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

I. Ohmine\textsuperscript{b)} and M. Karplus

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Klaus Schulten

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
and Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, Federal Republic of Germany

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Extensive configuration interaction (CI) is needed to achieve satisfactory descriptions of the optical spectra and photochemical properties of the \(\pi\)-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 \(\pi\)-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 \(1\text{B}_\text{u}^*, 1\text{B}_\text{g}^*, \text{and } 1\text{A}_\text{g}^*\) 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 experimental\textsuperscript{1} and theoretical studies\textsuperscript{2} that have demonstrated the inadequacy of the independent particle model, we have examined the magnitude of correlation effects on the \(\pi\)-electron spectrum\textsuperscript{3} of 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., \(1\text{B}_\text{u}^*, 1\text{A}_\text{g}^*\)) and the triplet states (e.g., \(3\text{B}_\text{u}, 3\text{A}_\text{g}^*\)) are reasonably well described by such calculations, the "covalent" singlet states (e.g., \(1\text{A}_\text{g}^*, 1\text{B}_\text{u}^*\)) are not; in particular, the lowest excited \(1\text{A}_\text{g}^*\) state, which is now known to be near-degenerate with the lowest \(1\text{B}_\text{u}^*\) 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 approximately 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 \(1\text{B}_\text{u}^*\) 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 \(\pi\) electrons are assumed to be fixed and a Pariser–Parr–Pople Hamiltonian is used to represent the \(\pi\) electron system. The advantages and limitations of a semi-empirical treatment of this type have been discussed previously by us\textsuperscript{3} and will not be repeated here; some recent related \textit{ab initio} results are given in Ref. 4. A localized SCF orbital basis\textsuperscript{5} is used for the \(\pi\) 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.\textsuperscript{6} Due to the spatial separation of excita-

\textsuperscript{a})Supported in part by the National Science Foundation and the National Institutes of Health.

\textsuperscript{b})Present address: Institute for Molecular Science, 38 Nishigongaka, Myodaiji, Okazaki, Aichi, 444, Japan.
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 ex-
citation can be decomposed into a single and a double ex-
citation. 7 Making use of this decomposition, it is possi-
able to show that the most important correlation con-
tributions 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 ef-
fects of the Pauli exclusion principle, the coupling be-
 tween 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 cal-
bulation but includes the higher order corrections in an
approximate manner is developed. In this method, ex-
citation configurations are generated relative to the cor-
related 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 sin-
glet states can not be calculated because they require
double excitations relative to the correlated ground
state.4,5 Hence only $1^2E_u$, $1^2A_g$, and $1^2B_g$ states are
properly described, while the $2^2A^*$ and $2^2B^*$ states re-
quire 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,6 Simpson,9 Pople and
Walmsley,10 Heilbronner,11 and others.12 Most of this
work involved use of a simple excitonic model for ap-
proximating 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
Mallrieu and co-workers,13 who used a completely lo-
calized ethylenic basis (i.e., non-SCF) to analyze the
effects of higher order excitations on excited state en-
ergies and to demonstrate the cancellation between the
correlation in the excited states and that in the ground
state. Also related are random phase approximation14-16
and Green's function17-20 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 ex-
amined the correlation correction to the excited states
introduced by the higher order excitations. An approxi-
mate 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 dem-
strate the approximate constancy, independent of chain
length, of the correlation correction to the excitation
energy. Conclusions are presented in Sec. VI.

II. THE $\pi$-ELECTRON HAMILTONIAN

The Pariser-Parr-Pople (PPP) Hamiltonian for the
$\pi$-electron system of a conjugated hydrocarbon is (en-
ergies are given in eV and distances in Å)

$$
H = \sum_{\kappa \lambda} Z_{\kappa} Z_{\lambda} R_{\kappa \lambda} + \sum_{\kappa \sigma} \left( I_{\kappa} - \sum_{\lambda \sigma} Z_{\lambda} R_{\kappa \lambda} \right) n_{\kappa \sigma}
$$

$$
+ \sum_{\kappa \sigma} c_{\kappa \sigma}^* c_{\kappa \sigma} + \frac{1}{2} \sum_{\kappa \sigma \kappa' \sigma'} R_{\kappa \kappa'} n_{\kappa \sigma} n_{\kappa' \sigma'},
$$

(1)

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

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

(2)

where $\beta_0$ is a constant and $r_{\kappa \lambda}$ is the distance between the
nuclear sites $\kappa$ and $\lambda$. 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 $\pi$
electrons. Two standard electron-electron repulsion for-
mulas were used; they are the Ohno formula

$$
R_{\kappa \lambda} = \frac{14.397}{[(2(14.397)/(R_{\kappa \lambda} + R_{\kappa \lambda}))^2 + r_{\kappa \lambda}^2]^{1/2}}
$$

(3a)

and the Mataga-Nishimoto formula,

$$
R_{\kappa \lambda} = \frac{14.397}{2(14.397)/(R_{\kappa \lambda} + R_{\kappa \lambda}) + r_{\kappa \lambda}}
$$

(3b)

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

$$
R_{\kappa \lambda} = R_{\kappa \lambda} \exp(-r_{\kappa \lambda}/D_0)
$$

(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); 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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_a$</td>
<td>11.16 eV</td>
</tr>
<tr>
<td>$Z_e$</td>
<td>1.0</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>-2.43 eV</td>
</tr>
<tr>
<td>$R_a$</td>
<td>11.13 eV</td>
</tr>
<tr>
<td>$r_{oa}$</td>
<td>1.35 Å (double bonds)</td>
</tr>
<tr>
<td></td>
<td>1.46 Å (single bonds)</td>
</tr>
</tbody>
</table>

empirical parameters $I_a$, $Z_e$, $\beta_0$, and $R_a$, 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 $2N \pi$ electrons a set of completely localized orbitals corresponds to the $N$ occupied orbitals $e_i$ and $N$ unoccupied orbitals $e_\pi$ of the ethylene units of which the polyenes are composed; they have the form

$$e_i = (1/\sqrt{2})(p_{2i-1} + p_{2i})$$

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

where the $p_i$ are the atomic $\pi$ 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 $\omega$, $\omega$; $i = 1, 2, \ldots, N$ can be defined; the symbols $\omega$, $\omega$ stand for the occupied and $\omega$ for the unoccupied orbitals of these sets are connected with the standard Hartree–Fock orbitals by the unitary transformation $U = (U^T)^{-1}$, where $U$ and $U$ are unitary matrices acting on the occupied ($\phi_i$) and the unoccupied ($\phi_\pi$) Hartree–Fock orbitals, respectively. Thus,

$$\omega_i = \sum_{j=1}^{N} U_{ij} \phi_j$$

$$\omega_\pi = \sum_{j=1}^{N} U_{ij} \phi_\pi$$

The corresponding transformations among the creation and annihilation operators $b_i$ and $b_\pi$ for the $\omega$

and $\omega$ orbitals and the operators $a_i$, $a_\pi$, and $a_\pi$, $a_\pi$ for the SCF orbitals are

$$b_i = \sum_{j=1}^{N} U_{ij} a_j$$

$$b_\pi = \sum_{j=1}^{N} U_{ij} a_\pi$$

$$b_i = \sum_{j=1}^{N} U_{ij} a_\pi$$

$$b_\pi = \sum_{j=1}^{N} U_{ij} a_\pi$$

The ground state $\psi_0$ expressed in terms of the orbitals $\omega_i$ is

$$\psi_0 = \prod_{i=1}^{N} \phi_i$$

where the usual notation of a bar superscript on the orbitals indicates a spin of $-1/2$. Correspondingly, the excited electron configurations over the orbitals $\omega_i$ and $\omega_\pi$ are

$$b_i^* b_i \psi_0 = \sum_{i,j} U_{ij}^* U_{ij} a_j^* a_i \psi_0$$

$$b_\pi^* b_\pi \psi_0 = \sum_{i,j} U_{ij}^* U_{ij} a_j^* a_\pi \psi_0$$

It is clear that the single excitations with respect to $\omega$ orbitals are linear combinations of the single excitations over SCF orbitals, the double excitations with respect to $\omega$ orbitals are linear combinations of the double excitations over SCF orbitals, etc. This shows that a complete CI calculation with the $\omega$ 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 $\omega_i$ and $\omega_i$ that have maximum overlap with the ethylene orbitals $e_i$ and $e_\pi$ of Eq. (4). For this purpose we define the projection operators $P$ and $Q$ onto the subspaces $V$ and $V'$ of the occupied and unoccupied SCF orbitals $\phi_i$ and $\phi_\pi$,

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

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

$$P + Q = 1$$

The set of projected orbitals

$$\langle \phi_i | e_i \rangle = \sum_{j=1}^{N} | \phi_j \rangle \langle \phi_j | e_i \rangle$$

$$\langle \phi_\pi | e_\pi \rangle = \sum_{j=1}^{N} | \phi_\pi \rangle \langle \phi_\pi | e_\pi \rangle$$

form nonorthogonal basis sets in $V$ and $V'$, respectively. The $P | e_i \rangle$ and $Q | e_\pi \rangle$ are linearly independent for all $i$, $i$ so that the overlap matrices with elements $| S_{ij} \rangle = | S_{ij} | | e_i \rangle$ (9) are real and symmetric

$$S_{ij} = \langle e_i | P | e_i \rangle$$

$$S_{ij} = \langle e_\pi | Q | e_\pi \rangle$$

Table II. Localized orbital coefficients $B_{ij}$ for decapentaene.*

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>0.707</td>
<td>0.698</td>
<td>0.696</td>
<td>0.0</td>
<td>-0.105</td>
<td>-0.116</td>
<td>0.0</td>
<td>0.038</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>0.111</td>
<td>0.123</td>
<td>0.707</td>
<td>0.699</td>
<td>0.685</td>
<td>0.0</td>
<td>-0.116</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.111</td>
<td>0.123</td>
<td>0.707</td>
<td>0.699</td>
<td>0.685</td>
<td>0.0</td>
<td>-0.116</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-0.022</td>
<td>-0.028</td>
<td>0.0</td>
<td>0.116</td>
<td>0.130</td>
<td>0.707</td>
<td>0.688</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.038</td>
<td>0.046</td>
<td>0.0</td>
<td>-0.106</td>
<td>-0.115</td>
<td>0.707</td>
<td>0.688</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.007</td>
<td>0.010</td>
<td>0.0</td>
<td>-0.024</td>
<td>-0.031</td>
<td>0.0</td>
<td>0.116</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-0.016</td>
<td>-0.022</td>
<td>0.0</td>
<td>0.038</td>
<td>0.047</td>
<td>0.0</td>
<td>-0.106</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-0.003</td>
<td>-0.004</td>
<td>0.0</td>
<td>0.007</td>
<td>0.010</td>
<td>0.0</td>
<td>-0.022</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.007</td>
<td>0.011</td>
<td>0.0</td>
<td>-0.016</td>
<td>-0.022</td>
<td>0.0</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Unoccupied orbitals

| $\omega_1$ | 0.707 | 0.698 | 0.696 | 0.0 | -0.105 | -0.116 | 0.0 | 0.038 | 0.046 |
| $\omega_2$ | -0.707 | -0.698 | -0.696 | 0.0 | -0.111 | -0.123 | 0.0 | 0.022 | 0.028 |
| | 0.0 | 0.111 | 0.123 | 0.707 | 0.699 | 0.685 | 0.0 | -0.106 | -0.115 |
| | 0.0 | 0.105 | 0.116 | -0.707 | -0.699 | -0.685 | 0.0 | -0.116 | -0.130 |
| | 0.0 | -0.022 | -0.028 | 0.0 | 0.116 | 0.130 | 0.707 | 0.688 | 0.683 |
| | 0.0 | -0.038 | -0.046 | 0.0 | 0.106 | 0.115 | -0.707 | -0.688 | -0.683 |
| | 0.0 | 0.007 | 0.010 | 0.0 | -0.024 | -0.031 | 0.0 | 0.116 | 0.130 |
| | 0.0 | 0.016 | 0.022 | 0.0 | 0.038 | 0.047 | 0.0 | 0.106 | 0.115 |
| | 0.0 | -0.003 | -0.004 | 0.0 | 0.007 | 0.010 | 0.0 | -0.022 | -0.028 |
| | 0.0 | 0.007 | 0.011 | 0.0 | -0.016 | -0.022 | 0.0 | -0.038 | -0.046 |

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

$\omega_{ij} = \sum_{k} B_{ik} \phi_{k}$ (occupied).

$\omega_{ij} = \sum_{k} B_{ik} \phi_{k}$ (unoccupied)

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

$$\sum_{i} S_{ij}^{1/2} P |e_i\rangle , \sum_{i} S_{ij}^{1/2} Q |e_i\rangle .$$

We now wish to show that these orbitals are the SCF orbitals that have maximum overlap with the $e_i$, $e_1$. Writing

$$|\omega_1\rangle = \sum_{k} U_{ij}^{*} S_{jk}^{1/2} P |e_k\rangle , \ |\omega_2\rangle = \sum_{k} U_{ij}^{*} S_{jk}^{1/2} Q |e_k\rangle ,$$

where $U$ and $U'$ are arbitrary unitary transformations, we demonstrate that the distance between $\omega_i$ and $e_i$ and that between $\omega_i$ and $e_1$, $d^2 = \sum_{i=1}^{N} \langle \omega_i - e_i | \omega_i - e_i \rangle , \ d^2 = \sum_{i=1}^{N} \langle \omega_i - e_1 | \omega_i - e_1 \rangle \ (11)$

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

$$d^2 = \sum_{i=1}^{N} \left\{ \langle \omega_i | \omega_i \rangle - \sum_{k} U_{ij}^{*} S_{jk}^{1/2} \langle e_i | P | e_k \rangle \right\} - \sum_{k} \langle e_i | P | e_i \rangle S_{ij}^{1/2} U_{ij}^{*}$$

$$+ \langle e_i | Q | e_i \rangle .$$

Since $S$ is symmetric,
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

\[
-\begin{array}{cccc}
  x & x & x & x \\
  -x & -x & x & x
\end{array}
\]

in which two electrons are promoted from the second orbital \( \phi_2 \) to the third orbital \( \phi_3 \); 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

\[
-\begin{array}{cccc}
  x & x & - & - \\
  - & - & x & x
\end{array}
\]

and

\[
-\begin{array}{cccc}
  - & - & x & x \\
  x & x & - & -
\end{array}
\]

in which two electrons are promoted within each ethylene unit. Since the ground state of an isolated ethylene unit can be written as \( \begin{array}{c} \alpha \end{array} + \begin{array}{c} \alpha \end{array} \), where \( \alpha \) 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

\[
-\begin{array}{cccc}
  - & - & x & - \\
  x & - & - & x
\end{array}
\quad -\begin{array}{cccc}
  - & - & - & x \\
  x & x & - & -
\end{array}
\quad -\begin{array}{cccc}
  x & - & x & - \\
  - & x & - & -
\end{array}
\]

the 50% contribution from single excitations involves

\[
-\begin{array}{cccc}
  - & - & x & - \\
  x & - & x & -
\end{array}
\quad -\begin{array}{cccc}
  - & x & - & x \\
  - & x & x & -
\end{array}
\]

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

\[
-\begin{array}{cccc}
  x & x & - & - \\
  - & - & x & x
\end{array}
\quad T 
\quad T
\]

in which the ethylene units are each excited to a triplet state, and the two triplets are coupled to give a singlet spin state; 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 \( \phi_2 \) to the lowest unoccupied orbital \( \phi_1 \). In the localized orbital picture, the state is a superposition of the ethylene singlet excitations \( \begin{array}{c} \alpha \end{array} \) and \( \begin{array}{c} \alpha \end{array} \) and the “charge transfer” excitations \( \begin{array}{c} \alpha \end{array} \) and \( \begin{array}{c} \alpha \end{array} \); this is the classic exciton description of the 1^1B_u state.14,15 The latter excitations describe the de-
<table>
<thead>
<tr>
<th>CL</th>
<th>Localized SCF orbitals CI coefficients</th>
<th>Delocalized SCF orbitals CI coefficients</th>
<th>CD&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;1&lt;/sup&gt;A&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2&lt;sup&gt;1&lt;/sup&gt;A&lt;sub&gt;x&lt;/sub&gt;</td>
<td>1&lt;sup&gt;1&lt;/sup&gt;B&lt;sub&gt;y&lt;/sub&gt;</td>
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<td>5.306</td>
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</tr>
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<td>x-x-</td>
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<td>x-x-</td>
<td>0.011</td>
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<td>0.0051</td>
</tr>
</tbody>
</table>

*Evaluated from PPP–Hamiltonian (1) with Ohno parametrization.

<sup>a</sup>CL: π-electron configurations defined over localized orbitals.

<sup>b</sup>CD: π-electron configurations defined over delocalized orbitals.

<sup>c</sup>CD: π-electron configurations defined over delocalized orbitals.
TABLE V. [S+D]–CI coefficients in decapentaene. 

<table>
<thead>
<tr>
<th>Major contributions to the ground state</th>
<th>Triplet–triplet excitations in the $2^1A_2^*$ state</th>
<th>Charge transfer excitations</th>
<th>$1^B_u$ state</th>
<th>$2^1B_u$ state</th>
<th>$3^1A_e^*$ state</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.941</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.240</td>
<td>x-x x-x x-x x-x x-x x-x</td>
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<td>-0.132</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.211</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.188</td>
</tr>
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<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.211</td>
<td>x-x x-x x-x x-x x-x x-x</td>
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<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.152</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.102</td>
</tr>
<tr>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.125</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.152</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.056</td>
</tr>
<tr>
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<td>-0.124</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.136</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.067</td>
</tr>
<tr>
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<td>0.136</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.067</td>
</tr>
<tr>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.124</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.136</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.067</td>
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<tr>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.124</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>0.136</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.067</td>
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<td>0.136</td>
<td>x-x x-x x-x x-x x-x x-x</td>
<td>-0.067</td>
</tr>
</tbody>
</table>

*Ohno parametrization.

Localization of the excited electron in the $1^1B_u^*$ state, in agreement with its valence–bond characterization as a noncovalent state. 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 $1^3B_u^*$ states as is made clear by the localized orbital description. It can be seen in Table V that the $1^1B_u^*$ state, as well as the next triplet state, $1^3A_e^*$, 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

$$|\psi_m^a\rangle = (1/\sqrt{2})(b_m^* b_i + b_m^* b_i)|\psi_0\rangle,$$

we show in Fig. 1 the absolute magnitude squares of the coefficients $|\psi_m^a\rangle$ multiplying the term $|\psi_m^a\rangle$ 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

$$\langle \psi_m^a | H | \psi_m^a \rangle = F_{mm} - F_{tt} - (ii \mid mm),$$

$$\langle \psi_m^a | H | \psi_m^a \rangle = F_{mm} - F_{tt} - (ii \mid mm) + 2(i\psi \mid i\psi),$$

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

![Fig. 1](image-url)
where the operator $\vec{R}$ 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 $C_{12}H_{20}$ for excitations from the fifth ethylene unit ($i = 5$). The excitation energy for the triplet excitation $m - i$ 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 intratetraethylene excitation ($m = i = 5$), but the energy well is more shallow. This is due to the fact that the exchange repulsion term $2(i \sigma \overline{m} | i \sigma \overline{m})$, absent in the triplet energy expression, takes on its maximum value at $i = m$.

### B. Length dependence of correlation correction

In a previous paper\(^3\) 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 $N \approx 5$ 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,
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

\[
D_1 \psi_0 \\
Q_{(i)} \psi_0 = D_1 D_i \psi_0 (i \neq j)
\]

\[
N_{t_1 \ldots t_n} \psi_0 = D_1 D_2 D_n \psi_0 (t_1 \neq t_2 \neq \ldots \neq t_n)
\]  

(18)

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

\[
\begin{pmatrix}
\beta_{2x} & 0 & 0 & \ldots & 0 \\
\beta_{2x} & \alpha_2 & 0 & \ldots & 0 \\
0 & \beta_{2x} & \alpha_4 & \beta_{2s} & \ldots \\
0 & 0 & \beta_{2s} & \alpha_{2s} & \ldots \\
\end{pmatrix}
\begin{pmatrix}
\psi_0 \\
\psi_2 \\
\psi_4 \\
\psi_6 \\
\end{pmatrix}
= E_0
\begin{pmatrix}
\psi_0 \\
\psi_2 \\
\psi_4 \\
\psi_6 \\
\end{pmatrix}
\]  

(19)

where \( f_0 \) is the CI coefficient of the SCF ground state \( \psi_0 \), \( f_2 \) is the vector of CI coefficients for the configurations \( D_i \psi_0 \) \( (i = 1, 2, \ldots, N) \), etc. The CI matrix in Eq. (19) contains submatrices \( \beta_{2s}, 2s + 2 \) and \( \alpha_{2s} \). The matrices \( \beta_{2s}, 2s + 2 \) describe the coupling between the \( 2s \) and the \( 2s + 2 \)-tuple excitations, and the \( \alpha_{2s} \) are diagonal matrices containing the transition energies of the \( 2s \)-tuple excitations.

\[
(\alpha_{2s})_{ij} = \delta_{ij} \langle \psi_0 | \tilde{H} D_j | \psi_0 \rangle
\]

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

\[
(\alpha_{2s})_{ij} = 2 \mu
\]  

(20)

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

\[
\langle D_i \psi_0 | \tilde{H} | D_i \psi_0 \rangle = \langle D_2 \psi_0 | \tilde{H} | D_2 \psi_0 \rangle = 11.02 \text{ eV}
\]

\[
\langle D_2 \psi_0 | \tilde{H} | D_2 \psi_0 \rangle = 11.70 \text{ eV}
\]

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

\[
\langle Q_{ij} \psi_0 | \tilde{H} | Q_{ij} \psi_0 \rangle = \langle D_i \psi_0 | \tilde{H} | D_i \psi_0 \rangle + \langle D_j \psi_0 | \tilde{H} | D_j \psi_0 \rangle
\]

\[
+ \{ (d^2 | j j) + (i j | j j) - (i j | j j) - (i j | j j) \}
\]

\[
- 2 \{ (i j | i j) + (i j | j j) - (i j | i j) - (i j | i j) \}
\]  

(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:

\[
\langle Q_{ij} \psi_0 | \tilde{H} | Q_{ij} \psi_0 \rangle = \langle Q_{12} \psi_0 | \tilde{H} | Q_{12} \psi_0 \rangle = 11.02 \text{ eV} + 11.70 \text{ eV} + 0.367 \text{ eV}
\]

\[
\langle Q_{14} \psi_0 | \tilde{H} | Q_{14} \psi_0 \rangle = 11.02 \text{ eV} + 11.02 \text{ eV} + 0.034 \text{ eV}
\]

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

\[
\langle N_{i_1 \ldots i_n} | \tilde{H} | N_{j_1 \ldots j_n} \rangle = \langle \psi_0 | \tilde{H} | D_{j_1 \ldots j_n} \psi_0 \rangle
\]

if \( \{ i_1, \ldots, i_n \} = \{ j_1, \ldots, j_n \} \)

0 otherwise.

The matrix elements \( \langle \psi_0 | \tilde{H} | D_2 \psi_0 \rangle \) are nearly independent of \( \kappa \), as can be seen from hexatriene, where

\[
\langle \psi_0 | \tilde{H} | D_2 \psi_0 \rangle = 1.62 \text{ eV}
\]

\[
\langle \psi_0 | \tilde{H} | D_2 \psi_0 \rangle = 1.54 \text{ eV}
\]

Consequently, we use the approximation

\[
\langle \psi_0 | \tilde{H} | D_2 \psi_0 \rangle = \gamma = \text{for} \ k = 1, 2, \ldots, N
\]  

(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

\[
\begin{pmatrix}
0 & \gamma & 0 & 0 & 0 \\
\gamma & 0 & 0 & 0 & 0 \\
0 & \gamma & 0 & 0 & 0 \\
0 & 0 & \gamma & 0 & 0 \\
0 & 0 & 0 & \gamma & 0
\end{pmatrix}
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4
\end{pmatrix}
= E_0
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4
\end{pmatrix}
\]  

(23)

In the case of butadiene we have

\[
\begin{pmatrix}
0 & \gamma & \gamma & 0 & 0 \\
\gamma & 0 & \mu & 0 & 0 \\
0 & \mu & 0 & \gamma & 0 \\
0 & 0 & \gamma & 2 \mu & 0 \\
0 & 0 & 0 & \gamma & 0
\end{pmatrix}
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4
\end{pmatrix}
= E_0
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2 \\
\psi_3 \\
\psi_4
\end{pmatrix}
\]

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

\[
E_0 = N \epsilon
\]

(24a)

where

\[
\epsilon = \frac{3}{2} \mu - \left( \frac{3}{2} \mu \right)^2 + \gamma^2
\]

(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

\[
\begin{pmatrix}
0 & \sqrt{N\gamma} & 0 & 0 & \ldots \\
\sqrt{N\gamma} & \mu & \sqrt{2(N-1)\gamma} & 0 & \ldots \\
0 & \sqrt{2(N-1)\gamma} & 2\mu & \sqrt{3(N-2)\gamma} & \ldots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
C_0 \\
C_1 \\
C_2 \\
\vdots
\end{pmatrix}
= E_0
\begin{pmatrix}
C_0 \\
C_1 \\
C_2 \\
\vdots
\end{pmatrix}
\tag{26}
\]

Expanding the matrix equation, we obtain

\[E_0 C_0 = \sqrt{N\gamma} C_1 \tag{26}'\]

and

\[B_{n-1} C_{n-1} + A_n C_n + B_n C_{n+1} = 0 \quad \text{for } n \geq 1, \tag{26}''\]

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

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

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

\[E_0 = \frac{-N\gamma^2}{\mu - E_0 - \frac{2(N-1)\gamma^2}{2\mu - E_0 - \frac{3(N-2)\gamma^2}{3\mu - E_0 - \ldots}}} \]

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

\[z = N\gamma^2/\mu - E_0 \tag{27a}\]

\[z = \frac{N}{\mu - z - 2(N-1)\gamma^2/(2\mu - z)} \tag{27b}\]

e.g. 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

\[\phi_0 \bigg( \sum_{i} D_i \frac{1}{\gamma} \bigg) = \sum_{D_i \gamma} D_i \phi_0, \quad \phi_0 \bigg( \sum_{D_i \gamma} D_i \phi_0 \bigg), \ldots, \tag{25}\]

where \(\gamma\) is the binomial coefficient. In terms of this basis, the ground-state wavefunction can be written

\[\phi_0 = \left( C_0 + C_1 \frac{1}{\gamma} \bigg) \sum_{D_i \gamma} D_i \phi_0 \bigg) \sum_{D_i \gamma} D_i \phi_0 \bigg) \ldots \phi_0, \tag{25}\]

where the coefficients $C_i$ obey the secular equation

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

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 $E_0^{(N)}$ is used as a first guess for the equation determining the ground-state excitation energy $E_0^{(N)}$, 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

\[E_0^{(1)} \approx -(2/\mu) N\gamma^2 \]

so that the double excitations ground-state correlation energy is seen to depend linearly on $N$. However, for long polyenes ($N \gamma^2 \gg (1/2\mu)^2$), 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 $N$.
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 for 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 $\psi$ can be expressed in terms of excitations in which one, two, ... electrons are promoted from the SCF ground state

$$\psi = (c_0 + \sum_i c_i^{m\sigma} \Omega_i^{m\sigma} + \sum_{i < j} c_{ij}^{m\sigma \sigma'} \Omega_{ij}^{m\sigma \sigma'} + \cdots) \psi_0 . \tag{28}$$

Here $\psi_0$ is the SCF ground state wavefunction, $i\sigma$, $m\sigma$, $j\sigma'$, $m\sigma'$ are localized orbitals with spin $\sigma$ or $\sigma'$ and the $\Omega_i^{m\sigma}$, $\Omega_{ij}^{m\sigma \sigma'}$ ... are composed of particle-hole excitation operators; i.e.,

$$\Omega_i^{m\sigma} = b_i^{m\sigma \dagger} b_i ,$$

$$\Omega_{ij}^{m\sigma \sigma'} = b_i^{m\sigma \dagger} b_j^{\sigma' \dagger} b_i^{m\sigma} b_j^{\sigma'} .$$

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 $(m \rightarrow i\sigma$, $m\sigma \rightarrow j\sigma')$ 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 $\psi_0$ in Eq. (28) by the exact ground state wavefunction $\psi_0$. We will refer to such expression as the renormalized CI expansion. Because of the spatial separation of the polyeval $\pi$ 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 $O_i^{m\sigma}$. If the excitation is relative to the SCF ground state [Eq. (28)],

$$\psi_i^{m\sigma} = O_i^{m\sigma} \psi_0 = b_i^{m\sigma \dagger} \psi_0 ,$$

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,

$$\psi_0 = \left( d_0 + \sum_{k \neq i} d_k D_k \right) \psi_0 , \tag{17}$$

the elementary excitation, which can be written

$$\psi_i^{m\sigma} = O_i^{m\sigma} \psi_0 , \tag{29}$$

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

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

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

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

where

$$\langle N_i^{m\sigma} \rangle^2 = \sum_{k \neq i} d_k^2 < 1 \tag{31}$$

Fig. 6. Pictorial representation of a localized single excitation $(m \rightarrow i)$; (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 $\sum_k d_k^2 = 1$. Consequently, the normalized excitations (for which we use the same symbol for simplicity) are]
\[ |\Psi_{10}^{\text{m}}\rangle = N_1^1 O_{10}^{\text{m}} |\Psi_0\rangle. \] (32)

Since the ground-state coefficients $d_1, d_2, \ldots$ are small, in general, the normalization constants $N_1^1$ 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 $|\Psi_{10}^{\text{m}}\rangle$ is
\[ E_{10}^{\text{m,corr}} = \langle \Psi_{10}^{\text{m}} | H | \Psi_{10}^{\text{m}} \rangle - \langle \Psi_{10}^{\text{m}} | H | \Psi_{10}^{\text{m}} \rangle. \] (33)

With the same simplifying assumptions as used in Sec. III, $E_{10}^{\text{m,corr}}$ reduces to
\[ E_{10}^{\text{m,corr}} = \sum_{l,m} \epsilon_l, \]
where $\epsilon_l$ is the ground state correlation energy of the $l$th ethylene unit. For large polyenes this correlation energy is comparable to the approximate ground state correlation energy of the entire polyene, $\sum l \epsilon_l$. 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, $\Psi_0$; that is,
\[ \Psi = \left( c_0 + \sum_{l,m} c_{10}^{\text{m}} O_{10}^{\text{m}} + \sum_{l,m,n} c_{1e}^{\text{m,n}} O_{1e}^{\text{m,n}} + \cdots \right) \Psi_0. \] (34)

Inserting the rhs of Eq. (17) into this expansion (i.e., approximating $\Psi_0$ by the function which includes intramethylene closed shell double excitations), we obtain
\[ \Psi = \left( c_0 d_0 \sum_{l,m} c_{10}^{\text{m}} O_{10}^{\text{m}} + c_0 \sum_k d_k D_k \right. \]
\[ + d_0 \sum_{l,m} c_{1e}^{\text{m,n}} O_{1e}^{\text{m,n}} + \sum_k d_k D_k \right. \]
\[ \left. + \sum_k d_k D_k \right) \Psi_0. \] (35)

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
\[ \{ \Psi_0, O_{1e}^{\text{m,n}} \Psi_0, O_{1e}^{\text{m,n}} O_{1e}^{\text{m,n}} \Psi_0, \cdots \} \]
is reduced to one in which the secular equation has the dimension of the smaller basis
\[ \{ \Psi_0, O_{1e}^{\text{m,n}} \Psi_0, O_{1e}^{\text{m,n}} O_{1e}^{\text{m,n}} \Psi_0 \cdots \}. \] (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
\[ \begin{aligned}
1.1 \langle \Psi_1^{\text{m,s}} \rangle &= N_1^1 1.1 \langle \Psi_0 \rangle = \frac{N_1^1}{\sqrt{2}} (O_{1e}^{\text{m,n}} + O_{1e}^{\text{m,n}}) \Psi_0,
\end{aligned} \] (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) subscripts unless they are required for clarity.

Given the basis in Eq. (37), the excited state wavefunction can be written
\[ |\Psi\rangle = \sum_{l,m} g_{l,m} |\Psi_{10}^{\text{m,s}}\rangle \] (38)

which is equivalent to
\[ |\Psi\rangle = \sum_{l,m} N_1^1 g_{l,m} \sum_{k \neq l,m} d_k D_k |\Psi_{10}^{\text{m,s}}\rangle, \] (39)

where $\Psi_{10}^{\text{m,s}}$ is given by Eq. (12) and the $g_{l,m}$ are the expansion coefficients; they are normalized to
\[ \sum_{l,m} |g_{l,m}|^2 = 1. \] (40)

The elements of the Hamiltonian matrix are
\[ \langle \Psi_{10}^{\text{m,s}} | H | \Psi_{10}^{\text{m,s}} \rangle = N_1^1 N_2^1 \left\{ \sum_{k \neq l,m} \left\langle \Psi_{10}^{\text{m,s}} | H D_k \right\rangle \right\} \]
\[ + \sum_{k \neq l,m} \langle \Psi_{10}^{\text{m,s}} | H D_k D_k H | \Psi_{10}^{\text{m,s}} \rangle \] (41)

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 octetetraene $(N=4)$, there are 25 elements.

A. Analysis of the method

The expansion of the excited-state wavefunctions in terms of the renormalized configurations $|\Psi_{10}^{\text{m,s}}\rangle$ 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
\[ |\Psi\rangle = \sum_{l,m,k} f_{l,m,k}^{\text{m,s}} |D_k \Psi_0\rangle, \] (42)

where
\[ |D_k \Psi_0\rangle = |\Psi_{10}^{\text{m,s}}\rangle \text{ for } k = 0, \]
\[ |D_k \Psi_0\rangle = |\Psi_{10}^{\text{m,s}}\rangle \text{ for } k \neq 0, \]

and $|\psi^m_i\rangle$, $|\psi^{N^2}_{im}\rangle$ are spin-symmetrized single $(m-i)$ and triple $(mk-kk)$ excitations. The single excitation coefficients $f_{10}^m (k=0)$ have $N^2$ degrees of freedom and the triple excitation coefficients $f_{10}^m (k \neq 0)$ 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,

$$f_{10}^m = N^2 g^m_i d_i$$

(43)

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

$$f_{10}^m = d_i$$

(44)

independent of $i$ and $m$.

An additional approximation is made by choosing the $d_i$ 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 $|D_k \psi^m_i\rangle$ as

$$\langle D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle = \langle \psi^m_i | \tilde{H} | \psi^m_j \rangle \delta_{lk} + (D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle \delta_{lk} \delta_{mn} + (D_k \psi^m_i | \tilde{V} | D_l \psi^m_j \rangle)$$

(45)

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

$$1^2 (D_k \psi^m_i | \tilde{V} | D_l \psi^m_j \rangle = (2kk | mm) - (km | km) - (2kk | mm)

+ (km | km) \delta_{lk} \delta_{mn} + (2kk | ij) \delta_{lk} \delta_{mn} + (kt | kt) \delta_{lk} \delta_{mn} + (kt | it) \delta_{lk} \delta_{mn}

+ (kt | it) \delta_{lk} \delta_{mn} + (kt | it) \delta_{lk} \delta_{mn} - (kt | ik) \delta_{lk} \delta_{mn} - (kt | ik) \delta_{lk} \delta_{mn})$$

(46a)

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

$$1^2 \langle D_k \psi^m_i | \tilde{V} | D_l \psi^m_j \rangle = (ii | jm) + (ji | jm) + (jm | jm) \delta_{lk} \delta_{mn}$$

- $(ii | jm) \delta_{lk} \delta_{mn} - (jm | jm) \delta_{lk} \delta_{mn}$

(46b)

for $k \neq 0$ 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

$$1^1 (D_k \psi^m_i | \tilde{V} | D_l \psi^m_j \rangle = 0$$

(46c)

for $k = 0$ and $l = 0$. The matrix $\tilde{V}$ 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)

$$E_{B} = \sum_{\langle i | m \rangle} N^2 N^2 g^m_i d_i \langle D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle$$

$$+ \sum_{\langle i | m \rangle} \left[ \sum_{\langle i | m \rangle} N^2 N^2 g^m_i d_i \langle D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle \right] \sum_{\langle i | m \rangle} \left[ \sum_{\langle i | m \rangle} N^2 N^2 g^m_i d_i \langle D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle \right]$$

$$+ \sum_{\langle i | m \rangle} \sum_{\langle i | m \rangle} N^2 N^2 g^m_i d_i \langle D_k \psi^m_i | \tilde{V} | D_l \psi^m_j \rangle$$

(47)

In the renormalized CI method, the excited state energy and wavefunction are obtained from Eq. (47) by assuming the $d_i$ to be known from the correlated ground state and minimizing with respect to the coefficients $g^m_i$. We justify this approximate procedure in what follows. If we assume [see Eq. (41)]

$$\sum_{\langle i | m \rangle} d_i^2 N^2 N^2 = 1$$

(48)

the first terms of Eq. (47) correspond to the energy expression in the $[S]-CI$ basis and has a minimum value when the coefficients $g^m_i$ are equal to the $[S]-CI$ coefficients $h^m_i$.

$$\Psi = \sum_{\langle i | m \rangle} h^m_i C^m_i \psi_i$$

A small difference between $g^m_i$ and $h^m_i$ 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 $\tilde{V}$ [third term of Eq. (47)], all of which are accounted for in the renormalized $[S]-CI$ calculation. The first term of Eq. (47) is approximately equal to the $[S]-CI$ energy expectation value $E_{B}^{[S]-CI}$. Its small deviation from $E_{B}^{[S]-CI}$ will be called the renormalization correction of $E_{B}^{[S]-CI}$, $\Delta_{B}^{[S]-CI}$; it is given by

$\Delta_{B}^{[S]-CI} = \sum_{\langle i | m \rangle} \left( N^2 g^m_i \langle \psi^m_i | \tilde{H} | \psi^m_i \rangle \right) \sum_{\langle i | m \rangle} d_i^2 (N^2 N^2) - E_{B}^{[S]-CI}$

(49)

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

$$\sum_{\langle i | m \rangle} \left( N^2 g^m_i \langle \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle \right) d_i d_j$$

(50)

$$= E_0 \sum_{\langle i | m \rangle} (N^2 g^m_i \langle \psi^m_i | \tilde{V} | \psi^m_i \rangle)^2 - \sum_{\langle i | m \rangle} (N^2 g^m_i \langle \psi^m_i | \tilde{V} | \psi^m_i \rangle)^2 C(i, m, k) \epsilon_k$$

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

$$E_0 = \sum_{\langle i | m \rangle} d_i d_j \langle D_k \psi^m_i | \tilde{H} | D_l \psi^m_j \rangle$$

Since
\[
\langle \phi_0 | \hat{H} | \phi_0 \rangle = 0
\]
and
\[
\langle D_k \psi_0 | \hat{H} | D_k \psi_0 \rangle = \delta_{k1} \langle D_k \psi_0 | \hat{H} | D_k \psi_0 \rangle
\]
for \( k \neq 0 \) and \( f \neq 0 \), we can write
\[
E_n = \sum_{k=1}^{N} \epsilon_k k, \tag{51}
\]
where \( \epsilon_k \), the correlation energy of an ethylene unit, is
\[
\epsilon_k = \langle \phi_0 | \hat{H} | D_k \psi_0 \rangle + \langle D_k \psi_0 | \hat{H} | \phi_0 \rangle d_k d_k \epsilon_k.
\]
If we set \( \Sigma_{i,m} (N_{i}^{m})^2 (g_{i}^{m})^2 = 1 \), the first term in Eq. (50) is approximately equal to \( \epsilon_0 \). Thus it is a reflection of the ground-state correlation energy in the excited state. The small deviation from \( \epsilon_0 \) will be called the renormalization correction to \( \epsilon_0 \); it is given by
\[
\Delta_0 = \epsilon_0 - \epsilon_0 \sum_{i,m} (N_{i}^{m})^2 (g_{i}^{m})^2 L(i, m) - E_0, \tag{52}
\]
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 \( \epsilon_0 \) 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, \( \epsilon_k \), for the one unit \((k = i = m)\) or for each of the two units \((k = i \neq m)\) 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
\[
E_p = - \sum_{i,m} (N_{i}^{m})^2 (g_{i}^{m})^2 L(i, m), \tag{53}
\]
where
\[
L(i, m) = \begin{cases} 1 & \text{for } i = m \\ 2 & \text{for } i \neq m \end{cases}
\]
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 \((E_p = -2\epsilon)\) if the excited states consist mainly of the 
interethylene excitations \((i = m, L(i, m) = 2)\), while it is smaller \((E_p = -\epsilon)\) for the states consisting mainly of intraethylene unit excitations \((i = m, L(i, m) = 1)\).

The last term in Eq. (47)
\[
E_{c} = \sum_{i,m} \sum_{i_{1},m_{1}} N_{i_{1}}^{m_{1}} N_{i}^{m} \beta_{i_{1}}^{m_{1}} d_{i_{1}} \langle D_k \psi_0 | \hat{H} | D_k \psi_0 \rangle \tag{55}
\]
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
\[
E_{RHF-CI} = E_{RHF} + N\kappa + E_p + E_C + \Gamma \Delta_{RHF-CI} + \Delta_0. \tag{56}
\]
The first two terms, which are dominant, are minimized by the coefficients \( (h_i^{m}, d_i) \). Use of \((g_i^{m}, d_i)\) in the \(E_{RHF-CI}\) corrects for the remaining terms in Eq. (56) under the assumption that the \( d_i \) can be employed for the excited states. Corrections to the coefficients \( d_i \) 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
\[
E_{RHF-CI} = N\kappa + \Delta, \tag{57}
\]
where \( \Delta \), the "rearrangement energy" is given by
\[
\Delta = E_p + E_C + \Gamma \Delta_{RHF-CI} + \Delta_0. \tag{58}
\]
It corresponds to the difference between the ground-state and the excited state correlation energy. In the excitation energy, the ground-state correlation energy \(N\kappa\) of the excited state cancels with the correlation energy of the ground state and we obtain a net excitation energy
\[
\Delta E_{RHF-CI} = E_{RHF-CI} + \Delta. \tag{59}
\]
where \(E_{RHF-CI}\) 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
\[
|\psi_{1}^{m} \rangle = N_{1}^{m} \mathcal{O}_{1}^{m} |\psi_0 \rangle, \tag{60}
\]
where the normalization factor \(N_{1}^{m}\) is defined by
\[
(N_{1}^{m})^2 = \sum_{i=0}^{\infty} d_i^2 < 1 \tag{61}
\]
and the operator \(\mathcal{O}_{1}^{m}\) is the spin-symmetrized double-excitation operator. Analogously to the \([S + D]\)–CI expansion function
\[
|\psi_1 \rangle = \mathcal{O}_{1}^{m} |\psi_0 \rangle + \sum_{i,m} h_{i,m}^{m} |\psi_i \rangle \tag{62}
\]
the wavefunction of the excited state is expanded in the renormalized CI basis given by Eqs. (37) and (60). It has the form
\[
|\psi_1 \rangle = g_0 |\psi_0 \rangle + \sum_{i,m} g_{i}^{m} |\psi_i \rangle + \sum_{i,j,i,j} g_{i,j}^{m} |\psi_{i,j} \rangle, \tag{63}
\]
where the $h$'s and $g$'s are expansion coefficients. The renormalized CI basis in Eq. (63) is not orthogonal; restricting $\Psi_0$ to closed-shell double excitations [Eq. (17)], we have the nonzero overlap

$$
\langle \Psi_0 | \psi_{ij}^{m} \rangle = \sum d_{i} d_{j} (d_{i}^{\dagger} d_{j}^{\dagger} \Psi_0 | \psi_{ij}^{m} \rangle)
$$

$$
= a_{ij} b_{im},
$$

(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

$$
\mathcal{E}_{R[S+D]-CI} = \mathcal{E}_{[S+D]-CI} + \mathcal{N}_e + \mathcal{E}_p
$$

$$
+ E_{C} + \Delta_{[S+D]-CI} + \Delta_0,
$$

(65)

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

$$
\mathcal{E}_p \simeq -\varepsilon \left\{ \sum_{i \neq m} \left( N_{ii}^{m} \langle \psi_i | \psi_m \rangle \right) \right\}
$$

$$
+ \sum_{i \neq m, n} \left( N_{ij}^{mn} \langle \psi_i | \psi_{mn} \rangle \right) M(i, j, m, n),
$$

(66)

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

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

(67)

The quantity $\mathcal{E}_C$ in Eq. (65) is the analog of $\mathcal{E}_C$ 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 $\Delta_{[S+D]-CI}$ and $\Delta_0$ 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 ($\mathcal{N}_e$) of the excited state cancels with the correlation energy of the ground state, and there results the expression

$$
\Delta \mathcal{E}_{R[S+D]-CI} = \mathcal{E}_{[S+D]-CI} + \Delta,
$$

(68)

where $\Delta$ is the rearrangement energy

$$
\Delta = \mathcal{E}_p + \mathcal{E}_C + \Delta_{[S+D]-CI} + \Delta_0.
$$

(69)

The divergence difficulties of the excitation energies in the $[S+D]-CI$ basis (see Sec. III.B) are removed in the renormalized $[S+D]-CI$ representation, because of the cancellation of the correlation energy ($\mathcal{N}_e$) between the excited and ground states. If the rearrangement energy $\Delta$ is neglected, the excitation energy $\Delta \mathcal{E}_{R[S+D]-CI}$ is equal to the energy relative to the SCF ground-state energy as zero ($\mathcal{E}_{[S+D]-CI}$). This approximation has been employed previously.\textsuperscript{24}

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,\textsuperscript{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

$$
\overline{O}_I | \psi_0 \rangle = \overline{Q}_I D_1 | \psi_0 \rangle,
$$

(70)

where $\psi_0$ is the correlation ground state and $\overline{O}_I$ is the symmetrized de-excitation operator,

$$
\overline{Q}_I = (1/\sqrt{3})(b_i^{\dagger} b_m^{\dagger} + b_i^{\dagger} b_m^{\dagger} + b_{im}^{\dagger} b_{im}^{\dagger}).
$$

(71)

These excitations are identical to single excitations from the SCF ground state $O_I | \psi_0 \rangle$. 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 $O_I | \psi_0 \rangle$ independent of the triple excitation amplitudes $O_1 D_1 | \psi_0 \rangle$; that is,

$$
(f_{1i}^{\dagger} f_{1o}^{\dagger} d_i d_o)
$$

(72)

instead of Eq. (44).

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

$$
\overline{O}_I | \psi_0 \rangle (i \neq m)
$$

(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,

$$
| \psi \rangle = \sum_{i,m} \bar{g}^{\dagger}_{i} d_{i} | \psi_{i} \rangle + \sum_{i,m} \bar{g}^{\dagger}_{i} \left\{ \sum_{m,n} d_{m}^{\dagger} | \psi_{i,m,n} \rangle \right\}
$$

(74)

where $d$'s are fixed as the ground-state wavefunction coefficients. The $\bar{g}^{\dagger}_{i}$ and $\bar{g}_{i}$ 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,

$$
\bar{g}^{\dagger}_{i} = \bar{g}_{i}.
$$

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

V. RESULTS

In this section, we apply the renormalized CI method to the $\pi$-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 $1^1B_2^+$ and $1^3B_2^+$ state of octatetraene, whose eight $\pi$-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.\(^a\)

<table>
<thead>
<tr>
<th>Excitation(^b)</th>
<th>([S+T'])(^6)</th>
<th>(R[S])</th>
<th>([S]–)</th>
<th>([S+T'])(^6)</th>
<th>(R[S])</th>
<th>([S]–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i \rightarrow m)</td>
<td>(\gamma^i)</td>
<td>(\beta^i)</td>
<td>(\gamma^m)</td>
<td>(\beta^m)</td>
<td>(\gamma^i)</td>
<td>(\beta^i)</td>
</tr>
<tr>
<td>1 (-) 1</td>
<td>0.3041</td>
<td>0.3057</td>
<td>0.2966</td>
<td>0.2668</td>
<td>0.2676</td>
<td>0.2707</td>
</tr>
<tr>
<td>1 (-) 2</td>
<td>0.1941</td>
<td>0.1928</td>
<td>0.2000</td>
<td>0.2425</td>
<td>0.2421</td>
<td>0.2451</td>
</tr>
<tr>
<td>1 (-) 3</td>
<td>0.1047</td>
<td>0.1031</td>
<td>0.1119</td>
<td>0.1509</td>
<td>0.1503</td>
<td>0.1550</td>
</tr>
<tr>
<td>1 (-) 4</td>
<td>0.0481</td>
<td>0.0471</td>
<td>0.0531</td>
<td>0.0781</td>
<td>0.0777</td>
<td>0.0821</td>
</tr>
<tr>
<td>2 (-) 1</td>
<td>0.1941</td>
<td>0.1828</td>
<td>0.2000</td>
<td>0.2425</td>
<td>0.2421</td>
<td>0.2451</td>
</tr>
<tr>
<td>2 (-) 2</td>
<td>0.4971</td>
<td>0.4988</td>
<td>0.4591</td>
<td>0.4108</td>
<td>0.4119</td>
<td>0.4412</td>
</tr>
<tr>
<td>2 (-) 3</td>
<td>0.2466</td>
<td>0.2449</td>
<td>0.2546</td>
<td>0.3012</td>
<td>0.3006</td>
<td>0.3013</td>
</tr>
<tr>
<td>2 (-) 4</td>
<td>0.1047</td>
<td>0.1031</td>
<td>0.1119</td>
<td>0.1509</td>
<td>0.1503</td>
<td>0.1550</td>
</tr>
</tbody>
</table>

\(^a\)Ono parametrization.
\(^b\)Localized orbital basis, the absolute magnitudes of the wavefunction coefficients for \(i \rightarrow m\) and \(m \rightarrow i\) are equal, i.e., \(|\gamma^i| = |\beta^i|\).
\(^c\)The coefficients \(\gamma^i/\beta^i\) and \(\gamma^m/\beta^m\) are normalized as \(\gamma^i/\beta^i = 1\) for comparison with \(\gamma^i/\beta^i\) and \(\gamma^m/\beta^m\).

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 \(g^s\) [from \(R[S]\)–CI; Eq. (38)] and \(f^s\) [from \([S+T']\)–CI; Eq. (42)] should be similar to each other and close to the coefficients \(h^s\) from an \([S]–\)CI calculation. In Table VII we list these coefficients and find good agreement among them for both the \(1^1B^+_u\) and \(1^3B^+_u\) 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 \(f^t/\beta^t = d/s\); 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 \(f^t/\beta^t\) obtained from the \([S+T']\) calculation and \(d/s\) from the ground state [Eq. (17)]. The agreement is found to be excellent for the \(1^1B^+_u\) state; the only exceptions are the configurations in which the single excitation "crosses" the double excitation as depicted in Fig. 7. For the \(1^1B^+_u\) state the agreement of the ratios is significantly worse, particularly for the double excitation \(22\rightarrow 22\).

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 \(1^3B^+_u\) state and only slightly worse for the \(1^1B^+_u\) state. The discrepancies depend only weakly on polyene chain length. Table IX also contains energy values obtained with the \(R[S]–\)CI basis, which includes both the basis of Eq. (37) and the de-excitation 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, in which de-excitation plays 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 \(1^1B^+_u\), \(1^3A^+_u\), and \(1^3B^+_u\) excitation energies for the polyenes.

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

<table>
<thead>
<tr>
<th>Excitation(^b)</th>
<th>(f^t_i/\beta^t_i) (_{\gamma^m/\beta^m})</th>
<th>(d_i/s_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 1 (-) 2 1 (_{1})</td>
<td>0.1275</td>
<td>0.1004</td>
</tr>
<tr>
<td>2 1 (-) 3 1 (_{1})</td>
<td>0.1300</td>
<td>0.1110</td>
</tr>
<tr>
<td>2 1 (-) 4 1 (_{1})</td>
<td>0.1311</td>
<td>0.1156</td>
</tr>
<tr>
<td>3 1 (-) 3 1 (_{1})</td>
<td>0.1365</td>
<td>0.1268</td>
</tr>
<tr>
<td>3 1 (-) 4 1 (_{1})</td>
<td>0.1390</td>
<td>0.1296</td>
</tr>
<tr>
<td>4 1 (-) 4 1 (_{1})</td>
<td>0.1382</td>
<td>0.1336</td>
</tr>
<tr>
<td>1 2 (-) 1 2 (_{2})</td>
<td>0.1169</td>
<td>0.0574</td>
</tr>
<tr>
<td>1 2 (-) 2 2 (_{2})</td>
<td>0.0657</td>
<td>0.0797</td>
</tr>
<tr>
<td>1 2 (-) 4 2 (_{2})</td>
<td>0.0652</td>
<td>0.0848</td>
</tr>
<tr>
<td>2 2 (-) 3 2 (_{2})</td>
<td>0.1154</td>
<td>0.0752</td>
</tr>
<tr>
<td>2 2 (-) 4 2 (_{2})</td>
<td>0.1159</td>
<td>0.0825</td>
</tr>
<tr>
<td>4 2 (-) 4 2 (_{2})</td>
<td>0.1213</td>
<td>0.1002</td>
</tr>
</tbody>
</table>

\(^a\)Ohno parametrization.
\(^b\)See Fig. 7.
\(^c\)Localized orbital basis.
TABLE IX. Comparison of excitation energies (eV) from $R(S)$ and $[S + T']$–CI calculations. 4

<table>
<thead>
<tr>
<th>Polyene length ($N$)</th>
<th>$R(S)$–CI $^b$</th>
<th>$R[S]–CI$ $^c$</th>
<th>$[S + T']$–CI $^b$</th>
<th>$[S]–CI$</th>
<th>$[C]–CI$ $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.8059</td>
<td>2.8049</td>
<td>2.8049</td>
<td>2.5182</td>
<td>2.7161</td>
</tr>
<tr>
<td>3</td>
<td>2.3683</td>
<td>2.3675</td>
<td>2.3645</td>
<td>2.0759</td>
<td>2.2256</td>
</tr>
<tr>
<td>4</td>
<td>2.1376</td>
<td>2.1371</td>
<td>2.1321</td>
<td>1.8468</td>
<td>...</td>
</tr>
</tbody>
</table>

$^b$Ohno parametrization.
$^c$Ground state energies are evaluated from the $[D']$–CI expansion, Eq. (17).
$^d$R$[S]$–CI calculation on the basis expansions Eqs. (37) and (70).
$^e$CI calculation with the complete excitation basis.

$C_9H_{2n+2}, N=2, 3, \ldots, 9$. 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 $\Psi_0$ 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 $r$ electrons, in accord with Eq. (57) and the fact that the rearrangement energy $\Delta$ is relatively independent of chain length (see Sec. IV and below); for $\Delta$ equal to a constant, $E_{\text{corr}}$ increases as $N\epsilon$, where $\epsilon$ is the correlation energy of a single ethylene unit. Since $\epsilon$ 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 $\Delta$ [Eq. (59)]. In Figs. 9(a) and 9(b) we plot the R$[S]$–CI and $[S]$–CI excitation energies and confirm that $\Delta$ 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 $\Delta$ consists of three terms, the Pauli exclusion energy $E_p$, the coupling energy $E_C$, and the renormalization correction, $\Delta' (\Delta' = \Delta_0 + \Delta_{\text{corr}})$. 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 $\Delta$ than do $E_C$ and $\Delta_0$, and is larger for the $1^1B_u$ state than for the $1^3B_u$ and $1^3A_u^*$ 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 $-2\epsilon$ and for an intratetraethylene excitation the Pauli exclusion energy is $-\epsilon$, where, by definition $\epsilon<0$ (see Sec. IV). Since the ex-

FIG. 8. Energies for the $1^1A_u^*$ (gr), $1^3B_u$, $1^3A_u^*$, and $1^1B_u$ excited states in the linear polyenes $C_9H_{2n+2}$ 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.
Ohmine, Karplus, and Schulten: Excited states of polyenes

<table>
<thead>
<tr>
<th>Length of polyene(N)</th>
<th>State</th>
<th>$E_p/(\langle - \epsilon \rangle + E_C/(\langle - \epsilon \rangle + \gamma \Delta/(\langle - \epsilon \rangle$)</th>
<th>$E_p/(\langle - \epsilon \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$^3B_u$</td>
<td>1.216 - 0.037 + 0.056</td>
<td>1.238 - 0.028 + 0.044</td>
</tr>
<tr>
<td>3</td>
<td>$^3B_u$</td>
<td>1.302 - 0.011 + 0.100</td>
<td>1.330 + 0.008 + 0.080</td>
</tr>
<tr>
<td>4</td>
<td>$^1B_u$</td>
<td>1.346 + 0.010 + 0.115</td>
<td>1.377 + 0.036 + 0.090</td>
</tr>
<tr>
<td>2</td>
<td>$^1A_g$</td>
<td>1.020 + 0.233 - 0.047</td>
<td>1.020 + 0.233 - 0.047</td>
</tr>
<tr>
<td>3</td>
<td>$^3A_g$</td>
<td>1.140 + 0.119 - 0.019</td>
<td>1.152 + 0.122 - 0.025</td>
</tr>
<tr>
<td>4</td>
<td>$^3A_g$</td>
<td>1.224 + 0.076 + 0.011</td>
<td>1.244 + 0.085 + 0.002</td>
</tr>
<tr>
<td>2</td>
<td>$^1B_u$</td>
<td>1.365 + 0.422 + 0.047</td>
<td>1.386 + 0.417 + 0.039</td>
</tr>
<tr>
<td>3</td>
<td>$^1B_u$</td>
<td>1.485 + 0.706 + 0.106</td>
<td>1.513 + 0.702 + 0.099</td>
</tr>
<tr>
<td>4</td>
<td>$^1B_u$</td>
<td>1.557 + 0.876 + 0.138</td>
<td>1.572 + 0.873 + 0.132</td>
</tr>
<tr>
<td>2</td>
<td>$^1A_g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$^1A_g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$^1A_g$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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. $\gamma \Delta = \gamma \Delta_{-C} + \gamma \Delta_{+}$.\n
The coupling energy $[E_C/(\langle - \epsilon \rangle)$ 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 $(kk - kk)$ with the particle state $m$ and \n
**TABLE XI.** Coupling and renormalization energy contributions for hexatriene (eV).\n
<table>
<thead>
<tr>
<th>State</th>
<th>$T-T$ [Eq. (46a)]</th>
<th>$S-T$ [Eq. (46b)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1st + 2nd)</td>
<td>1st term</td>
</tr>
<tr>
<td></td>
<td>$(+ 3rd$ term)</td>
<td>+ (2nd + 3rd) term</td>
</tr>
<tr>
<td>$^3B_u$</td>
<td>0.005 - 0.002</td>
<td>-0.052 + 0.046</td>
</tr>
<tr>
<td>$^1A_g$</td>
<td>0.003 + 0.000</td>
<td>0.009 + 0.013</td>
</tr>
<tr>
<td>$^1B_u$</td>
<td>0.005 - 0.004</td>
<td>0.092 + 0.058</td>
</tr>
</tbody>
</table>

*aOhno parametrization.\n
FIG. 9. Excitation energies corresponding to Fig. 8.
with the hole state \( i \). The total contribution from the Coulomb terms cancels,

\[
2 \langle kh | mm \rangle - 2 \langle kh | mm \rangle + 2 \langle kh | ii \rangle - 2 \langle kh | ii \rangle = 0
\]

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

The renormalization energy corrections, \( \Delta_0 \) and \( \Delta_0 \) [Eqs. (49) and (52), respectively], are also listed in Table XI. We can see that these energies are of the same magnitude as the \( S \rightarrow T \) coupling energy. Since \( \Delta_0 \) and \( \Delta_0 \) have opposite signs, their total contribution is less than half the value of the coupling energy \( E_C \) (except for \( \equiv \) 1 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.

**C. Estimate of the rearrangement energy**

The rearrangement energy \( \Delta \) 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 \( \Delta \). We have seen (Table VII) that the coefficients of the renormalized \( R[S] - CI \) expansion \( g_{nn}^T \) are close to the \( [S] - CI \) coefficients \( h_{nn}^T \). This allows a direct evaluation of the rearrangement energy \( \Delta \) on the basis of a \( [S] - CI \) calculation; that is, \( E_p \), \( E_C \), and \( \Delta \) can be evaluated from Eqs. (53), (55), and (46), (49), and (52) by replacing the \( R[S] - CI \) coefficients \( g_{nn}^T \) in these equations by the \( [S] - CI \) coefficients \( h_{nn}^T \). 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 \( h_{nn}^T \) of the excited states and the \( [D] - CI \) coefficients \( d_{nn} \) of the ground state [Eq. (77)].

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 \( E_p \), \( E_C \), \( \Delta_0 \), and \( \Delta_0 \) from Eqs. (66) and (68) by replacing the \( R[S + D] - CI \) coefficients \( g_{nn}^T \) and \( g_{nn}^T \) by the \( [S + D] - CI \) coefficients \( h_{nn}^T \) and \( h_{nn}^T \), 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 \( V \). The \( 2 \) \( A^2 \) state is found to have a large Pauli exclusion energy \( [E_p/(\epsilon = 2.0)] \), since this state consists mainly of double excitations involving two ethyl-

**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.

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 Å. At \( D_0 = 16 \) Å (long range potential; SCF limit) the ground-state correlation is small and the excitation energies for the \( 1 \) \( A^2 \), \( 2 \) \( A^2 \), \( 1 \) \( B^2 \), \( 1 \) \( B^2 \) states resulting from all methods are very similar. Smaller \( D_0 \) (9 Å, 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 (\( D_0 = 0.5 \) Å), higher order contributions become important and the \( [S] - CI \) 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>
<thead>
<tr>
<th>( D_0/\text{Å} ) state</th>
<th>( [S] - CI )</th>
<th>( [S + T'] - CI )</th>
<th>( [S + D] - CI )</th>
<th>exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( A_1 ) (exp)²</td>
<td>0.9 (0.05)</td>
<td>0.05</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>2.04</td>
<td>2.04</td>
<td>2.02</td>
<td>2.00</td>
</tr>
<tr>
<td>3 ( A_1 )</td>
<td>3.84</td>
<td>3.67</td>
<td>3.69</td>
<td>3.66</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>3.08</td>
<td>3.12</td>
<td>3.10</td>
<td>3.09</td>
</tr>
<tr>
<td>1 ( A_1 ) (exp)²</td>
<td>0.0 (0.05)</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>1.47</td>
<td>1.76</td>
<td>1.94</td>
<td>1.63</td>
</tr>
<tr>
<td>3 ( A_1 )</td>
<td>3.00</td>
<td>3.27</td>
<td>3.56</td>
<td>3.25</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>4.24</td>
<td>4.70</td>
<td>4.94</td>
<td>4.58</td>
</tr>
<tr>
<td>1 ( A_1 ) (exp)²</td>
<td>0.9 (1.55)</td>
<td>1.55</td>
<td>1.95</td>
<td>1.27</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>0.72</td>
<td>1.35</td>
<td>1.54</td>
<td>1.34</td>
</tr>
<tr>
<td>3 ( A_1 )</td>
<td>2.69</td>
<td>2.72</td>
<td>2.72</td>
<td>2.75</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>4.64</td>
<td>5.72</td>
<td>5.69</td>
<td>5.78</td>
</tr>
<tr>
<td>1 ( A_1 ) (exp)²</td>
<td>0.0 (4.00)</td>
<td>4.00</td>
<td>4.75</td>
<td>5.94</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>-0.09</td>
<td>0.07</td>
<td>0.04</td>
<td>0.93</td>
</tr>
<tr>
<td>0.5 ( A_1 )</td>
<td>0.66</td>
<td>1.87</td>
<td>1.86</td>
<td>1.98</td>
</tr>
<tr>
<td>1 ( B_1 )</td>
<td>4.97</td>
<td>6.51</td>
<td>6.50</td>
<td>7.68</td>
</tr>
</tbody>
</table>

²Repulsion defined in Eq. (5c), for this calculation, we assumed all bond lengths equal (1.397 Å).

Ground-state correlation energy, \( R[S] - [S + T'] - CI \) results are obtained for the ground state expansion in Eq. (17).
and the lowest optically allowed $1^1B_u^*$ state. The transition moment is defined by
\begin{equation}
M = \langle \Psi_r (t_f) | r | \Psi_0 \rangle,
\end{equation}
where $r$ is the dipole moment operator (in Å) and $\Psi_0$ and $\Psi_r (t_f)$ are the wavefunctions of the ground and the $1^1B_u^*$ state, respectively. The transition moments for the polyenes $C_{2n}H_{2n+2}$ ($N=2, 3, \ldots 9$) 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 $\Psi_0$ 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
\begin{equation}
f = 0.869 \frac{\Delta E}{M^2},
\end{equation}
where $\Delta E$ is the excitation energy (in units eV) and $M^2$ is the absolute square of the transition moment (in the units Å²) 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 ($N \approx 6$) the R[S]–CI values exceed the [S]–CI results. This is due to the fact that the energy factor $\Delta E$ involved in the oscillator strength [Eq. (75)] is larger in the R[S]–CI basis than in the [S]–CI basis and the ratio
\[
\frac{\Delta E_{[S+D]–CI}}{\Delta E_{[S]–CI}}
\]
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. 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; (----), [CI]–CI.](image)

![Fig. 11. Oscillator strengths corresponding to Fig. 10.](image)
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 produce of the appropriate single excitation coefficient with the double excitation coefficient in the correlated ground state. Use of this approach yields valid Rydberg 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, \(\bar{N}c\) (where \(c\) is the correlation energy of one ethylene unit in an \(N\)-unit polyene), and a rearrangement correction \(\Delta\). 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 \(\Delta\). Each excited state has a different value of \(\Delta\); for example, the \(1^2B^*\) and \(1^3A^*_1\) states, which consist mainly of intraethylene excitations, have small \(\Delta\) \(\Delta = 0.28\) eV (Onno) for hexatriene), while the \(2^1A^*_1\) and \(2^1B^*_2\) states, which involve interethylene excitations, have somewhat larger \(\Delta\) \(\Delta = 0.47\) eV (Onno) for hexatriene). The fact that \(\Delta\) is small and relatively independent of chain length (e.g., for the \(1^2B^*_2\) state, \(\Delta = 0.43\) eV (Onno) for butadiene and 0.52 eV (Onno) 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 \(2^1A^*_1\) and \(1^3B^*_2\) states. Even for the \(1^3B^*_1\), \(1^3A^*_1\), and \(1^3B^*_2\) states it is of importance because the doubly excited configurations make increasingly significant contributions for larger polyenes.