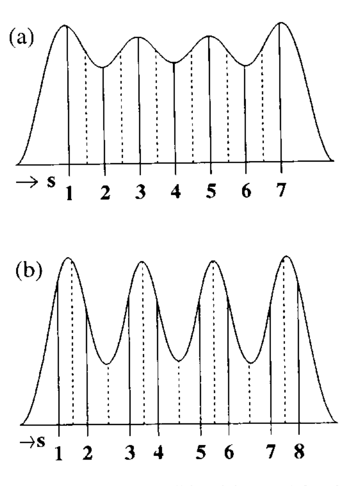


Fig. 1. Cyanines (a) and polyenes (b) with $n=4$ in the step-potential model. Charge density maxima at atoms 1, 3, 5, 7 (cyanines), at bonds 1–2, 3–4, 5–6, 7–8 (polyenes).

tween the heteroatom and carbon. The trough has width 0.3 Å and depth −12 eV for $H_2\bar{N}-$ or $H_2\overset{\oplus}{N}=$, −7.8 eV for $-\bar{N}=$, −20 eV for $-\underline{\bar{O}}-$ and −15.6 eV for $<\!O=$ or $\ominus|\underline{\bar{O}}-$. These numbers were obtained by modelling the troughs using Slater atomic orbitals [8,9].

Branched π-electron systems require another extension. We consider three branches 1, 2 and 3 that meet at a branching point P. The three parts of the wave function $\Psi_\nu(s_1)$, $\Psi_\nu(s_2)$ and $\Psi_\nu(s_3)$ must fulfil conditions that take care of the continuity requirement at this point. By setting at point P (defining s_1, s_2, s_3 to be zero at P):

$$\Psi_\nu(s_1)=\Psi_\nu(s_2)=\Psi_\nu(s_3)$$

$$\frac{\mathrm{d}\psi_\nu(s_1)}{\mathrm{d}s_1}+\frac{\mathrm{d}\Psi_\nu(s_2)}{\mathrm{d}s_2}+\frac{\mathrm{d}\Psi_\nu(s_3)}{\mathrm{d}s_3}=0 \tag{3}$$

This leads to a reasonable description of branched π-electron systems [10]. A recent application is the C_{60} where the bonds in the branched system are found to be alternant [11]. Calculated bond lengths are in agreement with experimental data in many cases of very differently branched systems such as aromatic hydrocarbons [12].

3. Excitation of π-electron systems in cases where correlation effects are small

Cyanine dyes and polyenes are prototypes where the strong absorption band, its position and its strength are almost unchanged by correlation effects beyond the effect of electronic interdependence of which $V(x,y,z)$ takes care. This approximation can be checked by comparison with a refined treatment considering correlation according to Section 4.

Typical organic dyes can be viewed as systems with uniform bond lengths. This follows from considerations according to Section 2. Thus the FE approach is reasonable. The excitation energy of the strong absorption band of a cyanine dye (transition from the highest occupied free electron orbital $\nu=n$ to $\nu=n+1$) is [5]

$$\Delta E=\frac{h^2}{8mL^2}(2n+1) \tag{4}$$

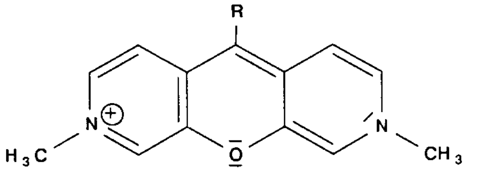
where h is Planck's constant and m is the mass of the electron. The light absorption of cyanine dyes is well described by this equation [5,12]. The effect of the potential troughs of the N atoms at the chain ends is neglected since both orbitals, $\nu=n$ and $\nu=n+1$, have antinodes at these troughs. As a consequence their energy levels are lowered by the same amount.

In polyenes, by their bond alternation, the situation is crucially different, since the electron, in essence, has to be removed from the double bonds (low potential) and brought to the single bonds, i.e. the excitation energy is increased due to bond alternation. The result of the numerical calculation using the step potential or more sophisticated potentials can be expressed by the equation [13]:

$$\Delta E=\frac{h^2}{8mL^2}(2n+1)+V_0\left(1-\frac{1}{2n}\right) \tag{5}$$

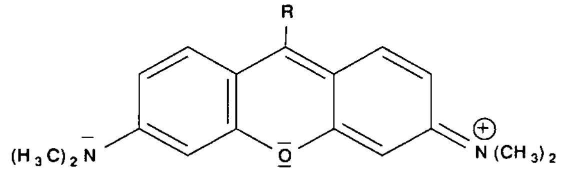
with $V_0=2.0$ eV. The observed absorption of polyenes is well represented by this equation.

In discussing the absorption of the more complex π-electron systems it is advisable to begin with the most simple model and to refine the approach gradually. In this way the nature of a given effect can be elucidated by investigating what is crucial and what is unimportant for it. This is in contrast to the conventional approach as shown in a recent example [14].



3

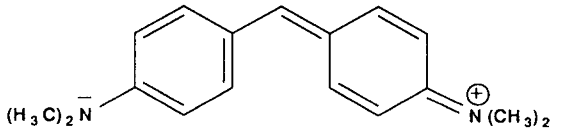
R=phenyl



4

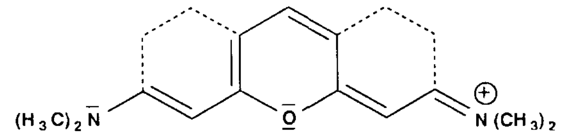
Dye **3** has been synthesized because a conventional calculation considering the configurational interaction of the 50 energetically lowest singly excited states, using a number of experienced adjusted parameters, leads to a prediction which was very surprising to the authors, that dye **3** should absorb at longer wavelengths than dye **4** with the more extended π-electron system. Indeed, the absorption maximum of dye **3** is observed at 630 nm; that of dye **4** at 554 nm. Is the effect a result of a complex interaction of configurations? Is the sophistication of the conventional treatment essential for understanding the effect or obscuring the reason of the unexpected shift?

We first discuss dyes of the kind of dye **4**.

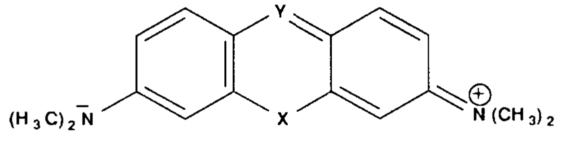


5

When proceeding from the cyanine **1** with $n=6$ to the corresponding branched system (dye **5**) the observed position of the absorption band is practically unchanged (it changes from 625 to 603 nm). Therefore, we first neglect this branching in considering dye **4** and treat this dye as if it is only branched by the O atom [15]:



The FE model of this system predicts a transition from the highest occupied orbital $|a\rangle$ to the lowest unoccupied orbital $|b\rangle$ at 393 nm. Orbital $|a\rangle$ has a node of the wave function at the O atom and $|b\rangle$ has an antinode. Therefore, if we consider the O atom as a potential trough, $|a\rangle$ is practically unaffected since this orbital has no charge accumulation at the O. In contrast, the charge of $|b\rangle$ is accumulated at the O atom, the level is lowered. The nitrogens at the ends, similar to the cyanines (dye **1**), have the same effect on the energy levels of $|a\rangle$ and $|b\rangle$ and can be neglected for the present purpose. The transition energy is lowered by the potential trough attributed to O; the predicted absorption maximum is shifted to 558 nm [15]. This is in good agreement with the measured value 550 nm. If the –O– atom is replaced for –N– the shift should be less since N is less electronegative, and the potential trough shallower. The predicted absorption maximum at 475 nm [15] agrees well with the experimental value 491 nm of dye **6** with X=NCH$_3$ and Y=CH.



6

If, in addition, the C atom in position Y is replaced by N, a further shift to smaller excitation energy is expected since $|a\rangle$ has a node and $|b\rangle$ an antinode also at this position. The predicted absorption maxima (at 610 nm for X=NCH$_3$ and Y=N, and at 758 nm for X=O and Y=N) are in reasonable agreement with experiment (565 and 648 nm, respectively) [15]. The refined approach including the additional branching leads essentially to the same results [16].

In the case of dye **3** the corresponding FE model (branching type of anthracene) predicts an absorption maximum for the transition from the highest occupied orbital $|a\rangle$ to the lowest unoccupied orbital $|b\rangle$ at 961 nm [17]. In contrast to the case of dye **4** orbital $|a\rangle$ has an antinode and orbital $|b\rangle$ a node at the position of the O atom. Therefore, the transition energy is expected to increase by about the same amount as it is decreased in the case of dye **4**.

Using the step-potential model taking care of all heteroatoms (potential troughs according to Section 2) and all branchings, the results in Table 1 and Fig. 2 are obtained. Good agreement with the measured values is obtained in all cases. Replacing R=phenyl in dye **3** by an electron-attracting group, the potential trough at the adjacent site should increase the excitation energy (antinode of HOMO (highest occupied molecular orbital) at the site) in contrast to dye **6** (antinode of LUMO (lowest unoccupied molecular orbital) at the corresponding site). This is indeed the case: dye **3** with R=4-CF$_3$–C$_6$H$_4$ has its absorption maximum at 614 nm [14].

Table 1
Absorption maximum (in nm) of some dyes with branched π-electron systems

	Dye 3	Dye 6			
		X=O Y=CH	X=NCH$_3$ Y=CH	X=O Y=N	X=NCH$_3$ Y=N
Theory	636	560	513	675	604
Experiment	630	550	491	648	565

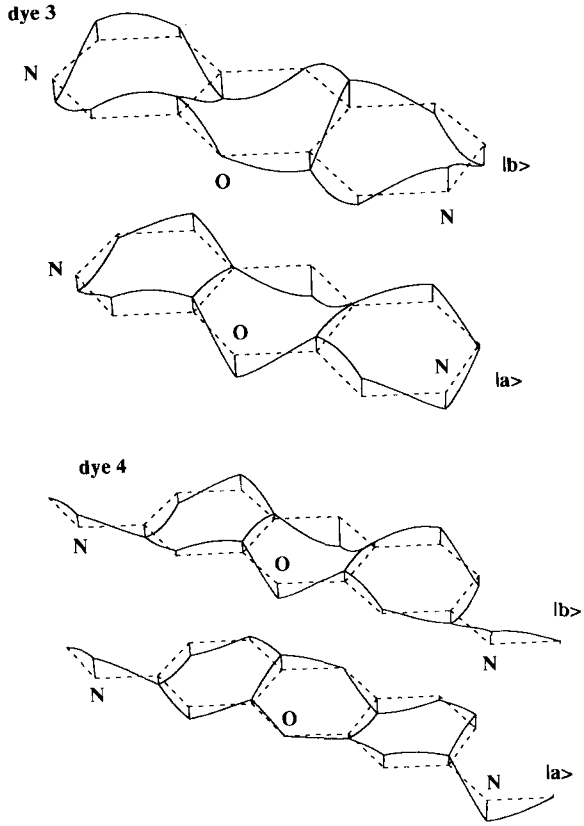


Fig. 2. Dyes **3** and **4**. Wave functions $|a\rangle$ and $|b\rangle$ in HOMO and LUMO. Potential troughs representing N and O atoms: width 0.3 Å, depth −12 eV (N), −20 eV (O), (see Section 2).

The intensities of the absorption bands are determined by the transition moment (x is the coordinate in the direction of the long axis of the chromophore; e is the elementary charge):

$$\mu_x = \langle \mathrm{a}|ex|\mathrm{b}\rangle \tag{6}$$

The oscillator strength of the transition is (if the transition moment is in the direction of the x-axis, and it is taken into account that two electrons are in the highest occupied state) [18]

$$f = \frac{2}{3}\frac{8\pi^2 m}{e^2 h^2}\Delta E \mu_x^2 \tag{7}$$

It is seen from the wave functions $|\mathrm{a}\rangle$ and $|\mathrm{b}\rangle$ that μ_x is large for the dyes of the kind of dye **4** and small for dye **3** (μ_x is zero in the FE case: wave function $|\mathrm{a}\rangle$ symmetric, $|\mathrm{b}\rangle$ anti-symmetric to both axes); it becomes different from zero when introducing the potential troughs of the heteroatoms causing a deformation of the wave functions (Fig. 2) and leading to the oscillator strength 0.26 for dye **3** as compared with 1.24 for dye **4**; ratio 4.8). Indeed, the extinction coefficient is 4.4 times larger for dye **4** than for dye **3** (oscillator strengths 0.9 and 0.2, respectively). The sophisticated treatment mentioned above predicts a factor of 16 [14]. Replacing R = phenyl in dye **3** for R = 4-CF_3–C_6H_4 should counteract the above effect on the wave functions and lead to a smaller oscillator strength, and this is indeed observed [14]. In conclusion, the absorption of dye **3** is well predicted by the step-potential model, showing that the effect is not due to a complex interaction of π-electrons requiring a sophisticated approach. The example demonstrates the merits of simple modelling in elucidating π-electron systems.

4. Excitation of π-electron systems in cases where correlation effects are important

4.1. General considerations

We consider the π-electron system in the perturbing electric field of the light wave and apply the time-dependent Schrödinger equation. The electron under consideration is treated as being exposed to the time-dependent field of the light and to the time-dependent field of all other electrons in the system. Thus, the essential point in our approach in treating the correlation of all electrons in the system is to neglect the requirement for antisymmetry of the total wave function. This leads to a strong simplification in the formalism, to a description which is sufficiently accurate for practical purposes, physically transparent and useful. Thus, the dogma that the single-electron approach fails in describing the spectra of π-electron systems cannot be sustained.

We first consider the light absorption of a one-electron system, an electron in wave function $|\mathrm{a}\rangle$ (ground state) which can be put into the excited state (wave function $|\mathrm{b}\rangle$), excitation energy ΔE). The system is exposed to light for a short time. The probability is determined to find the electron, after exposure, in the excited state $|\mathrm{b}\rangle$. The light is considered as an alternating electric field acting on the molecule. According to the theory of Dirac the interaction is strongest if the frequency of the light ν is given by $\Delta E = h\nu$. The oscillator strength of the transition is given by Eq. (7) if the x-axis is in the direction of the transition moment.

Now we consider the light absorption of a system of many electrons described by the wave functions of an electron in the potential $V(x,y,z)$. Electron i is assumed to be in orbital $|\mathrm{a}_i\rangle$; it can be excited (wave function $|\mathrm{b}_i\rangle$, excitation energy ΔE_i). The system in the ground state is exposed to the perturbing field of light. According to the time-dependent Schrödinger equation, the wave function of electron i becomes a time-dependent linear combination of $|\mathrm{a}_i\rangle$ and $|\mathrm{b}_i\rangle$ depending on the perturbing field of the light and on the fields of the time-dependent charge distributions of all other electrons. Each electron affects all the others, and again we ask for the probability, after light exposure, to find electron i in the excited state $|\mathrm{b}_i\rangle$. Then, by varying the frequency of the light, the positions and the oscillator strengths of the absorption bands attributed to each electron are obtained. For the present purpose it is sufficient to restrict ourselves to just two interacting electrons 1 and 2. Then, the positions ($\Delta E_{1,\mathrm{corr}}$ and $\Delta E_{2,\mathrm{corr}}$) and oscillator strengths ($f_{1,\mathrm{corr}}$ and $f_{2,\mathrm{corr}}$) are given by the relations [2]:

$$\Delta E_{1,\mathrm{corr}} = [A - B(1+\eta^2)^{1/2}]^{1/2} \tag{8}$$

$$\Delta E_{2,\mathrm{corr}} = [A + B(1+\eta^2)^{1/2}]^{1/2} \tag{9}$$

$$2A = (\Delta E_2)^2 + (\Delta E_1)^2 \tag{10}$$

$$2B = (\Delta E_2)^2 - (\Delta E_1)^2 \tag{11}$$

$$\eta = \frac{4}{B}(\Delta E_1 \Delta E_2)^{1/2} J \tag{12}$$

$$J = \langle \mathrm{a}_1(1)\mathrm{b}_1(1)|g(1,2)|\mathrm{a}_2(2)\mathrm{b}_2(2)\rangle \tag{13}$$

$$f_{1,\mathrm{corr}} = [C(f_1/2)^{1/2} - D(f_2/2)^{1/2}]^2 \tag{14}$$

$$f_{2,\mathrm{corr}} = [C(f_1/2)^{1/2} + D(f_2/2)^{1/2}]^2 \tag{15}$$

$$C = \left[1 + \frac{1}{(1+\eta^2)^{1/2}}\right]^{1/2} \tag{16}$$

$$D = \left[1 - \frac{1}{(1+\eta^2)^{1/2}}\right]^{1/2} \tag{17}$$

where $g(1,2)$ is the Coulomb repulsion energy of the two electrons.

These equations are formally identical with the equations for coupled classical oscillators, thus we call J the coupling term. The integral is identical with the essential matrix element in conventional treatments which takes care of the requirement for antisymmetry of the total wave function. The crucial question in treating correlation effects in practical cases is how to evaluate this integral J.

4.2. Evaluation of J in the present model and in conventional theories

We ask for the Coulomb repulsion energy $g(1,2)$ between electrons 1 and 2 with coordinates s_1 and s_2, averaged over the coordinates perpendicular to s. The repulsion energy is largest for $s_1=s_2$. In this case the electrons are roughly at an average distance equal to the distance d between the centres of the two lobes of a p_z orbital ($d=1.2$ Å). In this case the shielding by σ-electrons is considered to be negligible, the average repulsion energy $g(1,2)=e^2/d=12$ eV in accord with the conventional approach [19]. The repulsion decreases with the distance R between coordinates s_1 and s_2. If R is sufficiently large (larger than about $a/2$, which means that the distance between the two electrons is larger than about a) the shielding effect by the polarization of the σ-electrons is important. We consider this effect by assuming that the σ-electrons are polarized like a medium of the dielectric constant ϵ of a saturated hydrocarbon ($\epsilon=2.5$). This is expressed by the simple equation:

$$g(1,2)=\frac{e^2}{\epsilon(R^2+d^2)^{1/2}}\begin{cases}\epsilon=1 & \text{for } R<a/2\\ \epsilon=2.5 & \text{for } R\geqslant a/2\end{cases} \tag{18}$$

(for large values of R, $(R^2+d^2)^{1/2}$ is practically equal to R). With this rough but reasonable estimate, the integral J can be easily evaluated if the 1D wave functions are given by the FE model (example in Section 4.3) or by the step-potential model (examples in Section 4.4). The result is compiled in Table 2 for the cases in Sections 4.3 and 4.4 (column 2). In columns 3, 4 and 5 are listed the contributions to J for $R<(a/2)$, $(a/2)<R<a$; $R>a$. In the case of the porphyrin (Section 4.3) the contribution for $R<(a/2)$ is smaller than the contribution for $a/2<R<a$ because one or other wave function has a node in each atom. In contrast, in the polyenes (Section 4.4), J is governed by the contribution for $R<(a/2)$ because the large Coulomb repulsion at small distance is determining the value. In the conventional models [19] the orbital wave functions, $|a_1\rangle$, $|b_1\rangle$, $|a_2\rangle$, $|b_2\rangle$, are described as superpositions $\Sigma c_k\phi_k$ of atomic orbitals ϕ_k (coefficients c_k). Then J is evaluated by restricting to nearest-neighbour interaction terms:

$$U=\langle\phi_k^2(r)|g|\phi_k^2(r')\rangle \tag{19}$$

$$V_1=\langle\phi_k^2(r)|g|\phi_{k+1}^2(r')\rangle \tag{20}$$

$$2W=\langle\phi_k(r)\phi_{k+1}(r)|g|\phi_k(r')\phi_{k+1}(r')\rangle \tag{21}$$

$$X=\langle\phi_k^2(r)|g|\phi_k(r')\phi_{k+1}(r')\rangle \tag{22}$$

where $g=e^2/|r-r'|$ and r and r' are the coordinates of the two electrons. X and W are usually considered as negligible; U and V_1 as adjustable parameters. U values between 5 and 11 eV were recommended [19]. V_1 values between 1 and 9 eV were suggested, and values between 2.1 and 3.8 eV particularly recommended. In a frequently used approximation (Hubbard model [20]) a dramatic simplification is made: the restriction to the repulsion term U.

Table 2

Porphyrin and polyenes. Coupling integral J given by Eq. (13) and $|a_1\rangle$, $|b_1\rangle$, $|a_2\rangle$, $|b_2\rangle$ given by Eqs. (23)–(26) (porphyrin) and $|a_1\rangle=|n-1\rangle$, $|b_1\rangle=|n+1\rangle$, $|a_2\rangle=|n\rangle$, $|b_2\rangle=|n+2\rangle$ (polyenes). Contributions to J for $R<a/2$, $a/2<R<a$, $R>a$ in present model (columns 2–5) and integral J in LCAO approximation neglecting X and W (column 6)

	J (eV)	$J_{R<a/2}$ (eV)	$J_{a/2<R<a}$ (eV)	$J_{R>a}$ (eV)	J_{LCAO}
Porphyrin	0.41	0.17	0.23	0.01	$0.116V_1$
Polyene					
$n=2$	1.41	1.85	−0.02	−0.41	$0.2U+0.1V_1$
$n=4$	0.79	0.87	0.02	−0.11	$0.063U+0.05V_1$
$n=6$	0.58	0.58	0.01	−0.01	$0.042U+0.056V_1$

Are these simplifications reasonable? Are the adjusted values of U and V_1 reasonable in the present view? Is the use of V_1 values that differ by an order of magnitude physically plausible? We have studied this problem in the examples of Sections 4.3 and 4.4 by calculating the coefficients c_k of the Hückel molecular orbitals and evaluating J for these examples, neglecting W and X (Table 2, column 6).

In the porphyrin case (Section 4.3) the U term is missing (since one factor in the product of the coefficients c_k is always zero: at each site one of the four wave functions has a node). This is the only term considered in the Hubbard model in which correlation is assumed to be restricted to the case where both electrons are at the same site. However, there is a very strong correlation effect in the spectrum of porphyrin (see Section 4.3), showing that the Hubbard approximation is inappropriate in this case. On the other hand, when evaluating J using the Ohno equation [21] (which is identical with Eq. (18), but ϵ is set to unity in the whole range, i.e., the σ-electron polarization in the field of the π-electrons is not taken into account) the correlation should be overestimated.

The example of porphyrin then is a good case to estimate the value of V_1 by comparison with the present approach: neglecting W and comparing the value $0.116V_1$ with the value 0.41 eV (Table 2 and Section 4.3), gives $V_1=3.5$ eV. This is within the range of the particularly recommended adjusted V_1 values (2.1 to 3.8 eV). The comparison shows that these values are physically reasonable, but this is not the case for 1 and 9 eV.

The U term can be evaluated from the polyene data. We compare the contribution for $R<a$ (Table 1, sum of columns 3 and 4) with the sum of the U and the V_1 term (column 6) and find U for a given $V_1=3.5$ eV. The values $U=7.4$ eV ($n=2$), $U=11.3$ eV ($n=4$), and $U=9.3$ eV ($n=6$) are at the upper limit of the recommended adjusted values. It should be noted that the contribution to J for larger distances (usually neglected in LCAO (linear combinations of atomic orbital) treatments) ($R>a$, column 5) are considerable in polyenes with $n=2$ to 4.

The directness and easiness in evaluating J in the FE approach and beyond, avoiding separation into atomic orbital contribution and avoiding restriction to nearest neighbours, should be emphasized.

4.3. Porphyrin

Two bands are observed in the visible, a band at 550 nm ($f_1=0.14$) and a band at 423 nm ($f_2=2.80$). The strong difference in intensity of the two bands cannot be explained without taking correlation effects into account.

We consider the molecule as a system of 18 π-electrons moving along a ring of 16 sites [22] (thick line in Fig. 3, each bond of length $a=1.4$ Å, coordinate s along the bonds with $s=0$ at site 16) and eight separated π-electrons (indicated in the figure by double bonds). In a refined consideration [23] these electrons must be included and the molecule has to be considered as a branched 26 π-electron system. We neglect the branching in order to focus on the essential point in the present context.

The HOMOs:

$$|a_1\rangle=\frac{1}{(8a)^{1/2}}\sin\left(\frac{4\pi}{8a}s\right) \tag{23}$$

$$|a_2\rangle=\frac{1}{(8a)^{1/2}}\cos\left(\frac{4\pi}{8a}s\right) \tag{24}$$

are non-degenerate because $|a_2\rangle$ has antinodes (maximum density) at the positions of the N atoms, while $|a_1\rangle$ has nodes (zero density). Thus, treating N atoms as perturbations, $|a_2\rangle$ is at a lower level than $|a_1\rangle$.

In contrast, the LUMOs:

$$|b_1\rangle=\frac{1}{(8a)^{1/2}}\sin\left(\frac{5\pi}{8a}s\right) \tag{25}$$

$$|b_2\rangle=\frac{1}{(8a)^{1/2}}\cos\left(\frac{5\pi}{8a}s\right) \tag{26}$$

are degenerate, the overall density at the N atoms is the same. The first band in the FE description corresponds to transitions $|a_1\rangle$ to $|b_1\rangle$ (x-band with transition moment in the x-direction) and $|a_1\rangle$ to $|b_2\rangle$ (y-band); the second band corresponds to transitions $|a_2\rangle$ to $|b_1\rangle$ (y-band) and $|a_2\rangle$ to $|b_2\rangle$ (x-band). The following values are obtained for the corresponding excitation energies and oscillator strengths: $\Delta E_1=2.30$ eV (540 nm); $f_1=1.76$; $\Delta E_2=3.18$ eV (390 nm); $f_2=2.64$. The coupling treatment can be restricted to the y-bands, since there

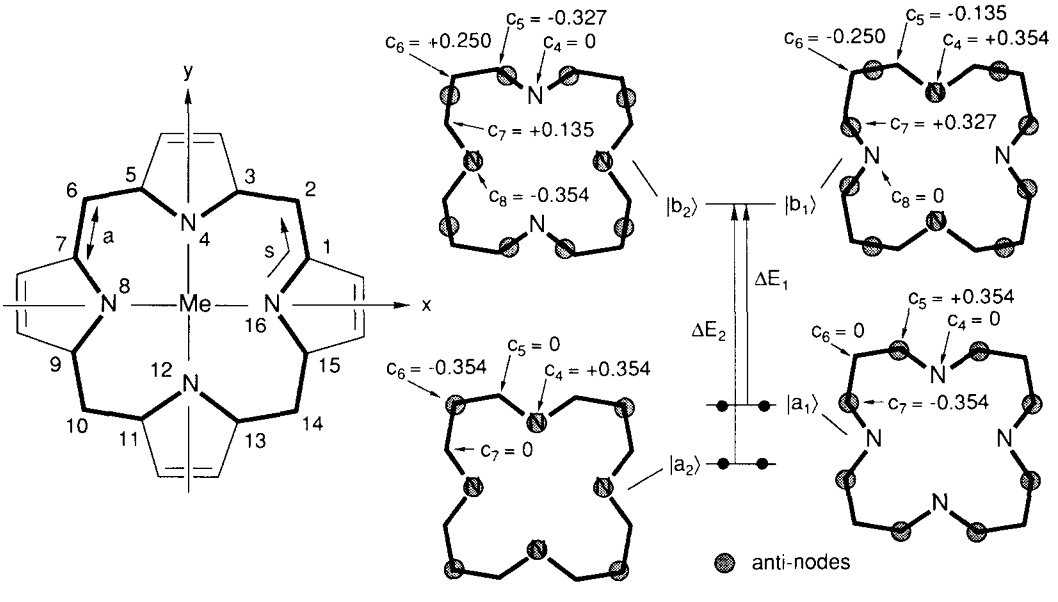


Fig. 3. Porphyrin (metal complex). Molecular lattice in xy-plane. 18 π-electrons moving along a ring (thick line) and eight separated π-electrons indicated by double bonds. Energy levels of HOMOs ($|a_1\rangle$, $|a_2\rangle$) and LUMOs ($|b_1\rangle$, $|b_2\rangle$) in the FE model treating N atoms as a perturbation. Wave functions $|a_1(s)\rangle$, to $|b_2(s)\rangle$ given by Eqs. (23) to (26): their anti-nodes are indicated by filled circles. Numerical values at atoms represent LCAO coefficients c_k.

is no coupling between x- and y-bands, and the x-bands couple in the same way as y-bands. With Eqs. (8) to (17) and $J=0.41$ eV (Table 2), we obtain the values: $\Delta E_{1,\mathrm{corr}}=1.63$ eV (763 nm); $f_{1,\mathrm{corr}}=0.04$; $\Delta E_{2,\mathrm{corr}}=3.57$ eV (347 nm); $f_{2,\mathrm{corr}}=4.36$. A refined treatment including atomic potential troughs gives $J=0.36$ eV and this leads to the slightly different values: $\Delta E_{1,\mathrm{corr}}=1.75$ eV (707 nm); $f_{1,\mathrm{corr}}=0.13$; $\Delta E_{2,\mathrm{corr}}=3.50$ eV (354 nm); $f_{2,\mathrm{corr}}=4.3$. Thus, the coupling effect on the intensities of the absorption bands is well represented by the model, but the separation of the two bands is overestimated and this is due to the neglect of branching, as seen by refining the treatment [23].

4.4. Polyenes

The fact that the 2^1Ag state of polyenes is below the 1^1Bu state has led to the so-called dogma that the single-electron approach used in early models fails in describing the spectra of π-electron systems. We have shown in [7] that the coupling approach (Eqs. (8) to (17)) leads to a simple explanation of this fact. We used a strongly simplified perturbation treatment focusing on the essence. Here we consider a more rigid approach. The Schrödinger equation for the step-potential model (Section 2) is solved numerically: the transitions from the ground state of a polyene with n double bonds into the 1^1Bu state (transition from orbital $|n\rangle$ to orbital $|n+1\rangle$, transition energy ΔE_1) and into the 2^1Ag state (coupling between transitions from $|n-1\rangle$ to $|n+1\rangle$ and $|n\rangle$ to $|n+2\rangle$, transition energies ΔE_2 and ΔE_3). The coupling between the two electrons engaged in each of the three transitions is first considered: transitions into singlets ($\Delta E_1^{(1)}$, $\Delta E_2^{(1)}$, $\Delta E_3^{(1)}$) and triplets ($\Delta E_1^{(3)}$, $\Delta E_2^{(3)}$, $\Delta E_3^{(3)}$), where e.g.,

$$\Delta E_1^{(1)}=(\Delta E_1^2+2\Delta E_1 J)^{1/2} \tag{27}$$

$$\Delta E_1^{(3)}=(\Delta E_1^2-2\Delta E_1 J)^{1/2} \tag{28}$$

J is given by Eq. (13) with $|a_1\rangle=|n\rangle$, $|b_1\rangle=|n+1\rangle$, $|a_2\rangle=|n\rangle$, $|b_2\rangle=|n+1\rangle$.

Then, the transitions $\Delta E_2^{(1)}$ and $\Delta E_3^{(1)}$ are coupled giving $\Delta E_{2,\mathrm{corr}}^{(1)}$ and $\Delta E_{3,\mathrm{corr}}^{(1)}$ (coupling integral J given by Eq. (13) with $|a_1\rangle=|n-1\rangle$, $|b_1\rangle=|n+1\rangle$, $|a_2\rangle=|n\rangle$, $|b_2\rangle=|n+2\rangle$). The coupling integrals are evaluated by numerical integration using Eq. (18) and the numerically obtained wave functions $|n-1\rangle$, $|n\rangle$, $|n+1\rangle$, $|n+2\rangle$. The approach is refined by additionally introducing a po-

Table 3
Polyenes with n double bonds. Transition energies and coupling elements (in eV)

n	2	3	4	5	6
ΔE_1	7.65 ^{a}	5.37 ^{a}	4.36 ^{a}	3.78 ^{a}	3.40^{a}
	5.25 ^{b}	4.34 ^{b}	3.82 ^{b}	3.50 ^{b}	3.29 ^{b}
	4.38 ^{c}	3.51 ^{c}	3.10 ^{c}	2.70 ^{c}	2.49 ^{c}
ΔE_2	9.57 ^{a}	6.38 ^{a}	4.79 ^{a}	3.83 ^{a}	3.19 ^{a}
	6.82 ^{b}	5.78 ^{b}	5.06 ^{b}	4.55 ^{b}	4.17 ^{b}
	6.0 ^{c}	4.95 ^{c}	4.24 ^{c}	3.74 ^{c}	3.38 ^{c}
ΔE_3	16.0 ^{a}	10.2 ^{a}	7.65 ^{a}	6.26 ^{a}	5.39 ^{a}
	9.98 ^{b}	7.20 ^{b}	5.80 ^{b}	4.97 ^{b}	4.43 ^{b}
	8.48 ^{c}	6.14 ^{c}	4.89 ^{c}	4.13 ^{c}	3.62 ^{c}
$\Delta E_1^{(1)}$	5.92 ^{c}	4.64 ^{c}	3.91 ^{c}	3.44 ^{c}	3.11 ^{c}
	5.91 ^{d}	4.93 ^{d}	4.40 ^{d}	4.02 ^{d}	3.65 ^{d}
$\Delta E_1^{(3)}$	1.83 ^{c}	1.75 ^{c}	1.69 ^{c}	1.65 ^{c}	1.64 ^{c}
	3.22 ^{d}	2.6 ^{d}	2.1 ^{d}	1.9 ^{d}	– ^{d}
$\Delta E_2^{(1)}$	7.50 ^{c}	6.02 ^{c}	5.10 ^{c}	4.46 ^{c}	4.00 ^{c}
$\Delta E_3^{(1)}$	9.77 ^{c}	7.08 ^{c}	5.66 ^{c}	4.78 ^{c}	4.18 ^{c}
$\Delta E_{2,\mathrm{corr}}^{(1)}$	5.59 ^{c}	4.54 ^{c}	3.78 ^{c}	3.28 ^{c}	2.92 ^{c}
	– ^{d}	– ^{d}	3.79 ^{d}	3.48 ^{d}	2.91 ^{d}
$\Delta E_{3,\mathrm{corr}}^{(1)}$	11.0 ^{c}	8.1 ^{c}	6.6 ^{c}	5.7 ^{c}	5.0 ^{c}
	– ^{d}	– ^{d}	– ^{d}	5.4 ^{d}	5.12 ^{d}
$J(\|n-1\rangle\rightarrow\|n+1\rangle;\ \|n\rangle\rightarrow\|n+2\rangle)$	1.41 ^{c}	0.97 ^{c}	0.79 ^{c}	0.67 ^{c}	0.58 ^{c}
$J(\|n\rangle\rightarrow\|n+1\rangle;\ \|n\rightarrow\|n+1\rangle)$	1.81 ^{c}	1.32 ^{c}	1.03 ^{c}	0.84 ^{c}	0.70 ^{c}
$J(\|n-1\rangle\rightarrow\|n+1\rangle;\ \|n-1\rangle\rightarrow\|n+1\rangle)$	1.69 ^{c}	1.18 ^{c}	0.94 ^{c}	0.79 ^{c}	0.68 ^{c}
$J(\|n\rangle\rightarrow\|n+2\rangle;\ \|n\rangle\rightarrow\|n+2\rangle)$	1.39 ^{c}	1.01 ^{c}	0.82 ^{c}	0.70 ^{c}	0.60 ^{c}

[a] Perturbation theory [1].
[b] Step-potential model (bond alternation); numerical solution of Schrödinger equation.
[c] Step-potential model (bond alternation, atomic potential troughs); numerical solution of Schrödinger equation.
[d] Experiment (see Ref. [14] in [7]).

tential trough of width 0.3 Å and depth 31 eV at each atom to take care of the atomic potential lowerings. The results are compiled in Table 3 for $n=2$ to 6.

The positions of the 1^1Bu and 2^1Ag states are essentially the same as in [7] [1]; the transition energies are in accord with experimental data.

5. Conclusions

The NFE model allows us to rationalize the spectroscopic properties of π-electrons. Electron repulsion is considered, but the antisymmetry of the total wave function, for simplicity, is neglected. In simple cases the extra correlation when exciting the molecule can be neglected, e.g., in the case of a recently synthesized dye, where this very simple model approach leads to a better agreement with experimental data than a conventional approximation including a great number of interacting configurations. This extra correlation is important in cases where electrons are engaged in transitions with equally oriented transition moments. For quantitative treatment an appropriate description of electron repulsion is crucial. In the FE model and beyond, this is attempted by numerically solving the Schrödinger equation for appropriately constructed model potentials and straightforward numerical integration in evaluating the coupling integral J. Thus, the difficulty is avoided of introducing errors by overstressing the perturbation theory and by making simplifying assumptions in evaluating J (writing each molecular orbital as a linear combination of atomic orbitals and making omissions which are not obvious). The free electron model and beyond has been recently considered as obsolete because it was tailor-made for analogue rather than digital computers and is less easy to handle than Hückel-type treatments [24]. However, in the form of the step-potential model, it can be easily handled with the digital computer and was successfully used to treat large π-electron systems (non-linear optical properties [8], solitons in polyacetylene [6] and their dynamics [25] and the bond lengths and the spectroscopy of C60 [11]).

---

[1] The errors due to the simplifications in [7] are largely compensated. The comparison of ΔE_1, ΔE_2 and ΔE_3, following from perturbation theory (Eq. (8) in [7]) with the values obtained by numerically solving the Schrödinger equation, shows that the perturbation theory was partially overstressed, particularly for $n=6$ where perturbation shifts ΔE_2 below ΔE_1. Discrepancies by overstressing the perturbation theory are seen in the present case where the numerical solution of the Schrödinger equation is simple. It is more hidden in sophisticated cases.

References

[1] R. Silbey, in J.D. Brédas and R.R. Chance (eds.), *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics,* Kluwer, Dordrecht, 1990, p. 4.
[2] W. Huber, G. Simon and H. Kuhn, *Z. Naturforsch., Teil A, 17* (1962) 99.
[3] H.D. Försterling, W. Huber and H. Kuhn, *Int. J. Quantum Chem., 1* (1967) 225.
[4] 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; H. Kuhn, in L. Zechmeister (ed.), *Progress in the Chemistry of Organic Natural Products,* Vol. 17, Springer, Berlin, 1959, p. 404; H.D. Försterling and H. Kuhn, *Int. J. Quantum Chem., 2* (1968) 413.
[5] H. Kuhn, *Helv. Chim. Acta, 31* (1948) 1441.
[6] C. Kuhn, *Phys. Rev. B, 40* (1989) 7776.
[7] H. Kuhn and C. Kuhn, *Chem. Phys. Lett., 204* (1993) 206. Errata: Eq. (2) should be $1/(2n)$ instead of $n/2$; line before Eq. (7) should be $(\Delta/a)^2$ instead of Δ/a^2; chemical formula for butadiene (p. 207) should be a single bond in the middle instead of a double bond.
[8] C. Kuhn, *Synth Met., 41–43* (1991) 3681; C. Kuhn, in H. Kuzmany, M. Mehring and S. Roth (eds.), *Electronic Properties of Polymers, Springer Series in Solid State Sciences,* Vol. 107, Springer, Berlin, 1992.
[9] H. Kuhn, *Helv. Chim. Acta, 34* (1951) 2371.
[10] H. Kuhn, *Helv. Chim. Acta, 32* (1949) 2247.
[11] C. Kuhn, in H. Kuzmany, J. Fink, M. Mehring and S. Roth (eds.), *Electronic Properties of Fullerenes, Springer Series in Solid State Sciences,* Vol. 117, Springer, Berlin, 1993.
[12] H.D. Försterling and H. Kuhn, *Moleküle und Molekülanhäufungen, Eine Einführung in die physikalische Chemie,* Springer, Berlin, 1983, p. 88.
[13] H. Kuhn, *J. Chem. Phys., 17* (1949) 1198.
[14] L. Eggers, W. Grahm, W. Lüttke, B. Knieriem, P.G. Jones and A. Chrapkowski, *Angew. Chem., 106* (1994) 903.
[15] W. Huber, H. Kuhn and W. Huber, *Helv. Chim. Acta, 36* (1953) 1597.
[16] H.D. Försterling, W. Huber, H. Kuhn, H.H. Martin, A. Schweig, F.F. Seelig and W. Stratmann, in W. Foerst (ed.), *Optische Anregung organischer Systeme, 2. Internationales Farbensymposium,* Verlag Chemie, Weinheim, 1966, p. 55.
[17] H.D. Försterling and H. Kuhn, *Praxis der physikalischen Chemie,* VCH, Weinheim, 1985, p. 346.
[18] H. Kuhn, *Helv. Chim. Acta, 34* (1951) 1308.
[19] D. Baeriswyl, D.K. Campbell and S. Mazumdar, in H.G. Kiess (ed.), *Conjugated Conducting Polymers, Springer Series in Solid State Sciences,* Vol. 102, Springer, Berlin, 1992; D. Baeriswyl and E. Jeckelmann, in H. Kuzmany, M. Mehring and S. Roth (eds.), *Electronic Properties of Polymers, Springer Series in Solid State Sciences,* Vol. 107, Springer, Berlin, 1992.
[20] A. Montorsi (ed.), *The Hubbard Model, A Reprint Volume,* World Scientific, Singapore, 1993.
[21] K. Ohno, *Theor. Chim. Acta, 2* (1964) 219.
[22] H. Kuhn and W. Huber, *Helv. Chim. Acta, 33* (1950) 363.
[23] H.D. Försterling and H. Kuhn, *Int. J. Quantum Chem., 2* (1968) 413.
[24] Hs.H. Günthard and E. Heilbronner, *Helv. Chim. Acta, 76* (1993) 631.
[25] C. Kuhn and W.F. van Gunsteren, *Solid State Commun., 87* (1993) 203; C. Kuhn, in P.L. Christiansen, J.C. Eilbeck, R.D. Parmentier and A.C. Scott (eds.), *Future Directions of Non-Linear Dynamics in Physical and Biological Systems,* Plenum Press, New York, 1993; C. Kuhn, *Synth. Met., 55–57* (1993) 4350.