

Renormalized configuration interaction method for electron correlation in the excited states of polyenes^{a)}

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Extensive configuration interaction (CI) is needed to achieve satisfactory descriptions of the optical spectra and photochemical properties of the π -electron systems of polyenes. Although a basis of single and double excitations with respect to the SCF ground state yields a qualitatively correct energy level scheme, such a treatment introduces an imbalance in the ground state correlation (well described) relative to that of the excited states (poorly described). The result is a divergence in the excitation energies with increasing size of the π -electron system. A *renormalized configuration interaction* method is developed to account correctly for the excited state correlation. The method is based on the finding that the main contribution to the correlation energy in the excited states is from the electrons not directly involved in the excitation, so that the correlation correction closely resembles that in the ground state. A detailed analysis of the excited state energy permits one to isolate the dominant ground-state correlation term and to determine the smaller, but not negligible, rearrangement correction. The former does not contribute to the excitation energy. The fact that the latter is approximately constant, independent of chain length, provides an explanation for the success achieved by appropriately parametrized single excitation calculations in the assignment of the optically allowed states of polyenes. To implement the renormalized CI method a localized SCF orbital set is employed and the basis functions used for the CI expansion are expressed in terms of single and double excitations with respect to the *correlated* ground state. It is demonstrated that for the ${}^1B_u^+$, ${}^3B_u^+$, and ${}^3A_g^+$ states, which can be characterized in terms of "elementary" single excitations, this approach gives excellent agreement with the results of more extended CI calculations. Further, it is shown that the correlation energy of the excited state can be estimated using the results of a single-excitation calculation and the ground-state double excitation coefficients.

I. INTRODUCTION

For a satisfactory understanding of the optical spectra and the photochemical reactions of polyenes, a detailed knowledge of their electronic states is necessary. Stimulated by recent experimental¹ and theoretical studies² that have demonstrated the inadequacy of the independent particle model, we have examined the magnitude of correlation effects on the π -electron spectrum³; a semi-empirical Hamiltonian of Pariser-Parr-Pople type was employed. For butadiene and hexatriene, a complete configuration interaction calculation [C] was performed. For longer polyenes, a more limited basis consisting of single [S] and double [D] excitations was used. It was found that configuration interaction with single excited configurations does not yield the correct spectrum. Although the "ionic" singlet states (e.g., ${}^1B_u^+$, ${}^1A_g^+$, ...) and the triplet states (e.g., ${}^3B_u^+$, ${}^3A_g^+$, ...) are reasonably well described by such calculations, the "covalent" singlet states (e.g., ${}^1A_g^-$, ${}^1B_u^-$, ...) are not; in particular, the lowest excited ${}^1A_g^-$ state, which is now known to be near-degenerate with the lowest ${}^1B_u^+$ state, is calculated to be much too high in energy. Introduction of double excitations provide qualitatively correct results in that the manifolds of ionic and covalent states have approxi-

mately correct relative positions. However, on a quantitative level the [S+D] calculation yields excitation energies that are significantly in error. More important, the dependence of the excitation energy on chain length is not correct for the longer polyenes due to the difference in the correlation error in an [S+D] calculation for the ground and excited states; e.g., the calculated excitation energy of the lowest ${}^1B_u^+$ state does not decrease monotonically to a limiting asymptotic value. The deficiencies of the [S+D] calculation could be overcome by including higher order (triple, quadruple, ...) excitations in the CI treatment. However, the required number of configurations becomes so large that the computations are too time consuming.

It is the purpose of this paper to analyze the correlation correction due to the higher order excitations and to develop a simplified method for their estimation. The σ electrons are assumed to be fixed and a Pariser-Parr-Pople Hamiltonian is used to represent the π electron system. The advantages and limitations of a semi-empirical treatment of this type have been discussed previously by us³ and will not be repeated here; some recent related *ab initio* results are given in Ref. 4. A localized SCF orbital basis⁵ is used for the π electrons. In this basis, the SCF orbitals are transformed to localize them as completely as possible in individual ethylenic units. This makes it possible to utilize effectively the spatial decay of the Coulomb and exchange interactions.⁶ Due to the spatial separation of excita-

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tions in the localized orbital description, the higher order excitations can be regarded approximately as a product of lower order excitations; e.g., a triple excitation can be decomposed into a single and a double excitation.⁷ Making use of this decomposition, it is possible to show that the most important correlation contributions to the excited states are the same as those present in the ground state. Correction terms, which are less important but not negligible, arise from the effects of the Pauli exclusion principle, the coupling between localized excitations and certain normalization factors that have to be included.

A configuration interaction method which has the same matrix dimension as the standard [S] or [S+D]-CI calculation but includes the higher order corrections in an approximate manner is developed. In this method, excitation configurations are generated relative to the correlated ground state rather than to the Hartree-Fock ground state. Only single excitations relative to the correlated ground state are included in the present work. This makes possible an accurate treatment of the triplet and the ionic singlet states. However, the covalent singlet states can not be calculated because they require double excitations relative to the correlated ground state.^{2,3} Hence only $1^3B_u^+$, $1^3A_g^+$, and $1^1B_u^+$ states are properly described, while the $2^1A_g^+$ and $2^1B_u^+$ states require an extension of the method.

The application of localized orbitals to polyenes has a long history. Contributions in this area have been made by Longuet-Higgins and Murrell,⁸ Simpson,⁹ Pople and Walmsley,¹⁰ Heilbronner,¹¹ and others.¹² Most of this work involved use of a simple excitonic model for approximating the lowest allowed states of polyenes and did not take into account ground-state correlation. Closest in spirit to the present study is the work of Malrieu and co-workers,¹³ who used a completely localized ethylenic basis (i.e., non-SCF) to analyze the effects of higher order excitations on excited state energies and to demonstrate the cancellation between the correlation in the excited states and that in the ground state. Also related are random phase approximation¹⁴⁻¹⁸ and Green's function¹⁹⁻²³ calculations for excited states. In both of these approaches, the excitations are relative to the exact ground state, in principle, though in practice an approximate ground state (often the SCF function) is used.

The Pariser-Parr-Pople Hamiltonian is described briefly in Sec. II. In Sec. III, the localized orbitals used for the ground and excited states are introduced. Effects of higher order excitations on the ground-state correlation energy are discussed. In Sec. IV we examined the correlation correction to the excited states introduced by the higher order excitations. An approximate CI method is developed to include the ground-state correlation in the excited states. The fundamental assumptions of the method are analyzed. The results obtained by the method are given in Sec. V. They demonstrate the approximate constancy, independent of chain length, of the correlation correction to the excitation energy. Conclusions are presented in Sec. VI.

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)

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

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 centers 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

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

where β_0 is a constant and $\gamma_{\kappa\lambda}$ is the distance between the nuclear sites κ and λ . The fourth term in H [the prime on the sum indicates that it excludes all terms $(\kappa, \sigma) = (\lambda, \sigma')$] describes the Coulomb repulsion of the π electrons. Two standard electron-electron repulsion formulas were used; they are the Ohno formula

$$R_{\kappa\lambda} = \frac{14.397}{\left\{ \left[2(14.397)/(R_{\kappa\kappa} + R_{\lambda\lambda}) \right]^2 + \gamma_{\kappa\lambda}^2 \right\}^{1/2}} \quad (3a)$$

and the Mataga-Nishimoto formula,

$$R_{\kappa\lambda} = \frac{14.397}{2(14.397)/(R_{\kappa\kappa} + R_{\lambda\lambda}) + \gamma_{\kappa\lambda}} \quad (3b)$$

The Mataga-Nishimoto formula introduces more correlation than the Ohno formula.³ In addition to these, an exponentially decaying repulsive potential of the form

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

was employed for testing the validity of the CI method developed in the present work. Variation of the decay constant D_0 simulates in a simple way the transition from the independent particle limit (D_0 large, long-range potential) to the limit of strong electron correlation (D_0 small, short-range potential)³; a range of values for D_0 between 0.5 and 16 Å was used. The values of the

TABLE I. Semiempirical parameters for conjugated hydrocarbons.

$I_{\kappa} =$	11.16 eV
$Z_{\kappa} =$	1.0
$\beta_0 =$	-2.43 eV
$R_{\kappa\kappa} =$	11.13 eV
$r_{\kappa\kappa 1} =$	1.35 Å (double bonds)
	1.46 Å (single bonds)

empirical parameters I_{κ} , Z_{κ} , β_0 , and $R_{\kappa\kappa}$ which enter into the PPP Hamiltonian are presented in Table I.

III. LOCALIZED ORBITAL DESCRIPTION

In this section, we introduce the localized orbital basis (LO) and illustrate its form by applying it to butadiene and decapentaene. Restricting the CI calculation to single and double excitations, we determine the length dependence of the correlation error for the ground and excited states. A simplified model is used to show analytically how higher excitations contribute to the ground-state correction correlation.

A. Localized orbitals

For polyenes with $2N$ π electrons a set of completely localized orbitals corresponds to the N occupied orbitals e_i and N unoccupied orbitals $e_{\bar{i}}$ of the ethylene units of which the polyenes are composed; they have the form

$$e_i = (1/\sqrt{2})(p_{2i-1} + p_{2i}) \quad i=1, 2, \dots, N, \quad (4)$$

$$e_{\bar{i}} = (1/\sqrt{2})(p_{2i-1} - p_{2i})$$

where the p_i are the atomic π orbitals introduced in Sec. II. The bar under the index i denotes an unoccupied orbital; this notation will be used throughout the section. Although the orbitals in Eq. (4) form a complete orthogonal set, it is convenient to replace them by localized SCF orbitals.

As is well known, the SCF orbitals can be specified by requiring that the Fock matrix has only zero elements between occupied and unoccupied orbitals; i. e., that it is block diagonal. This condition does not, however, provide a unique definition of the SCF orbitals. One applies customarily the more stringent condition that the SCF orbitals must diagonalize the Hartree-Fock matrix. If this restriction is relaxed, an infinite number of orthonormal orbital sets ($\omega_i, \omega_{\bar{i}}; i=1, 2, \dots, N$) can be defined; the symbols ω_i stand for the occupied and $\omega_{\bar{i}}$ for the unoccupied orbitals. These sets are connected with the standard Hartree-Fock orbitals by the unitary transformation $U = \begin{pmatrix} U & 0 \\ 0 & \bar{U} \end{pmatrix}$, where U and \bar{U} are unitary matrices acting on the occupied (ϕ_i) and the unoccupied ($\phi_{\bar{i}}$) Hartree-Fock orbitals, respectively. Thus,

$$\omega_i = \sum_{j=1}^N U_{ij} \phi_j, \quad (5)$$

$$\omega_{\bar{i}} = \sum_{j=1}^N \bar{U}_{ij} \phi_{\bar{j}}.$$

The corresponding transformations among the creation and annihilation operators b_i, b_i^* and $b_{\bar{i}}, b_{\bar{i}}^*$ for the ω

and $\bar{\omega}$ orbitals and the operators a_i, a_i^* , and $a_{\bar{i}}, a_{\bar{i}}^*$ for the SCF orbitals are

$$b_i = \sum_{j=1}^N U_{ij} a_j; \quad b_i^* = \sum_{j=1}^N U_{ij}^* a_j^*; \quad (6)$$

$$b_{\bar{i}} = \sum_{j=1}^N \bar{U}_{ij} a_j; \quad b_{\bar{i}}^* = \sum_{j=1}^N \bar{U}_{ij}^* a_j^*.$$

The ground state ψ_0 expressed in terms of the orbitals ω_i is

$$\psi_0 = |\omega_1 \bar{\omega}_1 \dots \omega_N \bar{\omega}_N\rangle = (\det U)^2 |\phi_1 \bar{\phi}_1 \dots \phi_N \bar{\phi}_N\rangle,$$

where the usual notation of a bar superscript on the orbitals indicates a spin of $-\frac{1}{2}$. Correspondingly, the excited electron configurations over the orbitals ω_i and $\omega_{\bar{i}}$ are

$$b_i^* b_j \psi_0 = \sum_{k_1} \bar{U}_{ik_1}^* U_{j k_1} a_{k_1}^* a_{k_1} \psi_0, \quad (7)$$

$$b_{\bar{i}}^* b_j b_{\bar{k}}^* b_l \psi_0 = \sum_{m_1 m_2} \bar{U}_{im_1}^* U_{jm} U_{ln} \bar{U}_{k_2}^* U_{l m} a_{m_1}^* a_{m_2}^* a_{m_1} a_{m_2} \psi_0.$$

It is clear that the single excitations with respect to ω orbitals are linear combinations of the single excitations over SCF orbitals, the double excitations with respect to ω orbitals are linear combinations of the double excitations over SCF orbitals, etc. This shows that a complete CI calculation with the ω orbital basis of a given type (i. e., all single excitations, all double excitations, etc.) must give results for molecular properties identical to those obtained from a corresponding calculation with SCF orbitals.

To obtain localized SCF orbitals, we wish to determine orbitals ω_i and $\omega_{\bar{i}}$ that have maximum overlap with the ethylene orbitals e_i and $e_{\bar{i}}$ of Eq. (4). For this purpose we define the projection operators P and Q onto the subspaces V and \bar{V} of the occupied and unoccupied SCF orbitals ϕ_i and $\phi_{\bar{i}}$,

$$P = \sum_{j=1}^N |\phi_j\rangle \langle \phi_j|, \quad (8)$$

$$Q = \sum_{\bar{j}=1}^N |\phi_{\bar{j}}\rangle \langle \phi_{\bar{j}}|,$$

$$P + Q = 1, \quad P^2 = P, \quad Q^2 = Q.$$

The set of projected orbitals

$$(P|e_i\rangle = \sum_{j=1}^N |\phi_j\rangle \langle \phi_j|e_i\rangle)$$

and

$$(Q|e_{\bar{i}}\rangle = \sum_{\bar{j}=1}^N |\phi_{\bar{j}}\rangle \langle \phi_{\bar{j}}|e_{\bar{i}}\rangle)$$

form nonorthogonal basis sets in V and \bar{V} , respectively. The $P|e_i\rangle$ and $Q|e_{\bar{i}}\rangle$ are linearly independent for all i, \bar{i} so that the overlap matrices with elements (S, \bar{S} are real and symmetric)

$$S_{ij} = \langle e_i | P | e_j \rangle, \quad (9)$$

$$\bar{S}_{\bar{i}\bar{j}} = \langle e_{\bar{i}} | Q | e_{\bar{j}} \rangle$$

TABLE II. Localized orbital coefficients $B_{i\kappa}$ for decapentane.^a

	A	B	C	A	B	C	A	B	C
Occupied orbitals ^b									
	ω_1			ω_2			ω_3		
p_1	0.707	0.698	0.696	0.0	-0.105	-0.116	0.0	0.038	0.046
p_2	0.707	0.698	0.696	0.0	0.111	0.123	0.0	-0.022	-0.028
p_3	0.0	0.111	0.123	0.707	0.689	0.685	0.0	-0.106	-0.115
p_4	0.0	-0.105	-0.116	0.707	0.689	0.685	0.0	0.116	0.130
p_5	0.0	-0.022	-0.028	0.0	0.116	0.130	0.707	0.688	0.683
p_6	0.0	0.038	0.046	0.0	-0.106	-0.115	0.707	0.688	0.683
p_7	0.0	0.007	0.010	0.0	-0.024	-0.031	0.0	0.116	0.130
p_8	0.0	-0.016	-0.022	0.0	0.038	0.047	0.0	-0.106	-0.115
p_9	0.0	-0.003	-0.004	0.0	0.007	0.010	0.0	-0.022	-0.028
p_{10}	0.0	0.007	0.011	0.0	-0.016	-0.022	0.0	0.038	0.046
Unoccupied orbitals ^b									
	ω_1			ω_2			ω_3		
p_1	0.707	0.698	0.696	0.0	-0.105	-0.116	0.0	0.038	0.046
p_2	-0.707	-0.698	-0.696	0.0	-0.111	-0.123	0.0	0.022	0.028
p_3	0.0	0.111	0.123	0.707	0.689	0.685	0.0	-0.106	-0.115
p_4	0.0	0.105	0.116	-0.707	-0.689	-0.685	0.0	-0.116	-0.130
p_5	0.0	-0.022	-0.028	0.0	0.116	0.130	0.707	0.688	0.683
p_6	0.0	-0.038	-0.046	0.0	0.106	0.115	-0.707	-0.688	-0.683
p_7	0.0	0.007	0.010	0.0	-0.024	-0.031	0.0	0.116	0.130
p_8	0.0	0.016	0.022	0.0	-0.038	-0.047	0.0	0.106	0.115
p_9	0.0	-0.003	-0.004	0.0	0.007	0.010	0.0	-0.022	-0.028
p_{10}	0.0	-0.007	-0.011	0.0	0.016	0.022	0.0	-0.038	-0.046

^aA, ethylene orbitals; B, localized SCF orbitals (Ohno parametrization); C, localized SCF orbitals (Mataga-Nishimoto parametrization).

^b $\omega_i = \sum_{\kappa} B_{i\kappa} p_{\kappa}$ (occupied).

^c $\omega_i = \sum_{\kappa} B_{i\kappa} p_{\kappa}$ (unoccupied).

are positive definite. Using the Löwdin symmetric orthogonalization,²⁴ we obtain the orthonormal basis sets

$$\sum_j S_{ij}^{-1/2} P |e_j\rangle, \quad \sum_j S_{ij}^{-1/2} Q |e_j\rangle.$$

We now wish to show that these orbitals are the SCF orbitals that have maximum overlap with the e_i , e_i . Writing

$$|\omega_i\rangle = \sum_{j,k} U'_{ij} S_{jk}^{-1/2} P |e_k\rangle, \quad |\omega_i\rangle = \sum_{j,k} \underline{U}'_{ij} S_{jk}^{-1/2} Q |e_k\rangle, \quad (10)$$

where U' and \underline{U}' are arbitrary unitary transformations, we demonstrate that the distance between ω_i and e_i and that between ω_i and e_i ,

$$d^2 = \sum_{i=1}^N \langle \omega_i - e_i | \omega_i - e_i \rangle, \quad \underline{d}^2 = \sum_{i=1}^N \langle \omega_i - e_i | \omega_i - e_i \rangle \quad (11)$$

take on minimum values for $U' = \underline{U}' = 1$. The quantity d^2 can be written

$$d^2 = \sum_{i=1}^N \left\{ \langle \omega_i | \omega_i \rangle - \sum_{j,k} U'_{ij} S_{jk}^{-1/2} \langle e_i | P | e_k \rangle - \sum_{j,k} \langle e_k | P | e_i \rangle S_{kj}^{-1/2} U'_{ji} + \langle e_i | P | e_i \rangle + \langle e_i | Q | e_i \rangle \right\}.$$

Since \underline{S} is symmetric,

$$d^2 = \sum_{i=1}^N \left\{ \langle \omega_i | \omega_i \rangle - \sum_j U'_{ij} S_{ji}^{1/2} - \sum_j S_{ij}^{1/2} U'_{ji} + \langle e_i | P | e_i \rangle + \langle e_i | Q | e_i \rangle \right\} \\ = \sum_{i=1}^N \langle e_i | Q | e_i \rangle + \text{Tr} \{ 1 + S - U' S^{1/2} - S^{1/2} U'^* \}.$$

Evidently, d takes on its minimum value for $U' = 1$ and, correspondingly, \underline{d} for $\underline{U}' = 1$. Thus, the orthonormal SCF orbitals closest to the ethylene orbitals e_i and e_i are given by Eq. (10) with $U' = \underline{U}' = 1$. The form of the localized SCF orbitals obtained from Eq. (10) is illustrated in Table II which compares the coefficients for decapentane from the Ohno (3a) and Mataga-Nishimoto (3b) formulas with the completely localized ethylenic orbitals [Eq. (4)]; only three occupied and three unoccupied orbitals are given since ω_4 (ω_4) and ω_5 (ω_5) are related by symmetry to ω_2 (ω_2) and ω_1 (ω_1), respectively. A localized orbital centered at a given ethylene unit is found to be 95% (Ohno) or 94% (Mataga-Nishimoto) at the unit, 2.5% (Ohno) or 3% (Mataga-Nishimoto) at the neighboring units, and negligibly small further away. Table II also demonstrates that the localized orbitals are translationally invariant to a very good approximation. Calculations on a variety of polyenes show that the localized orbitals are nearly independent of chain length.

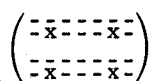
TABLE III. Localized and delocalized SCF orbitals of butadiene.^a

	Localized orbitals				Delocalized orbitals			
	ω_1	ω_2	ϕ_1	ϕ_2	ϕ_1	ϕ_2	ϕ_1	ϕ_2
Orbital energies (eV)								
	-12.15 ^b	-12.15 ^b	0.96 ^b	0.96 ^b	-13.53	-10.76	-0.43	2.34
Orbital coefficients								
p_1	0.699	-0.105	0.699	0.105	0.420	0.569	0.569	0.420
p_2	0.699	0.105	-0.699	0.105	0.569	0.420	-0.420	-0.569
p_3	0.105	0.699	0.105	-0.699	0.569	-0.420	-0.420	0.569
p_4	-0.105	0.699	0.105	0.699	0.420	-0.569	0.569	-0.420

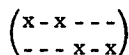
^aOhno parametrization [Eq. (3a)].^bDiagonal elements of Fock matrix.

To compare the CI wavefunctions resulting from the use of localized and delocalized SCF orbitals, we consider butadiene, which is small enough to allow presentation of the complete results. The butadiene wavefunctions exhibit all the characteristic features of the corresponding wavefunctions of longer polyenes. The orbitals and their energies are listed in Table III. The similarity of the localized orbitals of butadiene to those of decapentaene is clearly evident.

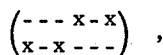
In Table IV are given the coefficients of localized and delocalized orbital configurations contributing to the wavefunctions of the lowest singlet states of butadiene ($1^1A_g^+$, $2^1A_g^+$, $1^1B_u^+$) obtained using [S+D]-CI. The diagrams in the table (and the subsequent text) give a self-explanatory pictorial representation of the orbital occupations in the different configurations (see Footnotes b and c). Although the two CI calculations yield identical results, the wavefunctions appear in very different forms. The ground-state correlation of butadiene ($1^1A_g^+$) in the delocalized orbital representation is described mainly through the configuration



in which two electrons are promoted from the second orbital ϕ_2 to the third orbital ϕ_3 ; a number of other doubly excited configurations are seen to make small but nonnegligible contributions. In the localized orbital basis, the correlation is dominated by the two double excitations

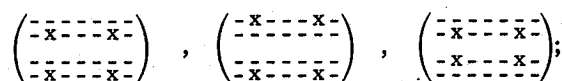


and

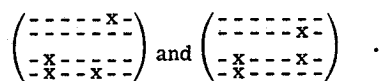


in which two electrons are promoted within each ethylene unit. Since the ground state of an isolated ethylene unit can be written as $\begin{pmatrix} - & - \\ - & - \end{pmatrix} + \alpha \begin{pmatrix} - & x \\ - & - \end{pmatrix}$, where α is the correlation coefficient, the butadiene ground state is approximately a superposition of ground-state correlated ethylene units. This description applies also to longer polyenes, as illustrated for decapentaene in Table V.

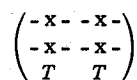
The excited $2^1A_g^+$ state of butadiene has a ~50% contribution from double-excited configurations as can be seen from Table IV: In the delocalized orbital picture the main double-excited components are



the 50% contribution from single excitations involves



In the localized orbital picture, the largest contribution comes from the configuration



in which the ethylene units are each excited to a triplet state, and the two triplets are coupled to give a singlet spin state^{2,3}; it is this characterization of the $2^1A_g^+$ state which leads to the result

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

The single excitation contributions to the $2^1A_g^+$ state in the localized description correspond to charge transfer from one ethylene unit to the other.

Table V shows that in a longer polyene, the triplet-triplet excitations still make the largest contributions to the $2^1A_g^+$ state. It can be seen that nearest neighbor excitations have large coefficients but that simultaneous excitations involving nonneighboring ethylene units are also very important.

The optically allowed $1^1B_u^+$ state has only very small contributions from double-excited configurations. In the delocalized orbital picture, the state consists almost exclusively of the promotion of one electron from the highest occupied orbital ϕ_2 to the lowest unoccupied orbital ϕ_1 . In the localized orbital picture, the state is a superposition of the ethylene singlet excitations ($\begin{pmatrix} - & x & - & - \\ - & - & - & - \end{pmatrix}$ and $\begin{pmatrix} - & - & - & - \\ - & x & - & - \end{pmatrix}$) and the "charge transfer" excitations ($\begin{pmatrix} - & - & - & - \\ - & x & - & - \end{pmatrix}$ and $\begin{pmatrix} - & - & - & - \\ - & - & - & x \end{pmatrix}$); this is the classic exciton description of the $1^1B_u^+$ state.⁷⁻¹² The latter excitations describe the de-

TABLE IV. π -electron wavefunctions of butadiene.^a

Localized SCF orbitals		Delocalized SCF orbitals						CD ^c
CL ^b	CI coefficients		CI coefficients					
	1 ¹ A _g	2 ¹ A _g	1 ¹ B _u	1 ¹ B _u	2 ¹ A _g	1 ¹ A _g		
	-0.554	4.853	5.306	5.306	4.853	-0.554		
---	---	0.973	-0.087	0.0	0.0	0.087	0.973	----- -x---x-
x-x	x-x							-x---x-
---	---	0.0	0.0	0.545	0.984	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
---	-x-	0.0	0.0	0.545	0.0	0.466	0.008	----- -x---x-
x-x	-x-							-x---x-
---	-x-	0.008	0.466	0.440	0.0	-0.466	-0.008	----- -x---x-
-x-	-x-							-x---x-
x-x	-x-	-0.008	-0.466	-0.440	0.105	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
x-x	-x-	0.063	0.644	0.0	0.0	-0.164	0.099	----- -x---x-
-x-	-x-							-x---x-
T	T							T T
---	---	-0.008	0.073	0.0	0.0	0.205	0.102	----- -x---x-
-x-	-x-							-x---x-
x-x	-x-							S S
---	---	-0.148	-0.028	0.0	0.0	0.250	-0.054	----- -x---x-
x-x	-x-							-x---x-
---	x-x	-0.148	-0.028	0.0	0.0	0.250	-0.054	----- -x---x-
x-x	---							-x---x-
---	x-x	0.038	0.178	-0.061	0.025	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
---	x-x	0.038	0.178	0.061	-0.097	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
x-x	---	-0.038	-0.178	-0.061	-0.097	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
---	x-x	-0.038	-0.178	0.061	0.025	0.0	0.0	----- -x---x-
-x-	-x-							-x---x-
---	x-x	-0.011	-0.067	0.051	0.0	-0.093	-0.051	----- -x---x-
-x-	-x-							-x---x-
x-x	---	0.011	-0.067	0.0051	0.0	-0.596	-0.159	----- -x---x-
x-x	---							-x---x-

^aEvaluated from PPP-Hamiltonian (1) with Ohno parametrization.

^bCL: π -electron configurations ω_1 defined over localized orbitals.

^cCD: π -electron configurations defined over delocalized orbitals.

----- ϕ_2
----- ϕ_1
----- ϕ_2
----- ϕ_1

TABLE V. [S+D]-CI coefficients in decapentaene.^a

(a) Major contributions to the ground state	(b) Triplet-triplet excitations in the 2^1A_g state	(c) Charge transfer excitations	$1B_g$ state	$3B_u$ state	$3A_g$ state
x-x x-x x-x x-x x-x	0.941	x-x -x- -x- -x- -x-	0.240	x-x -x- -x- -x- -x-	0.181 -0.185 -0.354
x-x -x- -x- -x- -x-	-0.132	-x- -x- -x- -x- -x-	0.211	-x- -x- -x- -x- -x-	0.188 0.156 -0.236
-x- x-x x-x x-x x-x	-0.132	-x- -x- -x- -x- -x-	0.211	-x- -x- -x- -x- -x-	0.148 0.110 0.087
x-x x-x x-x x-x -x-	-0.125	-x- -x- -x- -x- -x-	0.152	-x- -x- -x- -x- -x-	0.102 -0.067 -0.017
-x- -x- -x- -x- -x-	-0.125	-x- -x- -x- -x- -x-	0.152	-x- -x- -x- -x- -x-	0.056 0.033 0.000
x-x x-x x-x -x- x-x	-0.124	-x- -x- -x- -x- -x-	0.136	-x- -x- -x- -x- -x-	
x-x x-x -x- x-x x-x		-x- -x- -x- -x- -x-	0.136	-x- -x- -x- -x- -x-	
		-x- -x- -x- -x- -x-	0.075	-x- -x- -x- -x- -x-	

^aOhno parametrization.

localization of the excited electron in the 1^1B_u state, in agreement with its valence-bond characterization as a noncovalent state.³ Long-range charge transfer excitations contribute significantly to the 1^1B_u state of longer polyenes as is evident from the results for 1^1B_u state of decapentaene presented in Table V.

The lowest triplet state 1^3B_u also has only small contribution from double-excited configurations. In the delocalized orbital picture, this state, which is the triplet corresponding to the 1^1B_u state, is dominated by the promotion of one electron from the highest occupied to the lowest unoccupied orbital. However, there is some difference between the 1^1B_u and 1^3B_u state as is made clear by the localized orbital description. It can be seen in Table V that the 1^3B_u state, as well as the next triplet state, 1^3A_g , are composed more of intraethylene triplet excitations. The contribution from "charge transfer" excitations is smaller than for the 1^1B_u state.

The difference between the "delocalized" singlet state, 1^1B_u , and the more "localized" triplet state, 1^3B_u , which is covalent in character, is illustrated in Fig. 1. Defining the excitation

$$1^3|\psi_i^m\rangle = (1/\sqrt{2})(b_m^+ b_i + \mp b_m^+ b_{i+1})|\psi_0\rangle, \quad (12)$$

we show in Fig. 1 the absolute magnitude squares of the coefficients $1^3h_i^m$ multiplying the term $1^3|\psi_i^m\rangle$ in the 1^3B_u -state vector for the excitation from the fifth ethylene unit of the polyene. It is clear that the 1^3B_u state is significantly more localized than the 1^1B_u state. This can be compared with the behavior of the energy expectation values of singlet and triplet single-excited configurations. They are

$${}^3\langle\psi_i^m|\hat{H}|\psi_i^m\rangle = F_{mm} - F_{ii} - (ii|mm), \quad (13a)$$

$${}^1\langle\psi_i^m|\hat{H}|\psi_i^m\rangle = F_{mm} - F_{ii} - (ii|mm) + 2(im|im), \quad (13b)$$

where F_{mm} , F_{ii} are the diagonal elements of the Fock matrix and \hat{H} is the Hamiltonian defined as $\hat{H} = H - \langle\psi_0|H|\psi_0\rangle$ for the SCF-ground state ψ_0 ; the symbol $(ij|kl)$ represents the integral

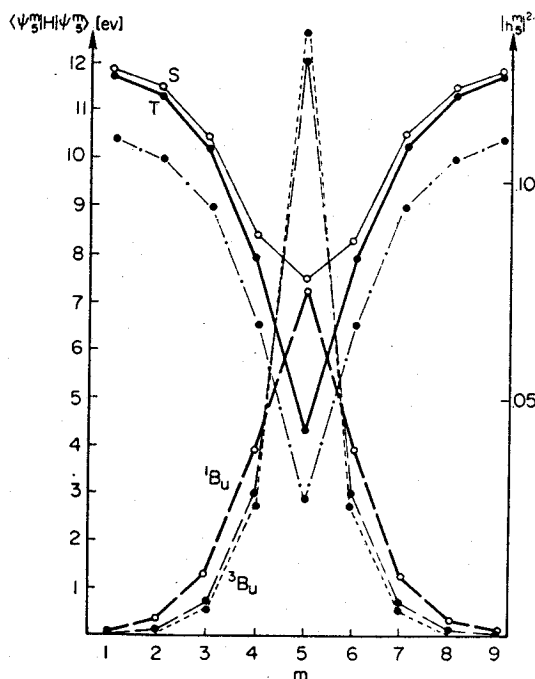


FIG. 1. Energy expectation values (left) and absolute amplitude squared of the wave vector coefficients h_i^m (right) of the excited configuration $1^3\langle\psi_i^m|\hat{H}|\psi_i^m\rangle$ in the linear polyene $C_{18}H_{20}$ ($i=5$, $m=1, 2, \dots, 9$). Energies: (—), 1^3B_u state; (---), 1^1B_u state; (-·-·), 1^3B_u state in renormalized CI basis. Coefficients: (-·-·), 1^3B_u state; (-—), 1^1B_u state; (····), 1^3B_u state in the renormalized CI basis. (Ohno parametrization is used.)

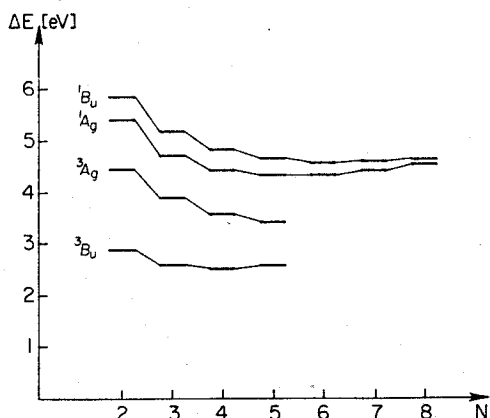


FIG. 2. Excitation energies of $1^3B_u^+$, $1^3A_g^+$, $1^1B_u^+$, and $2^1A_g^+$ states in linear polyenes $C_{2N}H_{2N+2}$ as evaluated from [S+D]-CI calculation with Ohno parametrization.

$$(ij|kl) = \langle \omega_i \omega_j | \hat{R} | \omega_k \omega_l \rangle \quad (14)$$

where the operator \hat{R} is the two-electron interaction part (the last term) of the Hamiltonian [Eq. (1)]. In Fig. 1 the triplet energies, Eq. (13a), and the singlet energies, Eq. (13b), are plotted for the polyene $C_{16}H_{20}$ for excitations from the fifth ethylene unit ($i=5$). The excitation energy for the triplet excitation $\bar{m}-i$ is smallest at $m=5$, i. e., for the intraethylene excitation ($m=i$). The singlet excitations also have their minimum at $m=5$ for the intraethylene excitation ($m=i=5$), but the energy well is more shallow. This is due to the fact that the exchange repulsion term $2(im|im)$, absent in the triplet energy expression, takes on its maximum value at $i=m$.

B. Length dependence of correlation correction

In a previous paper³ we have seen that 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. The comparison with experiments for the longer polyenes also showed that the results obtained with this basis exceed the experimental values and that the difference increases with the size of polyene, $C_{2N}H_{2N+2}$. Although the excitation energies of polyenes at first decrease in this approximation, for $N \geq 5$ they become a slowly increasing function of N , whereas experimental data show clearly that they decrease monotonically with N . This is illustrated in Fig. 2, where we present the calculated excitation energies for $C_{2N}H_{2N+2}$ polyenes ($N=2-8$). The source of this discrepancy is that the [S+D] basis, which accounts for most of the ground state correlation energy (but see below), yields a smaller fraction of the correlation correction for the excited states. Figure 3 presents the state energies in the [S] and [S+D] approximation. It is clear that the excitation energy increases with chain length due to the larger ground state correlation correction in the [S+D] approximation. We further observe that the correlation energy of the ground state increases nearly linearly with N ; that is,

TABLE VI. Ground state approximation.

	Ground-state correlation energies	
	Complete CI	D'-CI ^a
Butadiene	-0.566 eV	-0.466 eV (Ohno)
Hexatriene	-0.856 eV	-0.645 eV
Butadiene	-1.380 eV	-1.178 eV (Mataga-)
Hexatriene	-2.013 eV	-1.590 eV (Nishimoto)

^aEvaluated by the expansion $\Psi = \sum_k d_k D_k \psi_0$ in Eq. (17).

$$E_0 \approx N\epsilon, \quad (15)$$

where E_0 is the total correlation energy of the ground state and ϵ is that of a single ethylene unit. Higher (triple, quadruple, ...) excitations are needed to account for the missing correlation of the excited states. However, the configuration interaction treatment then becomes so large that the calculations are very time consuming. To avoid this difficulty, we will develop in Sec. IV a simplified method for estimating the correlation correction due to higher excitations. In what follows, we show that even for the ground state, higher than double excitations are needed in the larger polyenes to obtain the exact N dependence [Eq. (15)] of the correlation energy. In the localized orbital description, closed-shell configurations composed of intraethylene double excitations,

$$D_i \psi_0 = b_{i\sigma}^* b_{i-\sigma}^* b_{i\sigma} b_{i-\sigma} \psi_0, \quad (16)$$

where $\sigma, -\sigma$ represents the electron spin, make the dominant contribution. Hence, the correlated ground-state wavefunction can be expanded approximately in terms of these excitations (D'-CI basis)

$$|\Psi_0\rangle = d_0 |\psi_0\rangle + \sum_{k=1}^N d_k D_k |\psi_0\rangle \approx \sum_{k=0}^N d_k |D_k \psi_0\rangle. \quad (17)$$

The ground-state correlation energies obtained with this basis for butadiene and hexatriene are compared with the complete CI values in Table VI. We see that the

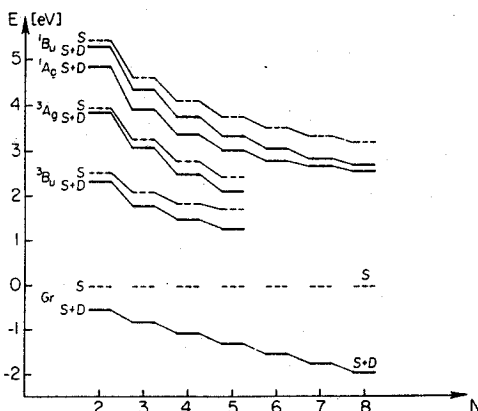


FIG. 3. Energies for the $1^1A_g^-(gr)$, $1^3B_u^+$, $1^3A_g^+$, $2^1A_g^+$, and $1^1B_u^+$ states in linear polyenes $C_{2N}H_{2N+2}$ as evaluated from [S]-CI (---), and [S+D]-CI (—) calculations with Ohno parametrization. The SCF ground state energy is taken as the zero of energy.

basis yields more than 75% of the exact correlation energy.

For larger polyenes, higher order excitations (quadruple, hextuple, ...) become important. To determine their contribution as a function of N , we carry out a model calculation in which we neglect all open-shell configurations and the closed-shell excitations which involve the simultaneous transfer of two electrons from one ethylene unit to another. The CI calculation involves the basis

$$\begin{aligned} D_i \psi_0 \\ Q_{ij} \psi_0 = D_i D_j \psi_0 (i \neq j) \\ \vdots \\ N_{i_1 \dots i_n} \psi_0 = D_{i_1} \dots D_{i_n} \psi_0 (i_1 \neq i_2 \neq \dots \neq i_n) \end{aligned} \quad (18)$$

for double, quadruple, ... and n -tuple excitations. This approximation leads to the problem of solving the secular equation

$$\begin{pmatrix} 0 & \beta_{02} & 0 & 0 & \dots \\ \beta_{02} & \alpha_2 & \beta_{24} & 0 & \dots \\ 0 & \beta_{24} & \alpha_4 & \beta_{46} & \dots \\ 0 & 0 & \beta_{46} & \alpha_6 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} f_0 \\ f_2 \\ f_4 \\ f_6 \\ \vdots \end{pmatrix} = E_0 \begin{pmatrix} f_0 \\ f_2 \\ f_4 \\ f_6 \\ \vdots \end{pmatrix}, \quad (19)$$

where f_0 is the CI coefficient of the SCF ground state ψ_0 , f_i is the vector of CI coefficients for the configurations $D_i \psi_0$ ($i = 1, 2, \dots, N$), etc. The CI matrix in Eq. (19) contains submatrices $\beta_{2s, 2s+2}$ and α_{2s} . The matrices $\beta_{2s, 2s+2}$ describe the coupling between the $2s$ and the $2s+2$ -tuple excitations, and the α_{2s} are diagonal matrices containing the transition energies of the $2s$ -tuple excitations;

$$(\alpha_{2s})_{ij} = \delta_{ij} \langle \psi_0 | D_i^{\dagger} \bar{H} D_j | \psi_0 \rangle.$$

To simplify Eq. (19), we introduce the approximation

$$(\alpha_{2s})_{ii} = s\mu, \quad (20)$$

i.e., we assume the transition energies for all $2s$ -tuple excitations to be identical and equal to s times the energy μ of a double excitation. This approximation neglects end-effects; for hexatriene, the values are

$$\langle D_1 \psi_0 | \bar{H} | D_1 \psi_0 \rangle = \langle D_3 \psi_0 | \bar{H} | D_3 \psi_0 \rangle = 11.02 \text{ eV},$$

$$\langle D_2 \psi_0 | \bar{H} | D_2 \psi_0 \rangle = 11.70 \text{ eV}$$

in the Ohno parametrization. Further, the approximation neglects exchange interactions between excitations in neighboring ethylene units. For the case of quadruple excitations, we have

$$\begin{aligned} \langle Q_{ij} \psi_0 | \bar{H} | Q_{ij} \psi_0 \rangle &= \langle D_i \psi_0 | \bar{H} | D_i \psi_0 \rangle + \langle D_j \psi_0 | \bar{H} | D_j \psi_0 \rangle \\ &+ 4[(ii|jj) + (ij|ij) - (ij|ji) - (ji|ij)] \\ &- 2[(ij|ij) + (ij|ij) - (ij|ij) - (ji|ji)]. \end{aligned} \quad (21)$$

The Coulomb integrals in the third set of terms cancel.

The fourth set of terms is composed of the exchange integrals that are neglected in the approximation of Eq. (20). To obtain an idea of the magnitude of the exchange interactions collected in the last set of terms we quote two examples for hexatriene:

$$\langle Q_{12} \psi_0 | \bar{H} | Q_{12} \psi_0 \rangle = \langle Q_{23} \psi_0 | \bar{H} | Q_{23} \psi_0 \rangle$$

$$= 11.02 \text{ eV} + 11.70 \text{ eV} + 0.367 \text{ eV},$$

$$\langle Q_{13} \psi_0 | \bar{H} | Q_{13} \psi_0 \rangle = 11.02 \text{ eV} + 11.02 \text{ eV} + 0.034 \text{ eV}.$$

This indicates that the neglected exchange contribution is small compared to the transition energies for adjacent ethylene units and decreases rapidly with increasing distance between the simultaneous double excitation.

The elements of the submatrices $\beta_{2s, 2s+2}$ are

$$\langle N_{i_1 \dots i_s} \psi_0 | \bar{H} | N_{j_1 \dots j_{s+1}} \psi_0 \rangle = \begin{cases} \langle \psi_0 | \bar{H} | D_{j_{s+1}} \psi_0 \rangle & \text{if } \{i_1, \dots, i_s\} = \{j_1, \dots, j_s\} \\ 0 & \text{otherwise.} \end{cases}$$

The matrix elements $\langle \psi_0 | \bar{H} | D_k \psi_0 \rangle$ are nearly independent of k , as can be seen from hexatriene, where

$$\langle \psi_0 | \bar{H} | D_1 \psi_0 \rangle = \langle \psi_0 | \bar{H} | D_3 \psi_0 \rangle = 1.62 \text{ eV},$$

$$\langle \psi_0 | \bar{H} | D_2 \psi_0 \rangle = 1.54 \text{ eV}.$$

Consequently, we use the approximation

$$\langle \psi_0 | \bar{H} | D_k \psi_0 \rangle = \gamma \quad \text{for } k = 1, 2, \dots, N. \quad (22)$$

With the approximations in Eqs. (20) and (22), the secular equation, Eq. (19), reduces to the one for a system of N identical, noninteracting ethylene units. The CI matrix for an isolated ethylene unit is

$$\begin{pmatrix} 0 & \gamma \\ \gamma & \mu \end{pmatrix}.$$

In the case of butadiene we have

$$\begin{pmatrix} 0 & \gamma & \gamma & 0 \\ \gamma & \mu & 0 & \gamma \\ \gamma & 0 & \mu & \gamma \\ 0 & \gamma & \gamma & 2\mu \end{pmatrix} \begin{pmatrix} f_0 \\ f_2^1 \\ f_2^2 \\ f_4 \end{pmatrix} = E_0 \begin{pmatrix} f_0 \\ f_2^1 \\ f_2^2 \\ f_4 \end{pmatrix} \quad (23)$$

in self-evident notation for the vector of CI coefficients. Clearly, the CI matrix in Eq. (23) corresponds to two ethylene units. The ground-state correlation energy for a polyene consisting of N identical independent ethylene units is

$$E_0 = N\epsilon, \quad (24a)$$

where

$$\epsilon = \frac{1}{2}\mu - \left[\left(\frac{1}{2}\mu \right)^2 + \gamma^2 \right]^{1/2} \quad (24b)$$

is the ground-state correlation energy of a single ethylene unit.

In order to obtain in a CI calculation the correct correlation energy, it is necessary to include all possible excitations. However, in common CI calculations only a

limited number of excitations is usually included. We now demonstrate that with the approximations of Eqs. (20) and (22) the CI problem (19) can be solved exactly for double, quadruple, etc., excitations included. Hence, we are able to examine the error introduced through neglect of higher excitations.

Since the N ethylene units are equivalent, we can use a (normalized) basis of collective excitations for the ground state of the form

$$\begin{pmatrix} 0 & \sqrt{N}\gamma & 0 & 0 & \dots \\ \sqrt{N}\gamma & \mu & \sqrt{2(N-1)}\gamma & 0 & \dots \\ 0 & \sqrt{2(N-1)}\gamma & 2\mu & \sqrt{3(N-2)}\gamma & \dots \\ \vdots & \vdots & \vdots & \vdots & \dots \\ \vdots & \vdots & \vdots & \vdots & \dots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \\ \vdots \end{pmatrix} = E_0 \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \\ \vdots \end{pmatrix} \quad (26)$$

Expanding the matrix equation, we obtain

$$E_0 C_0 = \sqrt{N}\gamma C_1 \quad (26')$$

and

$$B_{n-1} C_{n-1} + A_n C_n + B_n C_{n+1} = 0 \quad \text{for } n \geq 1, \quad (26'')$$

where

$$B_n = \sqrt{(n+1)(N-n)}\gamma$$

and

$$A_n = (n\mu - E_0)$$

The recursion relation, Eq. (26''), can be written as

$$\frac{C_n}{C_{n-1}} = \frac{-B_{n-1}}{A_n + B_n(C_{n+1}/C_n)} \quad \text{for } n \geq 1 \quad (26''')$$

Repeated substitution of Eq. (26''') into Eq. (26') yields the continued fraction solution for E_0 ,

$$E_0 = \frac{-N\gamma^2}{\mu - E_0 - \frac{2(N-1)\gamma^2}{2\mu - E_0 - \frac{3(N-2)\gamma^2}{3\mu - E_0 - \dots}}}$$

To determine the solution of this equation we consider the series of quadratic, cubic, etc., equations

$$z = -N\gamma^2/(\mu - z), \quad (27a)$$

$$z = \frac{-N}{\mu - z - 2(N-1)\gamma^2/(2\mu - z)}, \quad (27b)$$

etc. The roots $E_0^{(1)}$ [Eq. (27a)], $E_0^{(2)}$ [Eq. (27b)], etc., are the ground-state correlation energies obtained with double, double and quadruple, etc., excitations included in the CI treatment. Figure 4 illustrates for $N = 50$ that these energies form a monotonically decreasing series converging rapidly towards the limiting value $E_0^{(N)} = E_0$, the true ground-state correlation energy of the system. The energies $E_0^{(i)}$ can be evaluated starting from $i = 1$ [Eq. (27a)]; we have

$$\psi_0, \binom{N}{1}^{-1/2} \sum_i D_i \psi_0, \binom{N}{2}^{-1/2} \sum_{i>j} D_i D_j \psi_0, \dots,$$

where $\binom{N}{i}$ is the binomial coefficient. In terms of this basis, the ground-state wavefunction can be written

$$\Psi_0 = \left(C_0 + C_1 \binom{N}{1}^{-1/2} \sum_i D_i + C_2 \binom{N}{2}^{-1/2} \sum_{i>j} D_i D_j + \dots \right) \psi_0, \quad (25)$$

where the coefficients C_i obey the secular equation

$$E_0^{(1)} = \frac{1}{2}\mu - \left[\left(\frac{1}{2}\mu \right)^2 + N\gamma^2 \right]^{1/2}.$$

This solution of Eq. (27a) serves as a first guess for an iterative solution of Eq. (27b). Once the iteration of this equation has converged, the solution $E_0^{(2)}$ is used as a first guess for the equation determining the ground-state excitation energy $E_0^{(3)}$, etc.

In Fig. 5 we plot the correlation energies $E_0^{(i)}$ for polyenes as a function of the chain length N . For small polyenes ($N < 10$) double excitations alone give a good description of the ground state correlation of the model. Since $\gamma \ll \frac{1}{2}\mu$, we can expand $E_0^{(1)}$ for small N and write

$$E_0^{(1)} \cong - (2/\mu) N\gamma^2$$

so that the double excitations ground-state correlation energy is seen to depend linearly on N . However, for long polyenes ($N\gamma^2 \gg (\frac{1}{2}\mu)^2$), the correlation energy obtained from $E_0^{(1)}$ varies as \sqrt{N} . This result is clearly incorrect and requires the introduction of higher excitations to restore the expected linear dependence on N .

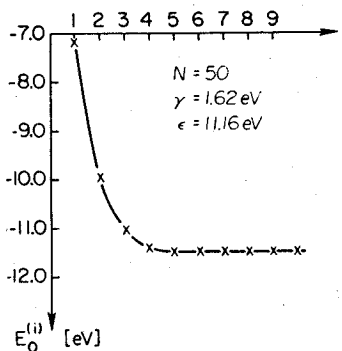


FIG. 4. Ground-state correlation energy of the model polyene $C_{100}H_{102}$ as a function of the extent of configuration interaction, i ; $i = 1$, [D]-CI; $i = 2$, [D+Q]-CI; $i = 3$, [D+Q+H]-CI; ... [see Eqs. (27)].

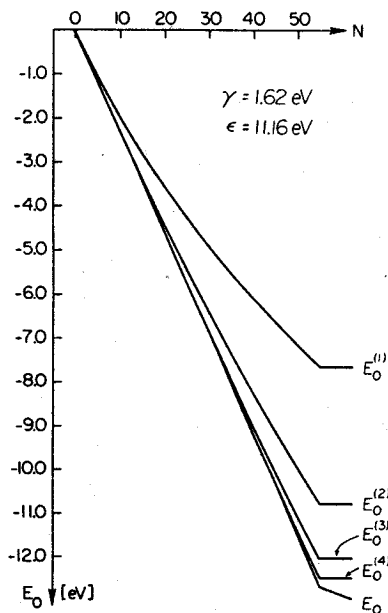


FIG. 5. Ground-state correlation energies of the model polyenes $C_{2N}H_{2N+2}$ as evaluated from the various levels of CI calculations; $E_0^{(1)}$, [D]-CI; $E_0^{(2)}$, [D+Q]-CI; $E_0^{(3)}$, [D+Q+H]-CI;

As can be seen from Fig. 5, $E_0^{(2)}$, $E_0^{(3)}$, . . . yields a significant improvement in the correlation energy result.

IV. RENORMALIZED CONFIGURATION INTERACTION METHOD

In this section, an approximate CI method is developed to account in the excited states for the correlation effects not described by single and double excited configurations. The basis of the method is that a large part of the ground-state correlation energy is present in the excited state. The validity of this assertion, which is formulated most directly in a localized orbital basis, is examined in detail. The results obtained with the CI method are presented and compared with more exact calculations in Sec. V.

Excited state wavefunctions Ψ can be expressed in terms of excitations in which one, two, . . . electrons are promoted from the SCF ground state

$$\Psi = \left(c_0 + \sum_{i,m} c_{i\sigma}^{m\sigma} O_{i\sigma}^{m\sigma} + \sum_{i,i',m,n} c_{i\sigma j\sigma'}^{m\sigma n\sigma'} O_{i\sigma j\sigma'}^{m\sigma n\sigma'} + \dots \right) \psi_0. \quad (28)$$

Here ψ_0 is the SCF ground state wavefunction, $i\sigma$, $m\sigma$, $j\sigma'$, $n\sigma'$ are localized SCF orbitals with spin σ or σ' and the $\bar{O}_{i\sigma}^{m\sigma}$, $\bar{O}_{i\sigma j\sigma'}^{m\sigma n\sigma'}$. . . are composed of particle-hole excitation operators; i. e.,

$$O_{i\sigma}^{m\sigma} = b_{m\sigma}^+ b_{i\sigma},$$

$$O_{i\sigma j\sigma'}^{m\sigma n\sigma'} = b_{m\sigma}^+ b_{n\sigma'}^+ b_{i\sigma} b_{j\sigma'}.$$

The upper indices m , n stand for the particle states (we have removed the underline bar of the superscripts for simplicity) and the lower indices stand for the hole states

in the localized basis. In each term that contributes to Eq. (28), the electrons that do not participate in the particular elementary excitations ($m\sigma - i\sigma$, $m\sigma n\sigma' - i\sigma j\sigma'$) are frozen in the SCF ground state. A more rapidly convergent expansion for the excited state wavefunction can be obtained by replacing the SCF function ψ_0 in Eq. (28) by the exact ground state wavefunction Ψ_0 . We will refer to such expression as the *renormalized* CI expansion. Because of the spatial separation of the polyene π electrons in localized orbitals, one expects that the elementary excitations do not seriously disturb the correlation of the electrons that are not excited.

To illustrate this point, we consider as an example the one-electron excitation $O_{i\sigma}^{m\sigma}$. If the excitation is relative to the SCF ground state [Eq. (28)], $\psi_{i\sigma}^{m\sigma} = O_{i\sigma}^{m\sigma} \psi_0 = b_{m\sigma}^+ b_{i\sigma} \psi_0$, it can be represented graphically as in Fig. 6(a). The electrons at the ethylene units $k \neq i$, m are expected to be only slightly perturbed. If we employ the approximation to the correlated ground state introduced in Sec. III,

$$\Psi_0 = \left(d_0 + \sum_{k=1}^N d_k D_k \right) \psi_0, \quad (17)$$

the elementary excitation, which can be written

$$\Psi_{i\sigma}^{m\sigma} = O_{i\sigma}^{m\sigma} \Psi_0, \quad (29)$$

corresponds to the representation shown in Fig. 6(b). Thus, the localized orbitals not involved in the excitation have the same correlation as in the ground state; for $i=k$ and/or $m=k$, we have

$$O_{i\sigma}^{m\sigma} D_k = 0 \quad (i=k \text{ or } m=k). \quad (30)$$

Although the excitations $\Psi_{i\sigma}^{m\sigma}$ are orthogonal, they are not normalized. To obtain the normalization constant we make use of Eq. (30). Thus, we have

$$\langle \Psi_{i\sigma}^{m\sigma} | \Psi_{i'\sigma'}^{m'\sigma'} \rangle = \delta_{i i'} \delta_{m m'} \delta_{\sigma \sigma'} (N_i^{m\sigma})^{-2},$$

where

$$(N_i^{m\sigma})^{-2} = \sum_{k=0}^N d_k^2 < 1 \quad (k \neq i, m) \quad (31)$$

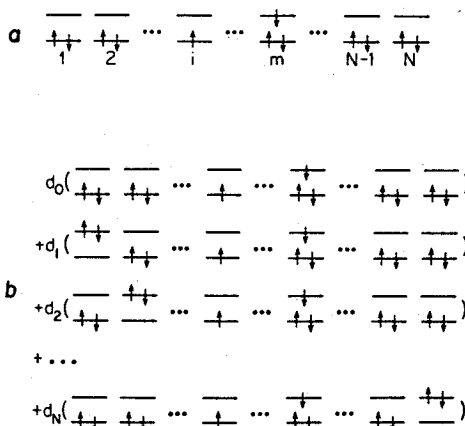


Fig. 6. Pictorial representation of a localized single excitation ($m-i$); (a) in the standard [S]-CI basis; (b) in the renormalized [S]-CI basis. Localized orbitals are represented by the corresponding ethylene orbitals.

[note that the d_k in Eq. (17) are normalized such that $\sum_{k=0}^N |d_k|^2 = 1$]. Consequently, the normalized excitations (for which we use the same symbol for simplicity) are

$$|\Psi_{i\sigma}^{m\sigma}\rangle = N_i^m O_{i\sigma}^{m\sigma} |\Psi_0\rangle. \quad (32)$$

Since the ground-state coefficients d_1, d_2, \dots are small, in general, the normalization constants N_i^m are close to unity. Double excitations from the correlated ground state, which we do not treat in detail here, can be constructed similarly; since they yield a nonorthogonal set, the calculations are more complicated (see below).

The correlation energy of the configuration corresponding to the elementary excitation $|\Psi_{i\sigma}^{m\sigma}\rangle$ is

$$E_{i\sigma}^{m\sigma, \text{corr}} = \langle \Psi_{i\sigma}^{m\sigma} | H | \Psi_{i\sigma}^{m\sigma} \rangle - \langle \psi_{i\sigma}^{m\sigma} | H | \psi_{i\sigma}^{m\sigma} \rangle. \quad (33)$$

With the same simplifying assumptions as used in Sec. III, $E_{i\sigma}^{m\sigma, \text{corr}}$ reduces to

$$E_{i\sigma}^{m\sigma, \text{corr}} \cong \sum_{k \neq i, m} \epsilon_k,$$

where ϵ_k is the ground state correlation energy of the k th ethylene unit. For large polyenes this correlation energy is comparable to the approximate ground state correlation energy of the entire polyene, $\sum_{k=1}^N \epsilon_k$. From Eqs. (17), (32), and (33) this part of the excited state correlation evidently originates from triple excitations. Consequently, it is not included in the [S+D] calculations and is a major source of the error in the excitation energies.

The above example indicates how to proceed to include the ground-state correlation contribution in the excited states. We replace the wavefunction expansion, Eq. (28), by the renormalized expansion in terms of elementary excitations with respect to the *correlated* ground state, Ψ_0 ; that is,

$$\Psi = \left(c_0 + \sum_{i,m} c_{i\sigma}^{m\sigma} O_{i\sigma}^{m\sigma} + \sum_{\substack{i,j \\ m,n \\ \sigma,\sigma'}} c_{i\sigma j\sigma'}^{m\sigma n\sigma'} O_{i\sigma j\sigma'}^{m\sigma n\sigma'} + \dots \right) \Psi_0. \quad (34)$$

Inserting the rhs of Eq. (17) into this expansion (i. e., approximating Ψ_0 by the function which includes intramethylene closed shell double excitations), we obtain

$$\begin{aligned} \Psi = & \left(c_0 d_0 + d_0 \sum_{i,m} c_{i\sigma}^{m\sigma} O_{i\sigma}^{m\sigma} + c_0 \sum_k d_k D_k \right. \\ & + d_0 \sum_{\substack{i,j \\ m,n \\ \sigma,\sigma'}} c_{i\sigma j\sigma'}^{m\sigma n\sigma'} O_{i\sigma j\sigma'}^{m\sigma n\sigma'} + \sum_k \sum_{\substack{i,m \\ \sigma}} c_{i\sigma}^{m\sigma} d_k O_{i\sigma}^{m\sigma} D_k \\ & \left. + \sum_k \sum_{\substack{i,j \\ m,n \\ \sigma,\sigma'}} c_{i\sigma j\sigma'}^{m\sigma n\sigma'} d_k O_{i\sigma j\sigma'}^{m\sigma n\sigma'} D_k + \dots \right) \psi_0. \quad (35) \end{aligned}$$

It is clear that the function includes single, double, triple, and quadruple, ... excitations with respect to the SCF ground state. By employing this expression, a CI calculation with a larger basis

$$\{ \psi_0, O_{i\sigma}^{m\sigma} \psi_0, O_{i\sigma j\sigma'}^{m\sigma n\sigma'} \psi_0, O_{i\sigma}^{m\sigma} D_k \psi_0, O_{i\sigma j\sigma'}^{m\sigma n\sigma'} D_k \psi_0, \dots \}$$

is reduced to one in which the secular equation has the dimension of the smaller basis

$$\{ \Psi_0, O_{i\sigma}^{m\sigma} \Psi_0, O_{i\sigma j\sigma'}^{m\sigma n\sigma'} \Psi_0, \dots \}. \quad (36)$$

To reduce the CI matrix, the calculations have been done with a spin-symmetrized basis of singlet and triplet configurations; for example, a single excitation has the form

$${}^{1,3} |\Psi_i^m\rangle = N_i^m {}^{1,3} O_i^m |\Psi_0\rangle = \frac{N_i^m}{\sqrt{2}} (O_i^{m-} \mp O_i^{m+}) |\Psi_0\rangle, \quad (37)$$

where the upper sign (-) is for the singlet state and the lower sign (+) is for the triplet state. In what follows we assume that spin-symmetrized configurations are being used, though we drop the singlet (triplet) superscripts unless they are required for clarity.

Given the basis in Eq. (37), the excited state wavefunction can be written

$$|\Psi\rangle = \sum_{i,m} g_i^m |\Psi_i^m\rangle \quad (38)$$

which is equivalent to

$$|\Psi\rangle = \sum_{i,m} N_i^m g_i^m \sum_{(k \neq i, m)} d_k D_k |\psi_i^m\rangle, \quad (39)$$

where ψ_i^m is given by Eq. (12) and the g_i^m are the expansion coefficients; they are normalized to

$$\sum_{i,m} |g_i^m|^2 = 1. \quad (40)$$

The elements of the Hamiltonian matrix are

$$\begin{aligned} \langle \Psi_i^m | H | \Psi_j^n \rangle = & N_i^m N_j^n \left\{ d_0^2 \langle \psi_i^m | H | \psi_j^n \rangle \right. \\ & + \sum_{k=1}^N d_0 d_k \langle \psi_i^m | H D_k + D_k H | \psi_j^n \rangle \\ & \left. + \sum_{k,l=1}^N d_k d_l \langle \psi_i^m | D_k H D_l | \psi_j^n \rangle \right\}. \quad (41) \end{aligned}$$

Each one of these elements is seen to incorporate $1 + 2N + N^2 = (N+1)^2$ matrix elements; that is one CI matrix element between single excitations (i. e., the one corresponding to use of an SCF ground state), $2N$ matrix elements between single and triple excitations, and N^2 matrix elements between triple excitations; e. g., for octatetraene ($N=4$), there are 25 elements.

A. Analysis of the method

The expansion of the excited-state wavefunctions in terms of the renormalized configurations $|\Psi_i^m\rangle$ is an approximation to a CI calculation which includes all single and certain triple excitations; we write the [S+T']-CI wavefunction in the form

$$|\Psi\rangle = \sum_{i,m,k} f_{i,m,k}^m |D_k \psi_i^m\rangle, \quad (42)$$

where

$$\begin{aligned} |D_0 \psi_i^m\rangle &= |\psi_i^m\rangle \quad \text{for } k=0, \\ |D_k \psi_i^m\rangle &= |\psi_{i,k,k}^m\rangle \quad \text{for } k \neq 0, \end{aligned}$$

and $|\psi_i^m\rangle$, $|\psi_{kk}^{mkk}\rangle$ are spin-symmetrized single ($m-i$) and triple ($mkk-ikk$) excitations. The single excitation coefficients f_{i0}^m ($k=0$) have N^2 degrees of freedom and the triple excitation coefficients f_{ik}^m ($k\neq 0$) have N^3 degrees of freedom. In the approximate CI method, the triple excitation coefficients are assumed to be equal to a product of single and double excitation coefficients [compare Eq. (39) with Eq. (42)]; that is,

$$f_{ik}^m = N_i^m g_i^m d_k \quad (43)$$

so that the degrees of freedom are $N^2 + N$ (N^2 for g_i^m and N for d_k). We term Eq. (43) the "cluster approximation" in analogy to the cluster expansion of Sinanoglu⁶ for the ground-state correlation problem. The equation implies that the ratio of triple and single excitation coefficients in Eq. (42) can be written

$$(f_{ik}^m : f_{i0}^m) = (d_k : d_0) \quad (44)$$

independent of i and m .

An additional approximation is made by choosing the d_k to be the same as the correlated ground-state wavefunction coefficients; that is, the electrons not directly involved in the excitation are assumed to be unaffected by it. The latter assumption brings the degrees of freedom down to N^2 , the same as in an ordinary [S]-CI expansion.

To examine the coupling between excitations, we expand the CI element for the function $|D_k \psi_i^m\rangle$ as

$$\begin{aligned} \langle D_k \psi_i^m | \bar{H} | D_l \psi_j^n \rangle &= \langle \psi_i^m | \bar{H} | \psi_j^n \rangle \delta_{kl} + \langle D_k \psi_0 | \bar{H} | D_l \psi_0 \rangle \delta_{ij} \delta_{mn} \\ &+ \langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle, \end{aligned} \quad (45)$$

where \bar{H} is the CI Hamiltonian [Eq. (13)] and the two-electron operator \hat{V} is defined in terms of its matrix elements (the singlet (triplet) matrix elements go with the upper (lower) signs)

$$\begin{aligned} {}^{1,3}\langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle &= \{2(\underline{kk} | \underline{mn}) - (\underline{km} | \underline{kn}) - 2(\underline{kk} | \underline{mn}) \\ &+ (\underline{km} | \underline{kn})\} \delta_{ij} \delta_{kl} + \{2(\underline{kk} | \underline{ij}) - (\underline{ki} | \underline{kj}) - 2(\underline{kk} | \underline{ij}) \\ &+ (\underline{ki} | \underline{kj})\} \delta_{mn} \delta_{kl} + \{(\underline{kk} | \underline{ll}) \pm (\underline{kk} | \underline{ll}) - (\underline{kl} | \underline{kl})\} \\ &\times \delta_{im} \delta_{il} \delta_{jn} \delta_{jk} (1 - \delta_{kl}) \end{aligned} \quad (46a)$$

for $k\neq 0$ and $l\neq 0$,

$$\begin{aligned} {}^{1,3}\langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle &= \{(\underline{ii} | \underline{jn}) + (\underline{ii} | \underline{jn}) \mp (\underline{in} | \underline{ji})\} \delta_{im} \delta_{il} \\ &- (\underline{ll} | \underline{jl}) \delta_{il} \delta_{mn} - (\underline{ln} | \underline{ll}) \delta_{ij} \delta_{ml} \end{aligned} \quad (46b)$$

for $k=0$ and $l\neq 0$ (a corresponding expression in which k, i, m are interchanged with l, j, n , respectively, holds for $k\neq 0$ and $l=0$), and

$${}^{1,3}\langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle = 0 \quad (46c)$$

for $k=0$ and $l=0$. The matrix \hat{V} represents the remaining terms coupling the excitations. If this coupling is much smaller than the other terms in Eq. (45), the cluster approximation is valid. We consider this point further in Sec. V.

To examine the partitioning of the energy contribution and the nature of the approximation in the renormalized CI treatment, we use Eqs. (42), (43), and

(45) to write the excited state energy expressions in the form (all quantities are assumed real for simplicity)

$$\begin{aligned} E_{RS-CI} &= \sum_{\substack{i,m,k \\ j,n,l}} N_i^m N_j^n g_i^m g_j^n d_k d_l \langle D_k \psi_i^m | \bar{H} | D_l \psi_j^n \rangle \\ &= \sum_{i,m} \left\{ g_i^m g_i^m \langle \psi_i^m | \bar{H} | \psi_i^m \rangle + \sum_{k \neq (i,m)} d_k^2 N_i^m N_j^n \right\} \\ &+ \sum_{i,m} \left\{ (N_i^m)^2 (g_i^m)^2 \sum_{k \neq i} \langle D_k \psi_0 | \bar{H} | D_i \psi_0 \rangle d_k d_i \right\} \\ &+ \sum_{\substack{i,m \\ j,n}} \sum_{k \neq (i,m)} N_i^m N_j^n g_i^m g_j^n d_k d_l \langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle \end{aligned} \quad (47)$$

In the renormalized CI method, the excited state energy and wavefunction are obtained from Eq. (47) by assuming the d_k to be known from the correlated ground state and minimizing with respect to the coefficients g_i^m . We justify this approximate procedure in what follows. If we assume [see Eq. (31)]

$$\sum_{k \neq (i,m)} d_k^2 N_i^m N_j^n = 1 \quad (48)$$

the first terms of Eq. (47) correspond to the energy expression in the [S]-CI basis and has a minimal value when the coefficients g_i^m are equal to the [S]-CI coefficients h_i^m ,

$$\Psi = \sum_{i,m} h_i^m O_i^m \psi_0.$$

A small difference between g_i^m and h_i^m is expected due to the normalization correction [first term of Eq. (47)], the coupling with the ground state correlation [second term of Eq. (47); see below] and the matrix \hat{V} [third term of Eq. (47)], all of which are accounted for in the renormalized [S]-CI calculation. The first term of (47) is approximately equal to the [S]-CI energy expectation value E_{S-CI} . Its small deviation from E_{S-CI} will be called the renormalization correction of E_{S-CI} , $\tau_{\Delta S-CI}$; it is given by

$$\tau_{\Delta S-CI} = \sum_{\substack{i,m \\ j,n}} \left\{ g_i^m g_j^n \langle \psi_i^m | \bar{H} | \psi_j^n \rangle + \sum_{k \neq (i,m)} d_k^2 (N_i^m N_j^n) \right\} - E_{S-CI}. \quad (49)$$

The second term in Eq. (47) may be separated into two contributions,

$$\sum_{i,m} \left\{ (N_i^m)^2 (g_i^m)^2 \sum_{k \neq i} \langle D_k \psi_0 | \bar{H} | D_i \psi_0 \rangle d_k d_i \right\} \quad (50)$$

$$= E_0 \sum_{i,m} (N_i^m)^2 (g_i^m)^2 - \sum_{i,m,k} (N_i^m)^2 (g_i^m)^2 G(i, m, k) \epsilon_k,$$

where E_0 is the correlation energy of a ground-state wavefunction of the form given in Eq. (17). It is given by the expression

$$E_0 = \sum_{k,l} d_k d_l \langle D_k \psi_0 | \bar{H} | D_l \psi_0 \rangle.$$

Since

$$\langle \psi_0 | \hat{H} | \psi_0 \rangle = 0$$

and

$$\langle D_k \psi_0 | \hat{H} | D_l \psi_0 \rangle = \delta_{k,l} \langle D_k \psi_0 | \hat{H} | D_k \psi_0 \rangle$$

for $k \neq 0$ and $l \neq 0$, we can write

$$E_0 = \sum_{k=1}^N \epsilon_k, \quad (51)$$

where ϵ_k , the correlation energy of an ethylenic unit, is

$$\epsilon_k = \{ \langle \psi_0 | \hat{H} | D_k \psi_0 \rangle + \langle D_k \psi_0 | \hat{H} | \psi_0 \rangle \} d_0 d_k + \langle D_k \psi_0 | \hat{H} | D_k \psi_0 \rangle d_k^2.$$

If we set $\sum_{i,m} (N_i^m)^2 (g_i^m)^2 = 1$, the first term in Eq. (50) is approximately equal to E_0 . Thus it is a reflection of the ground-state correlation energy in the excited state.

The small deviation from E_0 will be called the renormalization correction to E_0 , Δ_0 ; it is given by

$$\Delta_0 = E_0 \sum_{i,m} (N_i^m)^2 (g_i^m)^2 - E_0. \quad (52)$$

The ground-state correlation energy of the ethylene units that are involved in the excitation ($m-i$) are not present in unaltered form in the excited state. The required correction to E_0 is given by the second term in Eq. (50); it contains the factor $G(i, m, k)$, which has the form

$$G(i, m, k) = \begin{cases} 1 & \text{for } k=i \text{ or } k=m \\ 0 & \text{otherwise} \end{cases}$$

It introduces a correction corresponding to the correlation energy of an ethylene unit, ϵ_k , for the one unit ($k=i=m$) or for each of the two units ($k=i$ and $k=m$) involved in the excitation. To simplify the term, we assume, as suggested in Sec. III. B, that $\epsilon_k = \epsilon$ (independent of k) and write it in the form

$$E_p = -\epsilon \sum_{i,m} (N_i^m)^2 (g_i^m)^2 L(i, m), \quad (53)$$

where

$$L(i, m) = \begin{cases} 1 & \text{for } i=m \\ 2 & \text{for } i \neq m \end{cases}. \quad (54)$$

This contribution is termed the "Pauli exclusion energy" since it is the exclusion principle which forbids these excitations, which would have contributed to the correlation energy. The term is larger ($E_p \approx -2\epsilon$) if the excited states consist mainly of the interethylene excitations [$i \neq m$, $L(i, m) = 2$], while it is smaller ($E_p \approx -\epsilon$) for the states consisting mainly of intraethylene unit excitations [$i = m$, $L(i, m) = 1$].

The last term in Eq. (47)

$$E_C = \sum_{i,m} \sum_{\substack{k \neq i, m \\ j, n}} N_i^m N_j^n g_i^m g_j^n d_k d_l \langle D_k \psi_i^m | \hat{V} | D_l \psi_j^n \rangle \quad (55)$$

accounts for energy contributed by the coupling between triple excited configurations [Eq. (46a)] and between single and triple excited configurations [Eq. (46b)].

From the development in the preceding paragraph, the entire energy expression [Eq. (47)], which corresponds to the energy with respect to the Hartree-Fock ground state as zero, can be written

$$E_{RS-CI} \approx E_{S-CI} + N\epsilon + E_p + E_C + {}^r\Delta_{S-CI} + {}^r\Delta_0. \quad (56)$$

The first two terms, which are dominant, are minimized by the coefficients (h_i^m, d_k). Use of (g_i^m, d_k) in the E_{RS-CI} corrects for the remaining terms in Eq. (56) under the assumption that the d_k can be employed for the excited states. Corrections to the coefficients d_k are accounted for by the [S+T']-CI calculation; that they are small is demonstrated in Sec. V.

From Eq. (56) the excited state correlation energy accounted for by a renormalized S-CI calculation is

$$E_{RS-CI}^{corr} = N\epsilon + \Delta, \quad (57)$$

where Δ , the "rearrangement energy" is given by

$$\Delta = E_p + E_C + {}^r\Delta_{S-CI} + {}^r\Delta_0. \quad (58)$$

It corresponds to the difference between the ground-state and the excited state correlation energy. In the excitation energy, the ground-state correlation energy ($N\epsilon$) of the excited state cancels with the correlation energy of the ground state and we obtain a net excitation energy

$$\Delta E_{RS-CI} = E_{S-CI} + \Delta, \quad (59)$$

where E_{S-CI} is the energy (relative to the SCF ground state zero) in the S-CI calculation. Since $\Delta > 0$ in general, the excitation energies obtained from the renormalized [S]-CI calculations are larger than those from the [S]-CI calculations.

B. Extensions of the method

Some straightforward extensions of the method are described here.

1. Double excitations

To extend the renormalized CI method to include "elementary" double excitations in the excited state, we write

$$|\Psi_{ij}^{mn}\rangle = N_{ij}^{mn} O_{ij}^{mn} |\Psi_0\rangle, \quad (60)$$

where the normalization factor N_{ij}^{mn} is defined by

$$(N_{ij}^{mn})^{-2} = \sum_{\substack{k=0 \\ (k \neq i, j, m, n)}}^N d_k^2 < 1 \quad (61)$$

and the operator O_{ij}^{mn} is the spin-symmetrized double-excitation operator. Analogously to the [S+D]-CI expansion wavefunction

$$|\Psi\rangle = h_0 |\psi_0\rangle + \sum_{i,m} h_i^m |\psi_i^m\rangle + \sum_{i,j,m,n} h_{ij}^{mn} |\psi_{ij}^{mn}\rangle \quad (62)$$

the wavefunction of the excited state is expanded in the renormalized CI basis given by Eqs. (37) and (60). It has the form

$$|\Psi\rangle = g_0 |\Psi_0\rangle + \sum_{i,m} g_i^m |\Psi_i^m\rangle + \sum_{i,j,m,n} g_{ij}^{mn} |\Psi_{ij}^{mn}\rangle, \quad (63)$$

where the h 's and g 's are expansion coefficients. The renormalized CI basis in Eq. (63) is not orthogonal; restricting Ψ_0 to closed-shell double excitations [Eq. (17)], we have the nonzero overlap

$$\begin{aligned} \langle \Psi_0 | \Psi_{ij}^{mn} \rangle &= \sum_k d_k d_0 \langle D_k \psi_0 | \psi_{ij}^{mn} \rangle \\ &= d_i d_0 \delta_{ij} \delta_{im} \delta_{in} . \end{aligned} \quad (64)$$

Neglecting the small overlap contributions to the matrix elements, the energy expectation value (relative to the Hartree-Fock ground state) in the renormalized [S+D]-CI basis expansion can be written approximately as

$$\begin{aligned} E_{R[S+D]-CI} &= E_{[S+D]-CI} + N\epsilon + E_p \\ &\quad + E_C + {}^r\Delta_{[S+D]-CI} + {}^r\Delta_0 , \end{aligned} \quad (65)$$

where the $E_{[S+D]-CI}$ is the energy (relative to the SCF ground state as zero) obtained from the [S+D]-CI calculation. The Pauli exclusion energy E_p in Eq. (65) is given by

$$\begin{aligned} E_p \approx -\epsilon \left\{ \sum_{i,m} (N_i^m)^2 (g_i^m)^2 L(i, m) \right. \\ \left. + \sum_{i,j,m,n} (N_{ij}^{mn})^2 (g_{ij}^{mn})^2 M(i, j, m, n) \right\} , \end{aligned} \quad (66)$$

where $L(i, m)$ is defined in Eq. (54) and $M(i, j, m, n)$ is defined as

$$M(i, j, m, n) = \begin{cases} 1 & \text{if } i=j=m=n \\ 2 & \text{if three indices of } i, j, m, n, \text{ are} \\ & \text{equal or } i=m, j=n, \text{ or } i=n, j=m \\ 3 & \text{if two indices of } i, j, m, n \text{ are equal} \\ 4 & \text{if no indices of } i, j, m, n, \text{ are equal} . \end{cases} \quad (67)$$

The quantity E_C in Eq. (65) is the analog of E_C given in Eq. (55) and describes the coupling among single through quadruple excitation. The coupling matrix has a much more complicated form than Eq. (46) and is not presented here. The renormalization energies ${}^r\Delta_{[S+D]-CI}$ and ${}^r\Delta_0$ in Eq. (65) are the analog of those given in Eqs. (49) and (52).

For the calculation of the excitation energy, the ground-state correlation energy ($N\epsilon$) of the excited state cancels with the correlation energy of the ground state, and there results the expression

$$\Delta E_{R[S+D]-CI} = E_{[S+D]-CI} + \Delta , \quad (68)$$

where Δ is the rearrangement energy

$$\Delta = E_p + E_C + {}^r\Delta_{[S+D]-CI} + {}^r\Delta_0 . \quad (69)$$

The divergence difficulties of the excitation energies in the [S+D]-CI basis (see Sec. III.B) are removed in the renormalized R[S+D]-CI representation, because of the cancellation of the correlation energy ($N\epsilon$) between the excited and ground states. If the rearrangement energy Δ is neglected, the excitation energy $\Delta E_{[S+D]-CI}$ is equal to the energy relative to the SCF ground-state energy as zero ($E_{[S+D]-CI}$). This approximation has been employed previously.²⁵

2. De-excitation from ground state double excitations

In the correlated ground state [Eq. (17)], virtual orbitals are occupied due to the contribution of double excitations. Hence, in analogy with the random phase approximation,¹⁴⁻¹⁸ "excitations" can be introduced which "promote" electrons from the set of virtual to the set of orbitals occupied in the Hartree-Fock ground state. The contributing terms have the form

$$\bar{O}_i^m | \Psi_0 \rangle = \delta_{im} \bar{O}_i^m D_i | \psi_0 \rangle , \quad (70)$$

where Ψ_0 is the correlation ground state and \bar{O}_i^m is the symmetrized de-excitation operator,

$${}^{1,3}\bar{O}_i^m = (1/\sqrt{2})(b_i^m, b_{m,i}^m, \mp b_i^m, b_{m,i}^m) . \quad (71)$$

These excitations are identical to single excitations from the SCF ground state $O_i^m | \psi_0 \rangle$. This expansion (termed R'S-CI) introduces N degrees of freedom in addition to the N^2 degrees of freedom of the RS-CI method. These make the amplitudes of the single excitations $O_i^m | \psi_0 \rangle$ independent of the triple excitation amplitudes $O_i^m D_k | \psi_0 \rangle$; that is,

$$(f_{ik}^i : f_{i0}^i) \neq (d_k : d_0) \quad (72)$$

instead of Eq. (44).

If open shell excitations are included in the ground-state configuration, the de-excitations involving two ethylene units

$$\bar{O}_i^m | \Psi_0 \rangle \quad (i \neq m) \quad (73)$$

are also possible in the correlated ground state. The total degrees of freedom are $2N^2$ and the ratios of the single and the triple excitation amplitudes all become independent. This is equivalent to the CI expansion,

$$| \Psi \rangle = \sum_{i,m} \bar{g}_i^m d_0 | \psi_i^m \rangle + \sum_{i,m} \bar{g}_i^m \left\{ \sum_{\substack{j,k \\ n,o}} d_{jk}^{no} | \psi_{ijk}^{mno} \rangle \right\}$$

where d 's are fixed as the ground-state wavefunction coefficients. The \bar{g}_i^m and \bar{g}_i^m for single and triple excitations, respectively, are determined by minimizing the energy. The coefficients are independent in this case, in contrast to the cluster approximation [Eq. (43)], where they are identical; that is,

$$\bar{g}_i^m = \bar{g}_i^m .$$

If the cluster approximation [Eq. (43)] is valid, the effect of these de-excitations [Eqs. (70) and (73)] is small.

V. RESULTS

In this section, we apply the renormalized CI method to the π -electron spectra of polyenes in order to test the assumptions involved and to demonstrate its accuracy for these systems.

A. Test of assumptions

To test the validity of the renormalized CI method, we consider the $1^1B_u^+$ and $1^3B_u^+$ state of octatetraene, whose eight π -electron system is sufficiently large to yield significant results. As we have seen in Sec. IV,

TABLE VII. Comparison of [S+T']-, R[S]-, and [S]-CI coefficients.^a

Excitations ^b $i \rightarrow \underline{m}$	³ B _u state			¹ B _u state		
	[S+T'] ^c ³ f ₀ ^m	R[S] ³ g ₁ ^m	[S] ³ h ₁ ^m	[S+T'] ^c ¹ f ₀ ^m	R[S] ¹ g ₁ ^m	[S] ¹ h ₁ ^m
1 → <u>1</u>	0.3041	0.3057	0.2968	0.2668	0.2676	0.2707
1 → <u>2</u>	0.1941	0.1928	0.2000	0.2425	0.2421	0.2451
1 → <u>3</u>	-0.1047	-0.1031	-0.1119	-0.1509	-0.1503	-0.1550
1 → <u>4</u>	0.0481	0.0471	0.0531	0.0781	0.0777	0.0821
2 → <u>1</u>	-0.1941	-0.1828	-0.2000	-0.2425	-0.2421	-0.2451
2 → <u>2</u>	-0.4971	-0.4988	-0.4891	-0.4108	-0.4119	-0.4012
2 → <u>3</u>	0.2466	0.2449	0.2546	0.3012	0.3006	0.3013
2 → <u>4</u>	-0.1047	-0.1031	-0.1119	-0.1510	-0.1503	-0.1550

^aOhno parametrization.^bLocalized orbital basis, the absolute magnitudes of the wavefunction coefficients for $i \rightarrow \underline{m}$ and $m \rightarrow i$ are equal, i. e., $|f_{i0}^m| = |f_{0i}^m|$.^cThe coefficients ^{1,3}f₀^m are normalized as $\sum_{i,m} |{}^{1,3}f_{i0}^m|^2 = 1$ for comparison with ^{1,3}g₁^m and ^{1,3}h₁^m.

there are two conditions on the excitation coefficients involved in the renormalized CI calculation. The first is that, if the R[S]-CI calculation is a good approximation to a single plus triple CI ([S+T']-CI) calculation, the single excitation coefficients g_i^m [from R[S]-CI; Eq. (38)] and f_{i0}^m [from [S+T']-CI; Eq. (42)] should be similar to each other and close to the coefficients h_i^m from an [S]-CI calculation. In Table VII we list these coefficients and find good agreement among them for both the ¹B_u⁺ and ³B_u⁺ states. The other condition on the validity of the R[S]-CI calculation is that the triple excitation coefficients obey the cluster approximation [Eq. (43)]. This requires that $f_{ik}^m/f_{i0}^m = d_k/d_0$; that is, the ratio of triple to single excitation coefficients must be independent of i and m and depend only on the ground-state excitation k . This relationship is tested in Table VIII, which presents the ratios f_{ik}^m/f_{i0}^m obtained from the [S+T'] calculation and d_k/d_0 from the ground state [Eq. (17)]. The agreement is found to be excellent for the ³B_u⁺ state; the only exceptions are the configurations in which the single excitation "crosses" the double excitation as depicted in Fig. 7. For the ¹B_u⁺ state the agreement of the ratios is significantly worse, particularly for the double excitation 22 - 22.

The energy levels and excitation energies obtained from R[S]-CI and [S+T']-CI calculations for butadiene, hexatriene, and octatetraene are compared in Table IX. The agreement is excellent for the ¹B_u⁺ state and only slightly worse for the ³B_u⁺ state. The discrepancies depend only weakly on polyene chain length. Table IX also contains energy values obtained with the

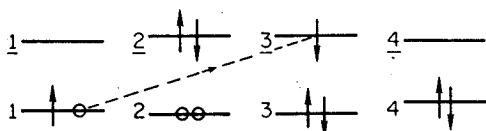


FIG. 7. "Cross over" excitation in octatetraene; the single excitation (3 - 1) crosses over the double excitation (22 - 22) in the triple excited configuration (322 - 122).

R'[S]-CI basis, which includes both the basis of Eq. (37) and the de-excitations defined in Eq. (70). Only a small improvement over the R[S]-CI results is found, though the changes are somewhat larger for the singlet than the triplet states. The inclusion of virtual to occupied SCF-orbital excitations has only an unimportant effect on the excitation energies in the renormalized CI method. This contrasts with the RPA calculations,¹⁴⁻¹⁸ in which de-excitations play an essential role by introducing the required self-consistency. This difference between the present method and the RPA method will be discussed elsewhere.

B. Spectra of polyenes in the renormalized single CI basis

We have used the R[S]-CI basis to evaluate the ¹B_u⁺, ³A_g⁺, and ¹B_u⁺ excitation energies for the polyenes

TABLE VIII. Test of the cluster approximation, Eq. (43).^a

Excitation ^b $i \ k \ k - \underline{m} \underline{k} \ \underline{k}$	(f_{ik}^m/f_{i0}^m)		
	³ B _u	¹ B _u	d_k/d_0
2 1 1 - <u>2</u> <u>1</u> <u>1</u>	0.1275	0.1004	
2 1 1 - <u>3</u> <u>1</u> <u>1</u>	0.1300	0.1110	
2 1 1 - <u>4</u> <u>1</u> <u>1</u>	0.1311	0.1156	0.1369
3 1 1 - <u>3</u> <u>1</u> <u>1</u>	0.1365	0.1268	
3 1 1 - <u>4</u> <u>1</u> <u>1</u>	0.1390	0.1296	
4 1 1 - <u>4</u> <u>1</u> <u>1</u>	0.1382	0.1336	
1 2 2 - <u>1</u> <u>2</u> <u>2</u>	0.1169	0.0574	
1 2 2 - <u>3</u> <u>2</u> <u>2</u> ^c	0.0537	0.0797	
1 2 2 - <u>4</u> <u>2</u> <u>2</u> ^c	0.0652	0.0848	0.1220
3 2 2 - <u>3</u> <u>2</u> <u>2</u>	0.1154	0.0752	
3 2 2 - <u>4</u> <u>2</u> <u>2</u>	0.1159	0.0825	
4 2 2 - <u>4</u> <u>2</u> <u>2</u>	0.1213	0.1002	

^aOhno parametrization.^cSee Fig. 7.^bLocalized orbital basis.

TABLE IX. Comparison of excitation energies (eV) from R[S]- and [S+T']-CI calculations.^a

Polyene length (N)	R[S]-CI ^b	R'[S]-CI ^{b,c}	[S+T']-CI ^b	[S]-CI	[C]-CI ^d
³ B _u state					
2	2.8059	2.8049	2.8049	2.5182	2.7161
3	2.3683	2.3675	2.3645	2.0759	2.2256
4	2.1376	2.1371	2.1321	1.8468	...
¹ B _u state					
2	5.8926	5.8672	5.8672	5.4654	5.8022
3	5.1230	5.1026	5.0890	4.6334	5.0254
4	4.6276	4.6125	4.5908	4.1118	...

^aOhno parametrization.^bGround state energies are evaluated from the [D']-CI expansion, Eq. (17).^cR'[S]-CI calculation on the basis expansions Eqs. (37) and (70).^dCI calculation with the complete excitation basis.

$C_{2N}H_{2N+2}$, $N=2, 3, \dots, 9$. These states were chosen because they are well known to be dominated by single excitations from the Hartree-Fock ground state. The results from the S-CI and R[S]-CI calculations are compared in Fig. 8(a) [Ohno parametrization, Eq. (3a)] and in Fig. 8(b) (Mataga-Nishimoto parametrization, Eq. (3b)). These figures give evidence for the importance of ground-state correlation in the excited states and for the effectiveness of the renormalized CI method. In the figures the exact ground and excited state energies obtained for butadiene and hexatriene from complete CI calculation are also given. The difference between the complete CI and the R[S]-CI energies is due mainly (i) to the missing open shell configurations in the correlated ground-state wavefunction Ψ_0 and (ii) to the neglect of double excitations in the excited states.

Figures 8(a) and 8(b) also illustrate that the excited state correlation energy increases linearly with the number of π electrons, in accord with Eq. (57) and the fact that the rearrangement energy Δ is relatively independent of chain length (see Sec. IV and below); for Δ equal to a constant, E_{RS-CI}^{corr} increases as $N\epsilon$, where ϵ is the correlation energy of a single ethylene unit. Since ϵ is larger in magnitude in the Mataga-Nishimoto parametrization than in the Ohno parametrization, this is reflected in the correlation corrections of the excited states in the two parametrization. Because of the cancellation expected between the ground and excited state correlation energies, the difference between the calculated excitation energy obtained from the R[S]-CI and [S]-CI methods is equal to the rearrangement energy Δ [Eq. (59)]. In Figs. 9(a) and 9(b) we plot the R[S]-CI and [S]-CI excitation energies and confirm that Δ is weakly dependent on polyene length. It can be seen that the S-CI and R[S]-CI calculations behave similarly with chain length but that the latter are much closer to the correct excitation energy than the former.

The analysis of Sec. IV showed that the rearrangement energy Δ consists of three terms, the Pauli exclusion energy E_P , the coupling energy E_C , and the renormaliza-

tion correction, ${}^r\Delta ({}^r\Delta = {}^r\Delta_0 + {}^r\Delta_{S-CI})$. In the first column of Table X under the heading R[S]-CI are listed the values of these three terms for butadiene, hexatriene, and octatetraene ($N=2, 3, 4$). We can see that the Pauli exclusion energy E_P makes a larger contribution to Δ than do E_C and ${}^r\Delta$, and is larger for the $1^1B_u^+$ state than for the $1^3B_u^+$ and $1^3A_g^+$ states. This difference is due to the greater contribution of interethylene excitation to the delocalized $1^1B_u^+$ state. For an interethylene excitation, the Pauli exclusion energy is -2ϵ and for an intraethylene excitation the Pauli exclusion energy is $-\epsilon$, where, by definition $\epsilon < 0$ (see Sec. IV). Since the ex-

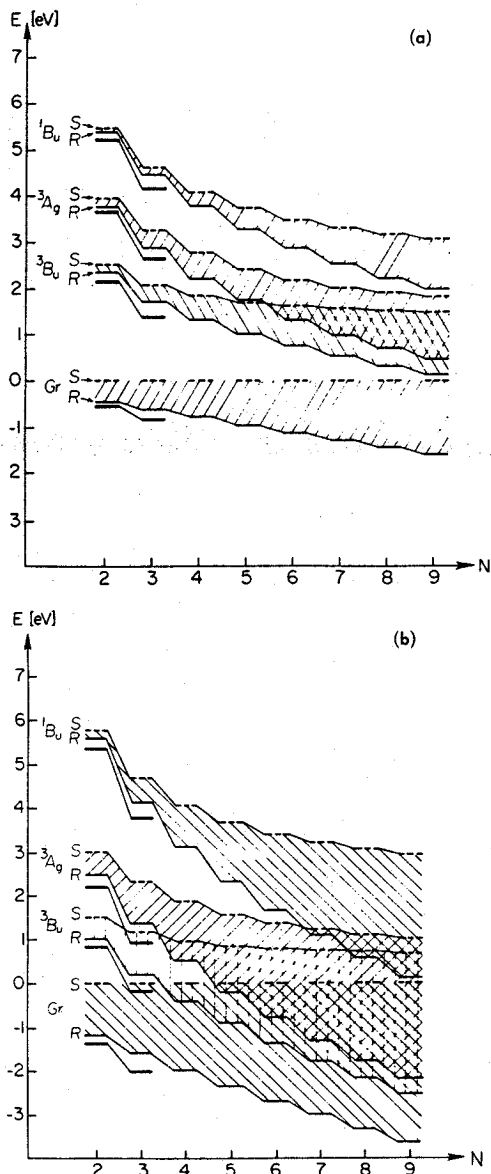


FIG. 8. Energies for the $1^1A_g^-(gr)$, $1^3B_u^+$, $1^3A_g^+$, and $1^1B_u^+$ excited states in the linear polyenes $C_{2N}H_{2N+2}$ relative to the SCF ground state as zero; (---), [S]-CI; (—), R[S]-CI; (—), [C]-CI. (a) in the Ohno parametrization and (b) in the Mataga-Nishimoto parametrization.

TABLE X. Pauli exclusion energy E_P , coupling energy E_C , and renormalization energy $\tau\Delta$ (eV).^a

Length of polyene (N)	State	$E_P/(-\epsilon) + E_C/(-\epsilon) + \tau\Delta/(-\epsilon)$		$E_P/(-\epsilon)$
		R[S]-CI	[S]-CI	[S+D]-CI
2	3B_u	1.216 - 0.037 + 0.056	1.236 - 0.028 + 0.044	1.280
3	3B_u	1.302 - 0.011 + 0.100	1.330 + 0.008 + 0.080	1.416
4	3B_u	1.346 + 0.010 + 0.115	1.377 + 0.036 + 0.090	1.494
2	3A_g	1.020 + 0.233 - 0.047	1.020 + 0.233 - 0.047	1.007
3	3A_g	1.140 + 0.119 - 0.019	1.152 + 0.122 - 0.025	1.209
4	3A_g	1.224 + 0.076 + 0.0011	1.244 + 0.085 + 0.002	1.333
2	1B_u	1.365 + 0.422 + 0.047	1.386 + 0.417 + 0.039	1.407
3	1B_u	1.495 + 0.706 + 0.106	1.513 + 0.702 + 0.099	1.560
4	1B_u	1.557 + 0.876 + 0.138	1.572 + 0.873 + 0.132	1.644
2	1A_g			1.983
3	1A_g			2.146
4	1A_g			2.253

^aOhno parametrization; for definitions, see text. The single ethylene correlation energy $\epsilon = -0.233$ eV for butadiene, -0.215 eV for hexatriene and -0.204 eV for octatetraene. $\tau\Delta = \tau\Delta_{g-CI} + \tau\Delta_0$.

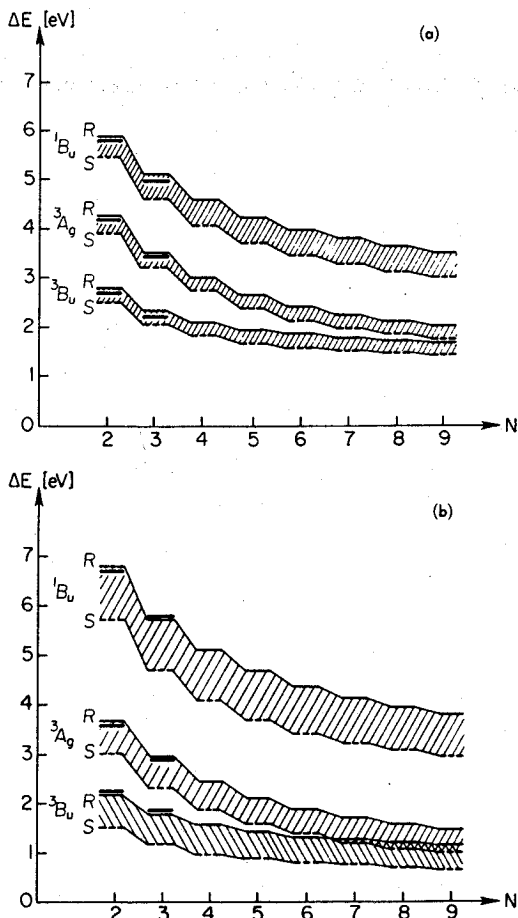


FIG. 9. Excitation energies corresponding to Fig. 8.

cited state is a superposition of inter- and intraethylene excitations, the Pauli exclusion energy [$E_P/(-\epsilon)$] has a value between 1 and 2. It is closer to 2 for delocalized states, like the $^1B_u^+$ state, and it is closer to 1 for localized states, such as the $^3B_u^+$ and $^3A_g^+$ states.

The coupling energy [$E_C/(-\epsilon)$] is always found to be smaller than the Pauli exclusion term. Its contribution is significantly larger for the $^1B_u^+$ state than for the triplet states. The term is made up of T - T couplings [Eq. (46a)] and S - T couplings [Eq. (46b)]. Table XI lists the magnitudes of the individual contributions to the coupling energy E_C for hexatriene. It is clear that the S - T coupling contributions are significant, while the T - T couplings are negligible. Comparing the $^3B_u^+$ state with the $^1B_u^+$ state, we see that the S - T terms make a small contribution to the former primarily because of cancellation. Elements of the T - T coupling term in Eq. (46a) can be significant only when $m=n$ and $i=j$. Then the terms in the first two parentheses represent the Coulomb and exchange interactions of the closed shell double excitation ($\underline{kk} - \underline{kk}$) with the particle state \underline{m} and

TABLE XI. Coupling and renormalization energy contributions for hexatriene (eV).^a

State	T - T [Eq. (46a)]	S - T [Eq. (46b)]	$\tau\Delta_{g-CI}$	$\tau\Delta_0$
	(1st+2nd) +3rd term	1st +(2nd+3rd) term		
3B_u	0.005 - 0.002	-0.052 + 0.046	0.036	-0.014
3A_g	0.003 + 0.000	0.009 + 0.013	0.009	-0.013
1B_u	0.005 - 0.004	0.092 + 0.058	0.039	-0.016

^aOhno parametrization.

with the hole state i . The total contribution from the Coulomb terms cancels,

$$2(kk|mm) - 2(kk|mm) + 2(kk|ii) - 2(kk|ii) = 0$$

and only small exchange terms remain. The third term in Eq. (46a) is also small; thus the T - T coupling is negligible.

The renormalization energy corrections, Δ_s and Δ_0 [Eqs. (49) and (52), respectively], are also listed in Table XI. We can see that these energies are of the same magnitude as the S - T coupling energy. Since Δ_s and Δ_0 have opposite signs, their total contribution is less than half the value of the coupling energy E_C (except for $1^3B_u^*$ state for which the value of E_C is very small). In a subsequent paper we use this result to formulate a simple approximation for the calculation of excited states.²⁶

C. Estimate of the rearrangement energy

The rearrangement energy Δ is the entire correlation correction to the excitation energies [Eq. (59)]. It is, thus, a quantity of great interest. The calculations described in the previous section have demonstrated that the rearrangement energy is relatively constant, independent of chain length. This is the fundamental reason for the fact that appropriately parametrized single-excitation methods work as well as they do for polyenes. The results given here suggest a simple approximate method for the direct evaluation of the rearrangement energy Δ . We have seen (Table VII) that the coefficients of the renormalized R[S]-CI expansion g_i^m are close to the [S]-CI coefficients h_i^m . This allows a direct evaluation of the rearrangement energy Δ on the basis of a [S]-CI calculation; that is, E_p , E_C , and Δ can be evaluated from Eqs. (53), (55), and (46), (49), and (52) by replacing the R[S]-CI coefficients g_i^m in these equations by the [S]-CI coefficients h_i^m . The results obtained are given in Table X under the heading [S]-CI for butadiene, hexatriene, and octatetraene. The agreement between the approximate and exact R[S]-CI results is excellent. This illustrates that it is possible to account for the effect of triple excited configurations on the excitation energies solely on the basis of a knowledge of the [S]-CI coefficients h_i^m of the excited states and the [D]-CI coefficients d_h of the ground state [Eq. (17)].

In a calculation including single plus double excitations, the wavefunction coefficients of the renormalized [S+D]-CI expansion are expected to be about equal to those of the [S+D]-CI expansion. This suggests an extension of the above ideas to the evaluation of E_p , E_C , $\Delta_{[S+D]-CI}$ and Δ_0 from Eqs. (66) and (69) by replacing the R[S+D]-CI coefficients g_i^m and g_{ij}^{mn} by the [S+D]-CI coefficients h_i^m and h_{ij}^{mn} , respectively. The Pauli exclusion energy E_p has been computed in this way, and the results are listed in the last column of Table X. The coupling energy E_C has not been included because of the difficulty in evaluating the complicated matrix elements of \hat{V} . The $2^1A_g^*$ state is found to have a large Pauli exclusion energy [$E_p/(-\epsilon) \approx 2.0$], since this state consists mainly of double excitations involving two ethyl-

ene units [$M(i, j, m, n) = 2.0$ in Eq. (67)]; the dominant contribution is from two ethylene units each excited to a triplet state (see Sec. III.A). It can be seen from Table X that for the $1^3B_u^*$, $1^3A_g^*$, and $1^1B_u^*$ states there is a very small difference between the [S]-CI and [S+D]-CI values for E_p , since these states have very small contributions from double-excited configurations.

D. Exponential potential

To test the renormalized CI method for different values of the correlation interaction, the exponential electron repulsion formula [Eq. (3c)] was used.³ The results of [S]-CI, R[S]-CI, [S+T']-CI, [S+D]-CI, and complete CI calculations on hexatriene are presented in Table XII, for $D_0 = 16, 4, 2, 0.5 \text{ \AA}$. At $D_0 = 16 \text{ \AA}$ (long range potential; SCF limit) the ground-state correlation is small and the excitation energies for the $1^3B_u^*$, $1^3A_g^*$, $1^1B_u^*$ states resulting from all methods are very similar. For smaller D_0 ($D_0 = 2, 4 \text{ \AA}$, increased correlation), the [S]-CI calculations predict excitation energies which are too low, and the R[S]-CI and [S+T']-CI calculations yield values which are in excellent agreement with each other and quite close to the exact values. Finally, in the limit of very strong correlation ($D_0 = 0.5 \text{ \AA}$), higher order contributions become important and the R[S]-CI method and [S+T']-CI calculation yield too small a correlation energy.

E. Transition moment and oscillator strength

The renormalized [S]-CI method can also be applied to an evaluation of the transition moment and the oscillator strength of the transition between the ground state

TABLE XII. Hexatriene excitation energies (eV) for exponential repulsion.^a

$D_0/\text{\AA}$	state	[S]-CI	R[S]-CI	[S+T']-CI	[S+D]-CI	exact
16	1^1A_g (gr) ^b	0.0	(-0.05)	(-0.05)	(-0.10)	(-0.10)
	3^1B_u	2.01	2.04	2.04	2.02	2.00
	3^1A_g	3.84	3.87	3.86	3.89	3.86
	1^1B_u	3.08	3.12	3.11	3.10	3.09
4	1^1A_g (gr) ^b	0.0	(-0.58)	(-0.58)	(-0.83)	(-0.87)
	3^1B_u	1.47	1.76	1.76	1.94	1.63
	3^1A_g	3.00	3.27	3.26	3.60	3.25
	1^1B_u	4.24	4.70	4.64	4.74	4.58
2	1^1A_g (gr) ^b	0.0	(-1.55)	(-1.55)	(-1.95)	(-2.17)
	3^1B_u	0.72	1.35	1.34	2.51	1.34
	3^1A_g	2.09	2.72	2.72	3.65	2.75
	1^1B_u	4.64	5.72	5.69	6.06	5.78
0.5	1^1A_g (gr) ^b	0.0	(-4.00)	(-4.00)	(-4.75)	(-5.94)
	3^1B_u	-1.09	0.07	0.04	2.63	0.93
	3^1A_g	0.46	1.87	1.86	4.11	1.98
	1^1B_u	4.07	6.51	6.50	7.68	7.45

^aRepulsion defined in Eq. (3c); for this calculation, we assumed all bond lengths equal (1.397 \AA).

^bGround-state correlation energy; R[S]- and [S+T']-CI results are obtained for the ground state expansion in Eq. (17).

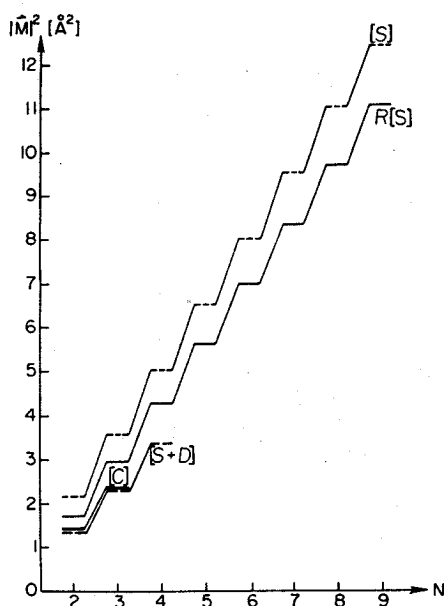


FIG. 10. Absolute square of the transition moments in the linear polyenes $C_{2N}H_{2N+2}$ with Ohno parametrization. (---), [S]-CI; (—), R[S]-CI; (- - -), [S+D]-CI; (—), [C]-CI.

and the lowest optically allowed $1^1B_u^+$ state. The transition moment is defined by

$$M = \langle \Psi(1^1B_u^+) | r | \Psi_0 \rangle, \quad (74)$$

where r is the dipole moment operator (in Å) and Ψ_0 and $\Psi(1^1B_u^+)$ are the wavefunctions of the ground and the $1^1B_u^+$ state, respectively. The transition moments for the polyenes $C_{2N}H_{2N+2}$ ($N=2, 3, \dots, 9$) evaluated in the [S]-CI and the R[S]-CI basis are presented in Fig. 10. The [S+D]-CI and complete-CI results for the small polyenes are also shown. One observes that the [S]-CI calculation overestimates the transition moment, while the [S+D]-CI calculation yields almost the exact results at least for small polyenes. The R[S]-CI results are between these two sets of values.

Both ground and excited state correlation effects are important for the transition moment. Within the PPP formulation, the valence-bond description of the optically allowed $1^1B_u^+$ state consists purely of ionic structures. This means that only the ionic components in the ground state couple with this state through the dipole operator r . Since the ionic components of the ground state are overestimated in the [S]-CI calculation (i. e., in the SCF ground state), the [S]-CI basis yields too large a transition moment. The correlation effects in the ground state Ψ_0 introduce more nonionic structures (covalent structures) and thus decrease the transition moment. The correlation effects in the $1^1B_u^+$ state also tend to lower the transition moment. In the R[S]-CI basis, the important correlation effects of the ground and $1^1B_u^+$ states are included by certain double and triple excited configurations (D' and T'), respectively; the [S+T']-CI results are very close to those from the R[S]-CI calculation. The R[S]-CI and [S+T']-CI basis provide a

smaller transition moment than the [S]-CI basis, but the results do not yet agree with the exact values. This error of the R[S]-CI calculation for the transition-moment can be attributed to the neglect of (i) double excitations in the excited state and (ii) the open-shell double excitations in the ground state. By examining the [S+D]-CI results, we found that these two types of corrections are both important.

The oscillator strength is given by

$$f = 0.869 \Delta E |M|^2, \quad (75)$$

where ΔE is the excitation energy (in units eV) and $|M|^2$ is the absolute square of the transition moment (in the units Å^2) defined in Eq. (74). In Fig. 11 we present the oscillator strength corresponding to the transition-moment values shown in Fig. 10. As expected from the results for the transition moment, the oscillator strengths for small polyenes obtained from the R[S]-CI basis are in better agreement with the exact values than those from the [S]-CI basis. However, for larger polyenes ($N \geq 6$) the R[S]-CI values exceed the [S]-CI results. This is due to the fact that the energy factor ΔE involved in the oscillator strength [Eq. (75)] is larger in the R[S]-CI basis than in the [S]-CI basis and the ratio

$$\Delta E_{R[S]-CI} / \Delta E_{[S]-CI}$$

increases rapidly with N . For large polyenes, even the [S+D]-CI calculations become unreliable, because the transition energy $\Delta E_{[S+D]-CI}$ is too large (nearly divergent as seen in Sec. III. B).

VI. CONCLUSION

Although a single plus double excitation basis configuration interaction calculation ([S+D]-CI) yields a qualitatively correct energy scheme for polyenes, quantitative results require the inclusion of higher excitations. To examine their effect we have expressed the

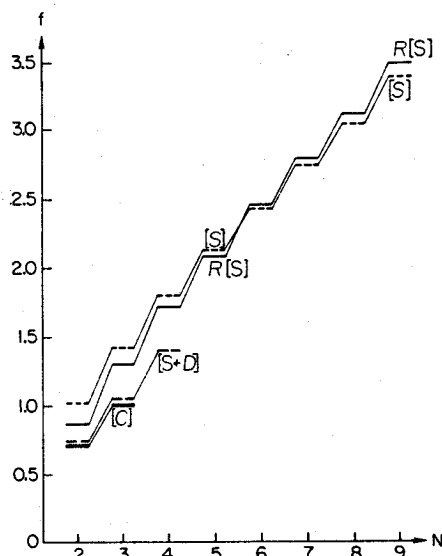


FIG. 11. Oscillator strengths corresponding to Fig. 10.

required configurations in terms of a localized SCF-orbital basis. The spatial separation of excitations in the localized orbital description makes it possible to approximate higher excitations as products of lower excitations; for example, triple excitations can be written as products of a small set of single and double excitations. It is demonstrated by this type of approach that the most important higher excitations introduce corrections for ground-state type correlation in the excited states. To estimate the contribution of these corrections to the excited state energy an approximate CI method, termed renormalized CI (i. e., R[S]-CI), has been developed. The essential element of the method in lowest order is to assume that only singly and triply excited configurations relative to the Hartree-Fock ground state are required, to calculate the singly excited contributions, and to approximate the effect of triple excitations by assuming that their contribution is given by the product of the appropriate single excitation coefficient with the double excitation coefficient in the correlated ground state. Use of this approach yields valid polyene excitation energies and their correct dependence on chain length.

An analysis of the renormalized CI method shows that the correlation in excited states can be expressed as a sum of the ground-state correlation energy, $N\epsilon$ (where ϵ is the correlation energy of one ethylene unit in an N -unit polyene), and a rearrangement correction Δ . Only the rearrangement energy contributes to the excitation energy. Thus, the excitation energy obtained from the R[S]-CI calculation is higher than the [S]-CI energy (relative to the SCF ground-state energy) by the amount of Δ . Each excited state has a different value of Δ ; for example, the $1^3B_u^*$ and $1^3A_g^*$ states, which consist mainly of intraethylene excitations, have small Δ [$\Delta \approx 0.28$ eV (Ohno) for hexatriene], while the $2^1A_g^*$ and $1^1B_u^*$ states, which involve interethylene excitations, have somewhat larger Δ [$\Delta \approx 0.47$ eV (Ohno) for hexatriene]. The fact that Δ is small and relatively independent of chain length (e. g., for the $1^1B_u^*$ state, $\Delta = 0.43$ eV (Ohno) for butadiene and 0.52 eV (Ohno) for octatetraene) provides a partial justification for the use of appropriately parametrized [S]-CI methods for polyenes.

The excitation energies resulting from the renormalized CI calculation are found to be in good agreement with the complete-CI values for butadiene and hexatriene. Since the R[S]-CI treatment results in similar equations of the same dimension as an [S]-CI calculation, the accurate results are obtained with less work than in the usual CI approach.

An extension of the present method is possible including (i) open shell double and some higher order excitations in the ground state and (ii) "elementary" double excitations in the excited states. Inclusion of the latter is essential for the discussion of the relative level ordering of the excited $2^1A_g^*$ and $1^1B_u^*$ states. Even for the $1^3B_u^*$, $1^3A_g^*$, and $1^1B_u^*$ states it is of importance be-

cause the doubly excited configurations make increasingly significant contributions for larger polyenes.

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