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Resonating Valence-Bond Theory for Polyenes and Polyacetylene

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Pauling's resonating valence-bond concepts are selectively reviewed and illustratively utilized to describe the ground and low-lying homopolar states of polyenes. Our computations are found to support a simple picture dominated by just a few resonance structures and are in agreement with qualitative experimental observations.

**Dedicated to Linus Pauling,
Great Scientist, Teacher and Humanitarian**

1. ORIENTATION

Linus Pauling's *The Nature of the Chemical Bond*¹ surely stands out as a major achievement in chemistry. This work provides a qualitative understanding of a great diversity of different chemical structures and their properties. Moreover, the concepts so introduced are suggested² to serve as key guideposts and tools in quantitative studies. The consequent ideas, especially the valence-bond (VB) theory, so impressively advocated by Pauling, have continued to progress. See for example, the wide-ranging surveys of refs. 3, 4 and 5.

Of course, there are alternative points of view. One is that the singular goal of quantum chemistry should be numerical computation, divorced from »explanation« or

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»understanding«. Perhaps it was first emphasized by Coulson⁶ that in such a paradigm one would »merely« have a new experimental tool, a »computer experiment«, and success would yield a huge catalog of numbers, the interpretation of which would remain. In a not always unrelated view, the molecular-orbital (MO) scheme has oft been espoused, though one of MO theory's strongest advocates (M. J. S. Dewar) has noted⁷:

One of the problems which has arisen with the development of sophisticated MO treatments is the difficulty of relating such calculations to the traditional picture of molecules in terms of localized bonds, resonance energy, etc. SCF (self-consistent field) expressions for the total energy are far more complex and it is much harder to see their relationship to traditional ideas.

Still, the MO theory has been and continues to be very popular, in part because of the wide availability of relatively user-friendly computer programs in this area. Also, there have been notable conceptual developments, such as the frontier orbital ideas of Fukui⁸ and the orbital-symmetry conservation ideas of Woodward and Hoffmann.⁹ Thence there has been a complex of themes tending to deemphasize VB-theoretic research, though now there seems to be a growing interest in its conceptual (and perhaps even computational) utility. A more detailed but still brief historical survey is found in ref. 10.

The application of Pauling's resonating VB ideas to solids or polymers, even to conjugated polymers, has been long neglected though Pauling and Wheland's first crucial papers¹¹ on resonance concerned (aromatic) conjugated hydrocarbons. Thence Chien's 1984 book¹² on polyacetylene references over a hundred theoretical papers all taking an MO (or band-theoretic) viewpoint. Indeed, the MO picture has dominated polymer studies, despite a recognized¹³ feature that the bands are somewhat narrow, this being the traditional mark of electron correlation and attrition (if not failure) of the (simple) MO picture. Further, the now popular solitonic excited state ideas^{12,14} lead to a »mid-gap« band that is extremely narrow, though there is a saving point in that the associated bond alternation tends to diminish electron correlation (and resonance).

With the oligomeric polyenes there is further general recognition of the limitations of the MO view, especially as regards¹⁵⁻¹⁷ the importance of electron correlation in describing low-lying optically weak excited states. For these excited states, and then also for the ground state, the typical¹⁸⁻²³ approach has been to carry out »heavy« configuration interaction (CI) computations, thereby generating a listing of energies (and properties). Support for the importance of CI (in the MO view) is found in the idea¹⁵ that the observed novel excitations are primarily combinations of pair excitations, with the primarily single-excitation states lying higher. It is also surmised that these excitations (along with the ground states) are largely homopolar, which would help explain the weakness of the optical transition. Thus, one might anticipate the possibility of a description both of the ground and low-lying excited states solely in terms of covalent VB structures.

In this paper, we explore the ground-state of the oligomers, the occurrence of bond localization and the nature of low-lying excitations all from a resonating VB-theoretic viewpoint. Although the focus is primarily on oligomers, our work has also some implications for the high-polymer limit. This study extends several earlier, rather independent, investigations: that of Coulson and Dixon²⁴ (»limited« to Kekulé structures, on annulenes), our ground-state infinite-chain work²⁵, and especially Surjan *et al.*'s²⁶ *ab initio* computations for and interpretation of triplet excitations.

Our present work and ideas are given in a sequence of steps. Section 2 reviews some fundamental VB ideas and nomenclature, which we find of use. Section 3 develops a quantitative description of the ground state for polyenes (or by a slight extension, for annulenes). This description, based upon (but not limited to) Kekulé structures, is chemically appealing and gives explicit dependencies on variations with the degree of bond alternation in these molecules. Section 4 develops our related resonance-theoretic description of the lowest excited states. Our overall view focuses on only a few key VB structures and is described in a qualitative »Paulingesque« fashion in section 5 here, which may be read without more detailed computational considerations of the intervening sections that, nevertheless, make use of resonating VB-theoretic ideas in a quantitative mode.

2. VB THEORY

The VB model of Pauling and Wheland^{11,27} for conjugated hydrocarbons is defined on the manifold of covalent structures. One way to represent their model is²⁸ as a Heisenberg spin Hamiltonian, which for the oligomeric polyenes takes the form

$$H = J \sum_{n=1}^{n-1} \{1 - (-1)^n \Delta\} 2 \vec{s}_n \cdot \vec{s}_{n+1} \quad (2.1)$$

where N is the number of sites, \vec{s}_m is the spin operator for site m , J is the (positive) exchange parameter, and Δ measures the extent of dimerization (or bond alternation). The operator $\vec{s}_i \cdot \vec{s}_j$ (or better $-2 \vec{s}_i \cdot \vec{s}_j - 1/2$) corresponds to a spin-free exchange (which perhaps relates more closely to Pauling and Wheland's representation). With it being understood that there is one electron affixed to each site, the coordinate-space part of the wave functions are fixed and the model may be constrained to spin space.

Solution of (2.1) may be attempted with reference to different bases. The VB or Rumer²⁹ basis utilizes disjoint products of singlet-coupled pairs of spins, as in the structure

$$|R\rangle = \prod_i^{\text{odd}} \{ \alpha(i) \beta(i_R) - \beta(i) \alpha(i_R) \} \quad (2.2)$$

where α and β are spin-up and -down spin-1/2 functions, and i_R denotes the site to which i is paired in structure R . Evidently, R may be pictorially represented with points identifying sites and lines connecting sites that are singlet spin-paired. See *e.g.* Figure 1. These structures (2.2) span the overall space of singlets for H , and indeed the subset of structures without »crossing« bonds forms³⁰ a basis for this space. Elegant pictorial graph-theoretic techniques for evaluating overlap and related matrix elements between pairs of structures were developed by Pauling.³¹ Some recent use of these techniques (along with some extensions) is indicated in ref.5.

There is a rationale to relate these Rumer basis structures to classical chemical concepts. The expectation value of H over any one of these structures is

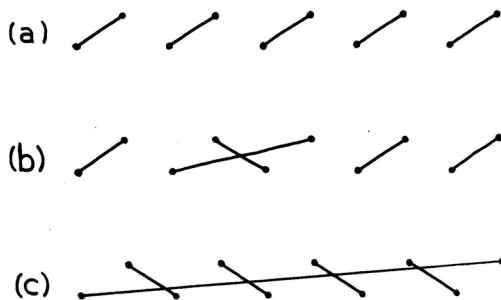


Figure 1. Three VB structures: (a) The $N=10$ linear-chain Kekulé structure with sites $2i-1$ and $2i$ paired for $i=10$ to 5 ; (b) A Thiele structure obtained as a slight modification of the Kekulé structure; and (c) An exceptional structure, almost a Kekulé structure, if the two end-sites were omitted.

$$\frac{\langle R|H|R\rangle}{\langle R|R\rangle} = -\frac{3}{2} \sum_n \sum_{\sigma+1} \{ 1 - \sigma \Delta (-1)^n \} \delta(n+\sigma, n_R) \quad (2.3)$$

Hence, the most important (more stabilizing) structures R in the ground state should be those with greater numbers of nearest-neighbor spin-pairings which correspond more closely to more strongly interacting (*i.e.* closer) sites. An approach taking into account such preferences is referred to as a *resonating* VB theory. A simple version of this theory approximates the ground state solely in terms of *Kekulé* structures (wherein only electrons on neighboring sites are paired). The next most important (Thiele) structures have a few longer-bond pairings, most preferably with shorter-long bonds (whence greater similarity to a Kekulé structure is achieved). Such ideas may be used qualitatively, as so often done by Pauling¹, and also they may be incorporated into wavefunction cluster expansions, as we show in the next section.

3. GROUND-STATE RESONATING VB CLUSTER EXPANSION

A chemical appealing ground-state wavefunction *ansatz* might be built from VB (or Rumer) structures in such a way as to allow local modifications to the imagined dominant Kekulé structures. Moreover, such local modifications should be made size consistently, more-or-less independently of one another, at least when well separated. Namely, they need to be included in the wavefunction in a more-or-less multiplicative manner (since to achieve independence it is the products of individual-event probabilities that give overall probabilities and wave functions are probability amplitudes). One of several^{25,32} ways to implement these ideas is *via* our present *ansatz*

$$|\Psi\rangle = \sum_R \prod_j \prod_i x_{ji}^{m(R,j,i)} |R\rangle \quad (3.1)$$

where the x_{ji} are variational parameters associated to the occurrence of i sites preceding site $j+1$ being spin-paired to i sites succeeding site j . That is,

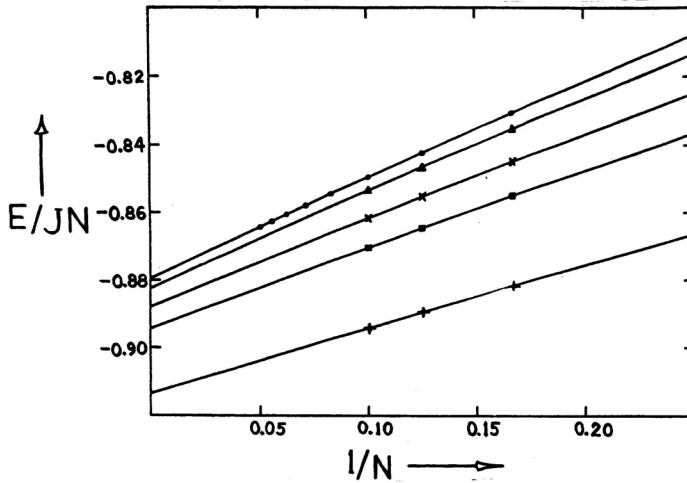


Figure 2. Plots of ground-state energy per site in units of J versus $1/N$, for $\Delta=0, 0.01, 0.03, 0.05$ and 0.10 from top to bottom.

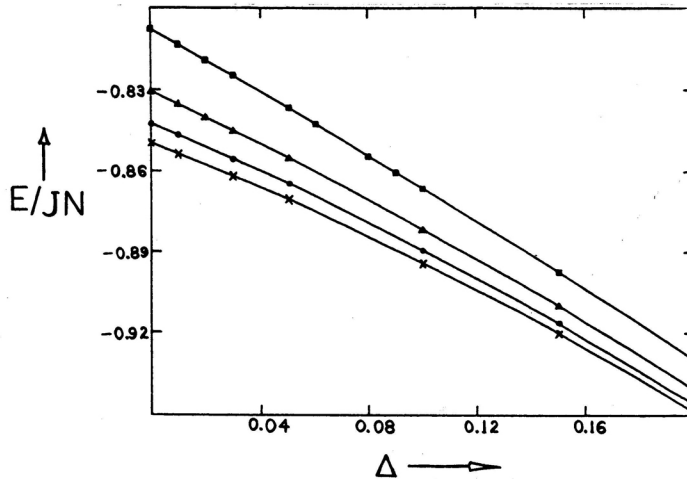


Figure 3. Plots of ground-state energy per site in units of J versus Δ , for $N=4, 6, 8,$ and 10 from top to bottom.

$$m(r;j,i) = \begin{cases} 1, & i \text{ spin-pairings traverse zone } j \text{ in } R \\ 0, & \text{otherwise} \end{cases} \quad (3.2)$$

where *zone* j refers to the region between j and $j + 1$. Thus, for example, the structure in Figure 1b has nonzero m -values for

$$(j,i) = (1,1),(2,0),(3,1),(4,2),(5,1),(6,0),(7,1),(8,0),(9,1)$$

We choose $x_{j_0} = 1$, thereby setting the normalization of Ψ . Then, the coefficient for $|R\rangle$ of Figure 1b is $x_{11}x_{31}x_{42}x_{51}x_{71}x_{91}$. Symmetry conditions may be invoked to make many pairs of x_{ji} equal, and in the infinite chain limit we anticipate that the j -dependence is largely quenched, that is, for j away from the chain ends x_{ji} should depend solely on i and the parity of j . In addition, since we anticipate that the importance of longer spin-pairings should be less, the x_{ji} should decrease (in magnitude) with increasing i .

Computations of Hamiltonian expectation values are a nontrivial task, especially for long chains. Nevertheless, this can be done using a powerful *transfer-matrix* technique,³³ much like that which is a standard tool in statistical mechanics. The overlap $\langle\Psi|\Psi\rangle$ has many of the features of a partition function, and the energy expectation value has many of the features of a logarithmic derivative of a partition function. The variational parameters are numerically optimized to find a minimum in the energy expectation value. Details for the present circumstance are found in a thesis.³⁴

In Table I we report on such computations for open chains at $\Delta=0$ and compare to some exact results. Here, the x_{ji} are set to 0 for the presumably less important $i>M=3$ for the sake of computational ease. From Table I it seems that the energies per site as given there are accurate to within a few percent, even for the $N\rightarrow\infty$ limit, the exact result there being due to Hulthen³⁵ and the exact finite N results being obtained by a unitary-group CI procedure.³⁶ In Table II, comparison to a variety of other infinite-chain approximations (at $\Delta=0$) is made. The present resonating VB *ansätze* are seen to be quite accurate. For dimerized models, *i.e.* with $\Delta\neq 0$, the effects of interdimer coupling should be less, and our *ansatz* should be even more accurate, becoming exact at $\Delta=1$ (within the limits of isolated dimers).

The total energy E being an extensive quantity should scale dominantly as N in the long-chain limit. We further presume an asymptotic form for the following leading terms

$$E / JN = \varepsilon_0(\Delta) + \varepsilon_1(\Delta) / N + \varepsilon_2(\Delta) / N^2 \quad (3.3)$$

Figure 2 supports this, the curves there being least-squares fit to this form. In (3.3), the parameters $\varepsilon_0(\Delta)$, $\varepsilon_1(\Delta)$ and $\varepsilon_2(\Delta)$ may, respectively, be thought of as: energy per

TABLE I
Ground-state energies per site at $\Delta=0$

N	E_{var}/JN	E_{exact}/JN
4	-0.80802	-0.80802
6	-0.83054	-0.83120
8	-0.84238	-0.84374
10	-0.84964	-0.85160
12	-0.85452	-0.85702
14	-0.85802	-0.86096
16	-0.86066	-0.86396
18	-0.86270	-0.86634
20	-0.86434	-0.86824
∞	-0.8690	-0.88630

TABLE II
Ground-state energies per site for $N \rightarrow \infty$ at $\Delta = 0$

Method	Ref.	e_0/J
Neél		-0.5000
Linderberg-Öhrn Green's Function approximant	a	-0.7500
Kekulé structure		-0.7500
3 to 1 renormalization (1st order perturbation)	37	-0.7826
Kasteleyn cluster wavefunction	b	-0.8156
Jordan-Wigner transformed RHF solution	c	-0.8383
9 to 1 renormalization (1st order perturbation)	d	-0.8424
Fisher-Oguchi variational spin-wave	e	-0.846
Neel-based cluster wavefunction (2-site)	f	-0.8558
Antiferromagnetic spin-wave	g	-0.8634
Jordan-Wigner transformed UHF solution	h	-0.8646
Present resonating VB <i>ansatz</i> ($M=2$)		-0.8716
Neel-based cluster wavefunction (4-site)	e	-0.8758
Present resonating VB <i>ansatz</i> ($M=3$)		-0.8790
Exact	35	-0.8863
Monte Carlo, for $N=48$ -site ring	i	-0.887
3 to 1 renormalization (2-site cluster)	j	-0.8969
Neel-state, 2nd order perturbation	k	-1.000
Hubbard Green's Function approximant	a	-1.2188

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site (for $N \rightarrow \infty$), energy for chain ends, and a higher-order correction. Alternatively, a second expansion may be considered about the uniform limit, where $|\Delta| = 0$, whence we write

$$E / JN = e_0(N) + e_1(N)\Delta + e_2(N)\Delta^2 \quad (3.4)$$

Figure 3 supports this form too, the lines again being least-squares fits. That the fits give $e_1(N) \neq 0$ (i.e., a term linear in Δ) as a significant: distortion of (partly) localized double bonding is indicated even in the $N \rightarrow \infty$ limit of long cyclic chains. This feature was earlier noted in ref. 24 for $N \rightarrow \infty$ with Kekulé structures only and in ref. 25 with a similar *ansatz* with more rigorous detail. Presumably, for cyclic chains the Δ -dependence for (2.1) should³⁷⁻³⁹ correctly be weaker, say as

$$E / JN - e_0(N) \sim \Delta^\nu \quad (3.5)$$

with ν perhaps being 4/3. But, with the inclusion in H of next-nearest-neighbor interactions (perhaps somewhat larger than relevant for conjugated organics), it is known²⁵

that $\nu=1$. Since the resonating VB *ansatz* of (3.4) (at least for our resonating VB energy) becomes better with such an inclusion, the rationale for the form of (3.4) is enhanced.

4. EXCITED STATES

The singlet excited states may also be treated⁴⁰ within the framework of our variational localized-site cluster expansion. From the ground state $|\Psi\rangle$, a natural way to form new states is by substitution of any of the optimized variational parameters by another value. That with x_{ji} replaced by x'_{ji} is denoted by $|\Psi_j\rangle$. Further, it is convenient to choose the value of x'_{ji} so that the generalized Brillouin condition⁴¹ is satisfied

$$\langle \Psi | \Psi_j \rangle = 0 \quad (4.1)$$

Then, if the original x_{ji} are variationally optimized, the Hamiltonian does not admix the $|\Psi_j\rangle$ with $|\Psi\rangle$, *i.e.*,

$$\langle \Psi | H | \Psi_j \rangle = 0 \quad (4.2)$$

We term these Ψ_j *single excitations*. They are largely »like« the ground state (Ψ_j being the same except for zone j), and diagonalization in this single-excitation space yields variational upper bound to lower-lying excited states.

The nomenclature adopted here has been chosen to provoke analogy to the SCFMO theory. The single excitations in neither case admix directly with the groundstate, though simultaneous excitations of (close) pairs do. In either case, the single excitation manifold exhibits internal mixing to yield good estimates of the low-lying eigenstates. Also, the present single excitations might be viewed as »quasi-particles« analogous to Frenkel excitons.

Computation of matrix elements within this manifold may be carried out by the transfer-matrix technique⁴⁰ again, and then CI within the manifold performed. Numerical results for the two lowest singlets are exhibited as a function of chain length N in Figure 4. The energy level pattern is rather like that of Mujica *et al*⁴², or Hashimoto⁴³ for slightly modified VB models, using quite different computational schemes. The lowest excited state is the optically forbidden 2^1A_g , in general agreement with numerous¹⁹⁻²³ CI computations on PPP and Hubbard models (though not so for simple MO-SCF schemes).

Evidently, in our approximation (like that of Hashimoto⁴³) there seems to be an excitation gap even in the infinite-chain limit (as $N \rightarrow \infty$). Though it has been proved⁴⁴ that no gap occurs for the $N \rightarrow \infty$ uniform ($\Delta=0$) chain with cyclic boundary conditions, the proof seems to fail for open chains, like the ones here. For cyclic alternating ($\Delta \neq 0$) chains, a gap is believed^{39,45} to occur – hence, with the strong electronic-structure premanifestations of alternation noted for our *ansatz* in the previous section one might anticipate it to mimic alternation and exhibit an excitation gap.

A further point of interest concerns the nature of the excited state wavefunctions. This is that the ratio x'_{ji}/x_{ji} turned out to be quite large in magnitude (often in the range of 20 to 30) for $i=3$, thereby favoring longer distance pairings, like in Figure 1c in the excited state. Thus, it seems the excited states might have significant contributions from VB structures with many close pairings, except for a long pair between two sites near opposite ends of the polyene chain.

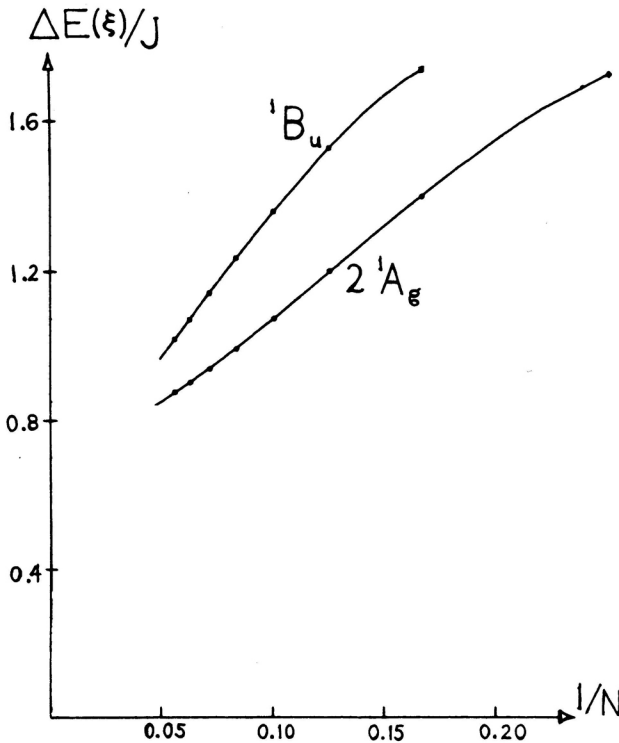


Figure 4. Plots of the variational excitation energies for 2^1A_g and 1^1B_u states.

Complete CI computations were carried out to check the extent of this long-range spin-pairing in the ground and first excited states. In particular, expectations

$$\langle \vec{s}_1 \cdot \vec{s}_N \rangle_\xi \equiv \frac{\langle \Psi(\xi) | \vec{s}_1 \cdot \vec{s}_N | \Psi(\xi) \rangle}{\langle \Psi(\xi) | \Psi(\xi) \rangle} \quad (4.3)$$

were computed for different states ξ . The results are reported in Figure 5. For the first excited singlet $\xi = 2^1A_g$, this expectation value is seen to be relatively large in magnitude though it evidently has not yet approached its asymptotic form which we might surmise to be

$$\langle \vec{s}_1 \cdot \vec{s}_N \rangle_\xi \sim 1/N \quad (4.4)$$

because the relevant long bond should more frequently be between sites near the chain ends, rather than at both extreme ends. If there are spins distantly paired to one another near opposite ends of the chain for $\xi = 2^1A_g$, then one would expect also the two triplet-paired spins of the lowest triplet ($\xi = ^3B_u$) to be near opposite ends of the chain. Then, $\langle \vec{s}_1 \cdot \vec{s}_N \rangle_\xi$ for $\xi = ^3B_u$ should be shifted upward, as we find to be the case. If long distance triplet-pairing occurs more frequently than singlet pairing, then this expectation value might even be positive, as is seen from Figure 4 to be the case.

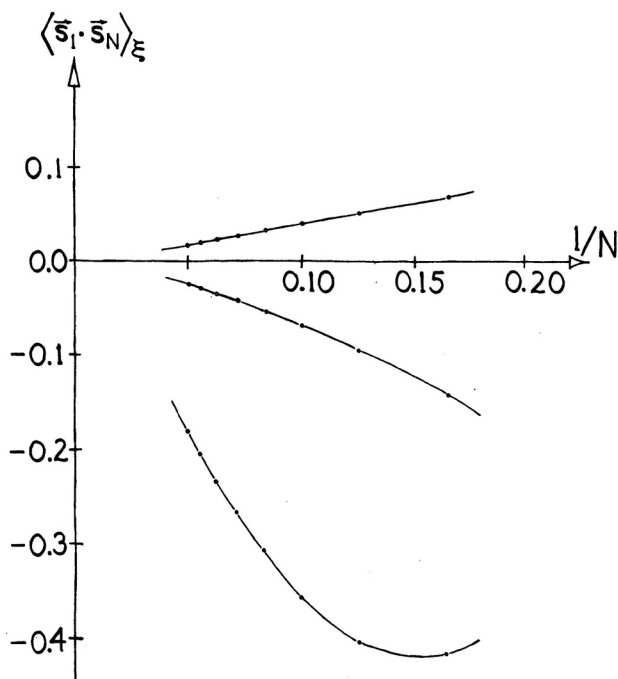


Figure 5. Exact end-to-end spin-spin correlations for the X^1A_g and 1^3B_u states.

5. QUALITATIVE OVERVIEW

As Pauling has emphasized, many consequences can often be naturally anticipated without recourse to extensive computation, and such we believe is the present case. First, the polyene ground state should be dominated by the lowest-energy VB structure: the Kekulé structure of Figure 1a. Second, the lowest (homopolar) excited states should retain as much stabilizing nearest-neighbor (singlet) spin-pairing as possible subject to the constraint of distinction from (*i.e.*, orthogonality to) the ground state. Thence for the N -site polyene, the ground state has $N/2$ neighbor spin-pairs while the lowest (singlet and triplet) excited states have $N/2-1$. For the lowest triplet state, the two electrons of the one triplet antipair tend to localize far apart since, when adjacent, there is a $+3J/w$ repulsive contribution to the energy (for the VB model), whereas when not so adjacent, each triplet-paired electron has a 0-interaction strength with the nearest neighbor sites. For the lowest singlet, one singlet pair is not to be adjacent (as in the ground state), and so should entail two more distantly separated electrons, the greatest dissimilarity and most easily achieved orthogonality to the ground state being achieved when separation is greatest. The ground state is of course totally symmetric (1A_g), at least in a spin-free sense. The symmetry of this lowest singlet excited state is, therefore, the same (1A_g) as the ground state, while the (spin-free) antisym-

metry of the triplet-pair in the lowest triplet leads to a 3B_u symmetry. The ground-state spin-pairing pattern of the Kekulé structure leads to bond alternation (with both end bonds being shorter). The spin-pairings of the excited states favor the opposite manner of bond alternation, with the end bonds being longer. Eventually (for large enough N) with this opposite manner of alternation, the equilibrium position of the 2^1A_g potential surface should »cross« below the ground-state X^1A_g surface (the two being of different »alternancy« symmetries). The symmetry and homopolarity of the excited states contributes to the weakness of optical transitions to them from the ground state. The bond-by-bond differences of the two-bond-alternating (and associated VB structure) patterns further enhances the weakness of the transition moment, ever more so the longer the polyene.

This overall view is supported by our results of sections 3 and 4. Further support for the ground state character is found elsewhere,^{24,25} and Surjan *et al.*'s²⁶ interpretation of the character of the excited triplet (3B_u) is much the same. Tavan and Schulten's²² recent excited singlet state computational results seem consistent with our present interpretation, though they propose a different interpretation of the excited states in terms of pairs of triplet (*anti*) pairs.

Some novel implications apply for the long-chain ($N \rightarrow \infty$) limit of polyacetylene. For the ground state, bond alternation is expected to persist, even with cyclic boundary conditions: asymptotically, the two Kekulé structures do not admix because they differ in N positions, so that resonance between the two is quenched. For the low-lying excited states, the two weakly coupled electrons can be distantly paired (or anti-paired) but so far separated that they behave independently. Such a single essentially unpaired electron then has characteristics of a soliton, with bond alternation on bonds of opposing parities before and after it. Further discussion of these ideas, including extensions to other conjugated polymers may be found elsewhere,^{6,47} though such ideas are relevant for small molecules too.^{46,48}

The present case of polyenes and polyacetylene seems to us to offer a nice example of the type of chemically and physically based resonating VB ideas championed by Linus Pauling. We believe there should be many more qualitative and quantitative applications – perhaps the area of solid-state chemistry is especially interesting because of the relative paucity of using such ideas in the past – and perhaps new computational tools will be of aid. Having a hierarchy of concepts and methods proceeding in an intimately interconnected way from classical chemical-bonding ideas to crude semiempirical models to high quality *ab initio* computations seems a worthwhile goal, and a way towards this end seems clearly to be *via* many of the ideas pursued by Pauling.

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SAŽETAK

Teorija rezonantnih valentnih struktura za poliene i poliacetilene

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Paulingova teorija rezonantnih valentnih struktura primijenjena je za opis i razumijevanje svojstava osnovnog stanja poliena i poliacetilena. Računi pokazuju da se rezultati mogu interpretirati s pomoću jednostavne slike koju daju svega nekoliko rezonantnih struktura. Teorijska predviđanja u skladu su s kvalitativnim eksperimentalnim opažanjima.