

Correlation effects in the spectra of polyenes*

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A Hamiltonian of the Pariser-Parr-Pople form is employed to investigate the effect of correlation on the π -electron spectrum of polyenes. Two limiting cases for the electron-electron interaction (short- and long-range limit) are considered, and it is shown that they yield descriptions corresponding to the standard valence-bond (Dirac-Heisenberg) and molecular-orbital models, respectively. The intermediate, chemically most interesting, range is examined in detail by means of a full configuration-interaction treatment with an exponential model potential that includes a variable effective range parameter. It is shown that correlation effects become more important as the effective range of the interaction decreases. The states of polyenes are classified as covalent or noncovalent, and it is found that the former are much more sensitive to correlation than the latter. Configuration interaction through double excitations yields a qualitatively correct ordering for all states in the chemical range, but triple and quadruple excitations are required for quantitative results. Applications to butadiene, hexatriene, and benzene demonstrate that correlation effects in these molecules lead to an important lowering in energy of the manifold of covalent states relative to that of the noncovalent states; most important, the first covalent ($^1A_g^-$) state of the polyenes is found to be near degenerate with the strongly allowed noncovalent ($^1B_u^+$) state. Density correlation functions and the fluctuation potential are obtained for the polyenes and used to clarify the nature of the correlation correction. Configuration interaction including double excitations is performed for polyenes through C_nH_n to exhibit the length dependence of the correlation effects. It is shown that with increasing chain length, an increasing number of covalent states appears in the energy range of the two usually observed excited $^1B_u^+$ and $^1A_g^+$ (*cis* peak) states.

I. INTRODUCTION

Molecules with extended conjugated π -electron systems have long been of interest, particularly because of their intense absorption bands in the optical region. Upon excitation, such molecules can undergo a variety of chemical reactions which makes them very suitable as light "harvesting" compounds in biological systems. Examples are the chlorophylls involved in the photosynthesis of bacteria and higher plants, and the carotenoid pigments of plants and animals; the latter include 11-*cis* retinal, which is the chromophore of the visual pigment in a wide variety of animals and is also found in the purple membrane of bacteria.

For a satisfactory understanding of the spectra and the photochemical reactions of conjugated molecules, a detailed knowledge of their electronic states is necessary. The quantum mechanical description of electronically excited π -electron systems is by now a classic part of theoretical chemistry.¹ The accepted theory can be characterized as based on a description of the π electrons as "independent" particles, each one moving in the average field of the other electrons. The results of this theory have for many years appeared to be in satisfactory agreement with the available spectral data and have been widely used for the assignment of observed absorption and emission bands. It has recently been demonstrated, however, that this description of the excited states is incomplete. The experimental observations of Hudson and Kohler² and of Christensen and Kohler³ showed that in diphenyloctatetraene and undecapentaene, respectively, the lowest singlet excited state is not an optically allowed state of 1B_u symmetry, as customarily assumed and calculated from the conventional theory, but instead is an optically forbidden state that has 1A_g symmetry according to the appropriate theoretical treatment.⁴ The low-lying 1A_g state is domi-

nated by a double excited configuration (relative to the ground state) that cannot be adequately described by the independent particle model.⁴⁻⁶ Recent spectral data for benzene suggest that there exists in this molecule a low-lying $^1E_{2g}$ state, which is also in disagreement with the standard theory.⁷⁻⁹ It is very likely on theoretical grounds that corresponding states are present in most conjugated systems and that they will be found by suitable experiments.¹⁰

In light of the above results, a re-examination of the independent particle model and the magnitude of correlation effects in the π -electron theory of conjugated molecules appears appropriate. It is our purpose in this paper to examine the importance of correlation with particular emphasis on its variation with the strength of the electron interaction. To make possible the study of larger polyenes, such as retinal, we assume that the σ electrons can be treated as an invariant core and employ a semiempirical Hamiltonian of the Pariser-Parr-Pople type for the π electrons. Butadiene and hexatriene are used as model systems, and comparisons are made of the results obtained as a function of the extent of configuration interaction up to the complete π -electron calculation. Both ground-state correlation and that in the excited states is considered. By varying the range of the electron interaction, the system behavior can be altered from one limit, satisfying the independent-electron SCF model to another, best described in terms of a localized valence-bond picture. The chemically interesting range of the electron interaction is shown to be intermediate, so that neither limiting model is adequate and a more complete treatment is required.

The Pariser-Parr-Pople Hamiltonian used in this paper is introduced in Sec. II. Two limiting cases of the electron interaction (short-range limit and long-

range limit) are considered in Sec. III. The more realistic intermediate range is described in Sec. IV; we included there a discussion of certain correlation functions and the fluctuation potential which permit one to evaluate the deviation from the limiting models. Applications to the analysis of the spectra of butadiene, hexatriene, and benzene are made in Sec. V. It is shown that the π -electron states in these compounds fall into two classes: noncovalent states that are well described by simple molecular orbital theory, and (optically forbidden) covalent states in which the electrons are strongly correlated. The calculations are extended to longer polyenes in Sec. VI to illustrate the nature of the correlated covalent states. In the calculations for longer polyenes, the configuration-interaction treatment is restricted to single and double excitations from the SCF ground state. The deficiencies of such a limited calculation can be overcome by an approximation that is described in a subsequent publication. The conclusions are presented in Sec. VII.

There have been many calculations on conjugated systems since they have played such an important role in the development of semiempirical theories. Closest in spirit to the present work are the studies of Koutecky *et al.*^{5,11} Related work has been done also by Murrell and McEwen,¹² Bloor *et al.*,¹³ Allinger and Tai,¹⁴ Vischer and Falicov,¹⁵ Shinoda *et al.*,¹⁶ Karwowski,¹⁷ and Knoop.¹⁸ CNDO calculations for various conjugated systems including double excitations for σ and π electrons have been carried out by Giessner-Prettre and Pullman.¹⁹ Since the present work was completed,⁴ a related study concerned with the symmetry properties of polyene excited states and the limits of weak and strong electron correlation was published by Cizek, Paldus, and Hubac.²⁰

The semiempirical calculations on conjugated molecules have been complemented recently by extensive *ab initio* calculations such as the frozen core π -electron treatment of Shavitt and co-workers for butadiene^{21a} and benzene^{21b} and of Shih *et al.*²² for butadiene. Both sets of calculations corroborate the importance of correlation effects in these systems and, in particular, find the low-lying 1A_g state in butadiene and the low-lying $^1E_{2g}$ state in benzene. These *ab initio* calculations also point to the importance of certain factors, which are included not at all or only indirectly by the semiempirical π -electron model used here. One of these is that some excited states (e.g., the lowest 1B_u state in butadiene and the $^1E_{1u}$ state in benzene) appear in these *ab initio* calculations to be "diffuse"; i.e., the excited state orbitals have much larger effective radii than those in the ground state. However, the diffuse character of these excited states is not confirmed by the careful work of Whitten and Ryan²³ on the V state of ethylene. Their results suggest that limitations on the basis set may introduce artificial diffuseness in the orbitals that permits them to account for electron correlation, analogous to the behavior found earlier in the excited states of simple atoms. Bender *et al.*²⁴ demonstrated that the effective radius of the ethylene V state reduces quite strongly with the number of configurations included in the CI treatment. This finding has been corroborated

most recently by Basch,²⁵ who stated that he actually did not reach convergence of the effective V -state radius in his extended MC-SCF calculations and that, hence, a characterization of the $^1B_{1u}$ state of ethylene as a Rydberg state is still "premature." Experimentally, the evidence on the size of the excited-state orbitals is not clear, although the smallness of the observed solvent shift suggests that they are not very diffuse.²⁶ A factor included by the π -electron treatment only in an average manner is the σ -electron reorganization on excitation. It appears likely that there is a difference in the reorganization energy for different types of states (e.g., covalent vs ionic) that is not accounted for in the model, though it may be significant.^{27,28} Finally, there is the possibility that certain of the observed states in polyenes correspond to $\sigma^* - \pi$ or $\pi^* - \sigma$ excitations. Since these are not described by the π -electron Hamiltonian, they would be misassigned by using it unless they could be distinguished from the π states. In spite of these limitations of the semiempirical Pariser-Parr-Pople model, it seems to us the one best suited, in terms of feasibility and generality, for examining the correlation effects in polyenes.

II. THE π -ELECTRON HAMILTONIAN

The Pariser-Parr-Pople (PPP) Hamiltonian for the π -electron system of a conjugated hydrocarbon is (energies are given in eV and distances in Å)

$$H = \sum_{\kappa < \lambda} Z_{\kappa} Z_{\lambda} R_{\kappa\lambda} + \sum_{\kappa, \sigma} \left(-I_{\kappa} - \sum_{\lambda \neq \kappa} Z_{\lambda} R_{\kappa\lambda} \right) n_{\kappa\sigma} + \sum_{\kappa \neq \lambda} t_{\kappa\lambda} c_{\kappa\sigma}^{\dagger} c_{\lambda\sigma} + \frac{1}{2} \sum_{\substack{\kappa, \lambda \\ \sigma, \sigma'}} R_{\kappa\lambda} n_{\kappa\sigma} n_{\lambda\sigma'}, \quad (1)$$

where $c_{\kappa\sigma}^{\dagger}$ and $c_{\kappa\sigma}$ are the fermion creation and annihilation operators which create and annihilate, respectively, an electron with spin σ in the mutually orthogonal atomic π orbitals p_{κ} ; the operator $n_{\kappa\sigma} = c_{\kappa\sigma}^{\dagger} c_{\kappa\sigma}$ is the π -electron number operator; $R_{\kappa\lambda}$ is the effective electron-electron repulsion integral between an electron in orbital p_{κ} and one in orbital p_{λ} ; $t_{\kappa\lambda}$ is the core integral between center κ and λ ; I_{κ} is the effective ionization potential of orbital p_{κ} ; and Z_{κ} is the net charge of the core at center κ ($Z_{\kappa} = 1$). The first term in H represents the repulsion of the nuclear framework of the conjugated molecule; for fixed geometries this term contributes a constant to the energy of the π electrons. The second term in H measures the energy of an electron placed in the atomic orbital p_{κ} . The energy is partitioned into a contribution arising from the ionization potential I_{κ} of a π electron residing at the isolated atomic site κ and a contribution arising from the attractive Coulomb interaction $Z_{\lambda} R_{\kappa\lambda}$ with the remaining atomic sites λ . The third term in H describes the coupling between different atomic orbitals due to the core integrals $t_{\kappa\lambda}$; they are assumed to vanish except for next neighbor orbitals p_{κ} , p_{λ} , in which case they are evaluated from the empirical formula

$$t_{\kappa\lambda} = \beta_0 + 3.21(r_{\kappa\lambda} - 1.397), \quad (2)$$

where β_0 is a constant and $r_{\kappa\lambda}$ is the distance between the nuclear sites κ and λ . The fourth term in H [the

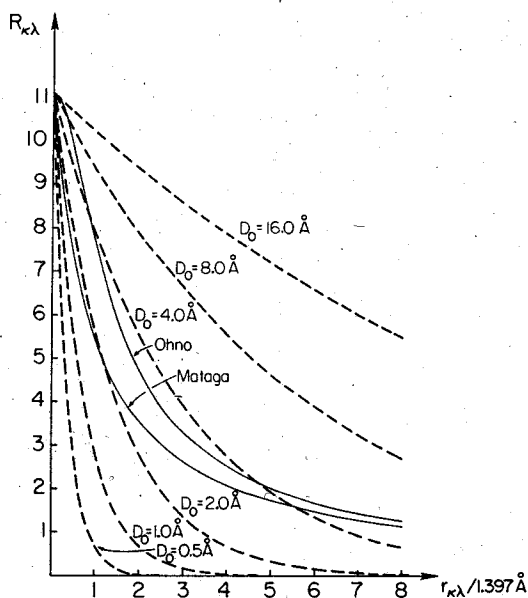


FIG. 1. Electron repulsion integral $R_{k\lambda}$ [Eq. (3), $\kappa=1$, $\lambda=1, 2, \dots, 6$] as function of the interatomic distance $r_{k\lambda}$ (see text).

prime on the sum indicates that it excludes all terms $(\kappa, \sigma) = (\lambda, \sigma')$ describes the Coulomb repulsion of the π -electrons.

To examine the effect on the electron correlation of the electron repulsion term in the Hamiltonian, a number of different forms were chosen for $R_{k\lambda}$. In addition to two standard Coulomb integral formulas,

$$R_{k\lambda} = \frac{14.397}{\{[2 \times 14.397 / (R_{\kappa\kappa} + R_{\lambda\lambda})]^2 + r_{k\lambda}^2\}^{1/2}} \quad (\text{Ohno formula}) \quad (3a)$$

or

$$R_{k\lambda} = \frac{14.397}{2 \times 14.397 / (R_{\kappa\kappa} + R_{\lambda\lambda}) + r_{k\lambda}} \quad (\text{Mataga-Nishimoto formula}), \quad (3b)$$

an exponentially decaying repulsive potential of the form

$$R_{k\lambda} = R_{\kappa\kappa} \exp(-r_{k\lambda}/D_0) \quad (3c)$$

was used. Variation of the decay constant D_0 simulates in a simple way the transition from the independent electron limit (D_0 large, long-range potential) to the limit of strongly correlated electron motion (D_0 small, short-range potential). In Fig. 1 the repulsion integrals $R_{k\lambda}$ from Eqs. (3a)–(3c) are shown as a function of the interatomic distance $r_{k\lambda}$; in Eq. (3c), a range of values for D_0 between 0.5 Å and 16 Å are used. The values employed in this paper for the empirical parameters I_κ , Z_κ , β_0 , and $R_{\kappa\kappa}$ which enter into the PPP Hamiltonian for conjugated hydrocarbons are presented in Table I.²⁹

III. LIMITING CASES OF π -ELECTRON CORRELATION

In this section we consider the two limiting cases for the PPP Hamiltonian [Eq. (1)]—that corresponding to the independent particle (molecular-orbital) model, and that described by a Dirac-Heisenberg (valence-bond)

spin Hamiltonian. The model exponential potential of Eq. (3c) is used in Sec. IV to examine the intermediate region.

In the limit of long-range repulsive interactions, the π -electron behavior is dominated by the one-electron part of the Hamiltonian, namely,

$$T = \sum_{\kappa, \lambda} t_{\kappa\lambda} C_{\kappa\sigma}^* C_{\lambda\sigma}, \quad (4)$$

where we define $t_{\kappa\kappa}$ as being equal to

$$t_{\kappa\kappa} = -I_\kappa - \sum_{\lambda} Z_\lambda R_{\kappa\lambda},$$

i. e., we have combined the second and third terms of Eq. (1) and neglected the electron interaction given by the fourth term of Eq. (1). In the opposite limit of short-range interactions, the π electrons are governed by the two-electron part of the Hamiltonian, namely,

$$V = \frac{1}{2} \sum_{\substack{\kappa, \lambda \\ \sigma, \sigma'}} R_{\kappa\lambda} n_{\kappa\sigma} n_{\lambda\sigma'}, \quad (5)$$

which correlates the motion of the electrons. Equations (4) and (5) as limits of the π -electron Hamiltonian lead to complementary descriptions of the π system; the first is of the independent particle (molecular-orbital) type, and the second of the Dirac-Heisenberg (valence-bond) type. The realistic repulsion potentials [(3a) and (3b)] are of intermediate range as exemplified in Fig. 1. However, it is useful for an understanding of the real situation to describe briefly the motion of π electrons in the well-known limits of short-range and long-range electron-electron interaction.

A. Long-range (weak) electron-electron interaction

We consider first a π -electron system in the limit of long-range electron-electron repulsive potentials, i. e., weak repulsive forces. In this limit, the π electrons can be described as independent fermions moving according to the one-electron part [Eq. (4)] of the PPP Hamiltonian. For a closed-shell π system, the ground state is then described by a single Slater determinant

$$\psi_0 = a_{1'}^* a_{1''}^* \cdots a_{N'}^* a_{N''}^* |0\rangle, \quad (6)$$

TABLE I. Semi-empirical parameters for conjugated hydrocarbons.^a

| | |
|--------------------------|---|
| I_κ | = 11.16 eV |
| Z_κ | = 1.0 eV |
| β_0 | = -2.43 eV ^b |
| $R_{\kappa\kappa}$ | = 11.13 eV |
| $r_{\kappa\kappa \pm 1}$ | = 1.35 Å (double bonds), 1.46 Å (single bonds), 1.397 Å (benzene) |

^aFrom Refs. 29(a) and 29(b).

^bIn some of the calculations (see Table II and Figs. 10 and 11), the parameters $\beta_0 = -2.60$ eV had been used to obtain better agreement with observed spectra.

where $|0\rangle$ denotes the π -electron vacuum state and the a_i^+ , and a_i^- , are linear combinations of the $c_{k_i}^+$ and $c_{k_i}^-$. With Eq. (4) as the Hamiltonian and appropriate choice of the $t_{k\lambda}$, the $a_{i\sigma}^+$, $a_{i\sigma}^-$ are Hückel molecular-orbital creation and annihilation operators, in terms of which T can be written

$$T = \sum_{i,\sigma} \epsilon_i^H a_{i\sigma}^+ a_{i\sigma}^- = \sum_{i,\sigma} \epsilon_i^H n_{i\sigma},$$

where ϵ_i^H is the Hückel orbital energy and $n_{i\sigma}$ is the Hückel orbital occupation number operator. An approximate independent particle description of π -electron systems can also be achieved without totally disregarding the potential energy term [Eq. (5)]. This is done in the self-consistent-field (SCF) approximation by using for the system the independent particle ground state [Eq. (6)], which minimizes the expectation value of the energy, $\langle \psi_0 | H | \psi_0 \rangle$. A variation of the ground state through use of the form

$$a_{i\sigma}^{\pm} = a_{i\sigma}^{\pm} + \sum_{m>N} \eta_{mi} a_{m\sigma}^{\pm}, \quad (7)$$

where the basis orbitals associated with the $a_{m\sigma}^{\pm}$ ($m > N$) are assumed orthogonal to those associated with the $a_{i\sigma}^{\pm}$ ($i \leq N$) and the η_{mi} are variational coefficients (independent of spin) gives a new ground state³⁰

$$\psi_0' = \exp\left(\sum_{\substack{m>N \\ i \leq N}} \eta_{mi} a_{m\sigma}^+ a_{i\sigma}^-\right) \psi_0. \quad (8)$$

The function ψ_0' may be expanded in orders of the coefficients η_{mi} in the form

$$\psi_0' = \psi_0 + \sigma^{(1)} \psi_0 + \sigma^{(2)} \psi_0 + \dots, \quad (9)$$

where $\sigma^{(1)} \psi_0$ collects the terms first order in η_{mi} ; $\sigma^{(2)} \psi_0$ the terms second order in η_{mi} ; and so on. The necessary condition for the SCF ground state is

$$\langle \sigma^{(1)} \psi_0 | H | \psi_0 \rangle = 0, \quad (10)$$

which leads to the well-known SCF equations for the $a_{i\sigma}^{\pm}$. The solution of these equations determines beside the ground state ψ_0 also the single excited configurations $a_{m\sigma}^+ a_{i\sigma}^- \psi_0$, the double excited configurations $a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{i\sigma_1}^- a_{j\sigma_2}^- \psi_0$, etc. ($m, n > N$; $i, j \leq N$). The first excited states of a π system in the limit of long-range electron-electron interaction are given by the single excited configurations or their appropriate linear combinations.

The sufficient condition for the stability³⁰ of the SCF ground state is that

$$\langle \psi_0' | H | \psi_0' \rangle - \langle \psi_0 | H | \psi_0 \rangle \langle \psi_0' | \psi_0' \rangle > 0. \quad (11)$$

As one goes to the short-range limit of the Coulomb repulsion, Eq. (11) cannot be satisfied and the SCF approximation breaks down. This point is discussed briefly in Appendix A.

B. Dirac-Heisenberg (valence-bond) limit

For a π -electron system governed by the electron interaction [Eq. (5)], the lowest energy states are given by the valence-bond model; the spin eigenstates correspond to linear combinations of determinants of the form

$$|p_1 \sigma_1 p_2 \sigma_2 \dots p_{2N} \sigma_{2N}|, \quad (12)$$

in which each atomic orbital p_n is singly occupied. Because of the neglect of atomic orbital exchange integrals in the PPP Hamiltonian, the energy is independent of the spin state; thus, all linear combinations of the 2^{2N} determinants [Eq. (12)] have the same energy, which is

$$E = \frac{1}{2} \sum_{\kappa \neq \lambda} R_{\kappa\lambda}, \quad (13)$$

where κ, λ go over all occupied orbitals. Higher in energy are the single, double, ... ionic valence-bond structures in which one, two, ... atomic orbitals are doubly occupied.

If the one-electron contribution T [Eq. (4)] is included in the Hamiltonian, a spin-dependent exchange term is introduced and the spin degeneracy is lifted. If T is small relative to V , the former can be treated by second-order perturbation theory. For the covalent states this yields a correction to Eq. (13) that can be written in the form of a simple effective Heisenberg spin Hamiltonian³¹

$$\Delta E = - \sum_{\kappa \neq \lambda} \frac{2t_{\kappa\lambda}^2}{R_{\kappa\kappa} - R_{\lambda\lambda}} (\mathbf{S}_\kappa \cdot \mathbf{S}_\lambda - \frac{1}{4}). \quad (14)$$

The net effect of the resonance integrals $t_{\kappa\lambda}$ is to stabilize spin configurations in proportion to the number of neighboring singlet pairs they contain. Thus, the set of covalent wavefunctions [Eq. (12)] is split into a narrow "band" [width $\sim t_{12}^2 / (R_{11} - R_{12})$] of "spin wave" states, with the perfect pairing (totally antiferromagnetic) singlet spin configuration lowest in energy. Higher in energy are the triplet states created through one spin flip from the antiferromagnetic ground state, the long-bonded singlet states that correspond to the family of two spin flips, etc. The transition dipole moments between any pair of these states vanish^{31b}; thus, all covalent singlet state transitions are optically forbidden from the ground state.

In addition to the covalent structures obtained from the determinants in Eq. (12), single ionic, double ionic, ... structures need to be included to obtain the complete set of π -electron wavefunctions. For strong electron repulsion (i. e., $R_{11} - R_{12} \gg |t_{\kappa\lambda}|$), the structures of increasing ionicity (covalent, single ionic, ...) are separated in energy by gaps on the order of $R_{11} - R_{12}$, the energy needed to move an electron from an occupied site to a neighboring occupied site. Hence, ionic structures are not expected to be important for low energy excited states in this limit.

The description of the electronic states just given is closely related to the valence-bond model. However, the latter makes use, in general, of nonorthogonal atomic orbitals p_κ , while the present formulation in terms of the PPP model employs orthogonal orbitals. It can be shown that the standard valence-bond Hamiltonian is connected with the PPP Hamiltonian by a symmetric orthogonalization transformation of the Löwdin type. This transforms the nonorthogonal valence-bond orbitals to a set of orthonormal orbitals, and the exchange interaction now appears in the resonance terms $t_{\kappa\lambda}$ of the transformed Hamiltonian.³²

IV. INTERMEDIATE RANGE ELECTRON INTERACTION

From the brief discussion in Sec. III, it is evident that for short-range electron repulsion, the Dirac-Heisenberg limit is valid and the electronic states separate into covalent low energy states (which are all forbidden from the ground state) and ionic higher energy states, many of which are reached by allowed transitions from the ground state; e.g., the lowest optically allowed 1B_u state belongs in the Dirac-Heisenberg limit to the manifold of ionic states. If the range of the electron repulsion increases, the quantity $R_{\kappa\kappa} - R_{\kappa\lambda}$ becomes smaller and the effective spin-spin interaction in the Dirac-Heisenberg Hamiltonian [i.e., the coefficient $t_{\kappa\lambda}^2/(R_{\kappa\kappa} - R_{\kappa\lambda})$ in Eq. (14)] increases. This increases the energy difference between the covalent spin wave states. Since $R_{\kappa\kappa} - R_{12}$ determines the energy gap between the covalent and the ionic states, the longer-range electron repulsion also lowers the excitation energy of the ionic states. Thus, for long-range potentials, covalent and ionic states become interspersed and, because of the resulting strong mixing, they retain their covalent and ionic character only in part. It is in this limit, as we have seen, that the SCF model becomes a good approximation.

To illustrate these conclusions, we consider the spectrum of the PPP Hamiltonian [Eq. (1)] as a function of the range of the electron-electron repulsion. For the calculations, we use the model exponential potential in Eq. (3c) and assign various values to the decay length D_0 , ranging from $D_0 = 16 \text{ \AA}$ (SCF limit) to $D_0 = 0.5 \text{ \AA}$ (Dirac-Heisenberg limit). The spectrum is obtained for butadiene (4π electrons) and hexatriene (6π electrons) with four different basis sets: (1) SCF-MO (S), which includes only single excited configurations; (2) SCF-MO (D), which also includes the double excited configurations; (3) restricted valence-bond basis (RV), which includes only the orthogonal atomic orbital valence-bond structures effectively accounted for by the Heisenberg spin Hamiltonian, namely, all covalent structures and all structures generated therefrom by moving a single electron to its adjacent site; and (4) complete basis (C), for which the choice of starting functions is immaterial. From the previous discussion, the (S) basis should provide a good description in the limit of long-range electron repulsion (i.e., D_0 large), whereas the (RV) basis should be sufficient for the low-lying covalent states in the limit of short-range electron repulsion (i.e., D_0 small). In this section, the exact expectation values of H in the (RV) basis are used, in contrast to the Dirac-Heisenberg spin Hamiltonian [Eq. (14)], which represents the energies for the covalent states evaluated by second-order perturbation theory. In the limit of small D_0 , where perturbation theory yields essentially exact results, the Dirac-Heisenberg Hamiltonian and the PPP Hamiltonian in the (RV) basis have nearly identical spectra.

In Figs. 2 and 3 we present energy level diagrams of butadiene and hexatriene, respectively, for different values of the decay constant D_0 . To visualize the effect of electron correlation on the energy levels, the lowest

eigenvalues of the PPP Hamiltonian in the four different bases are shown for each value of the decay constant D_0 (16, 8, 4, 2, 1, 0.5 \AA). From the figures, it is evident that the effect of electron correlation varies significantly with the type of electronic state involved. In what follows, we consider briefly some of the states and how they are altered by electron correlation effects.

A. Correlation effects on state energies

Ground State (${}^1A_g^-$). In the long-range limit ($D_0 = 16 \text{ \AA}$), the SCF ground-state energy $E_0(\text{SCF})$ nearly coincides with the ground-state energies $E_0(\text{D})$ and $E_0(\text{C})$; i.e., electron correlation is negligible. For faster decaying repulsive potentials (decreasing D_0), electron correlation becomes more important, as can be seen by the fact that the $E_0(\text{D})$ and $E_0(\text{C})$ values are lowered significantly relative to $E_0(\text{SCF})$. Double excitations account for the major part (>90%) of the correlation energy, except for very small values of D_0 . For $D_0 \leq 1 \text{ \AA}$, the SCF ground state (${}^1A_g^-$) is unstable since it lies above the ${}^3B_u^+$ (S) level (see Figs. 2 and 3). However, in a complete CI calculation, the ${}^1A_g^-$ state remains lowest. This "instability" of the SCF solution is of the spin-unrestricted type, with the unrestricted SCF ground state lying below the restricted SCF ground state.³⁰ In the short-range limit, the ground state evaluated in the complete basis set approaches the covalent "antiferromagnetic" (perfect pairing) ground state of the RV description.

Excited States (${}^3B_u^+$, ${}^3A_g^+$ and ${}^1B_u^+$). The low-lying triplet states ${}^3B_u^+$, ${}^3A_g^+$ and the optically allowed ${}^1B_u^+$ state show similar behavior in the response to the correlation correction for both butadiene and hexatriene, in spite of the fact that they have different "origins"²⁰; that is, in the short-range limit the ${}^3B_u^+$ and ${}^3A_g^+$ states correlate with low-lying covalent states (with one spin flip from the antiferromagnetic ground state), whereas the ${}^1B_u^+$ state correlates with a high-energy ionic valence-bond state not included in Figs. 2 and 3. In the long-range limit, these states are well described by the (S) basis. For shorter-range repulsion, they exhibit a significant energy lowering in the D basis. However, in contrast to the ${}^1A_g^-$ ground state, the additional lowering in going to the complete configurational basis (C) is relatively large, particularly for the triplet states. This demonstrates the importance of higher excitations (triple and quadruple excited configurations) for obtaining the correct energy of these states. The triplet excitation energies decrease rapidly with shorter-ranged potentials (i.e., the correlation effects are larger than in the ground state), whereas the singlet excitation energy increases (i.e., the correlation effect is smaller than in the ground state).

The States $2{}^1A_g^-$ and $2{}^1B_u^-$ (Hexatriene). The optically forbidden $2{}^1A_g^-$ state in butadiene and hexatriene and the $1{}^1B_u^-$ state in hexatriene (not included in butadiene with the basis used) are most strongly affected by electron correlation. In the short-range limit the $2{}^1A_g^-$ and $1{}^1B_u^-$ states both correspond to optically forbidden singlet states; in the RV basis they are generated by two simultaneous triplet spin flips relative to the antiferromagnetic ground state. They can, thus, be character-

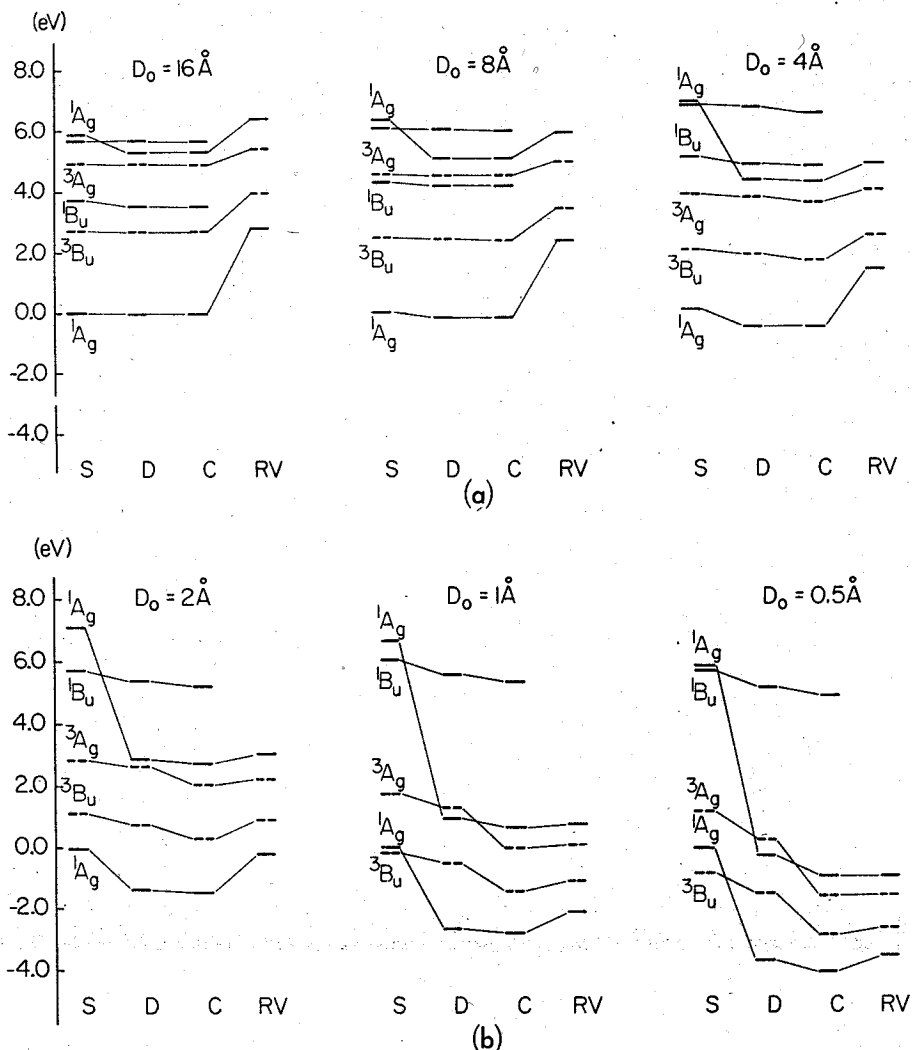


FIG. 2. Lowest butadiene energy levels with exponential potential [Eq. (3c)] as function of parameter D_0 ; equal bond lengths are assumed (1.397 Å). (S), basis of single excited configurations; (D), basis of single and double excited configurations; (C), all configurations; (RV), basis of covalent and adjacent single ionic valence bond structures.

ized as covalent states, as can all singlet (–) states (e.g., the ground state $1A_g^-$). As described already,⁴ the two lowest $1A_g^-$ states of butadiene correspond most closely to the “perfect pairing” and “long-bonded” π -electron valence-bond structures. The correlation corrections present in these simple valence-bond pictures of the molecules are essential for short-range electron interaction and require the inclusion of configurations beyond the (S) basis in the molecular orbital model.

Figures 2 and 3 show that correlation lowers the $2^1A_g^-$ and the $1^1B_u^-$ excited states more than the ground state. The large energy lowering observed in going from the (S) to the (D) basis is due to the fact that double excitations make the dominant contributions to the wavefunctions. To illustrate this point, we consider the $2^1A_g^-$ wavefunctions of butadiene in the (S) and in the (D) description evaluated with the Ohno repulsive potential [Eq. (3a)]:

$$2^1A_g^-(S): \psi = [0.707^0 \cdot 0^0 O_1^3 - 0.707^0 \cdot 0^0 O_2^4] \psi_0,$$

$$2^1A_g^-(D): \psi = [0.085 + 0.477^0 \cdot 0^0 O_1^3 - 0.477^0 \cdot 0^0 O_2^4 + 0.596^0 \cdot 0^0 O_{22}^{33} - 0.237^0 \cdot 0^0 O_{11}^{33} - 0.237^0 \cdot 0^0 O_{22}^{44} - 0.194 O_1 + 0.156^0 \cdot 0^0 \hat{O}_{12}^{34} + 0.085^0 \cdot 0^0 \hat{O}_{11}^{44}] \psi_0.$$

where ψ_0 is the SCF ground state. The excitation operators appearing in the equation are defined in Ap-

pendix B. The excitations O_1 and $0^0 \hat{O}_{12}^{34}$ differ in the spin coupling: in the first term the particle-hole pairs (1, 3) and (2, 4) are individually coupled to form singlet states which give a total singlet state; in the second term the particle-hole pairs (1, 3) and (2, 4) are individually coupled to form triplet states which in turn are coupled to give a total singlet state (see Appendix B). In the complete configurational basis (C), the $2^1A_g^-$ and the $1^1B_u^-$ state are lowered by an additional amount approximately equal to that for the optically allowed lowest $1^1B_u^-$ state.

It is of interest that the excitation energies of the $2^1A_g^-$ state can be estimated from the simple relation

$$\Delta E(2^1A_g^- - 1^1A_g^-) \approx 2\Delta E(1^3B_u^- - 1^1A_g^-)$$

in agreement with the characterization of the $2^1A_g^-$ state in the valence-bond picture as a concerted triplet-triplet excitation.

General Discussion. Figures 2 and 3 demonstrate that the ordering of the energy levels in polyenes is strongly dependent on the strength of the electron interaction between the π electrons. Although some states are more sensitive to electron correlation than are others, the figures show that *all* states are significantly altered in energy if the interaction is sufficiently short

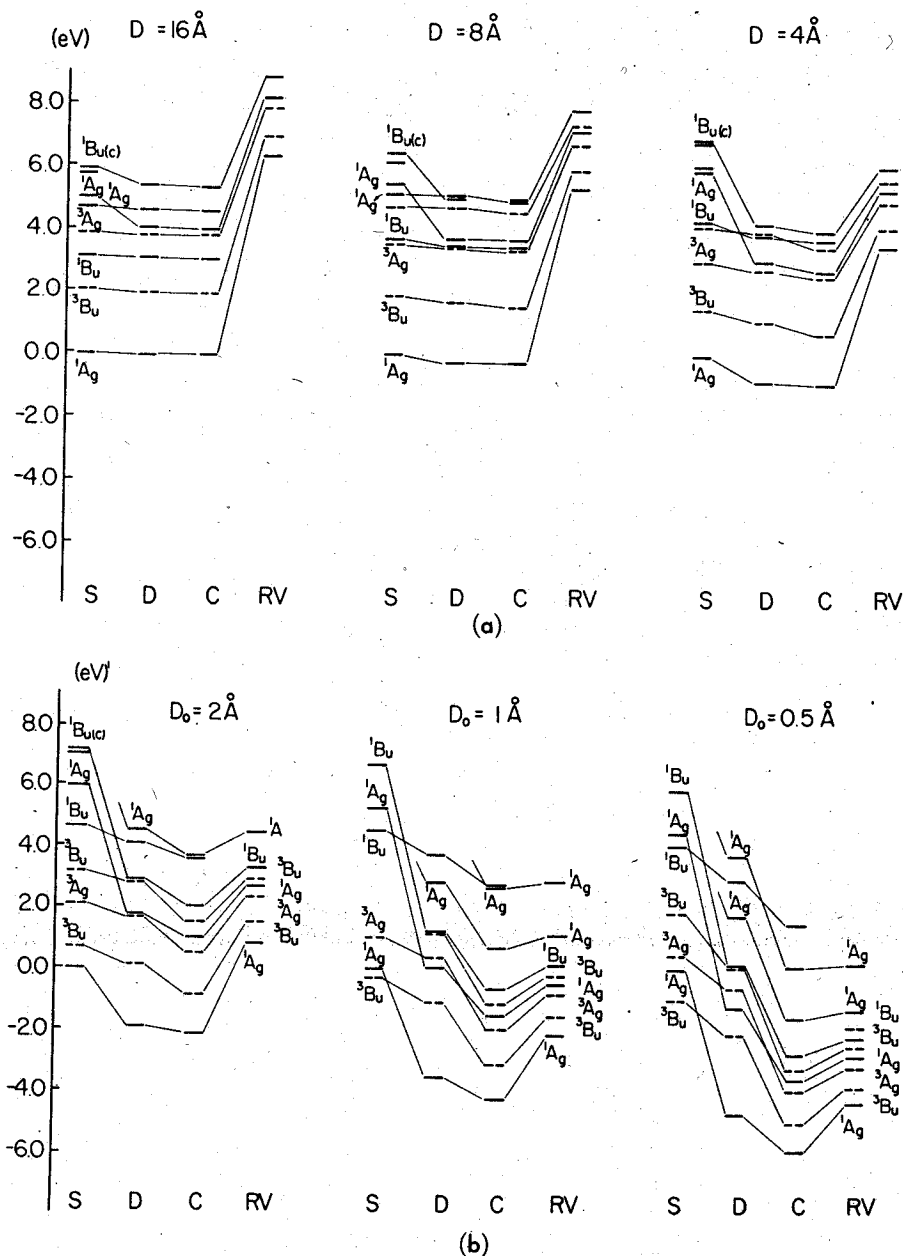


FIG. 3. Lowest hexatriene energy levels; for description, see Fig. 2.

range in character; this is the case for the "chemical region" of the parameter D_0 (2–4 Å). However, the magnitude of the effect is somewhat different for the different types of states. Thus, for the covalent states (e.g., $2^1A_g^-$, $1^1B_u^-$, $1^3B_u^+$, $1^3A_g^+$) the correlation is generally larger than for the ionic states (e.g., $1^1B_u^+$). Of particular interest is the fact that in the chemical region, the two lowest excited states ($2^1A_g^-$ and $1^1B_u^+$) are found to be close in energy, although their exact ordering (i.e., which is lower) depends on the details of the interaction and is very difficult to predict on the basis of a semiempirical model (see also Sec. V).

B. Fluctuation potential

From Eq. (5), the operator for the interaction between an electron at site κ (with spin σ) and an electron at site λ (with spin σ') can be written

$$R_{\kappa\lambda} c_{\kappa\sigma}^+ c_{\kappa\sigma} c_{\lambda\sigma'}^+ c_{\lambda\sigma'}. \quad (15)$$

The effective potential between the sites obtained in the independent particle (SCF) picture for the ground state ψ_0 is thus equal to

$$V_{\kappa\sigma, \lambda\sigma'}^{\text{SCF}} = \frac{1}{2} R_{\kappa\lambda} \{ \langle \psi_0 | n_{\kappa\sigma} | \psi_0 \rangle n_{\lambda\sigma'} + n_{\kappa\sigma} \langle \psi_0 | n_{\lambda\sigma'} | \psi_0 \rangle - \delta_{\sigma\sigma'} \langle \psi_0 | c_{\kappa\sigma}^+ c_{\lambda\sigma'} | \psi_0 \rangle c_{\lambda\sigma'}^+ c_{\kappa\sigma} - \delta_{\sigma\sigma'} \langle \psi_0 | c_{\lambda\sigma'}^+ c_{\kappa\sigma} | \psi_0 \rangle c_{\kappa\sigma}^+ c_{\lambda\sigma'} \}. \quad (15)$$

The difference between the true potential and the SCF-averaged result [Eq. (15)] is defined as the fluctuation potential operator,³³

$$V_{\kappa\sigma, \lambda\sigma'}^{\text{fl}} = R_{\kappa\lambda} \{ n_{\kappa\sigma} n_{\lambda\sigma'} - \frac{1}{2} \langle \psi_0 | n_{\kappa\sigma} | \psi_0 \rangle n_{\lambda\sigma'} - \frac{1}{2} n_{\kappa\sigma} \langle \psi_0 | n_{\lambda\sigma'} | \psi_0 \rangle + \frac{1}{2} \delta_{\sigma\sigma'} \langle \psi_0 | c_{\kappa\sigma}^+ c_{\lambda\sigma'} | \psi_0 \rangle c_{\lambda\sigma'}^+ c_{\kappa\sigma} + \frac{1}{2} \delta_{\sigma\sigma'} \langle \psi_0 | c_{\lambda\sigma'}^+ c_{\kappa\sigma} | \psi_0 \rangle c_{\kappa\sigma}^+ c_{\lambda\sigma'} \}. \quad (16)$$

The expectation value of this operator with respect to the full configuration-interaction wavefunction ψ^E ,

$$\langle \psi^E | V_{\kappa\sigma, \lambda\sigma'}^{f_i} | \psi^E \rangle,$$

expresses the strength of the interaction between the two electrons on centers κ and λ that is not accounted for by the SCF approximation. We find that for alternant neutral hydrocarbons

$$\langle \psi^E | V_{\kappa\sigma, \lambda\sigma'}^{f_i} | \psi^E \rangle = R_{\kappa\lambda} \{ \langle \psi^E | n_{\kappa\sigma} n_{\lambda\sigma'} | \psi^E \rangle - \frac{1}{4} + \frac{1}{4} \delta_{\sigma\sigma'} p_0(\kappa, \lambda) p_i(\kappa, \lambda) \}, \quad (17)$$

where $p(\kappa, \lambda)$ is the bond order,

$$\langle \psi_0 | c_{\kappa\sigma}^+ c_{\lambda\sigma} | \psi_0 \rangle = \langle \psi_0 | c_{\lambda\sigma}^+ c_{\kappa\sigma} | \psi_0 \rangle = \frac{1}{2} p_0(\kappa, \lambda), \quad (18)$$

and

$$\langle \psi^E | n_{\kappa\sigma} | \psi^E \rangle = \langle \psi_0 | n_{\kappa\sigma} | \psi_0 \rangle = \frac{1}{2} \quad (\sigma = \pm \frac{1}{2}). \quad (19)$$

The first term in Eq. (17) involves the two-particle density correlation function,^{1a}

$$\langle \psi^E | n_{\kappa\sigma} n_{\lambda\sigma'} | \psi^E \rangle,$$

which expresses the simultaneous probability of an electron with spin σ occupying site κ and another electron with spin σ' occupying site λ . If the two electrons move independently in the wavefunction ψ ,

$$\langle \psi | n_{\kappa\sigma} n_{\lambda\sigma'} | \psi \rangle = \langle \psi | n_{\kappa\sigma} | \psi \rangle \langle \psi | n_{\lambda\sigma'} | \psi \rangle.$$

Even for the independent particle (SCF) function given in Eq. (6), there is a correlation effect for the electrons with the same spin; that is, while for electrons with opposed spin, the result is

$$\langle \psi_0 | n_{\kappa\sigma} n_{\lambda-\sigma} | \psi_0 \rangle = \langle \psi_0 | n_{\kappa\sigma} | \psi_0 \rangle \langle \psi_0 | n_{\lambda-\sigma} | \psi_0 \rangle = \frac{1}{4} \quad (20)$$

for electrons with the same spin, the SCF function gives [see Eq. (15)]

$$\langle \psi_0 | n_{\kappa\sigma} n_{\lambda\sigma} | \psi_0 \rangle = \frac{1}{4} - \frac{1}{4} p_0^2(\kappa, \lambda) \quad (21)$$

due to the antisymmetry condition on the wavefunction; for even alternant hydrocarbons $p_0^2(\kappa, \kappa \pm 2n) = 0$ ($n=1, 2, \dots$) by the pairing theorem.^{1b}

To illustrate the above discussion, we present selected ground-state results for butadiene and hexatriene. Figure 4 shows the density correlation functions for hexatriene obtained with the Ohno repulsion and $\beta_0 = -2.43$ eV; the points are associated with each of the atoms ($\lambda=1, 2, \dots, 6$) for $\kappa=1$. For both antiparallel and parallel spin, it can be seen that the complete CI correlation function has an oscillatory form that decreases with distance. For antiparallel spin, the strong alternation relative to the uncorrelated value demonstrates that an antiferromagnetic spin arrangement, approximating the perfect pairing valence-bond result, applies to the fully correlated ground-state wavefunction. It is clear that there is a strong positive correlation for neighbors an odd number of atoms away (1-2, 1-4, 1-6). However, the correlation decreases with distance until it approaches the random value of $\frac{1}{4}$. For the parallel spin case [Fig. 4(b)], there is a positive correlation for neighbors an even number of atoms away (1-3, 1-5).

The correlation correction is seen in Figs. 4(a) and 4(b) to be overestimated by the restricted valence-bond calculation and underestimated by the SCF function. For the parallel spin case [Fig. 4(b)], both approximate results are much closer to the correct value than for the antiparallel spin case. Thus, the polyene calculations demonstrate very clearly the large difference between the behavior of electrons with the same and with opposed spin and the importance of the "correlation hole" present in the SCF function for electrons of the same spin.

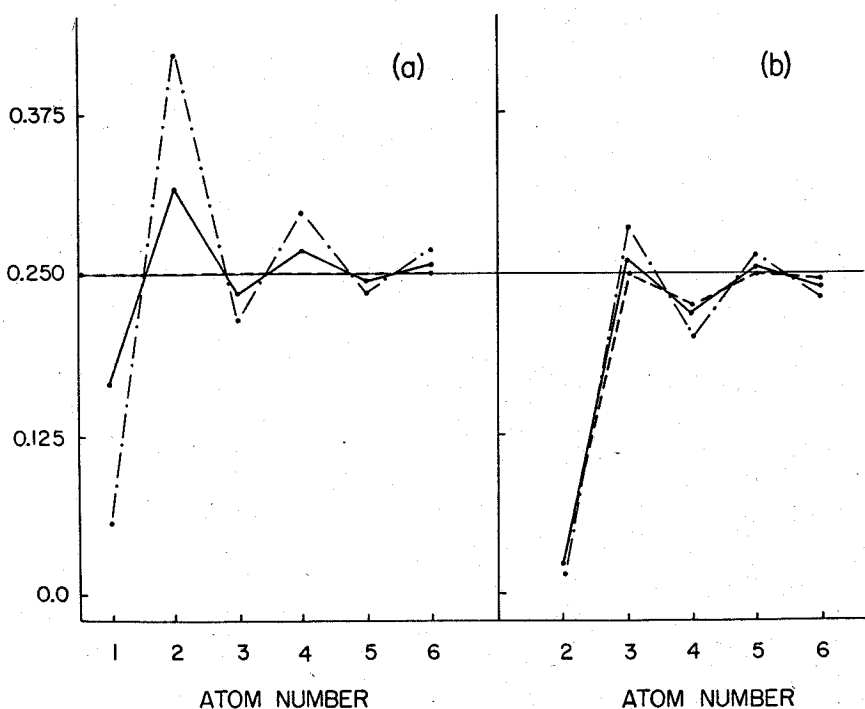


FIG. 4. Ground state density correlation function $\langle \psi | n_{\kappa\sigma} n_{\lambda\sigma'} | \psi \rangle$ for hexatriene with Ohno repulsion ($\kappa=1, \lambda=1, 2, \dots, 6$). (a) Antiparallel spin; (b) parallel spin. (—), complete CI; (---), SCF; (-·-), restricted VB (see text).

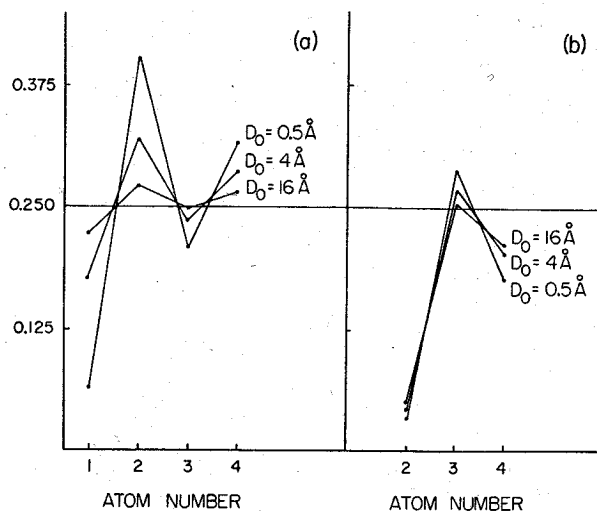


FIG. 5. Ground-state density correlation function $\langle \psi | n_{\kappa\sigma} n_{\lambda\sigma'} | \psi \rangle$ for butadiene with equal bond lengths and exponential repulsion. ($\kappa=1, \lambda=1, 2, \dots, 4$). (a) Antiparallel spin; (b) parallel spin.

Figure 5 shows the exact density correlation function for the ground state of butadiene as a function of the range of the exponential repulsive potential [Eq. (3c)]. As expected, the correlation is largest for the shortest range interaction ($D_0=0.5$) and decreases as the range of the interaction increases. For a very short range potential, we have seen that the SCF function is unstable; the unrestricted SCF solution introduces large correlation effects of the antiferromagnetic type.

Figure 6 shows the expectation value of the exact fluctuation potential

$$\langle \psi^\sigma | V_{1\sigma, \lambda\sigma'}^{f1} | \psi^\sigma \rangle + \langle \psi^\sigma | V_{1-\sigma, \lambda-\sigma'}^{f1} | \psi^\sigma \rangle \quad (\lambda=1, 2, \dots, 6)$$

as defined in Eq. (17) for the case $\sigma \neq \sigma'$ (antiparallel spin) on the left (a) and for the case $\sigma = \sigma'$ (parallel spin) on the right (b); the hexatriene ground state with the Ohno potential was used to obtain the values given in the

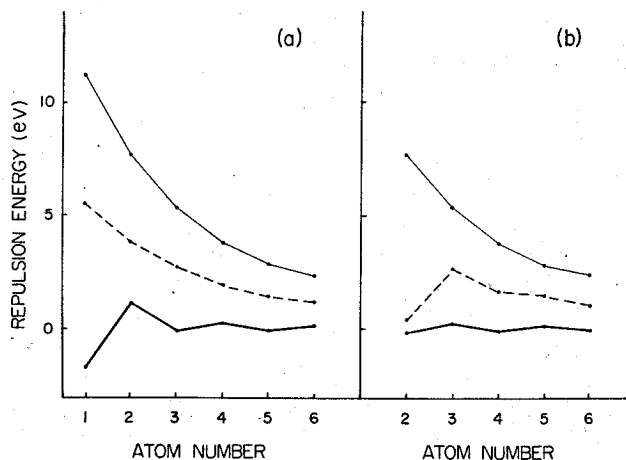


FIG. 6. Fluctuation potential in hexatriene ground state with Ohno potential. (a) Antiparallel spin; (b) parallel spin. (—), $R_{1\lambda}$; (---), $\{ \langle \psi_0 | V_{1\sigma, \lambda\sigma'}^{SCF} | \psi_0 \rangle + \langle V_{1-\sigma, \lambda-\sigma'} | \psi_0 \rangle \}$; (—), $\{ \langle \psi^c | V_{1\sigma, \lambda\sigma'}^{f1} | \psi^c \rangle + \langle \psi^c | V_{1-\sigma, \lambda-\sigma'}^{f1} | \psi^c \rangle \}$, where ψ^c is the complete CI wavefunction.

BUTADIENE SINGLET and TRIPLET STATES

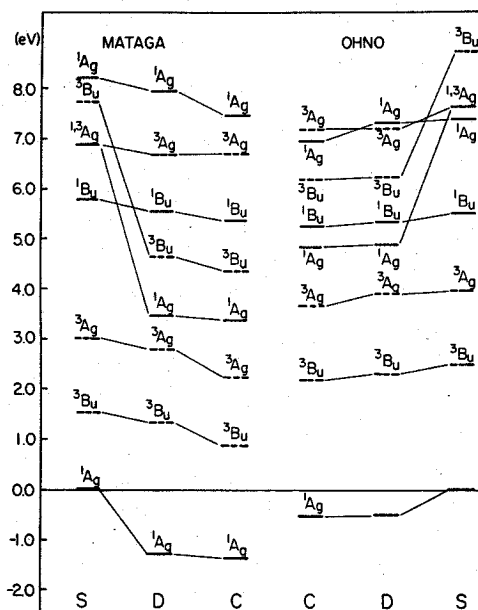


FIG. 7. Energy levels of butadiene evaluated with the Ohno and the Mataga-Nishimoto potential: (S), single excitation CI; (D), single plus double excitation CI; (C), complete CI.

figure. As indicated, we have summed over the two possible orientations of the spin component since on each atom there is a probability of $\frac{1}{2}$ that the spins is up and $\frac{1}{2}$ that it is down. We compare these results with the electron repulsion parameter, $R_{1\lambda}$, and the expectation value of the electron interaction operator for the SCF wavefunction

$$\langle \psi_0 | V_{1\sigma, \lambda\sigma'}^{SCF} | \psi_0 \rangle + \langle \psi_0 | V_{1-\sigma, \lambda-\sigma'}^{SCF} | \psi_0 \rangle.$$

It is seen that for both antiparallel and parallel spin, the fluctuation potential is relatively small. Important deviations from the SCF result are found only for the same atom and for the nearest neighbor atom in the antiparallel spin interaction. For the parallel spin case, there is only a negligible correction, as expected from the density correlation function results.

V. EXPERIMENTAL COMPARISON

To explore the practical significance of the results of the previous section, we make a comparison of calculations for butadiene, hexatriene, and benzene with experimental results for these systems. Rather than employing the exponential potential [Eq. (3c)] in the PPP Hamiltonian, we use the Ohno and Mataga-Nishimoto repulsion formulas [Eqs. (3a) and (3b)], which fall in the range of chemical interest and have been widely employed in semiempirical calculations by other workers. It is important to remember that the Ohno and Mataga-Nishimoto parameterizations were originally suggested for (S)-basis calculations on π systems. For such calculations, these formulas yield excellent values for the excitation energies of the optically allowed ${}^1B_u^+ - {}^1A_g^-$ and ${}^1E_{1u}^+ - {}^1A_g^-$ transitions in the polyenes and benzene, respectively. In Figs. 7-9 we present the energy level diagrams of butadiene, hexatriene, and benzene obtained

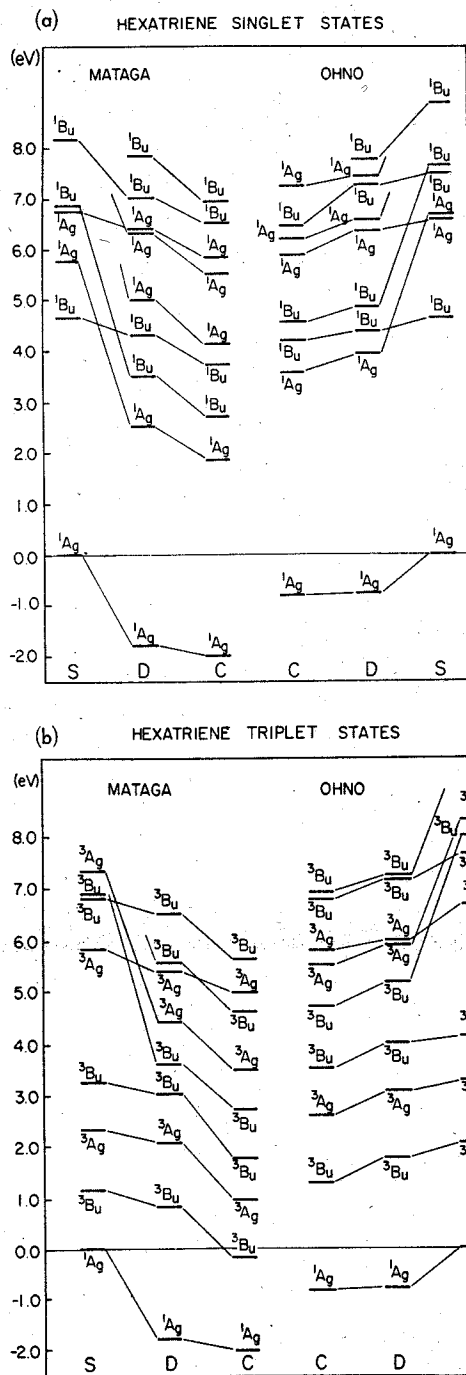


FIG. 8. Energy levels of hexatriene evaluated as in Fig. 7. (a) Singlet states; (b) triplet states.

for the two parameterizations with the (S), (D), and (C) approximations; the other parameters used are given in Table I. For all three molecules the Ohno and Mataga-Nishimoto formulas give similar results in the (S) approximation for the lowest allowed transition. However, even in the single excitation calculation, the two repulsion formulas give significantly different energies for the triplet states, with the Mataga-Nishimoto energies considerably lower than those from the Ohno formula. Also, particularly for hexatriene, the spacing between the $2^1A_g^-$ and $1^1A_g^-$ states is much larger for the Mataga-Nishimoto than for the Ohno calculation. If

the effect of electron correlation is included by a more complete configuration-interaction calculation (D or C), the differences between the energy level diagrams resulting from two formulas are greatly amplified; i. e., as expected from the discussion in Sec. IV, correlation effects are much stronger for the fast decaying Mataga-Nishimoto potential than for the Ohno potential. In benzene, for example, the correlation correction leads to a large depression of the $1^1B_{2u}^-$ state (below the $3^1B_{2u}^-$ state) and of the $1^1E_{2g}^-$ state (below the $3^1E_{2g}^-$ state). Both pairs of states are degenerate in a S-CI description of benzene but the introduction of correlation has a much larger effect on the singlet than on the triplet states. This is expected because the singlet (-) states are covalent while the triplet (-) states are ionic in origin.²⁰ The $1^1E_{2g}^-$ state, in particular, is analogous to the $1^1A_g^-$ state of polyenes discussed above; like the latter, it obeys the approximate relation

$$\Delta E(1^1E_{2g}^- - 1^1A_g^-) \approx 2\Delta E(3^1B_{1u}^+ - 1^1A_g^-),$$

as can be readily checked from the energy level diagram.

The large discrepancies between the level diagrams obtained from the two "standard" parameterization schemes requires that a decision be made as to what formula to use in studying the spectra of the molecules under consideration. For butadiene, hexatriene, and benzene there are a wide range of choices which yield reasonable results; certain of these have been described previously.^{5,13,15,16,18} Since the Mataga-Nishimoto electron repulsion in the complete CI calculation gives invalid results, we restrict the present discussion to the Ohno potential. This should be sufficient for a description of the essential features of the spectrum, though it may well introduce errors in detail. A core resonance integral ($\beta_0 = -2.60$ eV) is used (see Table I); this yields better agreement than does $\beta_0 = -2.43$ eV with the experimental data in the complete CI calcula-

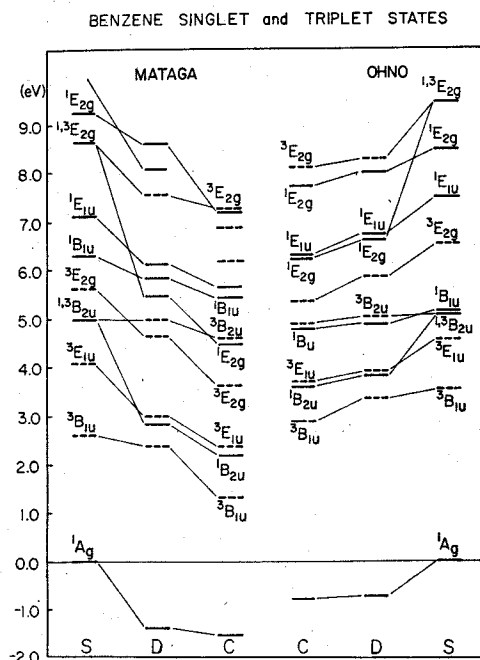


FIG. 9. Energy levels of benzene evaluated as in Fig. 7.

TABLE II. Excitation energies.^{a,b}

| A. Butadiene | | | | |
|---|--------------------|--------------------|--------------------|---------------------|
| Symmetry | (S) | (D) ^d | (C) ^d | Exptl. ^c |
| ³ B _u ⁺ | 2.745 | 3.085 | 2.924 | 3.22 |
| ³ A _g ⁺ | 4.328 | 4.790 | 4.593 | 4.91 |
| ¹ A _g ⁻ | 7.989 | 5.810 | 5.816 | |
| ¹ B _u ⁺ | 5.692 (f=1.086) | 6.057 (f=0.783) | 6.005 (f=0.775) | 5.92 |
| ³ B _u ⁺ | 9.228 | 7.320 | 7.273 | |
| ¹ A _g ⁺ | 7.738 | 8.175 | 7.872 | |
| B. Hexatriene | | | | |
| Symmetry | (S) | (D) ^e | (C) ^e | Exptl. ^c |
| ³ B _u ⁺ | 2.249 | 2.723 | 2.378 | 2.6 |
| ³ A _g ⁺ | 3.559 | 4.157 | 3.780 | 4.2 |
| ¹ A _g ⁻ | 6.946 | 5.015 | 4.732 | |
| ³ B _u ⁺ | 4.543 | 5.211 | 4.786 | |
| ¹ B _u ⁺ | 4.803 (f=1.524) | 5.311 (f=1.141) | 5.167 (f=1.103) | 4.9 |
| ¹ B _u ⁻ | 8.029 | 6.025 | 5.810 | 5.7 |
| ¹ A _g ⁺ | 6.885 | 7.459 | 7.001 | |
| ¹ A _g ⁻ | 11.832 | 7.960 | 7.623 | |
| ¹ B _u ⁺ | 7.858 (f=0.052) | 8.443 (f=0.027) | 7.924 (f=0.042) | 7.3 |
| ¹ A _g ⁻ | | 8.574 | 8.404 | |
| ¹ B _u ⁺ | 9.322 (f=0.238) | 8.990 (f=0.171) | 8.788 (f=0.163) | |
| ¹ A _g ⁺ | 9.679 | 9.920 | 9.576 | |
| C. Benzene | | | | |
| Symmetry | (S) | (D) ^f | (C) ^f | Exptl. ^c |
| ³ B _{1u} ⁺ | 3.872 | 4.358 | 3.975 | 3.9 |
| ¹ B _{2u} ⁻ | 5.395 | 4.885 | 4.700 | 4.9 |
| ³ E _{1u} ⁺ | 4.886 | 4.891 | 4.756 | 4.8 |
| ¹ B _{1u} ⁺ | 5.411 | 5.901 | 5.846 | See text |
| ³ B _{2u} ⁻ | 5.395 | 6.030 | 5.911 | 5.6 |
| ³ E _{2g} ⁺ | 6.997 | 7.014 | 6.607 | 6.6 |
| ¹ E _{1u} ⁺ | 7.819 | 7.755 | 7.374 | 7.0 |
| ¹ E _{2g} ⁻ | 9.919 | 7.827 | 7.532 | See text |

^aCalculation made with the Ohno potential (3a) and $\beta_0 = -2.60$ eV; see Table I.

^bAll energies in eV.

^cFor discussion of experimental values, see text.

^dThe ¹A_g⁻ ground state is lowered by 0.524 eV in (D) and by 0.535 eV in (C).

^eThe ¹A_g⁻ ground state is lowered by 0.777 eV in (D) and by 0.809 eV in (C).

^fThe ¹A_g⁻ ground state is lowered by 0.682 eV in (D) and by 0.710 eV in (C).

tion for the three molecules.¹⁸ The results obtained are given in Table II. The experimental and theoretical excitation energy values for the three molecules are shown in Fig. 10.

In order to compare the calculated results with ex-

periment, it is necessary to briefly consider the available data concerning the excited states of butadiene, hexatriene, and benzene. In butadiene and hexatriene, the strongly allowed transition can be assumed to involve the lowest ¹B_u⁺ excited state. As to higher excited singlet states, the situation is far less clear. Price and Walsh³⁴ observed transitions in gas phase *trans*-butadiene at 6.25 eV, 6.66 eV, 6.81 eV, and 7.27 eV, as well as higher energy Rydberg states. Very recently, McDiarmid³⁵ has assigned the series of sharp vibrational peaks descending the short-wavelength side of the diffuse ¹B_u band of gas phase butadiene to a low-lying ¹A_g⁻ state with origin at about 6.2 eV; however, whether this may well be another state than the ¹A_g⁻ state in question. For *trans*-hexatriene, the work of Gavin and Rice^{36a} shows a series of weak bands in the region 5.70–6.45 eV, a set of sharp, medium intensity bands in the region 6.53–7.1 eV, and another set of medium intensity bands starting at 7.37 eV; at about 7.8 eV a series of Rydberg transitions set in. Although considerable vibrational structure is present in certain of the bands, no experimental information on their symmetry characteristics is available.

The excitation energies of certain triplet states have been measured by electron impact,^{37–40} ion impact⁴¹ and high pressure oxygen-induced optical absorption.^{42–44} The electron impact studies by Mosher, Flicker, and Kuppermann⁴⁰ and by Brongersma *et al.*³⁸ on butadiene and by Knoop and Oosterhoff³⁹ on hexatriene yielded two states below the optically allowed ¹B_u⁺ state. The triplet character of these states was established by the variation of the relative intensities with the energy and scattering angle of the scattered electrons; the symmetry has not been determined. High energy He⁺ and H⁺ impact studies of Moore⁴¹ yielded two transitions below the ¹B_u⁺ state with He⁺; both of them were absent in H⁺-scattering processes. Since triplet excitations are induced through exchange between the electrons of the target and the scatterer, they are expected to occur with He⁺ but not with H⁺. Thus, the results of Moore are in agreement with the electron impact data. The oxygen-induced optical spectra of Evans^{42,43} have also demonstrated the existence of the two lowest triplet states of butadiene and hexatriene and provided resolution of their vibrational structure. Originally, Evans reported another triplet at ~1900 cm⁻¹ above the lowest triplet state for butadiene and for hexatriene, these "states" have now been identified as involving a simultaneous ¹Δ_g–³Σ_g⁻ transition of oxygen.⁴³ On the basis of the work of Evans, Brongersma *et al.*³⁸ were led to a similar assignment of their low energy electron impact spectra. These authors observed a broad peak in the range of the ³B_u–¹A_g transition at 3.8 eV and assigned to it both the ³B_u–¹A_g and the ³A_g–¹A_g transition. They concluded that a weak peak observed at 4.8 eV corresponds to a third triplet state. This transition appears to be the same as the rather strong transition observed by Mosher *et al.*⁴⁰ at a vertical transition energy of 4.91 eV and assigned by them to the second ³A_g state of butadiene. All of the measurements are thus in accord in demonstrating the existence of two low-lying triplet states for butadiene (3.2 eV, 4.9 eV) and for hexatriene

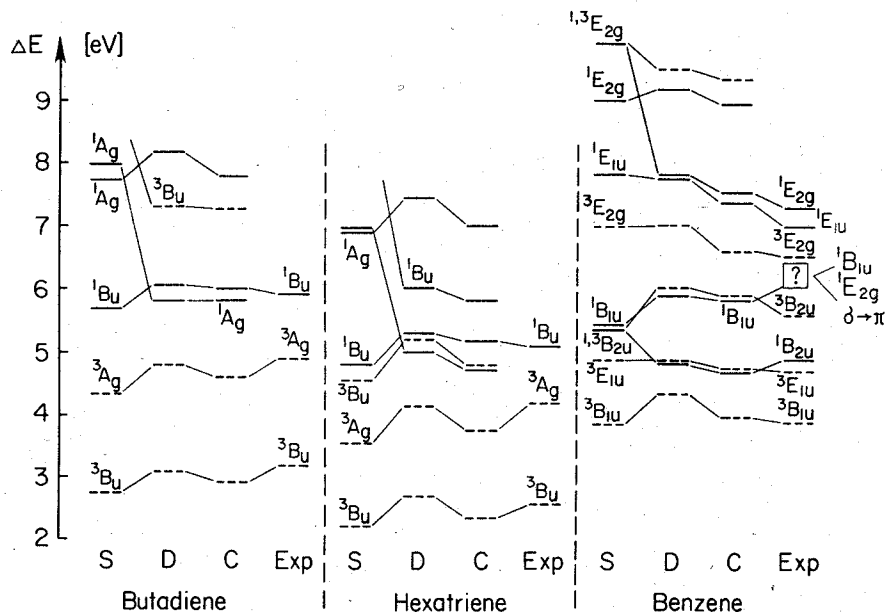


FIG. 10. Theoretical and experimental transition energies for butadiene, hexatriene, and benzene; the Ohno potential and $\beta_0 = -2.60$ eV were used. (S), (D), and (C) are defined in Fig. 7; see text for discussion.

(2.6 eV, 4.2 eV). On the basis of theoretical arguments, the first of these states is assigned, as already indicated, as 3B_u and the second as 3A_g .

Comparing the experimental data for butadiene with the present calculations (Table IIA), we see that there is satisfactory agreement for the lowest excited states (${}^3B_u^+$, ${}^3A_g^+$, ${}^1B_u^+$) with the assumed symmetries if either the (D) or (C) configuration interaction treatment is used. It should be noted that the (S) results are only slightly worse than the others. For the higher excited states, the relation between theoretical and experimental results is less clear. The states at 6.66, 6.81 eV have been suggested to be Rydberg states³⁴ and so would not be included in the PPP-Hamiltonian spectrum. The calculations yield a ${}^1A_g^+$ state at 7.87 eV, which could be the level at 7.3 eV; Mosher *et al.* have argued that the 7.3 eV level, which is observed in the electron impact spectrum, is a higher 1B_u state. There seems to be no level in the π spectrum to be identified with that at 6.25 eV unless the ${}^1A_g^-$ state is actually above the 1B_u state in contrast to the calculated order. An alternative possibility is that the state at 6.25 eV is a $\pi^* - \sigma$ excitation. Concerning the ${}^1A_g^-$ state, there is, in addition to the work of McDiarmid,³⁵ an observation by two photon absorption⁴⁵ of a forbidden state at 3.47 eV just below the ${}^1B_u^+$ state (3.57 eV) of diphenylbutadiene. However, this state may involve significant contributions from the phenyl substituents.

For hexatriene (Table IIB), the comparison between the calculations and the three lowest observed levels (${}^3B_u^+$, ${}^3A_g^+$, ${}^1B_u^+$) is analogous to that for butadiene. It is clear from the table that the singlet (+) states, which include the allowed 1B_u states, are generally less affected than the singlet (-) states by the inclusion of configuration interaction beyond single excitations. Thus, both the calculations yield an allowed ${}^1B_u^+$ state at approximately 7.9 eV, which can be identified with the observed excitation at 7.33 eV. As to the other transitions (5.7 eV, 6.5 eV) seen by Gavin and Rice,^{36a} the

situation is less clear. The complete CI calculation has a ${}^1B_u^+$ state at 5.81 eV, which corresponds reasonably well with the weak transition observed starting at 5.7 eV, but for the transition starting at 6.5 eV a pair of ${}^1A_g^-$ ($\pi\pi^*$) states would have to be suggested; they are the ${}^1A_g^+$ state at 7 eV and the ${}^1A_g^-$ state at 7.6 eV. However, such an identification appears rather unsatisfactory because the ${}^1A_g^-$ states are unlikely to have sufficient intensity to correspond to the observed value. An alternative interpretation is that the observed excitation corresponds to a $\pi^* - \sigma$ transition, which is not included in the π -electron Hamiltonian.^{36b}

Thus, from our discussion of both butadiene and hexatriene it appears that a knowledge of the higher excitations without a determination of their symmetries does not provide sufficient information for a definitive test of the magnitude of the correlation correction in the polyene spectra. In particular, it is clear that a knowledge of the positions of the forbidden excited states (e.g., the lowest ${}^1A_g^-$ state) would be the best way of obtaining the necessary calibration data. The two photon absorption experiment for diphenylbutadiene is suggestive in this regard, but comparable studies on the polyenes themselves are needed. In hexatriene, an unsuccessful search for the state ${}^1A_g^-$ was made by single photon absorption in the gas phase by Gavin, Risemberg, and Rice.⁴⁶ The excitation energy for this state is estimated to be at 5.2 eV for hexatriene from twice the experimental ${}^3B_u^+$ energy. This value is very close to the strong ${}^1B_u^+ - {}^1A_g^-$ transition at 4.9 eV. The present calculation yields an excitation energy of 4.73 eV, which is also in the vicinity of the allowed state. Although these estimates are approximate and cannot determine whether the ${}^1A_g^-$ state is above or below the 1B_u state, the fact that they are close together would make the forbidden ${}^1A_g^-$ state difficult to observe; e.g., it might appear as a weak shoulder on the intense ${}^1B_u^+$ state, particularly in low-resolution measurements. For butadiene, the situation is comparable; that is, the

empirical and calculated excitation energies of the ${}^1A_g^-$ state are 6.4 and 5.82 eV, respectively, while the allowed state ${}^1B_u^+$ is at 5.9 eV. In the higher polyene analogs (i. e., diphenyloctatetatriene and undecapentaene), the low-lying ${}^1A_g^-$ state has been identified below the ${}^1B_u^+$ state (the energy difference is 0.27 eV in the former and 0.40 eV in the latter compound) by the use of high-resolution spectroscopy in the solid state.^{2,3} However, this does not determine the level order for the simpler polyenes since a reversal of the two neighboring levels is not impossible and, as mentioned above, well within the limits of accuracy of the present calculations. Nevertheless, the larger polyene results do demonstrate that correlation plays an important role in the spectrum and that (S) calculations are not adequate for an analysis that includes the covalent levels.

In the levels of benzene (Fig. 9), the ${}^1B_{1u}^+$ and ${}^1E_{2g}^-$ states depend most sensitively on the parameterization of the PPP Hamiltonian. However, no unambiguous assignment exists for these levels. To illustrate the existing confusion, we mention that three recent publications on the 2000 Å band of benzene come to three different conclusions regarding the ${}^1B_{1u}^+$ and the ${}^1E_{2g}^-$ levels. Taleb, Munro, and Birks^{7c} reported a well-resolved spectrum of benzene in liquid perfluoro-*n*-hexane and assigned the ${}^1E_{2g}^-$ state to a band at 5.7 eV, below the ${}^1B_{1u}^+$ state that is assumed to have its onset at 6 eV. In the same spectral range, Brillante, Taliani, and Zauli⁸ studied the absorption of benzene single crystals with polarized light and concluded that there exists a possible $\pi^* - \sigma$ transition at 5.8 eV and an ${}^1E_{2g}^-$ state with a vertical transition energy at 5.9 eV. Allen and Schnepf⁹ studied the gas phase circular dichroism (CD) and the optical absorption spectrum of the benzene chromophore S-(+)-1-methylindan. From the structure of the CD spectrum, they suggested that there is a $\pi^* - \sigma^1E_{1g}$ state at 5.7 eV, below a ${}^1B_{1u}^+$ state with onset at 5.8 eV, and an ${}^1E_{2g}^-$ state at 6.3 eV. Evidence for two electronic states in this spectral range was also given some time ago by Lassetre, Skerbele, Dillon, and Ross.³⁷ These authors studied the electron impact spectrum of benzene in the 6.2 eV region and detected a pronounced change in relative intensity upon a variation of the scattering angle; they attributed this to the existence of two excited states with different symmetry properties at 6.2 eV and 6.3–6.5 eV.

A comparison of the theoretical excitation energies in Fig. 10 and Table IIC with the experimental spectrum of benzene²¹ reveals satisfactory agreement for a number of the lowest states of benzene (${}^3B_{1u}^+$, ${}^3E_{1u}^+$, ${}^1B_{2u}^-$, ${}^3B_{2u}^-$, and ${}^3E_{2g}^-$), though of course the symmetry assignments are mainly theoretical. Our calculation places the ${}^1B_{1u}^+$ state at 5.8 eV and the lowest ${}^1E_{2g}^-$ state at 7.5 eV [$2 \times \Delta E({}^3B_{1u}^+) \approx 8$ eV]. Spectroscopic evidence for an ${}^1E_{2g}^-$ state at 7.4 eV is available. In nanosecond flash photolysis of benzene in solution, Bonneau *et al.*^{7a} observed an absorption at 2.53 eV, which was interpreted by Birks^{7b} as a ${}^1E_{2g}^- - {}^1B_{2u}^-$ transition. Birks^{7c} also has made a preliminary report on a transition to this state directly from the ground state. He suggests that this state is the *second* ${}^1E_{2g}^-$ state of benzene, in disagree-

ment with the present calculation; but see Ref. 7(d). We find that the second ${}^1E_{2g}^-$ state is 9 eV above the ground state and believe that the state at 7.4 eV is in fact the lowest ($\pi\pi^*$) ${}^1E_{2g}^-$ state in benzene.

VI. SPECTRA OF LONGER POLYENES

To exhibit the length dependence of the correlation correction, we have extended the calculations to longer polyenes ($C_{2N}H_{2N+2}$, $N=2-6$). The PPP Hamiltonian given in Eq. (1) was employed with a configurational basis restricted to single and double excitations to reduce the dimension of the configuration-interaction problem. Table III gives the calculated numerical values for octatetraene ($N=4$), decapentaene ($N=5$), and dodecahexaene ($N=6$); the smaller polyenes results are given in Table IIA and IIB. In each of the polyenes, the lowest optically allowed transition ${}^1B_u^+ - {}^1A_g^-$, which is the one most easily detected spectroscopically,⁴⁷ is best known. Also available are the transition energies to the lowest triplet states in octatetraene^{42,43} and decapentaene.^{42,43} For octatetraene⁴⁸ ($N=4$), decapentaene^{48,49} ($N=5$), and dodecahexaene⁴⁸ ($N=6$), the transition to the noncovalent ${}^1A_g^-$ state at higher energies may have been observed. This is the transition which becomes optically allowed in *cis* isomers (the "*cis*" peak); in the all-*trans* molecule, it can pick up intensity from torsional deformations. The low-lying covalent ${}^1A_g^-$ state has been detected in undecapentaene ($N=5$) by Christensen and Kohler³ (0.40 eV below the optically allowed ${}^1B_u^+$ state) and very recently by Gavin (private communication) in octatetraene.

As we have seen (Secs. IV and V), a basis set restricted to single and double excitations results for butadiene and hexatriene in excitation energies which are somewhat too large compared with the energies arising from complete calculations (Fig. 10). The source of this discrepancy is that double excited configurations, which account for most of the ground-state correlation energy ($\approx 90\%$) yield a smaller fraction of the correlation correction for the excited states. Since the correlation energy increases in proportion to the number of electrons, the numerical shift of the excitation energies in the limited CI calculations is expected to increase in proportion to the number of double bonds in the polyene. This is illustrated in Fig. 11, where we show observed and calculated energy levels for $C_{2N}H_{2N+2}$ polyenes ($N=2-6$). It can be seen that the calculated correlation energies of the excited states (e. g., of the optically allowed ${}^1B_u^+$ state) increase more slowly with the polyene chain length than the ground-state correlation energy. Higher (triple, quadruple, etc.) excited configurations would be needed to account for the missing correlation in the excited states. The configuration interaction treatment thus becomes so large that calculations are very time consuming. To avoid this difficulty, we have developed a simplified method for estimating the correlation correction of ground and excited states in a balanced manner; the results will be presented in a subsequent publication.

In spite of the above limitation, the truncated CI calculations predict the same ordering of the lower excited

TABLE III. Excitation energies.^a

| A. Octatetraene | | | |
|---|--------------------|--------------------|---------------------|
| Symmetry | (S) | (D) ^c | Exptl. ^b |
| ³ B _u ⁺ | 1.988 | 2.626 | 2.10 |
| ³ A _g ⁺ | 3.012 | 3.762 | |
| ¹ A _g ⁻ | | 4.628 | |
| ³ B _u ⁺ | 3.990 | 4.825 | |
| ¹ B _u ⁺ | 4.245 (f=1.903) | 4.912 (f=1.506) | 4.08 |
| ¹ B _u ⁻ | | 5.578 | |
| ¹ A _g ⁻ | | 6.274 | |
| ¹ A _g ⁺ | 6.171 | 6.896 | 5.69 |
| B. Decapentaene ^a | | | |
| Symmetry | (S) | (D) ^d | Exptl. ^b |
| ³ B _u ⁺ | 1.831 | 2.647 | 1.9 |
| ³ A _g ⁺ | 2.636 | 3.552 | |
| ¹ A _g ⁻ | | 4.471 | 3.1 |
| ³ B _u ⁺ | 3.506 | 4.497 | |
| ¹ B _u ⁺ | 3.866 (f=2.278) | 4.702 (f=1.816) | 3.5 |
| ¹ B _u ⁻ | | 5.258 | |
| ³ A _g ⁺ | 4.239 | 5.203 | |
| ³ B _u ⁻ | | 5.572 | |
| ³ B _u ⁻ | 4.717 | 5.806 | |
| ¹ A _g ⁻ | | 6.035 | |
| ³ A _g ⁻ | | 6.069 | |
| ¹ B _u ⁻ | | 6.491 | |
| ¹ A _g ⁻ | 5.605 | 6.492 | 5.4 |
| ¹ A _g ⁺ | | 6.641 | |
| C. Dodecahexaene (singlet states only) ^a | | | |
| Symmetry | (S) | (D) ^e | Exptl. ^b |
| ¹ A _g ⁻ | | 4.439 | |
| ¹ B _u ⁺ | 3.595 | 4.605 | 3.42 |
| ¹ B _u ⁻ | | 5.080 | |
| ¹ A _g ⁻ | | 5.789 | |
| ¹ A _g ⁺ | 5.532 | 6.212 | 5.12 |
| ¹ A _g ⁻ | | 6.312 | |
| ¹ B _u ⁻ | | 6.367 | |

^aSee footnotes a and b in Table II.

^bSee footnote c of Table II.

^cThe ground state is lowered by 1.018 eV in (D).

^dThe ground state is lowered by 1.250 eV in (D).

^eThe ground state is lowered by 1.474 eV in (D).

states as does the complete treatment. This can be verified from Fig. 10 by a comparison of the (D) and (C)

calculations for butadiene and hexatriene and also from a comparison of the theoretical and experimental results for the ¹³B_u⁻, ²¹A_g⁻, and ¹¹B_u⁺ levels of undecapentaene in Fig. 11. From these results, it appears that, by including through double excitations, the excited state correlation energies are balanced with respect to each other, though not with respect to the ground state. Of course, this statement is only approximately true and is, moreover, limited to the lower excited states. Nevertheless, it suggests that, while a calculation including only single excitations is manifestly incomplete, one including single and double excitations is adequate for an understanding of the important features of polyene spectra.

The present calculations (see Table III and Fig. 11) show that, particularly in the longer polyenes, there are many low-lying covalent states of the same type as the ²¹A_g⁻ and ¹¹B_u⁻ states of butadiene and hexatriene. In the spectral range of the known ¹B_u⁻ and ¹A_g⁺ (*cis*-peak) states, we find two additional singlet covalent states in octatetraene and at least four such states in decapentaene and dodecahexaene. This demonstrates that, if the magnitude used here for the correlation correction due to the electron repulsion is valid, the covalent states outnumber the noncovalent states in the optical region of polyene spectra. Because of their forbidden character, these states are difficult to observe and may well have been missed until now. Only because they are the lowest excited states (below the allowed ¹B_u⁺ state) in diphenyloctatetraene and undecapentaene do they appear strongly in emission.^{2,3} It is to be hoped that some of the other covalent states will be searched for and found, now that they have been predicted theoretically.

Bond orders. A knowledge of low-lying covalent states of polyenes may well be of importance for an understanding of their photochemical behavior, particularly *trans-cis* isomerization. To look qualitatively at this problem, we utilize the bond orders

$$p_{\kappa,\lambda} = \langle \psi | \frac{1}{2} \left(\sum_{\sigma} c_{\kappa\sigma}^* c_{\lambda\sigma} + c_{\lambda\sigma}^* c_{\kappa\sigma} \right) | \psi \rangle$$

and assume that the relative strength of the bond ($\kappa, \kappa + 1$) is measured by the bond order $p_{\kappa, \kappa+1}$. The alternation of large (~ 0.9) and small (~ 0.3) bond orders in the polyene ground state (see Table IV) corresponds to the alternation of double and single bonds characteristic of linear polyenes. Upon excitation, electrons are promoted into different orbitals and the bond orders are significantly changed in some cases. Bond alternation is seen to be weaker in the excited states than in the ground state; for longer polyenes (e.g., dodecahexaene), the effect is most prominent in the middle portion of the molecules, and much weaker toward the ends. For the low-lying ¹A_g⁻ states (including the lowest excited ¹A_g⁻ state); the change in bond order can be significantly greater than for ¹B_u⁺ states in the same region. This suggests that *trans-cis* isomerization, which, in any case, appears to be most likely in the central part of the molecule, may well be facilitated in the ¹A_g⁻ states. Most striking, of course, is the result for butadiene

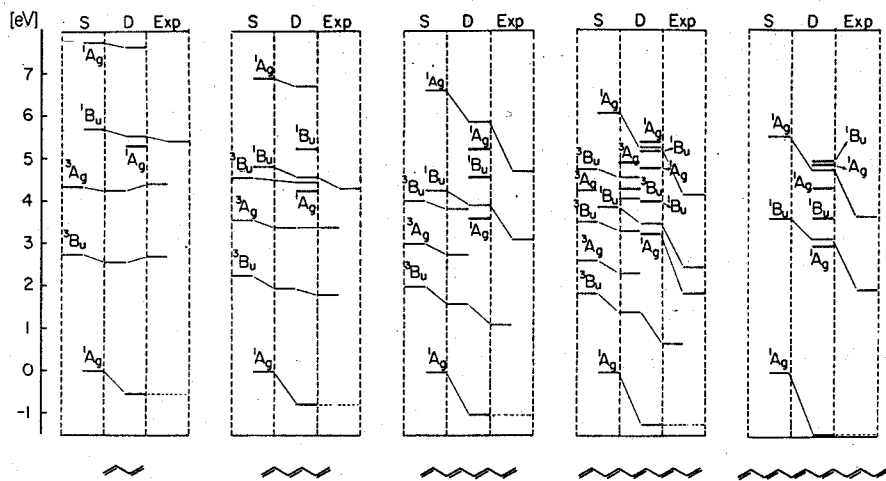


FIG. 11. Comparison of theoretical and experimental energy levels for the series of linear polyenes $C_{2N}H_{2N+2}$ ($N=2, 3, 4, 5, 6$). (S) and (D) are defined as in Fig. 7 ($\beta_0 = 7.60$ eV); see text for discussion.

(Table IVa), where we see that the p_{12} changes from 0.903 in the ground state to 0.154 in the ${}^1A_g^-$ state, while it remains at 0.497 in the 1B_u state. If the ${}^1A_g^-$ state is actually the lowest singlet excited state in the molecule (as it has been shown to be in undecapentaene), it would be likely to play an important role in photoisomerization. A quantitative understanding of the exact role of the ${}^1A_g^-$ states will have to await more detailed calculations (including dynamical studies⁵⁰), as well as an evaluation of the relative contributions of singlet and triplet states to the photoisomerization in these molecules. One case of particular interest, which has been discussed recently from this point of view,⁵¹ is the *cis-trans* isomerization of 11-*cis* retinal, the chromophore of the visual pigment rhodopsin. Another example of the possible importance of the ${}^1A_g^-$ state is found in the photocyclization of butadiene, which is known to occur by a disrotatory mechanism. In their discussion of the concerted reaction, Woodward and Hoffmann⁵² assumed that the photoprocess involves the ${}^1B_u^+$ state of butadiene. However, van der Lugt and Oosterhoff⁵³ suggested that the disrotatory motion of the terminal π orbitals of butadiene lowers the ${}^1A_g^-$ potential surface below the surface of the ${}^1B_u^+$ state, if it is not already below in the planar molecule. Bond order reversal has also been invoked in the photocyclization of hexatriene, e.g., in the work of Havinga *et al.*⁵⁴ on the phototransformations in vitamin D and related molecules.

VII. CONCLUSION

The observation of new low-lying electronic excitations in diphenyloctatetraene and undecapentaene which were assigned on theoretical grounds to highly correlated states of the π electrons made necessary a re-examination of correlation effects in conjugated π systems. For this purpose we have studied the spectrum of the PPP Hamiltonian commonly used to describe conjugated π systems as a function of the repulsive electron-electron interaction which is the source of the correlation effects. By varying the range of a screened electron-electron potential from the long-range limit (independent electron model) to the short-range limit

(Dirac-Heisenberg valence-bond model), we found that the electronic states can be classified as covalent and noncovalent. In the intermediate range of electron interaction corresponding to real polyenes, this classification is still valid, though considerable mixing occurs for many of the states. It is found that the noncovalent states (e.g., ${}^1B_u^+$, ${}^1A_g^+$, ...) are well described by the independent-particle (SCF) theory, with single excitation configuration interaction. Since the optically allowed transitions most easily observed in the polyenes belong to this class, apparently satisfactory treatments of polyene spectra have been limited to single excitation calculations. The covalent states (e.g., ${}^1A_g^-$, ${}^3B_u^+$, ...), which are optically inactive and therefore more difficult to observe are well described by valence-bond theory. For an accurate description of these states in the SCF model, higher excited configurations (at least double excited) have to be taken into account. When such calculations are done using the chemical range of the electron interaction, the covalent states are lowered drastically relative to the noncovalent states and there emerges a strongly altered picture of the excited state energy level scheme. Particularly for the longer polyenes (octatetraene, ...), an increasing number of covalent states are found in the range of the usually observed lowest ${}^1B_u^+$ and ${}^1A_g^+$ (*cis*) states.

Although single and double excitations yield a qualitatively correct energy level scheme for polyenes, quantitative results appear to require the inclusion of higher excitations. This is important to obtain the correct correlation for all excited states (covalent and noncovalent), as well as for the ground state. A complete configuration calculation for the π systems of butadiene, hexatriene, and benzene within the PPP approximation leads to satisfactory agreement with the observed energy levels and points to the importance of unobserved levels. Since some of the latter may well be of great interest for the dynamics of polyenes (photoisomerization, absorption and emission properties), it would be very useful to have more experiments confirming the present results, as well as additional calculations (particularly large scale *a priori* calculations) to validate and refine the Pariser-Parr-Pople Hamiltonian.

TABLE IV. Polyene bond orders.^a

| (a) Butadiene | | | | | | | |
|-----------------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------|
| $P_{\kappa,\kappa+1}$ | ${}^1A_g^-$ | ${}^3B_u^-$ | ${}^3A_g^+$ | ${}^1A_g^-$ | ${}^1B_u^-$ | ${}^1A_g^+$ | |
| 1-2 | 0.903 | 0.425 | 0.491 | 0.153 | 0.497 | 0.446 | |
| 2-3 | 0.319 | 0.693 | 0.096 | 0.642 | 0.547 | 0.225 | |
| (b) Hexatriene | | | | | | | |
| $P_{\kappa,\kappa+1}$ | 1A_g | 3B_u | 3A_g | 1A_g | 3B_u | 1B_u | 1A_g |
| 1-2 | 0.900 | 0.665 | 0.508 | 0.419 | 0.689 | 0.696 | 0.553 |
| 2-3 | 0.336 | 0.612 | 0.365 | 0.628 | 0.180 | 0.526 | 0.339 |
| 3-4 | 0.849 | 0.376 | 0.797 | 0.364 | 0.520 | 0.488 | 0.767 |
| (c) Octatetraene | | | | | | | |
| $P_{\kappa,\kappa+1}$ | 1A_g | 3B_u | 3A_g | 1A_g | 3B_u | | |
| 1-2 | 0.902 | 0.783 | 0.625 | 0.636 | 0.615 | | |
| 2-3 | 0.336 | 0.514 | 0.494 | 0.566 | 0.253 | | |
| 3-4 | 0.846 | 0.499 | 0.711 | 0.412 | 0.751 | | |
| 4-5 | 0.353 | 0.659 | 0.278 | 0.631 | 0.417 | | |
| | 1B_u | 1B_u | 1A_g | 1A_g | | | |
| 1-2 | 0.786 | 0.537 | 0.700 | 0.683 | | | |
| 2-3 | 0.485 | 0.489 | 0.401 | 0.387 | | | |
| 3-4 | 0.582 | 0.483 | 0.360 | 0.721 | | | |
| 4-5 | 0.557 | 0.589 | 0.480 | 0.355 | | | |
| (d) Decapentaene | | | | | | | |
| $P_{\kappa,\kappa+1}$ | 1A_g | 3B_u | 3A_g | 1A_g | 3B_u | | |
| 1-2 | 0.905 | 0.846 | 0.717 | 0.761 | 0.658 | | |
| 2-3 | 0.335 | 0.448 | 0.506 | 0.496 | 0.378 | | |
| 3-4 | 0.848 | 0.612 | 0.636 | 0.493 | 0.815 | | |
| 4-5 | 0.355 | 0.609 | 0.371 | 0.615 | 0.342 | | |
| 5-6 | 0.841 | 0.508 | 0.820 | 0.470 | 0.645 | | |
| | 1B_u | 1B_u | 3A_g | 3B_u | 3B_u | | |
| 1-2 | 0.836 | 0.641 | 0.696 | 0.673 | 0.835 | | |
| 2-3 | 0.449 | 0.499 | 0.227 | 0.508 | 0.261 | | |
| 3-4 | 0.657 | 0.615 | 0.713 | 0.495 | 0.682 | | |
| 4-5 | 0.543 | 0.539 | 0.364 | 0.471 | 0.241 | | |
| 5-6 | 0.596 | 0.403 | 0.821 | 0.601 | 0.648 | | |
| | 1A_g | 3A_g | 1B_u | 1A_g | 1A_g | | |
| 1-2 | 0.636 | 0.768 | 0.772 | 0.756 | 0.522 | | |
| 2-3 | 0.401 | 0.494 | 0.390 | 0.409 | 0.493 | | |
| 3-4 | 0.514 | 0.592 | 0.511 | 0.696 | 0.585 | | |
| 4-5 | 0.501 | 0.517 | 0.424 | 0.378 | 0.370 | | |
| 5-6 | 0.670 | 0.592 | 0.444 | 0.797 | 0.694 | | |
| (e) Dodecahexaene | | | | | | | |
| $P_{\kappa,\kappa+1}$ | 1A_g | 1A_g | 1B_u | 1B_u | 1A_g | 1A_g | 1B_u |
| 1-2 | 0.907 | 0.833 | 0.867 | 0.728 | 0.684 | 0.801 | 0.637 |
| 2-3 | 0.335 | 0.441 | 0.421 | 0.483 | 0.425 | 0.416 | 0.405 |
| 3-4 | 0.850 | 0.591 | 0.713 | 0.626 | 0.671 | 0.699 | 0.530 |
| 4-5 | 0.355 | 0.577 | 0.516 | 0.507 | 0.495 | 0.401 | 0.432 |
| 5-6 | 0.842 | 0.506 | 0.633 | 0.541 | 0.568 | 0.785 | 0.707 |
| 6-7 | 0.359 | 0.612 | 0.550 | 0.562 | 0.442 | 0.382 | 0.453 |

^aValues obtained for the indicated states by a calculation including single and double excitations with $\beta_0 = -2.60$ eV and the Ohno repulsion.

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APPENDIX A: STABILITY OF THE SCF GROUND STATE AS A FUNCTION OF THE ELECTRON-ELECTRON INTERACTION

In the ground state ψ_0 in Eq. (6) and its variation ψ'_0 in Eq. (8), electrons with different spins are restricted to move pairwise in identical spatial orbitals. This restriction is relaxed in the following discussion, where we admit variations of the ground-state orbitals in accord with Eq. (7) which can introduce different spatial orbitals for different spins. Such an unrestricted ground state can be written

$$\psi'_0 = \exp\left(\sum_{\substack{m>N \\ i \leq N \\ \sigma, \sigma'}} \eta_{m\sigma', i\sigma} a_{m\sigma'}^+ a_{i\sigma}\right) \psi_0, \quad (A1)$$

which is to be compared with the restricted variation shown in Eq. (8). On going from ψ_0 to ψ'_0 , the ground-state energy expectation value is changed. To second order in the mixing coefficients $\eta_{m\sigma', i\sigma}$ this change [Eq. (11)] is

$$\frac{1}{2} \left(\frac{\eta}{\bar{\eta}} \right)^* \begin{pmatrix} A & B \\ \bar{B} & \bar{A} \end{pmatrix} \begin{pmatrix} \eta \\ \eta \end{pmatrix}, \quad (A2)$$

where η stands for the column vector of coefficients $\eta_{m\sigma', i\sigma}$, \bar{X} stands for the complex conjugate of X , and X^* for the Hermitian conjugate. The elements of the matrices A and B are

$$A_{m_1\sigma_1', i_1\sigma_1; m_2\sigma_2', i_2\sigma_2} = \langle \psi_0 | a_{i_1\sigma_1}^+ a_{m_1\sigma_1} H a_{m_2\sigma_2}^+ a_{i_2\sigma_2} - H | \psi_0 \rangle,$$

$$B_{m_1\sigma_1', i_1\sigma_1; m_2\sigma_2', i_2\sigma_2} = \langle \psi_0 | H a_{m_1\sigma_1}^+ a_{i_1\sigma_1} a_{m_2\sigma_2}^+ a_{i_2\sigma_2} | \psi_0 \rangle.$$

If one uses real orbitals, the matrices A and B in (B2) are real and symmetric and the quadratic form (B2) is Hermitian. The condition that a variation of the ground-state wavefunction ψ_0 leads to an energy increase (i. e., that $\langle \psi_0 | H | \psi_0 \rangle$ is a minimum) is clearly that (B2) is positive for all variations η . This requires that the stability matrix

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}$$

be positive definite: i. e., all of its eigenvalues must be nonnegative. Hence, a diagonalization of the stability matrix determines unequivocally if the SCF ground state corresponds to a (local) energy minimum.

In Figs. A.1(a) and A.1(b) we present the lowest eigenvalue of the stability matrix for polyenes assuming various parameterizations of the PPP Hamiltonian [Eq. (1)]. Fig. A.1(a) shows for butadiene and hexatriene the dependence of the ground-state stability on the spatial decay of the Coulomb interaction. One observes that the SCF ground state is stable for the long-range repulsion [i. e., to a large decay constant D_0 in the potential formula Eq. (3c)]. However, for short-range electron-electron repulsion ($D_0 \lesssim 3.5$ Å), the SCF ground state is unstable. This instability, which is of the "triplet" type, arises from the possibility of spin-orbital

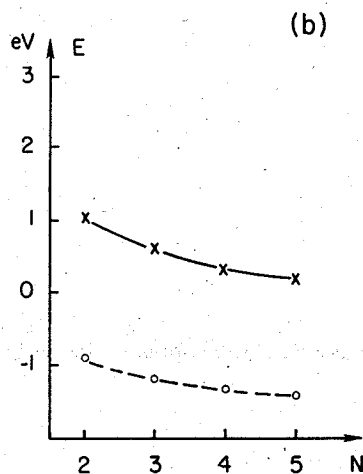
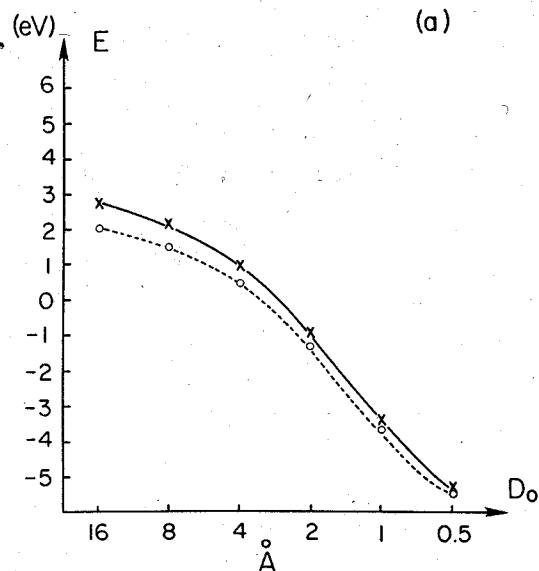


FIG. A. 1. Lowest eigenvalue of stability matrix: (a) as a function of exponential repulsion parameter D_0 ; $\beta_0 = -2.43$ eV; (0...0), Hexatriene; (x-x), butadiene. (b) as a function of the number of double bonds in the polyene $C_{2N}H_{2N+2}$; $\beta_0 = -2.60$ eV; (x-x), Ohno parameterization; (o---o), Mataga-Nishimoto parameterization.

variations that carry the spin-restricted SCF ground state over to a spin-unrestricted SCF ground state. Figure A.1(b) presents the lowest eigenvalue of the stability matrix for the polyenes butadiene to decapentaene, for the Ohno and Mataga-Nishimoto potentials given by Eqs. (3a) and (3b). For the Ohno potential, the ground state is stable for all polyenes, but in case of the Mataga-Nishimoto potential [Eq. (3b)], the restricted SCF ground state is unstable. This instability is again of the triplet type and leads to a function with different spatial orbitals for different spins. Thus, for the Mataga-Nishimoto potential, an unrestricted SCF ground state below the conventional SCF ground state can be found.

APPENDIX B: SPIN COUPLED SINGLE AND DOUBLE EXCITATIONS

The spin coupling for particle-hole excitations $O_{i\sigma}^{m\sigma}$ = $a_{m\sigma}^+ a_{i\sigma}$ is carried out algebraically by the use of the

expression⁵⁵

$$\sum_{\sigma, \sigma'} (-1)^{1/2-\sigma'} \left(\frac{1}{2} \sigma \frac{1}{2} - \sigma' \right) |SM_S\rangle O_{i\sigma'}^{m\sigma} \psi_0, \quad (B1)$$

where ψ_0 is the closed-shell SCF ground state and $(\frac{1}{2}\sigma\frac{1}{2} - \sigma'SM_S)$ stands for the Clebsch-Gordan coefficients coupling the particle spin $(\frac{1}{2}, \sigma)$ and the hole spin $(\frac{1}{2}, -\sigma')$ to the total spin (S, M_S) . In the following, we disregard total spin states with nonvanishing magnetic quantum number M_S , since they are not required in the present calculations. By use of Eq. (B1), the particle-hole excitations can be coupled to a singlet state ${}^0O_i^m \psi_0$ and a triplet state ${}^1O_i^m \psi_0$, the corresponding excitation operators are

$$i^0 O_i^m = 2^{-1/2} (O_{i\uparrow}^{m\uparrow} \mp O_{i\downarrow}^{m\uparrow}). \quad (B2)$$

For the double excitations, $mn - ij$, there are three possibilities to be considered:

- Particles as well as holes are located in the same spatial orbital ($m^2 - i^2$);
- Either particles or holes are located in the same spatial orbital ($mn - i^2, m^2 - ij$);
- Neither particles nor holes are located in the same spatial orbital ($mn - ij$).

The excitations in (a) are necessarily of a singlet character and have the form

$${}^0O_{ii}^{mm} = O_{i\uparrow}^{m\uparrow} O_{i\downarrow}^{m\downarrow}. \quad (B3)$$

The excitation in (b) can have singlet or triplet character,

$$i^0 O_{ij}^{mm} = 2^{-1/2} a_{m\uparrow}^+ a_{m\downarrow}^+ (a_i a_j \mp a_i a_j), \quad (B4)$$

$$i^1 O_{ii}^{mn} = 2^{-1/2} (a_{m\uparrow}^+ a_{n\uparrow}^+ \mp a_{m\downarrow}^+ a_{n\downarrow}^+) a_i a_{i\downarrow}. \quad (B5)$$

The excitations in (c) play a dominant role for the description of some excited states of conjugate molecules. (See also Ref. 16.) There are six possible excitations distinguished by their spin configurations: two singlet states, three triplet states, and a quintet state. The spin coupling is most easily performed in two steps. First, the four particle and hole spins are coupled in pairs to two intermediate spin states S_0 (singlet) and T_{-1}, T_0, T_1 (triplet) by means of Eq. (B1). Six intermediate spin configurations are possible: (I) S_0, S_0 ; (II) S_0, T_0 ; (III) T_0, S_0 ; (IV) T_0, T_0 ; (V) T_1, T_{-1} ; (VI) T_{-1}, T_1 . In the second step, these intermediate spin configurations are coupled to total spin states. In constructing the intermediate spin configurations, one can either couple the particle spins and the hole spins separately, or couple particle-hole spin pairs together. The particle-hole spin coupling scheme is used here to be able to describe most simply the simultaneous triplet excitations which are important for the correlation correction in the conjugated molecules. The intermediate spin configurations (I)-(IV) can be written

$$O_{I, II, III, IV} = \frac{1}{2} O_{i\uparrow}^{m\uparrow} O_{j\uparrow}^{n\uparrow} \pm O_{i\uparrow}^{m\uparrow} O_{j\downarrow}^{n\uparrow} \pm O_{i\downarrow}^{m\uparrow} O_{j\uparrow}^{n\uparrow} \pm O_{i\downarrow}^{m\uparrow} O_{j\downarrow}^{n\uparrow}, \quad (B6)$$

and (V) and (VI) are

$$O_V = O_{i\uparrow}^{m\uparrow} O_{j\downarrow}^{n\uparrow}, \quad (B7)$$

and

$$O_{VI} = O_{i_i}^{m_i} O_{j_i}^{n_i}, \quad (B8)$$

respectively.

From Eqs. (B6)–(B8), the total-spin excitation operators can be constructed. O_I is a total singlet excitation, and O_{II} and O_{III} are total triplet excitations. The excitations O_{IV} , O_V , and O_{VI} can be combined to form a singlet (${}^{00}\hat{O}_{ij}^{mn}$), a triplet (${}^{10}\hat{O}_{ij}^{mn}$), and a quintet (${}^{20}\hat{O}_{ij}^{mn}$) state; they are

$${}^{00}\hat{O}_{ij}^{mn} = 3^{-1/2}(O_{IV} + O_V + O_{VI}),$$

$${}^{10}\hat{O}_{ij}^{mn} = 2^{-1/2}(O_V - O_{VI}),$$

$${}^{20}\hat{O}_{ij}^{mn} = 6^{-1/2}(2O_{IV} - O_V - O_{VI}).$$

APPENDIX C: COMPLETE CI CALCULATION

The complete configuration-interaction calculations were carried out by use of a valence-bond formulation. This is a convenient way to proceed in the present case because the atomic orbitals are orthogonal and the matrix elements of the PPP Hamiltonian take a very simple form (see below). In this method, the wavefunction is expanded as a linear combination of Slater determinants constructed from atomic orbitals which satisfy the zero-differential overlap condition; for example, the wavefunction for butadiene with $S_z = 0$ can be written

$$|\psi\rangle = \sum_{\lambda\kappa\nu\mu} A_{\lambda\kappa\nu\mu} c_{\lambda}^* c_{\kappa}^* c_{\nu}^* c_{\mu}^* |0\rangle, \quad (C1)$$

where $A_{\lambda\kappa\nu\mu}$ is the expansion coefficient to be determined by minimizing the expectation value of the PPP Hamiltonian [Eq. (1)], $c_{\lambda\sigma}^*$ is the π -electron creation operator for atomic orbital λ with spin σ , and $|0\rangle$ is a π -electron vacuum state. It is to be noted that $\lambda \neq \kappa$ and $\nu \neq \mu$ by the Pauli exclusion principle; however, either λ or κ can be equal to either ν or μ . In general, for a system with $2N$ electrons and $2N$ atomic orbitals the total number of Slater determinants with total $S_z = 0$ is equal to

$$\left(\frac{(2N)!}{N!N!}\right)^2;$$

since there are $2N$ atomic orbitals to which N π electrons with spin $+\frac{1}{2}$ and N π -electrons with spin $-\frac{1}{2}$ are assigned. For the π electrons of butadiene, there are thus 36 determinants.

For a pair of Slater determinants over atomic orbitals, only the core integral term ($\sum_{\kappa\pm\lambda} t_{\kappa\lambda} c_{\kappa\sigma}^* c_{\lambda\sigma}$) of the PPP Hamiltonian has off-diagonal matrix elements. All other terms, including the two-particle operator, are diagonal. Thus, construction of the Hamiltonian matrix for a basis set composed of Slater determinants over atomic orbitals is very simple.

The above result is to be contrasted with that for determinants constructed from molecular orbitals. The creation operator $a_{i\sigma}^*$ of molecular orbital i with spin σ can be expanded in terms of the creation operator for atomic spin orbitals,

$$a_{i\sigma}^* = \sum_{\lambda} (D)_{i\lambda}^* c_{\lambda\sigma}^*,$$

inversely,

$$c_{\lambda\sigma}^* = \sum_i (B)_{\lambda i}^* a_{i\sigma}^*, \quad (C2)$$

where $\mathbf{B} = (\mathbf{D})^{-1}$ since the atomic and molecular orbitals are both orthogonal. Similarly, for the annihilation operator $a_{i\sigma}$, the result is

$$c_{\lambda\sigma} = \sum_i (B)_{\lambda i} a_{i\sigma}. \quad (C3)$$

Using Eqs. (C2) and (C3) to transform the PPP Hamiltonian, Eq. (1), which is given in terms of an atomic orbital basis to a molecular-orbital representation, we find

$$H = \sum_{\kappa\lambda} Z_{\kappa} Z_{\lambda} R_{\kappa\lambda} + \sum_{i,j,\sigma} \left[\sum_{\kappa} (-I_{\kappa} - \sum_{\lambda \neq \kappa} Z_{\lambda} R_{\kappa\lambda}) (B)_{\kappa i}^* (B)_{\kappa j} \right] a_{i\sigma}^* a_{j\sigma} + \sum_{i,j,\sigma} \left[\sum_{\kappa \neq \lambda} t_{\kappa\lambda} (B)_{\kappa i}^* (B)_{\lambda j} \right] a_{i\sigma}^* a_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l \\ \sigma_i \sigma_j}} \left[\sum_{\kappa\lambda} R_{\kappa\lambda} B_{\kappa i}^* B_{\lambda j}^* B_{\kappa k} B_{\lambda l} \right] a_{i\sigma}^* a_{j\sigma}^* a_{k\sigma} a_{l\sigma}. \quad (C4)$$

It is clear that all the terms (except the first constant term) in Eq. (C4) have off-diagonal matrix elements. The two-particle operator [the fourth term in Eq. (C4)] has four indices, which makes an evaluation of CI matrix elements much more difficult than in an atomic orbital expansion [Eq. (C1)].

In the valence-bond formulation, different orders of approximation can be defined in terms of the ionic determinants included. For example, the "restricted valence-bond" approximation described in the test includes all covalent and singly ionic adjacent structures.³² There are six covalent and 12 single ionic adjacent determinants for butadiene; an example of a covalent determinant is

$$c_1^* c_2^* c_3^* c_4^* |0\rangle,$$

and a single ionic adjacent determinant is

$$c_1^* c_2^* c_2^* c_4^* |0\rangle.$$

In general, a $2N$ atomic orbital, $2N$ -electron system (with $S_z = 0$) has $(2N)!/(N!)^2$ covalent determinants and $(2N)!/[n!(N-n)!]^2$ n th ionic determinants; the total number of determinants is, in agreement with the result given above,

$$\sum_{n=0}^N \frac{(2N)!}{[n!(N-n)!]^2} = \left[\frac{(2N)!}{(N!)^2} \right]^2.$$

A further simplification in the calculation is that off-diagonal elements of the core integral in the PPP Hamiltonian can exist only between determinants with the same degree of ionic terms or those having one more

or one less ionic terms; e.g., a single ionic structure can couple only with single ionic determinants, with covalent determinants, or with double ionic determinants.

The dimension of the Hamiltonian matrix can be reduced by introducing space and spin symmetry in the usual way. Spatial symmetry can easily be imposed; e.g., linear combinations of the form

$$\Phi_{\pm} = [c_1^{\pm}, c_2^{\pm}, c_3^{\pm}, c_4^{\pm}, \pm c_1^{\pm}, \pm c_2^{\pm}, \pm c_3^{\pm}, \pm c_4^{\pm}] | 0 \rangle$$

have A_g symmetry (+) and B_u symmetry (-), respectively. Spin eigenstates are obtained in the same way as in the molecular orbital methods (see Appendix B). There are two singlet covalent structures (with ${}^1A_g^+$) for butadiene and five singlet covalent structures (four with 1A_g and one with 1B_u) for hexatriene. Inclusion of all ionic determinants for butadiene yields 12 1A_g , eight 1B_u , seven 3A_g , and eight 3B_u , and for hexatriene, 92 1A_g , 83 1B_u , 90 3A_g , and 99 3B_u . The computing time required for a complete calculation of all hexatriene singlet and triplet states of a given spatial symmetry is less than 20 sec on the IBM 360-91 computer.

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