The low-lying electronic excitations in long polyenes: A PPP-MRD-CI study

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A correct description of the electronic excitations in polyenes demands that electron correlation is accounted for correctly. Very large expansions are necessary including many-electron configurations with at least one, two, three, and four electrons promoted from the Hartree–Fock ground state. The enormous size of such expansions had prohibited accurate computations of the spectra for polyenes with more than ten π electrons. We present a multireference double excitation configuration interaction method (MRD-CI) which allows such computations for polyenes with up to 16 π electrons. We employ a Pariser–Parr–Pople (PPP) model Hamiltonian. For short polyenes with up to ten π electrons our calculations reproduce the excitation energies resulting from full-CI calculations. We extend our calculations to study the low-lying electronic excitations of the longer polyenes, in particular, the gap between the first optically forbidden and the first optically allowed excited singlet state. The size of this gap is shown to depend strongly on the degree of bond alternation and on the dielectric shielding of the Coulomb repulsion between the π electrons.

I. INTRODUCTION

Polyenes are well known for their intense optical absorption which originates from an optically allowed singlet state of B_u symmetry. For a long time this state had been assumed to be the lowest singlet electronic excitation of polyenes and to be the starting point for the fast polyene photochemistry. However, in 1972 it had been discovered that in a diphenylpolyene a lower, optically forbidden singlet electronic excitation of A_g symmetry exists and it had been suggested that such state can be found in all polyene compounds.[1,2] This expectation was based on self-consistent field configuration interaction calculations (SCF-CI) involving a Pariser–Parr–Pople (PPP) Hamiltonian. The existence of this state below the optically allowed B_u singlet state in polyenes with 3–6 double bonds is by now a well established fact.[3] The early prediction that this state occurs also in butadiene has been confirmed recently by resonance Raman spectroscopy.[4] In this latter molecule the excited A_g state has been identified about 0.2 eV below the B_u state. *Ab initio* calculations fail to describe the excitation energies of these two states properly.[5–7]

In this paper we want to investigate the electronic level ordering of long polyenes. The interest in these materials stems from the observation of large conductivities in doped derivatives of very long polyenes, i.e., of polyacetylene. Investigations of the physical properties of these compounds are currently being persued in many laboratories.[8] These investigations have been stimulated very much by the intriguing suggestion that solitonic excitations, i.e., low energy states which involve a strong coupling between electronic and nuclear degrees of freedom, mediate the conductivity of polyacetylene.[9,10] However, the existence of solitonic excitations in polyacetylene has not been proven conclusively and their original theoretical description based on a single-electron picture was found to be at variance with a number of experimental findings. This issue has been discussed in Refs. 11, 12, 13, and 14. But in spite of the shortcomings of the original treatment, which are due to the neglect of electronic correlations, it appears that the concept of solitons in these materials is actually correct. Our aim is to investigate electronic excitations and their vibronic coupling in a wide range of polyenes in order to relate the well understood properties of short conjugated chains to the emerging notions on the properties of polyacetylene.[13] A prerequisite for such an investigation is a knowledge of the energies and wave functions of the ground state and of the excited A_g and B_u singlet states in polyenes of all sizes.

Due to the importance of electron correlation effects a description of the electronic excitations in long polyenes is a rather complicated task. For the description one has to resort to semiempirical Hamiltonians. *Ab initio* methods cannot be applied to longer polyenes because of the large total number of electrons in these compounds. Besides, as pointed out above, *ab initio* methods appear to be incapable of correctly describing the excitation energies of even the smallest polyene. In this paper we will employ the PPP Hamiltonian as it proved to describe properly the electronic excitations in the smaller polyenes.

In the following we will denote excited singlet states by the symbols $n\,^1A_g$ and $n\,^1B_u$ where A_g and B_u denote the spatial symmetry of the states and n counts in order of increasing energy the excitations of a particular symmetry type. In this notation the ground state will be denoted by $1\,^1A_g$.

The singlet ground state $1\,^1A_g$ of polyenes customarily is described by a single Hartree–Fock determinant. This description to a large part neglects the effect of electron correlation. Since the $1\,^1B_u$ state and, in particular, the $2\,^1A_g$ state are dominated by electron correlation the determination of accurate excitation energies requires that electron correlation is also properly described for the ground state. Actually, the aim of any computational method for excitation energies is to account for the contributions of electron correlation in a "balanced" way, i.e., to determine the contributions of the correlation energy to the same degree of completion in both the ground state and the excited state.

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Starting from the Hartree–Fock determinant the effect of electron correlation on the ground state can be described by a configuration interaction expansion which includes double excitations. Such description renders an accurate description for small polyenes, however, falls short in the description of longer polyenes. In fact, the correlation contribution to the ground state energy is proportional to $\sqrt{N}$, whereas the exact correlation contribution should increase linearly with the polyene length N. The error obviously becomes very large for longer polyenes. An estimate of this error has been presented in Ref. 15. The results of these authors let us expect that the inclusion of configurations with up to four electrons excited from the Hartree–Fock ground state should provide accurate ground state energies for polyenes that are as long as considered in this work, i.e., $N \leqslant 16$.

The description of the optically allowed $1\,^1B_u$ state is rather straightforward. In zeroth order approximation this state can be constructed by promoting a single electron from the highest occupied to the lowest unoccupied molecular orbital. To account in a first approximation for the effect of electron correlation all one particle–one hole excitations have to be included in the description. The resulting expansion describes properly the Coulomb attraction between electron and hole.[15] The energy contribution of this interaction grows with the size of the polyene.[16,17] Further correlation effects in the $1\,^1B_u$ state due to electron–electron repulsion are very similar to the electron correlation effects in the ground state. For a proper description of these effects one needs to include configurations in the CI expansion in which at least three electrons are simultaneously excited from the Hartree–Fock ground state.[15]

The low-lying excited $2\,^1A_g$ state has been characterized to involve two simultaneous triplet excitations of ethylenic units which combine to an overall singlet state.[2,8,18,19] For a proper representation of this state all π-electron configurations with one and two electrons promoted from the Hartree–Fock ground state have to be included in a CI expansion (D-CI). However, such a minimal representation does not provide a balanced description of the correlation energies of the ground and the excited state and, as a result, fails to describe excitation energies accurately, the error increasing with increasing lengths of the polyenes as $\sqrt{N}$.[15] This deficiency is repaired, at least for the shorter polyenes, when all triply and quadruply excited configurations are included in the CI expansion (Q-CI). The resulting description predicts that the energy gap between the excited $2\,^1A_g$ and $1\,^1B_u$ states increases with increasing polyene length, a finding which is in agreement with the available spectral data. This has been demonstrated previously[19] for the polyene series C_NH_{N+2}, $N = 4,6,8,10$. The results were confirmed in a series of investigations by Soos and co-workers[20–23] who employed a full-CI description. However, for the longer polyenes ($N > 10$) a satisfactory description of the $2\,^1A_g$ state is still missing.

Actually, Soos and co-workers chose a parametrization of the PPP Hamiltonian different from that in Refs. 18 and 19. In order to avoid unneccessary confusion about the accuracy of the different methods we will adopt the parametrization of Soos *et al.*[23] This allows a direct comparison of results and, as demonstrated below, proves that full-CI calculations reproduce very closely the results obtained by our previous Q-CI method.

There are two problems connected with a description of longer polyenes. First, the larger the π-electron system, the more important is the effect of electron correlation. Actually, for a description which is to reproduce for short and long polyenes the energies of ground and excited states to the same degree of accuracy one needs to include electron configurations for the longer polyenes which are excited to a higher degree than those of the shorter polyenes.[15] Second, the dimension of the many-electron Hamiltonian increases exponentially with the number N of π electrons. Even with the use of supercomputers and very efficient algorithms for the matrix element evaluation a CI dimension of about 10^5 currently represents the upper computational limit. Employing an orthonormal basis of antisymmetrized, spin- and symmetry-adapted configurational functions this limit is reached at $N = 14$ for Q-CI expansions and at $N = 12$ for full-CI expansions. In order to overcome these difficulties one needs to employ an approximation scheme which selects in a suitable way the most important electron configurations. On the one hand the selection has to guarantee that the resulting dimensions of the CI expansions remain within realistic bounds. On the other hand, the selection should achieve a balanced description of correlation effects in ground and excited states. For this purpose we have adopted the multireference double excitation configuration interaction (MRD-CI)[24] scheme. In our implementation of this scheme the relevant matrix elements of the many-electron Hamiltonian are evaluated from a small set of general formulas.[25] These formulas render an efficient algorithm for the matrix element generation allowing the treatment of CI expansions comprising several 10^4 spin-adapted, antisymmetrized functions.

In the following we will demonstrate that the MRD-CI expansion furnishes accurate descriptions of the five lowest excited states in polyenes comprising up to 16 π electrons. The accuracy of the MRD-CI expansion is proven by comparing for polyenes with up to 10 and 12 π electrons our results to those of full-CI[23] and Q-CI calculations. We then extend our calculations to longer polyenes. The results show that the $2\,^1A_g$–$1\,^1B_u$ energy gap increases from butadiene to the longest polyene investigated. The energy gap is found to depend on the degree of bond alternation as well as on a possible dielectric screening of the Coulomb repulsion between the π electrons. In a subsequent publication the calculated MRD-CI excitation energies and wave functions are employed for a study of the properties of electronic states in the long polyenes and for an extrapolation to polyacetylene, i.e., to the "infinite" polyene limit.[26]

II. METHOD: PPP-MRD-CI

The excited π-electron valence states of the polyenes are described here as in our previous work[2,18,15,19] by a Pariser–Parr–Pople (PPP) parametrized model Hamiltonian:

$$H=\sum_{n<m} U_{nm}+\sum_{m,\sigma}\left(-I-\sum_{n\neq m} U_{nm}\right)c^{+}_{m\sigma}c_{m\sigma}$$

$$+\sum_{\substack{n,m,\sigma\\ n\neq m}} t_{nm}c^{+}_{n\sigma}c_{m\sigma}+\frac{1}{2}\sum_{\substack{n,m,\sigma,\sigma'\\ (n,\sigma)\neq(m,\sigma')}} U_{nm}c^{+}_{n\sigma}c_{n\sigma}c^{+}_{m\sigma'}c_{m\sigma'}. \tag{2.1}$$

The first term describes the nuclear repulsion, the second term the attraction between π electrons and nuclear cores, the third term the kinetic energy of the electrons and the last term their mutual Coulomb repulsion. The Fermion creation (annihilation) operators $c^{+}_{n\sigma}$ ($c_{n\sigma}$) position the π electrons in an orthonormal set of atomic orbitals. The effective Coulomb repulsion integrals U_{nm} between orbitals at atoms n and m are given by the Ohno formula[27]

$$U_{nm}=U/\sqrt{1+0.6117r^{2}_{nm}}, \tag{2.2}$$

where r_{nm} is the atomic distance in Å. For the repulsion energy U of two π electrons at the same atomic site we have adopted the standard value of 11.26 eV such that at large distances the electron repulsion falls off as e^2/r_{nm}. To investigate how a faster decay of the Coulomb repulsion of the π electrons affects the polyene spectra we have employed also a modified formula U^{sc}_{nm} which is related to Eq. (2.2) by

$$U^{sc}_{nm}(r)=U_{nm}(2r). \tag{2.3}$$

At large distances this expression mimics a dielectric screening with an intramolecular dielectric constant $\epsilon=2$. For the effective ionization potential I of a π electron at a carbon site we assumed the value 11.16 eV. The resonance integral t_{nm} between centers n and m is given by (distances r_{nm} in Å)

$$t_{nm}=\begin{cases}-2.4\times[1.0+1.4(1.4-r_{nm})]\,\text{eV} & \text{for } n=m\pm1;\\ 0 & \text{else.}\end{cases} \tag{2.4}$$

With atomic distances of 1.45 Å for single bonds and of 1.35 Å for double bonds this parametrization is identical to that employed by Sool and Ramasesha[23] in their full-CI study on the π-electron excitations of shorter polyene chains. Since we have adopted the parameters of these authors we can employ the full-CI results as a reference for the accuracy of our description. To study the effects of the degree of bond length alternation on the polyene spectra, we have also investigated model polyenes with all bond lengths equal to 1.40 Å.

For alternating hydrocarbons the PPP Hamiltonian (1) in addition to spatial and spin symmetries exhibits an additional symmetry, the so-called "alternancy symmetry," which classifies (−) and (+) states.[28,29] In a valence bond (VB) description the (−) states are characterized by covalent diagrams corresponding to spin wave excitations, whereas the (+) states are purely ionic. Hence, the (−) states depend much more sensitively on the electron correlation than the (+) states[19] such that much larger CI expansions have to be chosen for a proper description of the (−) states than for the (+) states. To underline this difference we will classify all states by their (−) and (+) alternancy symmetry. In our calculations we have dealt separately with the four symmetry classes, i.e., with $^1A_g^+$, $^1A_g^-$, $^1B_u^+$, and $^1B_u^-$ states, in order to reduce the dimension of the CI matrix.

Exact calculations of the low-energy spectrum of the Hamiltonian (1) for the polyenes appear to be limited to systems with at most 12 π electrons. This is due to the enormous dimension d of the corresponding many-electron Hilbert space which increases exponentially with the number N of electrons. For instance, in the VB basis the subspace of singlet states of the 12-electron system is spanned by 226 512 VB diagrams.[23] Therefore, for larger systems one has to rely on approximations which are based on some kind of selection of "important" contributions.

A selection of the main contributions to a given state is difficult in the VB basis but is straightforward when Hartree–Fock molecular orbitals are chosen for the construction of the many-electron states. In the latter case the many-electron functions can be classified according to the number of particle–hole excitations from the Hartree–Fock ground state. Such a classification corresponds to an energetic ordering according to increasing energy. Higher excited many-electron configurations should give successively smaller contributions to the low-lying excited states and one may hope to achieve rather accurate descriptions by truncating the configurational basis at some chosen degree of excitation.

The choice of the CI basis is determined by the character of the states to be described. The covalent (−) states of the polyenes require single, double, triple, and quadruple excitations for a correct description.[19] Consequently, we include such excitations in our CI expansion. However, the inclusion of all such excitations leads to very high dimensions d of the many-electron basis. As shown in Table I a Q-CI description of the singlet excitations of the 14-electron polyene for each space and alternancy symmetry class leads to a dimension of

TABLE I. Dimensions d of the CI matrices employed for the Q-CI and MRD-CI expansions of the $1\,^1A_g^-$, $2\,^1A_g^-$, and $1\,^1B_u^+$ states. Pariser's alternancy symmetry has been taken into account in order to reduce d. In the MRD-CI method d varies strongly with the number n_r of reference configurations used for the zeroth order description of the respective state. Dimensions marked with an * have been estimated assuming $d_{\text{Q-CI}}/4$ where $d_{\text{Q-CI}}$ has been calculated according to a formula given in Ref. 24.

	Q-CI	MRD-CI				Q-CI	MRD-CI	
	$^1A_g^-$	$1\,^1A_g^-$		$2\,^1A_g^-$		$^1B_u^+$	$1\,^1B_u^+$	
N	d	n_r	d	n_r	d	d	n_r	d
4	9	2	9	2	9	6	1	6
6	53	2	29	3	47	45	1	25
8	332	2	80	3	183	306	1	74
10	1 727	2	180	5	668	1 664	1	178
12	7 230	2	359	6	2 056	7 088	1	367
14	24 700*	2	647	9	6 699	24 700*	1	682
16	73 545*	2	1086	16	17 623	73 545*	1	1167

about 25 000 of the Hamiltonian matrix. Considering that the corresponding many-electron basis is made up of about 50 000 spin-adapted antisymmetrized functions for which matrix elements of the Hamiltonian have to be calculated, the 14-electron system appears to be the upper limit for a Q-CI treatment in a conventional CI approach even on current supercomputers. For larger electron systems a more detailed truncation scheme of the CI basis is necessary which selects the basis more carefully than a scheme which cuts off all excitations beyond a certain degree of excitation.

Such an alternative scheme is offered by the multireference double excitation CI method (MRD-CI) of Buenker and Peyerimhoff.[24] This method is based on perturbation theoretical arguments and is characterized by a two-step individual selection of the CI basis for each electronic state.

In the first step n_r "reference" configurations $|K_r\rangle$ describing the main contributions to the respective wave function are selected. The representation of the wave function in terms of the references $|K_r\rangle$ defines the unperturbed state. In our implementation of the MRD-CI method the references are determined in a trial D-CI calculation. For each state those single and double excitations are included into the set of references which have the largest coefficients in the D-CI expansion of the wave function. The number of references is chosen such that the contribution of the references to the D-CI electron density exceeds a certain threshold X.

In the second step the "interacting" configurations $|K_i\rangle$ which are actually employed in the CI expansion are generated from the reference configurations $|K_r\rangle$. The $|K_i\rangle$ include the configurations $|K_r\rangle$ and all those configurations which are singly or doubly excited with respect to one of the reference configurations. Hence, the set of $|K_i\rangle$ comprises all those single, double, triple, and quadruple excitations which in second order perturbation theory can give a correction to the energy of the unperturbed state.

The dimensions d of the MRD-CI basis sets and, consequently, the resulting excitation energies depend on the choice of the thresholds X, i.e., on the number n_r of reference configurations $|K_r\rangle$ employed for the zeroth order approximation of the various states. These zeroth order descriptions are chosen such that the correlation effects neglected are of similar magnitude for all states, in which case the MRD-CI *excitation* energies may be closer to the exact values than the energies of the individual electronic states, i.e., of the ground state and of the excited states. Unfortunately, there is no general *a priori* criterion which guarantees that a certain choice of X yields approximations of similar quality for all electronic states of the polyene series such that the desired cancellation of errors actually occurs. A "balanced" description was determined by comparisons with the exact results available for small polyenes. The values of n_r and d rendering a balanced description are given in Table I for the $1\,^1A_g^-$, $2\,^1A_g^-$, and $1\,^1B_u^+$ states. The table demonstrates the strong reduction of the computational effort achieved by the MRD-CI expansion as compared to the Q-CI expansion. This reduction is particularly significant for the ground state and for the ionic $1\,^1B_u^+$ and $1\,^1A_g^+$ states, the MRD-CI basis of which results from only two ($1\,^1A_g^-$) and one ($1\,^1A_g^+$, $1\,^1B_u^+$) reference configurations. Up to the 16-electron polyene the MRD-CI dimensions are small enough to allow a calculation also of the strongly correlated covalent $2\,^1A_g^-$, $1\,^1B_u^-$, and $3\,^1A_g^-$ states for which many reference configurations have to be taken into account.

TABLE II. Excitation energies (energies relative to the CI ground state) of the low energy states of the polyenes with N conjugated π electrons as determined from PPP-MRD-CI calculations for which a geometry of alternating bonds described by $\delta = 0.10$ Å has been assumed (energies given in eV).

N	$2\,^1A_g^-$	$1\,^1B_u^+$	$1\,^1B_u^-$	$3\,^1A_g^-$	$1\,^1A_g^-$
4	5.343	5.828	10.230	9.304	7.547
6	4.365	5.046	5.345	6.976	6.751
8	3.782	4.558	4.714	5.359	6.098
10	3.405	4.231	4.211	4.924	5.600
12	3.169	4.006	3.855	4.510	5.217
14	3.003	3.849	3.578	4.149	4.918
16	2.865	3.742	3.387		4.683

We would like to note that the 16-electron system is not the largest system which currently can be treated in the MRD-CI scheme since this scheme leads quite naturally to a couple of further approximations.[24,30,31] For instance, instead of calculating the energies and wave functions variationally in the full MRD-CI basis, one can divide the set of interacting configurations $|K_i\rangle$ into subsets of strongly and weakly interacting configurations $|K_{is}\rangle$ and $|K_{iw}\rangle$ using as a selection criterion the second order energy correction to the energy of the unperturbed state defined through the reference configurations $|K_r\rangle$. The Hamiltonian is then diagonalized in the $|K_{is}\rangle$ basis (SEL-MRD-CI) and the corrections due to the weakly interacting configurations $|K_{iw}\rangle$ are approximated by perturbation theory. An investigation and comparison of such approximations using the polyenes as model systems together with a systematic study of the criteria how to achieve balanced descriptions of the ground and excited states in the framework of the MRD-CI method will be published elsewhere.[32] For the present study we restrict the discussion to the results of the fully variational MRD-CI method outlined above.

In spite of the strongly reduced computational effort for a MRD-CI expansion as compared to a Q-CI expansion very large Hamiltonian matrices had to be evaluated for the description of the covalent excited states of the 16-electron polyene. For the $2\,^1A_g^-$ state, for instance, the CI basis comprised about 35 000 spin-adapted antisymmetrized functions. The necessary calculations became feasible only after the development of efficient algorithms for the evaluation of the matrix elements of the Hamiltonian and required a CRAY-1 supercomputer. The algorithms and the corresponding general matrix element formulas for spin-coupled particle–hole excitations have been presented in detail in Ref. 25.

III. RESULTS

The calculated MRD-CI excitation energies for the five energetically lowest excited singlet states of the polyene series C_NH_{N+2}, $N = 4,6,...,16$ are collected in Table II. For comparison Table III shows the corresponding Q-CI results for $N \leqslant 12$ including one further excited state.

TABLE III. Excitation energies of the low energy states of the polyenes with N conjugated π electrons as determined from PPP-CI calculations including all single, double, triple, and quadruple excitations.

N	$2\,^1A_g^-$	$1\,^1B_u^+$	$1\,^1B_u^-$	$3\,^1A_g^-$	$1\,^1A_g^+$	$4\,^1A_g^-$
4	5.343	5.828	10.230	9.304	7.547	11.174
6	4.360	5.049	5.337	6.977	6.755	8.085
8	3.768	4.564	4.712	5.331	6.110	6.001
10	3.418	4.244	4.228	4.925	5.628	5.309
12	3.217	4.024	3.892	4.542	5.267	4.837

A. The spectra of the long polyenes

The length dependence of the polyene spectra resulting from an MRD-CI description is shown in Fig. 1. With increasing polyene length the excitation energies of the covalent ($-$) states decrease faster than those of the ionic ($+$) states. Therefore, the $2\,^1A_g^- - 1\,^1B_u^+$ energy gap continues to grow even for the longest polyene investigated. Furthermore, as observed previously by Ramasesha and Soos,[22] a second covalent excited state, the $1\,^1B_u^-$ state, in decapentaene ($N=10$), falls just below the strongly absorbing $1\,^1B_u^+$ state. In the longer polyenes this $1\,^1B_u^-$ state moves further below the $1\,^1B_u^+$ state and appears to approach the $1\,^1A_g^-$ state. Extrapolations have demonstrated that for $N\to\infty$ the excitation energies of the covalent states $2\,^1A_g^-$, $1\,^1B_u^-$, and $3\,^1A_g^-$ tend towards a common finite value, the covalent gap ΔE_c measuring about 2 eV. Similarly the excitation energies of the ionic states $1\,^1B_u^+$ and $1\,^1A_g^+$ converge to a common value, the optical gap ΔE_i of about 3 eV. Hence, for polyacetylene a band of homopolar singlet states is predicted below the conduction band of optically allowed ionic states. The extrapolations and a discussion of the dependence of the covalent gap ΔE_c on bond alternation and on the range of the Coulomb interaction of the electrons are presented in Ref. 26.

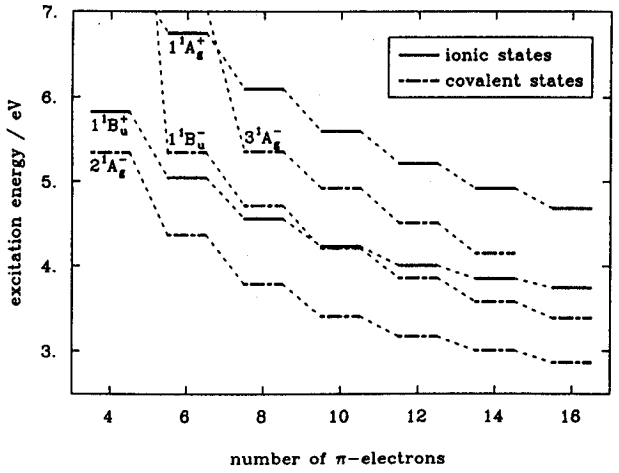

FIG. 1. Excitation energies of the five lowest excited singlet states resulting from PPP-MRD-CI expansions for the polyenes with $N=4,6,\ldots,16$ conjugated π electrons. The bond length alternation has been described by the standard value $\delta=0.10$ Å and for the description of the Coulomb interaction equation (2.2) has been employed.

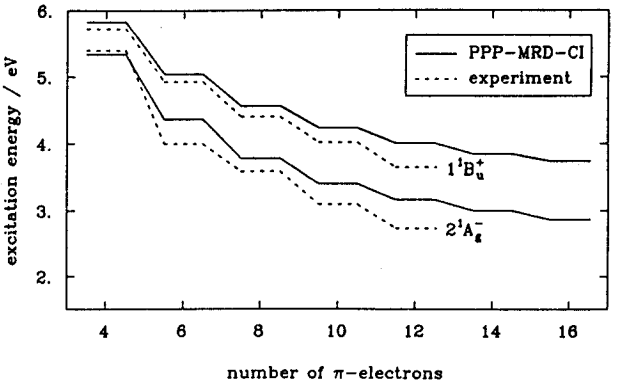

FIG. 2. Comparison of the PPP-MRD-CI excitation energies and the spectral data for the two lowest polyene singlet states; the experimental data are from Refs. 3, 4, and 32; see caption to Fig. 1 for further explanation.

B. Comparison with experiment

Figure 2 compares the MRD-CI excitation energies of the $2\,^1A_g^-$ state and of the $1\,^1B_u^+$ state with the available experimental data taken from Refs. 3, 4, and 33. The observed excitation energies refer to the 0–0 transitions in isolated, unsubstituted polyenes. All these values are somewhat smaller than those predicted by the PPP model. Such a difference has to be expected, however, because the theoretical excitation energies do not refer to 0–0 transitions but rather to vertical transitions.[34] In octatetraene, decapentaene, and dodecahexaene, for instance, the vertical transitions to the $2\,^1A_g^-$ state have been observed 0.2–0.4 eV above the 0–0 bands.[3]

The relaxation of the molecular geometry in the excited state which is not accounted for in the theoretical description does not explain all discrepancies between the observations and the predictions of the PPP model Hamiltonian. Most remarkable in this respect is the observation, that the experimentally determined excitation energies decrease faster with increasing polyene length than those predicted by our calculations. As a measure for the dependence of the excitation energies on the size of the compounds one may consider the differences $\Delta E_{4,12}(2\,^1A_g^-)$ and $\Delta E_{4,12}(1\,^1B_u^+)$ of the excitation energies in the $N=4$ and $N=12$ polyenes. For these differences the values $\Delta E_{4,12}(2\,^1A_g^-)\approx 2.7$ eV and $\Delta E_{4,12}(1\,^1B_u^+)\approx 2.1$ eV have been observed whereas our description yields the values 2.2 and 1.8 eV, respectively. In search for the reasons of this shortcoming we have investigated two possibilities.

A first source for the mentioned error may be the assumption that the pattern of bond alternation of polyenes is independent of the polyene length. In our calculations the bond alternation has been described by a parameter δ which is equal to the length difference of single and double bonds. We have assumed a value $\delta=0.10$ Å. In the case of the short polyenes butadiene and hexatriene such a value of δ is actually too small. Electron diffraction yields the value $\delta=0.12$ Å.[35,36] For the long polyenes the value assumed for δ is rather too large. Nutation NMR experiments revealed values of 1.44 Å for the single bonds and 1.36 Å for the double bonds in polyacetylene, i.e., in the polyene of infinite length.[37] The

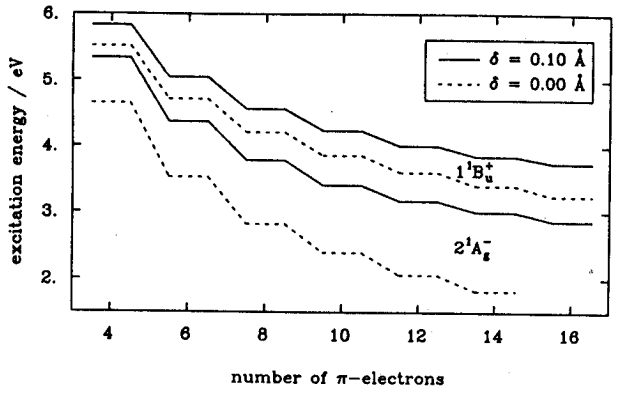

FIG. 3. The effect of the bond length alternation on the excitation energies of the two lowest polyene singlet states as calculated by PPP-MRD-CI expansions.

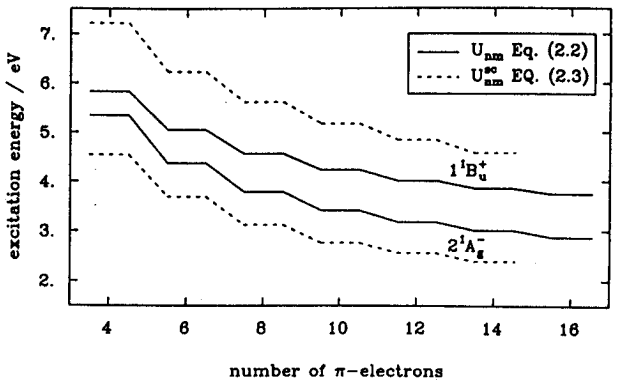

FIG. 4. The effect of a dielectric shielding of the Coulomb interaction U_{nm} of the π electrons on the excitation energies of the two lowest polyene singlet states as calculated by PPP-MRD-CI expansions; see the text for discussion.

corresponding value $\delta = 0.08$ Å can lead to considerable alterations of the excitation energies.

In order to investigate the dependence of the excitation energies on the degree of bond alternation we have carried out MRD-CI calculations for $\delta = 0$. Figure 3 compares the MRD-CI excitation energies of the $2\,^1A_g^-$ and $1\,^1B_u^+$ states of model polyenes calculated for $\delta = 0.10$ Å and $\delta = 0$. The numerical values for the latter case are provided in Table IV. Figure 3 shows that the excitation energies of both low-lying states increase strongly upon bond dimerization. We denote these energy increments by $\Delta E_\delta(N,S) = E(N,S,\delta) - E(N,S,0)$, i.e., the energy difference between excitation energies of the state S in polyenes of length N characterized by $\delta \neq 0$ and $\delta = 0$. These energy increments are larger for the covalent state than for the ionic state and more pronounced in the long compounds than in the short ones. Hence, small changes in the assumed model geometry can entail considerable variations in the calculated bond length dependence of the excitation energies. Assuming a linear dependence of δE_δ on δ and bond alternation parameters $\delta = 0.12$ Å for $N = 4$ and $\delta = 0.08$ Å for $N = 12$ one may obtain from Fig. 3 a crude estimate on the corrections to the $\delta E_{4,12}$ values which might result if instead of the intermediate alternation more realistic polyene geometries would be employed. One finds corrected values $\Delta E_{4,12}(2\,^1A_g^-) = 2.6$ eV and $\Delta E_{4,12}(1\,^1B_u^+) = 2.1$ eV which reproduce the observations rather well.

A second source of errors in the description of the length dependence of the polyene excitation energies might be the specific form of the Ohno formula (2.2). Although one must expect an effective shielding of the electric field of the π electrons due to correlations with the electrons in the σ core[38–40] this formula assumes a vacuum type asymptotic e^2/r dependence for the effective π-electron repulsion. In order to reveal to which extent the polyene spectra depend on a dielectric shielding of the π-electron interaction we have replaced the Ohno formula (2.2) by Eq. (2.3). This latter expression certainly oversimplifies the description of dielectric shielding. However, application of Eq. (2.3) can provide a qualitative measure to which extent dielectric shielding affects excitation energies. [At this point we would like to note that the unrestricted Hartree–Fock (UHF) treatment of the dependence of the $1\,^1B_u^+$ excitation energy and of the structure of the ground state of polyacetylene on the dielectric shielding of the Coulomb potential in Refs. 38–40 appears to underestimate the effects of electron correlation. This is indicated by the erroneous[14] UHF prediction of a charge density wave ground state for strong shielding of the long range part of the Coulomb potential.]

In Fig. 4 we compare the excitation energies for both the $2\,^1A_g^-$ and the $1\,^1B_u^+$ states for a shielded (2.3) and an unshielded (2.2) Coulomb interaction. Table V presents the corresponding numerical values. The results illustrate that a dielectric shielding increases the $2\,^1A_g^- - 1\,^1B_u^+$ energy gap by pushing the excitation energy of the ionic state upward and that of the covalent state downward. Furthermore, with

TABLE IV. Excitation energies of the low energy states of the polyenes with N conjugated π electrons as determined from PPP-MRD-CI calculations for polyenes with $\delta = 0$.

N	$2\,^1A_g^-$	$1\,^1B_u^+$	$1\,^1B_u^-$	$2\,^1A_g^+$
4	4.647	5.520	9.638	7.379
6	3.524	4.712	4.692	6.545
8	2.814	4.206	3.951	5.885
10	2.376	3.858	3.357	5.385
12	2.064	3.602	2.922	4.995
14	1.818	3.402	2.569	4.673
16		3.242		4.415

TABLE V. Excitation energies of the low energy states of the polyenes with N conjugated π electrons as determined from PPP-MRD-CI calculations. The Coulomb repulsion between the π electrons has been described by the scaled Ohno formula (2.3).

N	$2\,^1A_g^-$	$1\,^1B_u^+$
4	4.539	7.217
6	3.725	6.231
8	3.246	5.613
10	3.006	5.171
12	2.758	4.836
14	2.607	4.573

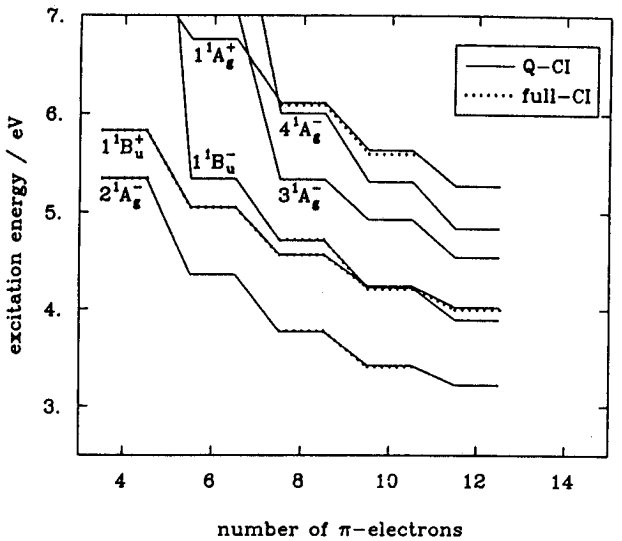

FIG. 5. Comparison of polyene excitation energies obtained from Q-CI and full-CI expansions; the full-CI results have been taken from Ref. 22; see the caption to Fig. 1 for further explanation.

a shielded π-electron repulsion the excitation energy of the $1\,^1B_u^+$ state decreases more rapidly with increasing polyene length. Comparison with Fig. 2 shows that in this respect the shielded Coulomb repulsion yields a length dependence of the excitation energies which is closer to the observed behavior. Hence, one can expect that an appropriately reparametrized PPP Hamiltonian including, in particular, a shielded π-electron interaction and a size-dependent bond alternation, should reproduce all observed features of the low energy spectra of the polyenes rather well.

C. The accuracy of the CI methods

MRD-CI is an approximate method for the determination of the excitation energies of low-lying excited states which relies on an assumed cancellation of errors. If, in particular, MRD-CI excitation energies of long compounds are used for extrapolations to the polyacetylene case[26] then small deviations from the exact results can cause large errors in the extrapolations. For this reason it is important to discuss the magnitude of the errors connected with the results reported here. The errors depend strongly on the properties of the Hamiltonian under consideration.

Comparing Tables II and III for the standard polyene PPP Hamiltonian at intermediate bond alternation we first note that MRD-CI reproduces the Q-CI excitation energies very closely. The mean square deviation of the excitation energies for the first five singlet state of decapentaene ($N = 10$) measures 0.017 eV even though the dimensions of the corresponding variational spaces differ by factors in the range 3–10 (cf. Table 1). The high accuracy of the Q-CI excitation energies, on the other hand, can be judged from Fig. 5 which compares the Q-CI data of Table III with the available full-CI data.[23] In the case of decapentaene the mean square deviation of the Q-CI energies from the full-CI energies for the first four singlet states measures 0.023 eV. The MRD-CI excitation energies match the exact results even somewhat better, the mean square deviation measuring only 0.006 eV. However, for a judgment on the latter agreement one has to keep in mind that the selection of the number of reference configurations for the MRD-CI description had been chosen to minimize deviations from the exact results on the short polyenes ($N = 4,6,8,10$).

TABLE VI. Ground state correlation energies E_{corr}/N per site determined from full-CI, Q-CI, and MRD-CI calculations for various polyene PPP Hamiltonians. The correlation energy E_{corr} is defined here as the difference of the CI and SCF ground state energies.

	$\delta = 0.10$ Å, U_{nm} Eq. (2.2)			$\delta = 0.0$ Å	U^{sc}_{nm} Eq. (2.3)
N	Full-CI	Q-CI	MRD-CI	MRD-CI	MRD-CI
4	−0.1491	−0.1491	−0.1491	−0.1759	−0.4238
6	−0.1547	−0.1504	−0.1470	−0.1787	−0.4040
8	−0.1555	−0.1512	−0.1438	−0.1780	−0.3791
10	−0.1560	−0.1515	−0.1402	−0.1752	−0.3554
12	−0.1564	−0.1515	−0.1367	−0.1712	−0.3348
14			−0.1334	−0.1665	−0.3173
16			−0.1303	−0.1616	

Table VI compares the ground state correlation energies per carbon atom as resulting from full-CI,[23] Q-CI, and MRD-CI calculations. The correlation energy is defined here as the difference of the Hartree–Fock and CI ground state energies. A comparison of the energy values reveals the magnitude of the errors in the absolute energies for the Q-CI and the MRD-CI method. For decapentaene, for instance, Q-CI reproduces 97% of the correlation energy of a full-CI calculation, whereas the MRD-CI expansion involving a tenfold smaller variational space reproduces 90% of this energy. The absolute errors are 0.045 and 0.158 eV, respectively. Hence, for both Q-CI and MRD-CI the excitation energies of the low-lying states are much better described than their absolute energies, i.e., the desired cancellation of errors actually occurs.

For the standard PPP model the MRD-CI excitation energies are rather insensitive to the zeroth order description of the excited states. Adding, for example, a sixth configuration to five reference configurations describing the $2\,^1A_g^-$ state of decapentaene results in a 22% enlargement of the CI dimension. However, this considerable increase of the computational effort reduces the excitation energy only by 0.3%. The MRD-CI excitation energies are more sensitive to the description of the ground state. Adding a third configuration to the reference configurations for the ground state of decapentaene expands the CI basis by 145% and results in an increase of the excitation energy by 1%–2%. Summing up all the mentioned effects on the MRD-CI excitation energies one expects that for the polyenes with 12–16 carbons the error in the MRD-CI excitation energies is likely to be much smaller than 0.1 eV.

These statements on the high accuracy of the MRD-CI results remain true as long as the correlation effects, on an absolute scale, are not much larger than in the case of the standard polyene PPP Hamiltonian. A comparison of the MRD-CI correlation energies in Table VI reveals that these energies increase for both modifications of the standard PPP model, i.e., in case of vanishing bond alternation and in case of dielectric shielding. For the model with $\delta = 0$ the ground state correlation energy increases by about 20%. The dielec-

tric shielding of the Coulomb interaction as described by Eq. (2.3) leads to a strong increase of the ground state correlation energies. One expects that the uncertainties connected with the choice of a particular MRD-CI basis are considerable in the latter case. For example, adding in the case of decapentaene one further reference configuration for the ground state increases the calculated excitation energies by 5%–10%, i.e., much more than in the case of an unshielded Coulomb interaction. But even in such a strongly correlated case one can achieve a satisfactory MRD-CI description of the large electron systems if the exact results for the corresponding small compounds are known. Then the optimal MRD-CI descriptions of the large systems can be extrapolated from those of the small ones.[32] If exact results are unavailable, like in the case of dielectric shielding, and if one has to resort to Q-CI approximate results for the fit of the MRD-CI description, then, of course, the results may be less reliable. In the strongly correlated case we estimate errors in the excitation energies smaller than 0.2 eV.

IV. SUMMARY

We have presented an MRD-CI method for the calculation of the spectra of extended conjugated systems comprising up to 16 π electrons in a PPP parametrization. The MRD-CI expansions cover only a small part of the complete many-electron basis of such systems and, consequently, entail certain errors in the calculation of the absolute energies of the ground and excited states. However, the selection procedure of the many-electron basis employed in the MRD-CI scheme individually for each state is designed to lead to an approximate cancellation of these errors and, thereby, to rather accurate predictions of the spectra.

The MRD-CI method has been employed to describe the excited singlet states of polyenes. For short polyenes with up to ten π electrons the MRD-CI expansions have been shown to render excitation energies which match the exact results[23] very well. It has been demonstrated that the errors in the MRD-CI excitation energies should be very small also for the longer polyenes with up to 16 π electrons. Differences between observations and predictions must be attributed to shortcomings of the PPP model rather than to inaccuracies of the MRD-CI approximation.

A comparison with spectral data has lead to the conclusion that the PPP model furnishes a qualitatively correct description of the observed energy gap between the excited $2\,^1A_g^-$ and $1\,^1B_u^+$ states. This gap increases with increasing length of the polyenes. For polyenes with more than 12 π electrons for which up to now no experimental data are available this behavior is predicted to continue. However, a PPP model of the polyenes which assumes a constant bond length alternation underestimates the decrease of the excitation energies and the increase of the energy gap associated with an increasing length of the polyenes. To a large degree these deficiencies can be repaired if one follows the experimental evidence and assumes a weakening of the bond length alternation. Calculations which assume no bond length alternation to exist predict smaller excitation energies for both low-lying states and a steeper decrease of the $2\,^1A_g^-$ excitation energy with increasing chain length. To a lesser degree the shortcoming of the PPP model might arise from the assumption that the Coulomb interaction of the π electrons decays like e^2/r at large distances. Calculations assuming an intramolecular dielectric shielding predict larger $2\,^1A_g^- - 1\,^1B_u^+$ energy gaps and a steeper decrease of the $1\,^1B_u^+$ excitation energy with increasing polyene length. Altogether we expect that an appropriately reparametrized PPP model Hamiltonian should be capable of describing quantitatively the low-lying excitations in polyenes.

Since accurate descriptions of the electronic excitations in long polyenes are now available these results can be used for an extrapolation to polyacetylene, i.e., the polyene of "infinite" length. The reader is referred to Ref. 26 for a presentation and discussion of such extrapolation.

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