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Correlated electronic structure of conjugated π-systems*

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Abstract

The electron correlations are shown to modify the predictions of the Huckel theory for conjugated systems and bring experiments and theory into closer agreement.

Key words: Alternant hydrocarbons, electron correlations, solutions, polarons, bipolarons, charge density waves.

1. Introduction

Conjugated π-organic systems have been of long standing interest to chemists, due to their high reactivity, their long wavelength uv absorption and their large response to external electric and magnetic fields. Benzene, naphthalene, biphenyl, stilbene and polyenes are some of the famous systems that belong to this class. Basic description of bonding in these systems is given by carbon atoms in sp^2 hybridization, with C–C π-bonds forming the backbone and p_Z orbitals involved in π-conjugation along the backbone. The remaining sp^2 hybrid orbitals are σ-bonded to the hydrogen atoms.

In most electronic structure theories of conjugated systems, it is assumed that the σ-orbitals are energetically removed from the π-orbitals and the focus is thus entirely on the π-electrons of these systems. In the next section, we give a brief introduction to the Huckel theory and discuss some of its predictions. This is followed by a section on the discrepancies between Huckel predictions and experiments. In section four, we give a brief introduction to the correlated electronic structure models and comparison between their predictions and experiment. In the final section, we discuss the current status of theory and experiment in conjugated systems.

2. The Huckel theory and its predictions

The simplest model for studying the electronic structure of conjugated organic systems

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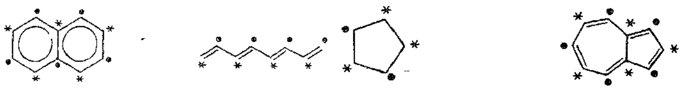

(a) (b)

FIG. 1. Examples of some well-known alternant and nonalternant conjugated hydrocarbons.

was introduced by Huckel in 1931[1]. This model is essentially topological and depends upon the connectivity of the sp^2 carbon atoms in the system. The Huckel Hamiltonian can be written as

$$H_{Huck} = \sum_{i,\sigma} \epsilon_i \, a^*_{i,\sigma} \, a_{i,\sigma} + \sum_{\langle ij \rangle,\sigma}{}' \, \beta_{ij} \, (a^*_{i,\sigma} \, a_{j,\sigma} + H.C.) \tag{1}$$

where ϵ_i is the energy of the p$_z$ orbital, on the ith carbon atom, β_{ij} the resonance integral between the bonded pair of carbon atoms i and j and $a^+_{i,\sigma}$ ($\alpha_{i,\sigma}$) creates (annihilates) an electron in the p$_z$ orbital on atom i and n_i are the corresponding occupation number operators. This model neglects explicit electron–electron interactions but includes static electron–lattice interactions by assuming the resonance integrals to depend upon the bond length.

The unsubstituted homoconjugated systems can be classified as alternant or nonalternant systems[2]. Alternant systems are those in which the carbon atoms belong to one of two sublattices (the starred or the unstarred) such that starred atoms are only surrounded by unstarred atoms and *vice versa*. Nonalternant systems are those in which such a bipartite partitioning is not possible. Examples of some alternant and nonalternant conjugated hydrocarbons are given in Fig. 1. This symmetry is variously known as alternancy symmetry, charge–conjugation symmetry or electron–hole interchange symmetry and is associated with the invariance of the Hamiltonian when the creation and annihilation operators are interchanged.

The consequences of alternancy symmetry in Huckel theory are immense. Among the various predictions made on the basis of this symmetry, the following are of considerable importance. The theory predicts that the bonding and antibonding molecular orbitals (MOs) always occur in pairs. That is for every bonding MO at an energy $-E_k$ there is an antibonding MO at an energy $+E_k$ and that the atomic orbital (AO) coefficients of these states (for $|E_k|$ not zero) can be written as

$$\psi_{+E_k} = \Sigma^* \, C_r \, \phi_r + \Sigma^0 \, C_s \, \phi_s \, ; \tag{2a}$$

$$\psi_{-E_k} = C_r \, \phi_r + \Sigma^0 \, C_s \, \phi_s . \tag{2b}$$

From this it follows that the lowest energy excitation, which defines the optical gap, E_g, in an alternant system is always dipole allowed. Thus, techniques such as two-

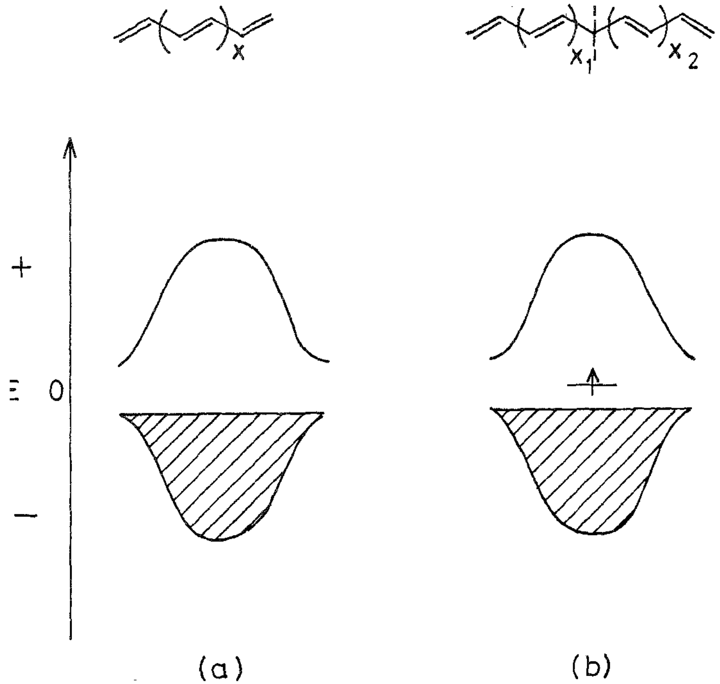

FIG. 2. Electronic energy levels of (a) a very long chain even polyene and (b) of a very long chain odd polyene. Note the mid-gap state in (b).

photon spectroscopies or those that probe different spin states of the system, according to Huckel theory, should not find states below the optical gap.

This symmetry also makes a prediction for infinite polyenes which is quite stunning[3,4]. In very long polyenes with odd number of carbon atoms, there would exist a nonbonding MO at zero of energy while in the one with even number of carbon atoms such a nonbonding MO does not exist. To a first approximation, the system being infinite, we can assume that all the bonding and antibonding MO energies are identical in the two systems. Since polyenes are known to have bond alternation, *i.e.*, the single and double bond lengths in infinite systems are unequal[5], by Peierl's theorem[6], there exists a nonzero energy gap between the occupied and the

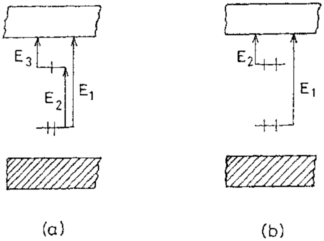

Fig. 3. Split-off states and the associated absorptions below E_g in (a) polaronic systems, and (b) bipolaronic systems.

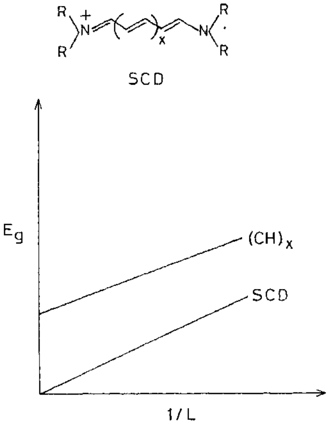

Fig. 4. A schematic of the dependence of optical gap in polyenes (upper curve) and symmetric cyanine dyes (lower curve).

unoccupied states. Therefore, Huckel theory would predict that, for very long odd-polyene chains, the lowest energy optical absorption would be at twice the wavelength of the corresponding absorption in even polyene system (Fig. 2).

This absorption is associated with a solution since a polyene system with odd number of carbon atoms would show a crossover in the bond alternation pattern in going from one end of the chain to another. The mid-gap state could have zero, one or two electrons. When the number of electrons in the mid-gap state is one then we have a neutral polyene radical and a spin is associated with the soliton. In other cases, the polyene is ionized and we have charged solitons.

The MO coefficients of the nonbonded state in Huckel theory is nonzero at odd-numbered carbon atoms and is zero at even-numbered carbon atoms. Thus, the theory makes yet another prediction about the spin density distribution in the neutral solitons, namely, that the spin densities are all of same sign at odd-numbered carbon sites and are zero at even-numbered carbon sites.

In even polyene systems, when a charge is introduced by doping, then electron–lattice interaction would distort the lattice around the charged site and we would have two split-off states[7]. The alternancy symmetry, being topological, still exists and hence these states are symmetrically placed about the mid-gap. These split-off states are known as the polaronic states and we would have a polaron if the doping is by a single charge and a bipolaron if the doping is by two charges (Fig. 3).

The Huckel theory makes very strong predictions about the optical spectra of the polarons and the bipolarons. The polarons in this theory should show three optical absorptions below the optical gap of the neutral even polyene and the bipolarons should show two such absorptions. It also predicts that the sum of the two excitation energies in the bipolaron and that of the two higher energy excitations (below E_g) in polarons should add to E_g, as shown in Fig. 3. Furthermore, in the case of bipolarons, the energies of these absorptions should not depend upon the spin states.

Among the predictions of the Huckel theory that cannot be directly verified by experiments, is the nature of spin correlations in the ground state. The theory predicts that the spin correlation function, $\langle s_i^z s_j^z \rangle$, where s_i^z is the z-component of the site spin operator, reflects antiferromagnetic spin coupling with odd-numbered neighbours but is nonmagnetic with even-numbered neighbours[8].

3. Experimental observations in π-systems

Conjugated organic systems that are closely related to polyenes are the symmetric cyanine dyes (SCD) (Fig. 4). If Huckel theory is correct, then it is to be expected that in the limit of large chain lengths, the polyenes and the SCDs should show identical optical absorptions, involving π electrons, as the end effects would become progressively weaker. However, from Fig. 4, we see that the experimental optical gap of the polyenes extrapolates to a finite value while that of SCDs[9] to zero.

Two-photon spectroscopies have shown the presence of states below the optical gap in many π-electron systems, contrary to the predictions of the Huckel theory[10]. Furthermore, there is also no strong evidence for the existence of mid-gap absorption in neutral odd-polyene chains. The spin density pattern in these neutral radical chains, obtained from electron spin resonance studies, shows that at even-numbered carbon sites the spin density is opposite in sign to that at odd-numbered carbon sites[11]. The observation of negative spin density is in direct conflict with the prediction of the Huckel theory.

The optical spectra of polarons and bipolarons are rather complex and hence difficult to analyse in detail. However, from the limited analysis that exists, there is neither any evidence for the precise number of absorption bands predicted by the Huckel theory in the two cases nor is there evidence for the sum rule for the absorption maxima discussed above.

Even where the Huckel theory is qualitatively correct, there exist, quantitative discrepancies. The oscillator strengths predicted by Huckel theory is an order of magnitude larger than found experimentally[2]. To obtain the correct optical gap in the system, the Huckel theory also has to assume rather large electron–phonon coupling constant. Another quantity of interest is the aromatic ring currents in neutral and charged annulenes which can indeed be inferred from nmr experiments. Huckel theory predicts smaller ring currents for charged annulenes when compared to neutral annulenes while, experimentally, the opposite is found to be true.

4. Correlated model Hamiltonians and predictions

The simplest level at which electron–electron interactions can be introduced into the Huckel model is by assuming that two electrons repel only when they are in the same orbital. The model which incorporates this feature is known as the Hubbard model[13] and is given by

$$H_{Hub} = H_{Huck} + U \sum_{i} \hat{n}_i \, (\hat{n}_i - 1)/2 \tag{3}$$

where U is the Hubbard on-site repulsion parameter and $\hat{n}_i$ are the occupation number operators. This model can be justified in the case of metals where the screening due to mobile conduction electrons is effective in drastically cutting down the range of Coulomb interactions[14]. Although this model is simple, it incorporates the essential physics of electron correlations. Exact solutions to this model, for infinite lattices, exist only in one-dimension for uniform resonance integrals[15].

In systems wherein the screening is not as effective as in metals, we need to include longer-range Coulomb interactions. A model which includes these in the zero differential overlap approximation is known as the Pariser–Parr–Pople (PPP) or the extended Hubbard model[16,17]. The Hamiltonian in this approximation is given by

$$H_{PPP} = H_{Hub} + \sum_{i>j} V_{ij} \, (\hat{n}_i - 1) \, (\hat{n}_j - 1). \tag{4}$$

The electron repulsion integrals between electrons on two different sites, V_{ij}, usually parametrized as

$$V_{ij} = U \, (1 + 0{\cdot}6117 \, r_{ij}^2)^{-1/2} \tag{5}$$

where r_{ij} is the distance between the sites. In the context of polyenes, another parameter besides U that enters in these models is the degree of dimerization, δ, wherein the short bonds have a transfer integral of $t(1 + \delta)$ and the long bonds of $t(1 - \delta)$. Thus, PPP model for polyenes is essentially a two-parameter model. The parameter used for U of carbon in the PPP models is 11·2eV and t corresponding to a bond length of 1·397Å is 2·4eV with a linear coupling constant of −3·2eV/Å. This parameter set has reproduced excitation gaps in a large number of homoconjugated organic systems.

The interacting model Hamiltonians for the infinite polyene cannot be solved exactly for alternating transfer integrals. However, exact solutions for finite chains can be obtained and the properties can be extrapolated to infinite system size. The results of the PPP calculations for finite chains are also significant since these correspond to finite polyenes which have been extensively studied experimentally[19].

Figure 5 gives the correlation diagram for the energy levels of decapentane. We note that there exist two singlet states below the optical gap. Existence of the 2^1A_g

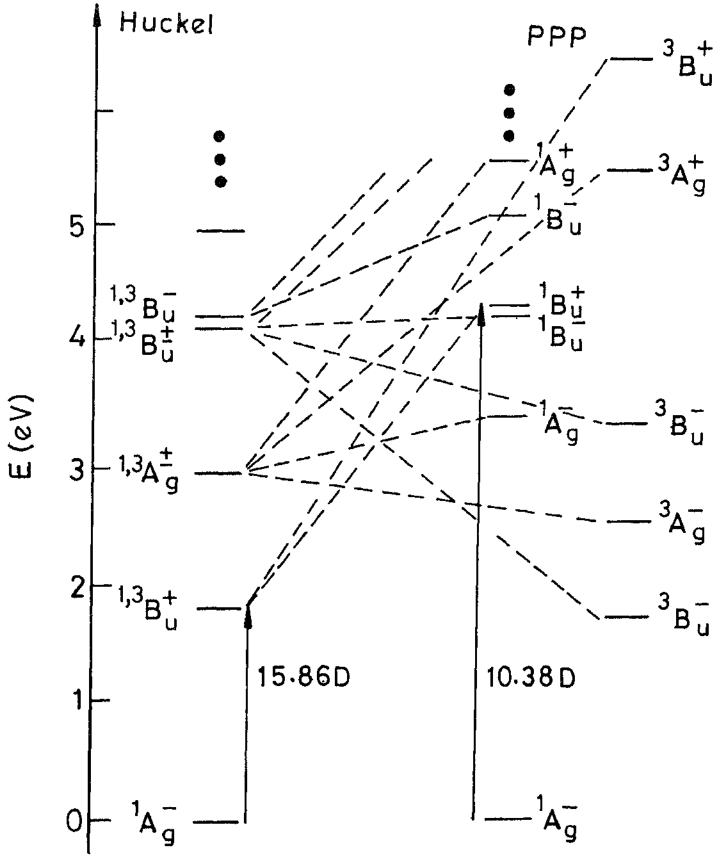

FIG. 5. Correlation between the Huckel excitations and the PPP excitations in decapentane.

state, below the optical gap of 4·02eV, at 3·10eV in this system has indeed been confirmed experimentally. Besides, Fig. 5 also shows that the transition moment for the dipole-allowed transition has been reduced from the Huckel value.

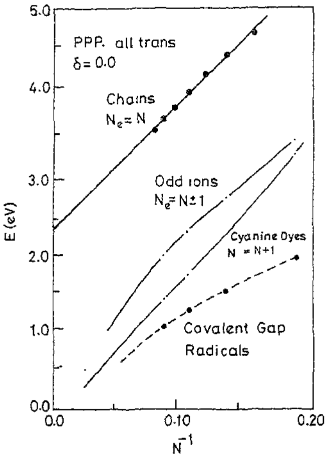

FIG. 6. Excitation gaps *vs* N^{-1} (N is the number of atoms in conjugation) for uniform (δ = 0) PPP systems. The covalent gaps are dipole forbidden.

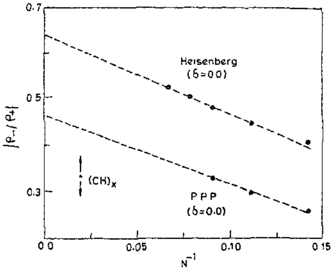

FIG 7 Absolute ratio of total negative to total positive spin density *vs* N^{-1} for Heisenberg spin chains and the PPP Hamiltonian. $(CH)_x$ value is from Thomann *et al*[11].

Figure 6 shows the extrapolated excitation gaps of PPP chains with no bond alternation (all transfer integrals equal and all bond lengths equal) for the polyenes, ions of odd polyenes and cyanine dyes. The optical gap of the even and odd neutral polyenes fall on the same line and extrapolate to a finite gap while Huckel results for uniform chains would extrapolate to zero gap and the line for even polyenes would be above that of the odd polyene. The PPP results show that the optical gap of cyanine dyes extrapolates to zero as also that of the singly charged ions of odd polyenes.

The above result can be rationalized on the basis that in the limit of infinite chain ength, the charge density distribution would correspond to an incommensurate charge density wave (CDW). By changing the phase of this wave, it is possible to create a tate which would have a nonvanishing transition dipole with the ground state. The nergy of such a state would however be the same as the ground state since the CDW is not pinned to the lattice and can be slided without any cost in energy.

It is also interesting to see from Fig. 6 that the covalent gaps also vanish as the hain length increases. In a uniform chain, in the limit of large effective U, these ecome spin wave excitations of a uniform Heisenberg chain. In such a spin chain it known that the singlet gap vanishes[20].

The spin density calculations in the odd polyene radicals show the presence of negative spin density at even-numbered sites, in agreement with experiments (Fig. 7). Besides, some detailed studies on the singlet and triplet excitation gaps of a Heisenberg chain with two alternation reversals show that these gaps do not converge to the same value when the distance between the alternation reversals is increased[21]. If the spin solitons were noninteracting, as they should be if solitons are elementary excitations of the system, then the triplet and the singlet gaps should have converged to the same value in the limit of infinite separation. The spin–spin correlation function, in the presence of electron correlations, shows antiferromagnetic spin alignment over the chain and thus passes on to the Heisenberg limit correctly[18].

The aromatic ring currents in PPP and Hubbard models have been computed, exactly, for annulenes and their monoions. Correlated models correctly predict the ring currents in ions to be greater than in neutral annulenes. These studies also show that the aromatic stabilization of the $4n + 2$ system gradually decreases with increase in correlation strength and system size, as should be expected on physical grounds.

Another aspect of recent interest has been the strong fluorescence exhibited by some homoconjugated polyenes such as polyparaphenylenevinylene (PPV)[22]. The monomer in this system is divinylbenzene and hence the strength of electron correlations in this system should be nearly the same as in polyenes. Yet, to show strong fluorescence, according to Kasha rule[23], this system should not have states below the optical gap, unlike in polyenes.

The above puzzling fact can be rationalized if one recognizes that a para-substituted benzene ring in an extended system can be exactly replaced, in Huckel theory, by a linear chain of four sites with large bond alternation and a pair of localized orbitals[24]. Recent studies have shown that, for the same correlation strength, the one-photon state gradually descends below the two-photon state, on increasing bond alternation. Thus, it appears that in the PPV system, the enhanced alternation due to the topology of the system leads to a one-photon state as the lowest energy-excited state and hence to strong fluorescence.

In the above system, studies of dianions, triplets and singlet excited states show that the bond orders in these states, which can be identified as triplet bipolaron, charged bipolaron or singlet bipolaron, are qualitatively different[25]. Thus, the relaxation energies associated with these states would show charge and spin dependence. Furthermore, correlated models would predict several charged bipolaronic states below the optical gap. The broad solution spectra observed in dianions of oligomers of PPV, however, precludes a proper accounting of the number of such excitations.

5. Summary

In this paper, we briefly reviewed the Huckel model and its predictions for homoconjugated organic systems. The experimental status, with particular reference to polyenes, was presented and the discrepancy between Huckel predictions and experimental observations were highlighted. Phenomenological Hamiltonians that capture the essential features of the electron correlations were introduced and solutions of these models were shown to be in broad agreement with experimental findings.

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