

Dimerization of polyacetylene treated as a spin-Peierls distortion of the Heisenberg Hamiltonian

M. A. Garcia-Bach

Departament de Física Fonamental, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

P. Blaise

Faculté des Sciences, Université de Perpignan, Avenue de Villeneuve, 66000 Perpignan, France

J.-P. Malrieu

Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse CEDEX, France

(Received 3 August 1992)

Extracting a bond-length-dependent Heisenberg-like Hamiltonian from the potential-energy surfaces of the two lowest states of ethylene, it is possible to study the geometry of polyacetylene by minimization of the cohesive energy, using both variational-cluster and Rayleigh-Schrödinger perturbative expansions. The dimerization amplitude is satisfactorily reproduced. Optimizing the variational-cluster-expansion total energy with the equal-bond-length constraint, the barrier to reversal of alternation is obtained. The alternating-to-regular phase transition is treated from the Néel-state starting function and appears to be of second order.

I. INTRODUCTION

The well-known bond alternation of the one-dimensional (1D) conjugated linear polyenes, the so-called polyacetylene (PA), has been interpreted for a long time^{1,2} at the mono-electronic level of description of the π -electron half-filled band as a Peierls distortion³ stabilizing the ground state and opening a band gap at the Fermi level. Often only electron-lattice coupling was taken into account, partially including electron-electron interactions through the empirically determined values of the Fermi-liquid parameters entering the noninteracting model. However, some Hartree-Fock (HF) calculations⁴⁻⁶ can be found in the literature. Nevertheless, in contradiction to the predictions of band theory the lowest excited state in long polyenes has been determined to be an optically "forbidden" 2^1A_g state instead of the optically allowed 1^1B_u state.^{7,8} The characterization of this 2^1A_g state is poorly described without extensive configuration interaction (CI). The importance of e - e interactions in PA is also emphasized by the nonvanishing negative spin density on alternate carbon atoms in polyacetylene (see Ref. 9 and references therein), or the absence of midgap absorption associated to neutral soliton levels in photoinduced optical absorption¹⁰ and photothermal deflection spectroscopy.¹¹ So in recent years many theories have been developed to deal with the electron repulsion mainly from the extended Hubbard model point of view. One can find mean-field and perturbation theories,¹² the valence-bond method,¹³⁻¹⁵ Monte Carlo simulations,^{16,17} the renormalization-group method,^{18,19} the Gutzwiller variational approach,^{20,21} among others. Paldus and co-workers²² have treated the case of large polyenes rings, using the HF level as the starting point on a Pariser-Parr-Pople (PPP) Hamiltonian with unscreened e - e repulsion and exchange, and including correlation effects by

several different means. The PPP Hamiltonian has also been used by Tavan and Schulten²³ with a multireference double-excitation expansion on long polyenes. Suhai²⁴ has performed second-order Møller-Plesset perturbation theory *ab initio* quantum-chemical calculations with an extended basis set on an infinite chain of *trans*-polyacetylene. For a review see Ref. 25. Nevertheless results are still controversial depending on the interactions included and the level of the calculation performed (see, for instance, Refs. 15 and 26-33 and references therein).

The present work seeks to demonstrate that the same problem may be successfully treated in a purely magnetic model as a "spin-Peierls" distortion, i.e., a geometrical symmetry breaking for the lowest eigenstate of a Heisenberg Hamiltonian as proposed earlier³⁴⁻³⁹ and studied in several contexts; see, for instance, Refs. 40-46.

Heisenberg Hamiltonians or the equivalent covalent-structure valence-bond model have been applied successfully to many physical systems. This applicability sometimes appears surprising since most derivations of the model proceed via degenerate perturbation expansions based upon the atomic limit,^{47,48} which have been shown⁴⁹⁻⁵² to be adequate only for rather small delocalization versus the on-site electronic repulsion ratio ($|4t| < U$). Within this approximation Coulomb interactions in polyacetylene are argued to be not large enough to justify a truncated perturbation theory spin model, as has been pointed out by Fukutome and Sasai.⁶ Nevertheless in the literature one can find other derivations, such as those of Refs. 52-58, that have a wider range of applicability than perturbation theory. The possible treatment of the weakly correlated system through a magnetic Hamiltonian is discussed more precisely in Sec. III.

Following these approaches to obtain Heisenberg Hamiltonians, for the present type of conjugated hydrocarbon a nonempirical nonperturbative Heisenberg-like

Hamiltonian has been obtained in Ref. 59. This Hamiltonian involves a scalar term characterizing the interaction between two σ -bonded carbon atoms with parallel spins in the π system, and a spin operator part,

$$\mathbf{H} = \sum_{\langle i,j \rangle} \{ R(r_{i,j}) + g(r_{i,j})[(i,j) - 1] \}, \quad (1)$$

where $\langle i,j \rangle$ means i and j are nearest neighbors and (i,j) simply denotes a transposition of spin indices i and j and is related to the usual spin operators via the Dirac identity,

$$(i,j) = 2\mathbf{s}_i \cdot \mathbf{s}_j + \frac{1}{2}. \quad (2)$$

Both $R_{i,j} \equiv R(r_{i,j})$ and the effective exchange integral $g_{i,j} \equiv g(r_{i,j})$ are distance dependent. Their values as functions of the bond distance (and eventually of torsion θ of the bond) can be obtained from the spectroscopy of the ethylene molecule, the lowest states of which are

$$E(^1A_g) = R - 2g, \quad (3)$$

$$E(^3B_u) = R. \quad (4)$$

The two functions $R(r)$ and $g(r)$ are provided by the potential energy surfaces of these two states, as known from either good *ab initio* calculations or experiment. Previous work⁵⁹ has used a polynomial development of R and g which resulted from *ab initio* extended-basis-set CI calculations. This Heisenberg Hamiltonian happened to give highly accurate ground-state geometries and transition energies to the lowest excited states of a wide range of conjugated molecules.⁵⁹ Regarding finite linear polyenes, bond alternation was obtained; the largest calculation on $C_{18}H_{20}$ by Cioslowski⁶⁰ gave $r_s = 1.366 \text{ \AA}$ and $r_l = 1.433 \text{ \AA}$ for the most internal short and long bond lengths, in good agreement with experimental values on E polyacetylene (1.36 and 1.44 \AA).^{61,62}

We thought that the problem deserved to be reanalyzed regarding (i) the treatment of an infinite 1D chain, in order to exclude the propagation of end effects, and (ii) the study of the transition from alternating-to-regular geometries, i.e., the bifurcation appearing in the potential-energy surface $E(r_s, r_l)$ or $E(\bar{r}, \delta)$ with $2\bar{r} = r_s + r_l$ and $\delta = (r_l - r_s)/(r_l + r_s)$.

II. METHOD

Two methods have been used to treat the infinite system, namely a Rayleigh-Schrödinger perturbative expansion

and a variational localized-site cluster expansion (VLSCE) development, both starting from the same zeroth-order descriptions. Two starting descriptions have been considered.

(i) For the strongly distorted region, the best zeroth-order description is of course the *product of bond singlet pairs* localized on the short bonds,

$$\phi_0^s = \prod_i^{\text{odd}} S_{i,i+1} \quad (5)$$

with

$$S_{i,j} = \frac{1}{\sqrt{2}} [\alpha(i)\beta(j) - \beta(i)\alpha(j)]. \quad (6)$$

This starting function is symmetry broken as regards the treatment of bonds. One may use it for a research of a tentatively distorted minimum energy and associated geometry, but the nondistorted structures and bifurcation behavior cannot be studied from approximate developments based on that symmetry-broken function.

(ii) The $r_s \simeq r_l$ region and the bifurcation should be studied from a starting function which treats all bonds on the same grounds, i.e., without any prejudice. The most natural zero-order function of that type is the Néel state,

$$\phi_0^N = \prod_{i=1}^{n/2} \alpha(2i-1)\beta(2i), \quad (7)$$

where all bonds (short and long) present a spin alternation.

A. Product of singlets-based approximations

1. RVB variational cluster expansion Ansatz

Our resonating valence-bond (RVB) variational localized-site cluster expansion *ansatz* is defined⁶⁴ by

$$|\phi^{\text{RVB}}\rangle = \sum_s \prod_j \prod_i x_i^{m(j,i,s)} |s\rangle, \quad (8)$$

where s is restricted to all the linearly independent overall singlets made as a product of noncrossing spin pairings with no more than M pairings crossing any plane perpendicular to the chain; x_i is the variational parameter associated with the occurrence of i sites preceding a site $j+1$ being spin paired to i sites succeeding site j . That is,

$$m(j,i,s) \equiv \begin{cases} 1 & \text{if in } s \text{ there are } i \text{ bonds crossing the } j, j+1 \text{ intersite zone,} \\ 0 & \text{otherwise.} \end{cases}$$

In our case we truncate to $M=4$, while the zero-order state in Eq. (5) corresponds to $M=1$.

The energy per atom for a chain of length L is given by

$$E(\phi^{\text{RVB}}) = \frac{1}{L} \sum_i \left[R_{i,i+1} + g_{i,i+1} \left[2 \frac{\langle \phi^{\text{RVB}} | \mathbf{s}_i \cdot \mathbf{s}_{i+1} | \phi^{\text{RVB}} \rangle}{\langle \phi^{\text{RVB}} | \phi^{\text{RVB}} \rangle} - \frac{1}{2} \right] \right]. \quad (9)$$

The last term in Eq. (9) is easily obtained using a transfer matrix⁶⁵⁻⁶⁷ T that allows us to deal with matrix elements locally by (reduced) unit cells. In the long length limit, $L \rightarrow \infty$, the largest eigenvalue Λ of T dominates and

$$\frac{\langle \phi | \mathbf{s}_i \cdot \mathbf{s}_{i+1} | \phi \rangle}{\langle \phi | \phi \rangle} \approx \frac{(\Lambda, l | C_{i,i+1} | \Lambda, r)}{\Lambda^2}, \quad (10)$$

where (Λ, l) and (Λ, r) are the transfer matrix left and right biorthonormal eigenvectors corresponding to Λ and $C_{i,i+1}$ is a connection matrix containing the additional features of the single interaction $\mathbf{s}_i \cdot \mathbf{s}_{i+1}$, while the transfer matrix T acts on the other cells.

2. Perturbative approach

The perturbative approach from ϕ_0^s perturbs it under the effect of singlet-double excitations which are products of triplet excitations, of $S_z = 0, 1$, or -1 value, on adjacent bonds I and J ,

$${}^1\phi_{IJ}^* = \frac{1}{\sqrt{3}} (T_I^+ T_J^- + T_I^- T_J^+ - T_I^0 T_J^0) \prod_{K \neq I, J} S_K. \quad (11)$$

The zeroth- and second-order energies per atom are easily expressed as functions of R_s , R_l , g_s , and g_l ,⁶⁸

$$E_s^{(0)} = \frac{1}{2} (R_s + R_l - 2g_s - \frac{1}{2}g_l), \quad (12)$$

$$E_s^{(2)} = -\frac{3}{8} \frac{g_l^2}{4g_s - g_l}. \quad (13)$$

B. Néel-based approximations

1. Variational localized-site cluster expansion

The present variational localized-site cluster expansion *Ansatz* based upon the Néel state is a generalization for alternating chains of a previous one,⁶⁹

$$|\phi^N\rangle = \mathcal{U}(e^{S^+})|\phi_0^N\rangle \quad (14)$$

with

$$S^+ \equiv \sum_{i,m} S_{i(m)}^+, \quad (15)$$

where \mathcal{U} indicates that only the unlinked portion of e^{S^+} is to be retained, i.e., a product as $\prod_{i(m)} S_{i(m)}^+$ is to be retained in the Taylor series expansion of e^{S^+} only if none of the sets $i(m) \equiv i_1, i_2, \dots, i_m$ of sites has a site in common. And here the nonzero $S_{i(m)}^+$ are selected to be

$$S_{i,i+1}^+ \equiv x_i(i, i+1) \quad (16)$$

and

$$S_{i,i+1,i+2,i+3}^+ = y_i(i, i+1)(i+2, i+3) + z_i(i, i+3), \quad (17)$$

where x_i , y_i , and z_i are variational parameters with alternating translational symmetry conditions

$$v_{i+2} = v_i, \quad v = x, y, z. \quad (18)$$

The energy per atom as a function of variational parame-

ters and interatomic distances is obtained,

$$E(\phi^N) = \frac{1}{L} \sum_i \left[R_{i,i+1} + g_{i,i+1} \left[\frac{\langle \phi^N | (i, i+1) | \phi^N \rangle}{\langle \phi^N | \phi^N \rangle} - 1 \right] \right], \quad (19)$$

where, following a generalization to alternating chains of the procedure suggested in Ref. 69, transposition energy as a function of x_i , y_i , and z_i is easily obtained,

$$E_i \equiv g_{i,i+1} \frac{\langle \phi^N | (i, i+1) | \phi^N \rangle}{\langle \phi^N | \phi^N \rangle} = \frac{2g_{i,i+1}}{ff_{i+1}} \left[f_{i+1} - 1 + \frac{x_i(f_{i+1}f_i + y_i)}{f_{i+1}f_i - y_i} + \frac{z_i^2}{f_{i+1}f_i} + \frac{y_{i+1}z_{i+1}}{f_i^2} + \frac{x_{i+1}^2 z_{i+1} f_{i+1}^2}{(f_{i+1}f_i - y_{i+1})^2} \right], \quad (20)$$

with

$$f_i \equiv 1 + \frac{y_i^2 + z_i^2}{f_{i+1}^2 f_i} + \frac{x_i^2}{f_{i+1}} \frac{f_{i+1}f_i + y_i}{f_{i+1}f_i - y_i} \quad (21)$$

and

$$f \equiv 1 + \frac{2(y_i^2 + z_i^2)}{f_{i+1}^2 f_i} + \frac{2(y_{i+1}^2 + z_{i+1}^2)}{f_{i+1} f_i^2} + \frac{x_i^2 y_i (2f_i f_{i+1} - y_i)}{f_{i+1} (f_i f_{i+1} - y_i)^2} + \frac{x_{i+1}^2 y_{i+1} (2f_i f_{i+1} - y_{i+1})}{f_i (f_i f_{i+1} - y_{i+1})^2}. \quad (22)$$

2. Perturbative approach

The perturbative expansion from the Néel state is quite classical for regular lattices and has been pushed to the sixth order by Parinello and Arai.⁷⁰ Here we have established the cohesive energy up to the fourth order for the distorted system,

$$E_N^{(0)} = \frac{1}{2} (R_s + R_l - g_s - g_l), \quad (23)$$

$$E_N^{(2)} = -\frac{1}{2} \left[\frac{g_s^2}{2g_l} + \frac{g_l^2}{2g_s} \right], \quad (24)$$

$$E_N^{(4)} = \frac{1}{8} \left[g_s + g_l - \frac{g_s^4}{2g_l^3} - \frac{g_l^4}{2g_s^3} \right]. \quad (25)$$

The fourth order included both exclusion principle violating (EPV) and normal linked-diagrams corrections. One may easily check that for equal bond lengths these expressions coincide with Arai and Parinello values [$-g/2$ at order 2, $g/8$ at order 4, i.e., $-0.5g$ and $-0.375g$ for the total correction to the energy, respectively, the exact value being $-0.38629g$ (Ref. 71)].

An infinite summation of EPV-type diagrams has also been performed following a method employed in the many-body problem⁷² and giving a modified expression of the second-order and fourth-order energies, $E_N^{(2\infty)}$ and

TABLE I. Optimized geometries of butadiene and benzene for the two parametrizations P_1 and P_2 .

		P_1	P_2	Experimental
Butadiene	r_s	1.351	1.346	1.344
	r_l	1.444	1.441	1.467
Benzene		1.393	1.389	1.399

$E_N^{(4\infty)}$, where in the denominators g_s and g_l are replaced by \tilde{g}_s and \tilde{g}_l with

$$\tilde{g}_s = g_s \left[1 + \left(\frac{g_s}{2g_l} \right)^2 + 2 \left(\frac{g_l}{2g_s} \right)^2 \right], \quad (26)$$

$$\tilde{g}_l = g_l \left[1 + \left(\frac{g_l}{2g_s} \right)^2 + 2 \left(\frac{g_s}{2g_l} \right)^2 \right]. \quad (27)$$

The corresponding total energies $-0.286g$ and $-0.332g$ at orders 2 and 4 (for equal bond lengths) are poorer approximations of the exact one but the series have a less oscillatory behavior and one may expect a less dangerous evolution of the basic perturbative ratio $g_s/2\tilde{g}_l$ versus that of $g_s/2g_l$ which may become too large when the distortion becomes large, making the unresummed series divergent.

C. Parametrization of the Hamiltonian

Finally two parametrizations have been used. The first one (P_1) is the original *ab initio* proposal⁵⁹ which, for an ethylene molecule, gives $r_{C-C}=1.344$ Å, $k_{C-C}=9.29$ mdyn Å, and vertical singlet-triplet transition energy $\Delta E_{S-T}=2g(r_0)=4.23$ eV; the second one (P_2) keeps the same function for R and slightly corrects $g(r)$ in order to obtain the experimental distance, $r_{C-C}=1.339$ Å,⁷³ $k_{C-C}=9.39$ mdyn Å,⁷⁴ and the experimental vertical transition energy $\Delta E_{S-T}=4.54$ eV.⁷⁵ We have tested that on finite problems as butadiene and benzene, the calculated geometries from these $g(r)$ functions give comparable accuracies (see Table I).

III. RESULTS AND DISCUSSION

(1) Starting from the Néel state, for the variational localized-site cluster expansion *Ansatz* of Sec. II B 1, when geometry is optimized, both parametrizations P_1 and P_2 yield an alternant geometry (cf. Table II) with interatomic distances that compare very well with experimental values.^{61,62} Studying this energy as a function of δ for different values of \bar{r} allows us to obtain the bifurcation for the regular-to-dimerized transition. Results are similar for both the original parametrization of Said *et al.*,⁵⁹ P_1 , and the modified parametrization P_2 of Sec. II C. In Fig. 1 energy per site is plotted as a function of δ for different values of \bar{r} for the original P_1 parametrization, being qualitatively identical for P_2 . The bifurcation is found for $\bar{r}_c \simeq 1.32$ Å. The whole calculated potential-energy surface is very flat. In particular for the optimal \bar{r} (1.40 Å), the energy gain brought by the dimerization is ~ 0.0118 eV per C_2H_2 unit for P_1 and ~ 0.0136 eV for P_2 . These values are very close to those shown in Table III, obtained as the difference between the cluster expansion ground-state energies when optimization is performed with and without the $r_1=r_2$ constraint. Those are about four times the value predicted by Mintmire and White using a local-density-functional approach,²⁸ but still smaller than 0.07 eV suggested by Ashkenazi *et al.* [32] to be compatible with PA being dimerized well above room temperature, or the Suhai (0.09 eV) HF calculation and second-order Møller-Plesset perturbation theory.²⁴ HF stabilization energies brought by dimerization are in general still higher (see Ref. 63 and references therein), though this approximation is not reliable in this precise problem, due to the charge-density wave HF instability occurring for $\delta=0$ as discussed later on. Still higher-order Néel-based cluster expansion approximations should yield higher values of the barrier than this *Ansatz*.

The choice of the Néel state as zero-order wave function might seem to imply that our perturbed state retains the same type of spin-orienting *long-range order* as the Néel state. Nevertheless, as already discussed explicitly for the cluster expansion treatment,⁶⁹ this *long-range spin order* approaches zero for the linear chain as we increase the extent of the cluster expansion, i.e., the perturbation

TABLE II. Results of perturbative and variational localized-site cluster expansions from either a Néel state or a product of bond singlets for two different parametrizations of $g(r)$. \bar{r}_c is the critical bifurcation mean bond length, r_s and r_l are the optimized short and long bond distances (in Å), $r_s \simeq 1.36$ Å and $r_l \simeq 1.44$ Å being the experimental values (Ref. 61). E is the energy per carbon atom (in eV), taking the energy of the Néel state with 1.40-Å equal bond lengths as zero of energy.

ϕ_0	Method	\bar{r}_c	P_1		E	P_2		E	
			r_s	r_l		r_s	r_l		
Néel state	Perturbative (fourth order)	1.43	1.401	1.401	-0.616	1.46	1.398	1.398	-0.659
	VLSCE:								
	lower level	1.46	1.400	1.400	-0.661	1.46	1.397	1.397	-0.705
	higher level	1.32	1.360	1.443	-0.704	1.32	1.356	1.440	-0.751
Product of bond singlets	Perturbative (second order)		1.361	1.438	-0.720		1.351	1.441	-0.769
	VLSCE		1.364	1.436	-0.720		1.359	1.433	-0.772

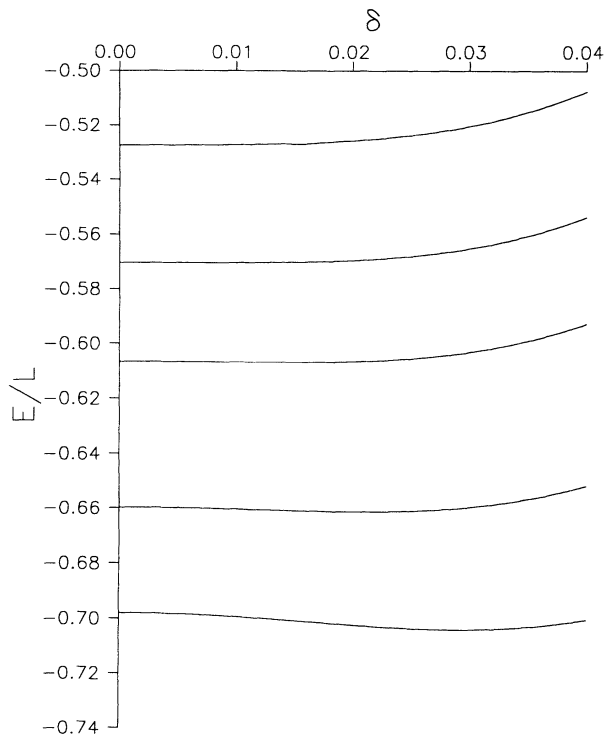


FIG. 1. Néel-based variational localized-site cluster expansion energy per atom (in eV) as a function of δ for $\bar{r}=1.32, 1.33, 1.34, 1.36,$ and 1.40 (in Å), from top to bottom, respectively, for parametrization P_1 , taking the energy of the Néel state with 1.40 -Å equal bond lengths as zero of energy.

or the exponential cluster expansion tend to destroy the long-range spin correlation of the zero-order state. For the present distorted ground-state geometry, this remanent *long-range spin order*, when computed with the optimal cluster expansion wave function, is still smaller (~ 0.009 for both P_1 and P_2 parametrizations) than its value for the regular chain (~ 0.052) yield by this *Ansatz*.

(2) The Néel-based variational localized-site cluster expansion *Ansatz*, when optimization is performed at lower order imposing $y_i = z_i = 0$, leads to the same conclusions as the most refined fourth-order perturbation expansions for both parametrizations (cf. Table II). The lowest energy is obtained for a nondimerized geometry $r_s = r_l = 1.40$ Å and the bifurcation takes place for a stretched system,

TABLE III. Optimized regular interatomic distance (in Å) and gain in energy per C_2H_2 unit (in eV) of regular PA by report to the alternating ground state for the two parametrizations P_1 and P_2 with the Néel-based higher order and the RVB cluster expansions.

		P_1	P_2
Néel based	r	1.399	1.395
	ΔE	0.0118	0.0122
RVB	r	1.398	1.394
	ΔE	0.0391	0.0417

the critical distance \bar{r}_c being 1.46 Å in the cluster expansion with both P_1 and P_2 parametrizations, and 1.43 and 1.46 Å in the perturbative approach with P_1 and P_2 parametrizations, respectively. The success of the most refined cluster expansion approach and the failure of both the perturbative and lower-level cluster expansion may be interpreted as due to (i) the poor convergence of the Néel-based perturbation expansion for such a low-dimensional material, and (ii) the necessity to go beyond exchange between nearest neighbors in the excitation operator in the cluster expansion. In all cases the phase transition is of second order.

(3) Starting from the *product of bond singlets* one may have a better energy evaluation for the distorted region and actually the energies are lower (cf. Table II). Furthermore, the RVB cluster expansion already yields lower energy than the Néel-based one even when applied to the regular $s = \frac{1}{2}$ Heisenberg linear chain (cf. Table IV). For both parametrizations the optimized geometries are almost identical for the cluster expansion and perturbative estimates; the bond distances lie between 1.351 and 1.365 Å for the short bond, and between 1.433 and 1.443 Å for the long bond. The mean distance \bar{r} and the relative distortion δ have reasonable values whatever the parametrization and the expansion. Thus, starting from the *product of bond singlets* zeroth-order picture, one always obtains a reasonable estimate of the dimerized geometry; the so-obtained values are slightly better than the most internal bond distances given by the exact solution for the finite C_{18} molecule and better than the CEPA *ab initio* estimate of König and Stollhoff ($r_s = 1.343$ Å, $r_l = 1.436$ Å).³³ Optimizing the geometry with the constraint of equal bond length, we have estimated the stabilization energy gain by dimerization. The barrier to inversion of dimerization is higher with the RVB than the Néel-based variational cluster expansion, being 0.0391 and 0.0417 eV for P_1 and P_2 parametrizations, respectively, as shown in Table III.

While the RVB *Ansätze* yield better energy and interatomic distances, they do not enable the study of the $r_s \simeq r_l$ region and the bifurcation. In a general way, all methods which start with a symmetry-broken description are unable to treat correctly the weakly dimerized region and of course the bifurcation point. That is the case of RVB *Ansätze*. With this problem in mind, one has to analyze the usual way to solve the N -electron problem: One generally starts from the HF description, which is used as a zero-order description. But as it is well known, HF symmetry breaking takes place for nondimerized geometries, leading to bond-centered charge-density waves, i.e., bond alternation of the density matrix without any bond-length alternation. Then, any strategy based on the HF solutions will be unable to study the region around $\delta=0$, since it is symmetry broken for the nondimerized geometries. This fact is manifested by the energy cusp for $\delta=0$ in Ref. 33 or in RVB *Ansätze* as also pointed out for the Heisenberg Hamiltonian in Ref. 36. These cusps are induced by the broken-symmetry character of the starting ground-state wave function. Therefore, the possible existence and location of the bifurcation between nondimerized and dimerized structures is very

TABLE IV. Ground-state Heisenberg energies per site for $L \rightarrow \infty$ at $\delta=0$ (see Refs. 69, 64, and references therein for other available results).

Method	$\langle (i, i+1) \rangle$
Néel state	0.000
Product of bond singlets (RVB, $M=1$)	-0.2500
EPV infinite summation of Sec. II B 2 (second order)	-0.2860
EPV infinite summation of Sec. II B 2 (fourth order)	-0.3320
Lower-order Néel-based cluster expansion	-0.3558
Product of bond-singlets perturbative expansion (second order)	-0.3750
Néel-based perturbative expansion (fourth order)	-0.3750
Higher-order Néel-based cluster expansion	-0.3758
RVB cluster expansion ($M=4$)	-0.3791
Exact result of Hulthén (Ref. 71)	-0.3863
Néel-based perturbative expansion (second order)	-0.5000

difficult to study from the exact or Hubbard Hamiltonian as long as one starts from the HF solution. Exploring that zone from a Heisenberg Hamiltonian was one success of the present work.

The treatment of the one-dimensional polyacetylene problem through a carefully parametrized r -dependent magnetic Hamiltonian proved to give reliable results for the mean bond length, the existence, and the extent of bond alternation; it also is able to give information regarding the transition from alternating to nonalternating structures and the barrier to inversion of dimerization. Nevertheless that success does not prove by itself that polyacetylene is a strongly correlated electronic system, since all studies agree on a value of $|t|/U > \frac{1}{4}$. This work is intending to illustrate the possibility of treating such a material from either the traditional (delocalization + correlation) approach or from a magnetic approach which incorporates delocalization through effective exchanges. For spin-nonfrustrated lattices there is a large domain around the $|t|/U = \frac{1}{4}$ perturbative critical value for which both approaches are relevant. This is especially true for one-dimensional chains where the Gutzwiller-type *Ansatz*^{76,77} remains efficient in the strongly correlated domain^{78,79} and conversely the magnetic treatments provide reliable ground-state and lowest-excited-state properties in the weakly correlated region [see, for instance, RVB (Ref. 64) and exact⁵⁹ calculations of low-lying homopolar states of polyenes]. Obtention of excited states for the dimerized chain is in progress. This wide duality of description is due to the fact that the projection of the delocalized single determinant ϕ_0 onto the neutral VB subspace closely resembles the Heisenberg

eigenstate, the antisymmetrization introducing per se the correct spin ordering among the neutral components of ϕ_0 . Of course, the Heisenberg Hamiltonian must be considered as an effective Hamiltonian built on neutral valence-bond configurations from the exact Hamiltonian or from an approximation to it (such as the Hubbard Hamiltonian), and it cannot bring more physics than the original Hamiltonian. However, its use may be interesting when the solution of the exact or simplified Hamiltonian is difficult to approach. That is an important point, since it has been argued that the widely used Hubbard model describes reasonably only those states that are also capable of being so described by a Heisenberg model.⁵²

We would like to point out that a very similar problem, namely the metal-insulator transition of phosphorus, has been treated with the same strategy as a spin-Peierls distortion using a Heisenberg Hamiltonian for the half-filled π band extracted from the spectroscopy of P and the P_2 diatom.⁸⁰

One final point to notice is that all these calculations have been obtained, within seconds, with a 286 IBM compatible PC with a mathematical coprocessor.

ACKNOWLEDGMENTS

M.A.G.B. acknowledges support from the DGICYT (Project PS90-0061), and also acknowledges Professor D. J. Klein's valuable comments. The Laboratoire de Physique Quantique is Unité associée de Centre Nationale de la Recherche Scientifique.

¹H. C. Longuet-Higgins and L. Salem, Proc. R. Soc. (London) Ser. A **25**, 172 (1959).

²W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2095 (1980).

³R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955).

⁴R. Dovesi, Int. J. Quantum Chem. **26**, 197 (1984).

⁵J. Delhalle, Int. J. Quantum Chem. **26**, 717 (1984).

⁶H. Fukutome and M. Sasai, Prog. Theor. Phys. **67**, 41 (1982); **69**, 1 (1983); **69**, 373 (1983).

⁷B. S. Hudson, B. E. Kohler, and K. Schulten, in *Excited States*,

edited by E. C. Lim (Academic, New York, 1982), Vol. 6, and references therein; B. S. Hudson and B. E. Kohler, Synth. Met. **9**, 241 (1984).

⁸E. A. Imhoff and D. B. Fitchen, Solid State Commun. **44**, 329 (1982); D. B. Fitchen, Synth. Met. **9**, 341 (1984).

⁹H. Thomann, L. R. Dalton, Y. Tomkiewicz, N. S. Shiren, and T. C. Clarke, Phys. Rev. Lett. **50**, 533 (1983); H. Thomann, L. R. Dalton, M. Grabowski, and T. C. Clarke, Phys. Rev. B **31**, 3141 (1985).

¹⁰J. Orenstein, Z. Vardeny, G. L. Baker, G. Eagle, and S. Etemad, Phys. Rev. B **30**, 786 (1984).

- ¹¹B. R. Weinberger, C. B. Roxlo, S. Etemad, G. L. Baker, and J. Orenstein, *Phys. Rev. Lett.* **53**, 86 (1984).
- ¹²S. Kivelson and D. Heim, *Phys. Rev. B* **26**, 4278 (1982).
- ¹³Z. Soos and S. Ramasesha, *Phys. Rev. B* **29**, 5410 (1984).
- ¹⁴S. Mazumdar and S. N. Dixit, *Phys. Rev. Lett.* **51**, 292 (1983).
- ¹⁵S. N. Dixit and S. Mazumdar, *Phys. Rev. B* **29**, 1824 (1984).
- ¹⁶J. E. Hirsch, *Phys. Rev. Lett.* **51**, 296 (1983).
- ¹⁷D. Campbell, T. A. DeGrand, and S. Mazumdar, *Phys. Rev. Lett.* **52**, 1717 (1984).
- ¹⁸G. Hayden and E. Mele, *Phys. Rev. B* **32**, 6527 (1985).
- ¹⁹B. Horovitz and J. Solyom, *Phys. Rev. B* **32**, 2681 (1985).
- ²⁰P. Horsch, *Phys. Rev. B* **24**, 7351 (1981).
- ²¹D. Baeriswyl and K. Maki, *Phys. Rev. B* **31**, 6633 (1985).
- ²²J. Paldus and E. Chin, *Int. J. Quantum Chem.* **24**, 373 (1983); J. Paldus, E. Chin, and G. Grey, *ibid.* **24**, 395 (1983); R. Pauncz and J. Paldus, *ibid.* **24**, 411 (1983); M. Takahashi, J. Paldus, and J. Cizek, *ibid.* **24**, 707 (1983); J. Paldus and M. Takahashi, *ibid.* **25**, 423 (1984); M. Takahashi and J. Paldus, *ibid.* **26**, 349 (1984).
- ²³P. Tavan and K. Schulten, *Phys. Rev. B* **36**, 4337 (1987).
- ²⁴S. Suhai, *Phys. Rev. B* **27**, 3506 (1983); *Int. J. Quantum Chem.* **23**, 1239 (1983).
- ²⁵H. W. Streitwolf, *Phys. Status Solidi B* **127**, 11 (1985); A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- ²⁶C. Wu, X. Sun, and K. Nasu, *Phys. Rev. Lett.* **59**, 831 (1987); **63**, 2535 (1989).
- ²⁷S. Kivelson, W.-P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **58**, 1899 (1987); **60**, 72 (1988).
- ²⁸J. W. Mintmire and C. T. White, *Phys. Rev. B* **35**, 4180 (1987); *Phys. Rev. Lett.* **63**, 2532 (1989).
- ²⁹D. Baeriswyl, P. Horsch, and K. Maki, *Phys. Rev. Lett.* **60**, 70 (1988).
- ³⁰J. T. Gammel and D. K. Campbell, *Phys. Rev. Lett.* **60**, 71 (1988).
- ³¹J. L. Bredas and J. Heeger, *Phys. Rev. Lett.* **63**, 2534 (1989).
- ³²J. Ashkenazi, W. E. Pickett, H. Krakauer, C. S. Wang, B. M. Klein, and S. R. Chubb, *Phys. Rev. Lett.* **62**, 2016 (1989); **63**, 2533 (1989).
- ³³G. König and G. Stollhoff, *Phys. Rev. Lett.* **65**, 1239 (1990).
- ³⁴C. A. Coulson and T. Dixon, *Tetrahedron* **17**, 215 (1961).
- ³⁵H. M. McConnell *et al.*, *J. Chem. Phys.* **36**, 2393 (1962); **39**, 2321 (1963).
- ³⁶D. J. Klein and M. A. Garcia-Bach, *Phys. Rev. B* **19**, 877 (1979).
- ³⁷M. C. Cross and D. S. Fisher, *Phys. Rev. B* **19**, 402 (1979).
- ³⁸J. Kondo, *Physica* **98B**, 176 (1980).
- ³⁹T. Nakano and H. Fukuyama, *J. Phys. Soc. Jpn.* **49**, 1679 (1980).
- ⁴⁰C. Tsallis, *J. Appl. Phys.* **53**, 8012 (1982).
- ⁴¹Y. Lépine, *Solid State Commun.* **43**, 375 (1982); *J. Appl. Phys.* **53**, 8029 (1982).
- ⁴²J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1983), Vol. III, p. 353.
- ⁴³J. Kondo, *Physica* **123B**, 169 (1984).
- ⁴⁴J. Solyom, *Phys. Rev. B* **37**, 5781 (1988).
- ⁴⁵C. Coulon, B. Gallois, T. Granier, and P. Vaca, *Synth. Met.* **27**, B449 (1988).
- ⁴⁶N. Read and S. Sachdev, *Phys. Rev. B* **42**, 4568 (1990).
- ⁴⁷P. W. Anderson, in *Solid State Physics. Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1963), Vol. 14, pp. 99–214.
- ⁴⁸B. H. Brandow, *Adv. Phys.* **26**, 651 (1977).
- ⁴⁹L. N. Bulaewskii, *Zh. Eksp. Teor. Fiz.* **51**, 230 (1966) [*Sov. Phys. JETP* **24**, 154 (1967)].
- ⁵⁰W. A. Seitz and D. J. Klein, *Phys. Rev. B* **9**, 2159 (1974).
- ⁵¹M. Takahashi, *J. Phys. C* **10**, 1289 (1977).
- ⁵²R. D. Poshusta, T. G. Schmalz, and D. J. Klein, *Mol. Phys.* **66**, 317 (1989).
- ⁵³L. F. Matheiss, *Phys. Rev.* **123**, 1209 (1961).
- ⁵⁴E. N. Economu and C. T. White, *Phys. Rev. Lett.* **38**, 289 (1977); E. N. Economu and P. Mihás, *J. Phys. C* **10**, 5017 (1977).
- ⁵⁵R. D. Poshusta and D. J. Klein, *Phys. Rev. Lett.* **48**, 1555 (1982); *J. Mol. Struct.* **229**, 103 (1991).
- ⁵⁶S. Kuwajima, *J. Chem. Phys.* **77**, 1930 (1982).
- ⁵⁷D. J. Klein and D. C. Foyt, *Phys. Rev. A* **8**, 2280 (1973); D. J. Klein, W. A. Seitz, M. A. Garcia-Bach, J. M. Picone, and D. C. Foyt, *Int. J. Quantum Chem. Symp.* **17**, 555 (1983).
- ⁵⁸J.-P. Malrieu and D. Maynau, *J. Am. Chem. Soc.* **104**, 3021 (1982); **104**, 3029 (1982); *Ph. Durand, Phys. Rev. A* **28**, 3184 (1983); J.-P. Malrieu, D. Maynau, and J. P. Daudey, *Phys. Rev. B* **30**, 1817 (1984); D. Maynau, M. A. Garcia-Bach, and J.-P. Malrieu, *J. Phys. (Paris)* **47**, 207 (1986).
- ⁵⁹M. Said, D. Maynau, J.-P. Malrieu, and M. A. Garcia-Bach, *J. Am. Chem. Soc.* **106**, 571 (1984); **106**, 580 (1984).
- ⁶⁰J. Cioslowski, *Theor. Chem. Acta* **75**, 271 (1989).
- ⁶¹C. S. Yannoni and T. C. Clarke, *Phys. Rev. Lett.* **51**, 1191 (1983).
- ⁶²H. Kalhert, O. Lertner, and G. Leising, *Synth. Met.* **17**, 467 (1987).
- ⁶³M. Springborg, *Phys. Rev. B* **33**, 8475 (1986).
- ⁶⁴M. A. Garcia-Bach, R. Valentí, S. Alexander, and D. J. Klein, *Croat. Chem. Acta* **64**, 415 (1991).
- ⁶⁵D. J. Klein, D. G. Hite, and T. G. Schmalz, *J. Comput. Chem.* **7**, 443 (1986); D. J. Klein, M. A. Garcia-Bach, and W. A. Seitz, *J. Mol. Struct.* **185**, 287 (1989).
- ⁶⁶D. J. Klein, M. A. Garcia-Bach, and W. A. Seitz, *J. Mol. Struct.* **185**, 275 (1989).
- ⁶⁷M. A. Garcia-Bach, A. Peñaranda, and D. J. Klein, *Phys. Rev. B* **45**, 10 891 (1992).
- ⁶⁸P. Blaise, J.-P. Malrieu, D. Maynau, and B. Oujia, *J. Mol. Struct.* **169**, 469 (1988).
- ⁶⁹D. J. Klein and M. A. Garcia-Bach, *Int. J. Quantum Chem.* **12**, 273 (1977).
- ⁷⁰M. Parinello and T. Arai, *Phys. Rev. B* **10**, 265 (1974); M. Parinello, M. Scire, and T. Arai, *Lett. Nuovo Cim.* **6**, 138 (1973).
- ⁷¹L. Hulthén, *Ark. Mat. Astron. Phys.* **26A**, 1 (1938).
- ⁷²M. B. Lepetit and J.-P. Malrieu, *J. Chem. Phys.* **87**, 5937 (1987).
- ⁷³J. L. Ducan, I. J. Wright, and D. Vam Leberghe, *J. Mol. Spectrosc.* **42**, 462 (1972).
- ⁷⁴C. W. Bock, Ph. George, and M. Trachman, *J. Mol. Spectrosc.* **76**, 191 (1979).
- ⁷⁵D. F. Evans, *J. Chem. Soc. (London)* **1960**, 1735.
- ⁷⁶M. C. Gutzwiller, *Phys. Rev. A* **134**, 993 (1964).
- ⁷⁷G. Stollhoff and P. Fulde, *Z. Phys. B* **26**, 257 (1977); **29**, 231 (1978).
- ⁷⁸T. A. Kaplan, P. Horsch, and P. Fulde, *Phys. Rev. Lett.* **49**, 889 (1982).
- ⁷⁹B. Oujia, M. B. Lepetit, and J.-P. Malrieu, *Chem. Phys. Lett.* **58**, 559 (1989).
- ⁸⁰A. Pellegatti and J.-P. Malrieu, *Phys. Rev. B* **46**, 9946 (1992).