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Stability Conditions for the Solutions of the Hartree-Fock Equations for Atomic and Molecular Systems. VI.*

Singlet-Type Instabilities and Charge-Density-Wave Hartree-Fock Solutions for Cyclic Polyenes†

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The singlet-stability conditions of the symmetry-adapted Hartree-Fock (HF) ground state of cyclic polyenes (linear metal with Born-Kármán cyclic boundary conditions) are studied, using the Pariser-Parr-Pople Hamiltonian and three different parametrization schemes. It is shown that the HF ground states are singlet-unstable for large enough cycles, so that the diamagnetic (pure singlet) symmetry-nonadapted HF solutions (broken-symmetry HF solutions), having lower energy than the symmetry-adapted HF solutions, must exist. In fact a number of broken-symmetry diamagnetic HF solutions, displaying the charge density waves (CDW's), exist for large enough cyclic polyenes. The most important ones, corresponding to the maximum quasi-momentum transfer and having lowest energy, are studied. The HF equations for these symmetry-nonadapted solutions are given in the BCS-Bogoliubov form, and their solutions are found numerically for cycles containing up to 170 atomic sites. It is shown that these new HF solutions display different types of CDW's, which may be conveniently classified as diagonal and off-diagonal CDW's. Finally, it is shown that the diagonal CDW HF solutions not only have generally higher energy than the off-diagonal HF solutions, but are, moreover, singlet-unstable, while the off-diagonal CDW solutions are singlet-stable. The implications of the existence of singlet instabilities for the occurrence of the energy-gap and bond-length alternation (sublattice formation), as well as for the applicability of some many-body techniques to these systems, are briefly discussed.

I. INTRODUCTION

In the first paper[1] of this series we have rederived Thouless's stability conditions[2] for the solutions of the Hartree-Fock (HF) equations and specified them to the closed-shell atomic and molecular systems. In this case, assuming a spin-independent Hamiltonian, we can achieve significant simplification of the stability conditions due to the possible factorization of the latter. Simultaneously, this enables us to classify the instabilities of the closed-shell HF solutions into two basic classes, which we refer to as *singlet* and *nonsinglet*[3] (or *triplet*) *instabilities*.

By nonsinglet instability we mean the instability of the restricted HF solution with respect to the variations characteristic of the unrestricted HF method, i.e., variations, which do not preserve the double occupancy of the spatial orbitals and, therefore, the singlet character of the HF single-determinantal wave function. If the restricted HF solution is nonsinglet-stable, this means that it represents a true local minimum with respect to such variations of the trial wave function.

On the other hand, the singlet instability conditions are much more restrictive and, consequently, occur less frequently. They mean the instability of the symmetry-adapted restricted HF determinant to variations, which preserve the double occupancy of the orbitals. Consequently, if the restricted HF solution is *singlet*-unstable, this means that it does not represent a true minimum with respect to the variations mentioned above and that another pure singlet solution, having lower energy than the restricted HF solution, must exist. It may be shown[1] that this new solution violates the space-symmetry conservation laws, while it preserves the spin symmetry. Therefore, it displays the so-called charge density waves (CDW's) while the unrestricted HF solutions, which clearly exist if the restricted HF solution is nonsinglet-unstable, display the spin density waves (SDW's).

Clearly, the nonsinglet instability is only a necessary condition for the existence of unrestricted HF solutions with lower energy than the corresponding restricted HF solution. This is due to the fact that the stability problem is concerned with the local properties of the restricted HF solutions and cannot give any information as regards the absolute minima of the energy-mean-value functional. This is the subject of a much more general problem of the symmetry dilemma,[4] first clearly formulated by Löwdin.

The singlet instability and the corresponding CDW HF solutions have been demonstrated in Paper I of this series for the π-electronic models of cyclic polyenes, as well as in Paper III,[5] where singlet stability of linear polyacenes was studied. In Paper III we have also presented simple rules which make it possible to predict the singlet stability of the symmetry-adapted HF solutions of π-electronic systems on the basis of the symmetry properties of pertinent Kekulé structures.

Recently a number of papers have been devoted to the problems, which are closely related to the HF stability problem studied in this series. A brief review of these papers may be found in the Introduction to Paper II[6] of this series, where the stability problem has been extended to the restricted HF solutions of simple open-shell systems, as well as in another recent review paper.[7]

In particular a number of papers appeared recently, which are closely connected with the problem of singlet instabilities in cyclic polyenes.[8-14] As already mentioned, this problem has been briefly studied in Paper I of this series as an illustration of singlet instabilities. In addition to demonstrating the singlet instability of symmetry-adapted HF solutions of larger cyclic polyenes, we have also given the convenient equations for the new HF solutions and found its solutions. These new HF solutions clearly displayed the CDW's.

In the meantime, Fukutome[8] rederived the singlet and nonsinglet stability conditions and also applied them to the cyclic polyenes. However, he has missed[9] the bond-order alternating solutions; he has calculated and formulated rather the HF equations for the atomic-charge alternating solutions. Fukutome[8] presented the equations for the new atomic-charge alternating HF solutions in the form of the BCS-Bogoliubov equations, similar to the formulation given by Shi[15] for the case of nonsinglet instabilities. On the basis of his study he then made implications with respect to the existence of the bond-length alternation in long polyenes.

Very recently, Harris and Falicov[10] published a series of papers dealing with the problems of bond alternation in cyclic polyenes and with the existence of CDW and SDW solutions. Their preliminary communication[10(a)] has been commented on by Salem[11] and by Tric.[12(a)] Together with Cazes, they have also recently considered[12(b)] the stability problem for long polyenes. Tric[12(a)] has also studied a very interesting problem of the compatibility of instability mixing.[13]

In their studies Harris and Falicov[10(b)] claim the nonexistence of CDW HF ground-state solutions for cyclic polyenes in spite of their well-known existence.[1,8,16] This is because their study is based in principle on the Hubbard Hamiltonian,[17] in which only the electrons on the same site may interact. One can indeed show[14] that this over-simplified Hamiltonian cannot yield the CDW HF solutions for cyclic polyenes. However, using at least a slightly more realistic interelectronic potential, as did for example Ooshika,[16] one can show that the CDW ground states do exist for large enough cyclic polyenes.

As may be seen from this brief review, there has been a considerable confusion in this respect. We consider it, therefore, very useful to give a detailed account and united formulation of these problems in this paper and to carry out a number of actual calculations, considering the cycles having up to the 170 atoms, in order to clarify these problems.

Simultaneously, we would like to point out that the cyclic polyenes may be thought not only as an interesting quantum chemical model, but also as a model of a linear metal with Born-Kármán cyclic boundary conditions. This model is also essentially equivalent to the model of an electron in a box with proper boundary conditions.[12,18]

Indeed, the π-electronic systems in general represent an interesting finite Fermi systems to which the methods of many-body theories might be applied, as pointed out by Gutfreund and Little,[19] in whose paper one can also find a very nice and concise description of these models. The semiempirical Hamiltonian used in these model calculations has been formulated in the second-quantized form earlier by Harris[20] and Koutecký.[21]

II. CLOSED-SHELL STABILITY CONDITIONS

Let us first recall the form of the singlet and nonsinglet (triplet) stability conditions for the restricted solutions of the HF equations, given in Paper I.

These conditions ensure that the HF single-determinantal wave function represents a true local minimum of the mean-energy functional or, in other words, that the second variation of the mean-energy functional, within the variational space considered, is positive definite.

In general, the variational space considered is spanned by all single-determinantal functions, which are not orthogonal to the HF wave function, whose stability is studied. These general stability conditions had been first formulated by Thouless.[2] The first application of these conditions to the molecular problems and their formulation in terms of density matrices was given by Adams.[22]

However, these general stability conditions may be considerably simplified, if the Hamiltonian of the system is spin independent. Indeed, in this case we can separate the general variational space into two independent subspaces and, henceforth, obtain an independent stability condition for each subspace. This separation is easily achieved by a proper unitary transformation, as shown in Paper I, where the two independent stability conditions obtained were called singlet and nonsinglet (triplet) stability conditions.

In the case of the singlet stability problem, the corresponding variational subspace is spanned by the single-determinantal functions with doubly occupied orbitals, i.e., by the Slater determinants which are pure singlet eigenfunctions of the operator S^2. However, in the case of the nonsinglet (triplet) stability problem, the restriction of the double occupancy is lifted and the corresponding variational space is, therefore, typical of the unrestricted HF method. This factorization of the general stability criteria into the singlet and nonsinglet stability conditions not only simplifies the problem, but also leads to a useful classification of the instabilities, as shown in Paper I.

In order to formulate the singlet and nonsinglet stability conditions, let us write the Hamiltonian of our closed-shell $2n$-electronic system as a sum of one- and two-particle operators $\hat{z}_i$ and $\hat{v}_{ij}$, respectively, i.e.,

$$H = \sum_i \hat{z}_i + \sum_{i<j} \hat{v}_{ij} \quad . \tag{1}$$

Let us, further, designate by $\phi_1, \phi_2, \ldots,$ etc., the HF molecular orbitals, which are numbered in such a way that first n orbitals are occupied in the ground state, so that the HF solution may be written, up to a normalization factor, as follows:

$$\Phi_0 = \det \| \phi_1\alpha, \ \phi_1\beta, \ \phi_2\alpha, \ldots, \phi_n\alpha, \ \phi_n\beta \| \quad , \tag{2}$$

where α and β are spin-up and spin-down functions, respectively. We can now state the stability conditions as follows: The HF solution (2) is nonsinglet ($x=t$) and/or singlet ($x=s$) stable, if the eigenvalue problem

$$\begin{pmatrix} A^x & B^x \\ \bar{B}^x & \bar{A}^x \end{pmatrix} \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix} = \lambda \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix} \tag{3}$$

has only positive eigenvalues. In this eigenvalue problem, A^x and B^x are square matrices, whose rows and columns are labeled with all possible monoexcitations $i \to j$, describing excitation from the occupied HF molecular orbital ϕ_i to the virtual orbital ϕ_j. Further, $\bar{X}$ designates the complex-conjugate matrix to the matrix X. We will find it useful to label each monoexcitation by a single index. This may be easily achieved by numbering consecutively all monoexcitations and writing, generally, the ith excitation u_i, in which an occupied orbital $\phi_{k_i} \equiv \langle x | k_i \rangle$ is replaced with the virtual orbital $\phi_{l_i} \equiv \langle x | l_i \rangle$ as follows:

$$u_i \equiv \begin{pmatrix} l_i \\ k_i \end{pmatrix} \quad . \tag{4}$$

Obviously, the matrix elements of the A or B matrices may now be designated by one of the following symbols as convenient:

$$X_{u_i,u_j} = \langle u_i | X | u_j \rangle \equiv \left\langle \begin{matrix} l_i \\ k_i \end{matrix} \middle| X \middle| \begin{matrix} l_j \\ k_j \end{matrix} \right\rangle \equiv X_{k_i l_i ; k_j l_j} \quad , \tag{5}$$

where $X = A^s, \ B^s, \ A^t, \ B^t$. For the nonsinglet stability problem, these matrix elements have the following form (see Paper I):

$$\begin{aligned} \left\langle \begin{matrix} l \\ k \end{matrix} \middle| A^t \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle &= \langle l | \hat{f} | l' \rangle \langle k | k' \rangle - \langle k' | \hat{f} | k \rangle \langle l | l' \rangle \\ &\quad - \langle l k' | \hat{v} | l' k \rangle \quad , \\ \left\langle \begin{matrix} l \\ k \end{matrix} \middle| B^t \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle &= - \langle l l' | \hat{v} | k' k \rangle \quad , \end{aligned} \tag{6}$$

while for the singlet case we have

$$\begin{aligned} \left\langle \begin{matrix} l \\ k \end{matrix} \middle| A^s \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle &= \left\langle \begin{matrix} l \\ k \end{matrix} \middle| A^t \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle + 2 \langle l k' | \hat{v} | k l' \rangle \quad , \\ \left\langle \begin{matrix} l \\ k \end{matrix} \middle| B^s \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle &= \left\langle \begin{matrix} l \\ k \end{matrix} \middle| B^t \middle| \begin{matrix} l' \\ k' \end{matrix} \right\rangle + 2 \langle l l' | \hat{v} | k k' \rangle \quad , \end{aligned} \tag{7}$$

where we have denoted

$$\langle i|\hat{f}|\,j\rangle = \langle \phi_i\,|\,\hat{z}\,|\phi_j\rangle + \sum_{k=1}^{n} (2\langle ik\,|\hat{v}\,|\,jk\rangle - \langle ik\,|\hat{v}\,|kj\rangle) \quad ,$$

and, further

$$\langle i\,|\,j\rangle = \langle \phi_i\,|\,\phi_j\rangle \quad ,$$

$$\langle ij\,|\hat{v}\,|kl\rangle = \langle \phi_i\phi_j\,|\hat{v}\,|\,\phi_k\phi_l\rangle \quad .$$

From the above definitions we see immediately that matrices A^x, $x=s$, t, are Hermitian matrices, while B^x, $x=s$, t, matrices are not, since

$$(B^x)^\dagger = \bar{B}^x \quad , \tag{8}$$

where $B^\dagger$ designates the Hermitian conjugate matrix to the matrix B. However, the supermatrix of the eigenvalue problem (3) is again Hermitian. Consequently, the above-stated stability conditions imply that the quadratic form

$$\Delta^{(2)}\tilde{E}^x = \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix}^\dagger \begin{pmatrix} A^x & B^x \\ \bar{B}^x & \bar{A}^x \end{pmatrix} \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix} \tag{9}$$

is positive definite. In fact, this quadratic form expresses, up to a constant factor, the second variation of the mean-energy value at the point of the variational space corresponding to the HF solution considered.

The same stability conditions have also been recently derived by Fukutome,[8] who calls the singlet and nonsinglet (triplet) instabilities, instabilities to charge-density and spin-density fluctuations, respectively. Fukutome's terminology has the advantage of indicating directly the nature of the instabilities, while our terminology has the advantage of being more concise.

When the matrices A^x and B^x, $x=s$, t, are real matrices, as is usually the case, the stability problem (3) may be further simplified. Indeed, (3) may be factored into two subproblems

$$[A^x + (-1)^y B^x]E^{x,y} = \lambda^{x,y}E^{x,y}\,, \quad y=0,1 \tag{10}$$

while $D^x = E^{x,0}$ for the $y=0$ case, and $D^x = iE^{x,1}$ for the $y=1$ case.

Further, it may be easily shown[1] that the eigenvector, corresponding to the lowest eigenvalue λ_0 of the stability condition (3), gives the direction of the steepest descent ($\lambda_0 < 0$) or slowest ascent ($\lambda_0 > 0$) on the mean-energy hypersurface in the given variational subspace. In fact, the elements d_{ij} of the eigenvector D_0, corresponding to the lowest eigenvalue λ_0, determine the ratios in which the virtual molecular orbitals must be admixed to the occupied orbitals in order to obtain the variational function corresponding to the direction of the energy's steepest descent (slowest ascent).

Finally, let us recall that the existence of singlet instability implies the existence of another HF solution, which has lower energy than the studied singlet-unstable HF solution and which is, moreover, a pure singlet eigenfunction of S^2. In finding these new singlet solutions it is advantageous, especially in the case of cyclic polyenes, to use as a first approximation in the HF equations a wave function corresponding to the minimum energy in the direction of steepest descent discussed above. This procedure is described in greater detail in Sec. V.

III. CYCLIC POLYENES

We shall study the model systems, which have been often used in the correlation-energy studies and are generally called cyclic polyenes.[23,24] These models do not represent any real existing molecules except for the first term (benzene). However, they are useful for the study of the correlation effects in one-dimensional systems. In the limiting case of infinitely large polyenes, they may be considered as models of very long linear polyenes.

On the other hand, the same model may be thought of as a model of a linear metal with Born-Kârmân cyclic boundary conditions. As a matter of fact this model is essentially equivalent to the model of an electron in a box with proper boundary conditions.[12,18]

Let us now describe the model of cyclic polyenes which we shall study. These are π-electronic models of hypothetical cyclic polyenes C_NH_N, $N=2n=4\nu+2$, $\nu=1,2,\ldots$, which are assumed to form a regular polygon, so that the point group of the corresponding Hamiltonian is D_{Nh}. The semiempirical model Hamiltonian describing the π-electronic system of these model systems may be written conveniently in the second-quantized form

$$H = \sum_{\mu,\nu,\sigma} z_{\mu\nu} a^\dagger_{\mu\sigma} a_{\nu\sigma} + \tfrac{1}{2} \sum_{\mu,\nu,\sigma,\tau} \gamma_{\mu\nu} a^\dagger_{\mu\sigma} a^\dagger_{\nu\tau} a_{\nu\tau} a_{\mu\sigma}\,, \tag{11}$$

where $a^\dagger_{\mu\sigma}$ and $a_{\mu\sigma}$ designate the creation and annihilation operators, respectively, defined on the basis of spin orbitals $|\mu\sigma\rangle$, $|\mu\sigma\rangle = |\mu\rangle|\sigma\rangle$, $\sigma=\alpha$ or β. For the one-particle-operator matrix elements $z_{\mu\nu}$, the tight-binding approximation is used, so that all off-diagonal elements vanish except when μ and ν are nearest neighbors, when

$$z_{\mu\nu} = \beta_{\mu\nu} \quad , \tag{12}$$

where $\beta_{\mu\nu}$ is a resonance integral. The diagonal elements are approximated as follows:

$$z_{\mu\nu} = \alpha_\mu - \sum_{\nu(\neq\mu)} Z_\nu \gamma_{\mu\nu} \quad , \tag{13}$$

where α_μ is a Coulombic integral, approximated usually by the corresponding valence-state ionization potential and Z_μ designates the number of π electrons contributed by the μth site. Finally, $\gamma_{\mu\nu}$ are Coulomb repulsion integrals, describing the interelectronic potential,

$$\gamma_{\mu\nu}=\langle\mu\nu|\hat{v}|\mu\nu\rangle \quad , \tag{14}$$

which result from the general terms $\langle\mu\nu|\hat{v}|\mu'\nu'\rangle$ using the zero-differential overlap approximation.[25]

The semiempirical values of these integrals take into account the correlation effects, σ-electron and other π-electron screening. In particular the value of the one-center integral $\gamma_{\mu\mu}$, giving the interaction energy between two $2p_z$ electrons located on the same atomic site, is found in the semiempirical theories as a difference of the valence-state ionization potential and electron affinity.[25] Furthermore, due to the symmetry of the cyclic-polyene model, we have

$$\beta_{\mu\nu}=\beta, \quad \alpha_\mu=\alpha \quad ,$$

and, since $Z_\mu=1$, we have also $z_{\mu\mu}=z_0$. Clearly, without any loss of generality, we can choose the energy scale in such a way that $z_0=0$, and obtain the following simple model Hamiltonian:

$$H=\beta\sum_{\mu,\nu}{}'\sum_{\sigma}a^\dagger_{\mu\sigma}a_{\nu\sigma}+\tfrac{1}{2}\sum_{\mu\nu,\sigma\tau}\gamma_{\mu\nu}a^\dagger_{\mu\sigma}a^\dagger_{\nu\tau}a_{\nu\tau}a_{\mu\sigma} \ , \tag{15}$$

where the prime at the first summation symbol indicates the summation over nearest neighbors only. Since also $\gamma_{ii}=\gamma_{00}$, we can further write

$$H=\beta\sum_{\mu,\nu}{}'\sum_{\sigma}a^\dagger_{\mu\sigma}a_{\nu\sigma}+\tfrac{1}{2}\sum_{\mu,\nu}{}'\gamma_{\mu\nu}\sum_{\sigma,\tau}n_{\mu\sigma}n_{\nu\tau} +\gamma_{00}\sum_{\mu}n_{\mu\alpha}n_{\mu\beta} \quad , \tag{16}$$

where $n_{\mu\sigma}$ is the number operator corresponding to the spin orbital $|\mu\rangle|\sigma\rangle$, i.e.,

$$n_{\mu\sigma}=a^\dagger_{\mu\sigma}a_{\mu\sigma} \quad . \tag{17}$$

Needless to say, the basis orbitals $|\mu\rangle$, used as the atomic-orbital basis for the LCAO approximation and to define our creation and annihilation operators, are assumed to be orthonormal. These may be thought of as Löwdin-orthogonalized $2p_z$ carbon atomic orbitals, which yield essentially the semiempirical values of the integrals β and $\gamma_{\mu\nu}$, which we are going to use. Clearly, each carbon atom of our model contributes one such atomic orbital, which we can label consecutively along the chain from 0 to $N-1$.

The symmetry-adapted HF molecular orbitals in the LCAO form are, in the minimum basis set we use, fully determined by the symmetry of our model, independently of the actual form of the Hamiltonian, as long as it has the symmetry of the point group D_{Nh}. Indeed, using Bloch's theorem we can write the rth HF molecular orbital as follows[26]:

$$\left|r\right\rangle=\frac{1}{\sqrt{N}}\sum_{\mu=0}^{N-1}\exp\left(\frac{2\pi i r\mu}{N}\right)\left|\mu\right\rangle , \qquad r=0,1,\ldots,N-1 \quad . \tag{18}$$

The corresponding orbital energies ϵ_r are

$$\epsilon_r\equiv\langle r|\hat{f}|r\rangle=\langle r|\hat{z}|r\rangle + \sum_{k\in\omega}(2\langle rk|\hat{v}|rk\rangle-\langle rk|\hat{v}|kr\rangle) \quad , \tag{19}$$

where ω designates the set of orbitals occupied in the ground-state HF wave function,

$$k\in\omega: \quad k=0,1,\ldots,\nu \ \text{ and }$$
$$k=N-1,\ N-2,\ldots,N-\nu \ .$$

Using the Hamiltonian (16), we get

$$\langle r|\hat{z}|r\rangle=2\beta\cos(2\pi r/N) \quad , \tag{20}$$

$$\langle rs|\hat{v}|tn\rangle=K(r-t)\,\delta_{r+s,t+n} \quad , \tag{21}$$

where

$$K(r)=[\gamma_{00}+(-1)^r\gamma_{0n}+2\sum_{\mu=1}^{n-1}\gamma_{0\mu}\cos(2\pi\mu r/N)]/N \quad .$$

We get, therefore, finally

$$\epsilon_r=2\beta\cos(2\pi r/N)+NK(0)-\sum_{k\in\omega}K(r-k) \quad . \tag{22}$$

The schematic representation of the orbital energies ϵ_k, $k=0,1,\ldots,N-1$, and their numbering is shown schematically in Fig. 1.

The total π-electronic energy E_0 of the system is then given by

$$E_0=\sum_{k\in\omega}(\epsilon_k+\langle k|\hat{z}|k\rangle) \quad . \tag{23}$$

Finally, in the actual calculations, we use the following parametrizations for the resonance- and Coulomb-repulsion integrals.

a. Pariser-Parr parametrization[25,27] (PP). We take $\beta=-2.388$ eV, and Coulomb-repulsion integrals are calculated using the charged-spheres approximation[28] using Slater effective nuclear charge $Z=3.25$ and $\gamma_{00}=10.840$ eV.

b. Mataga-Nishimoto parametrization[29] (MN). We take again $\beta=-2.388$ eV and $\gamma_{00}=10.840$ eV, while the other Coulomb-repulsion integrals are given by the formula

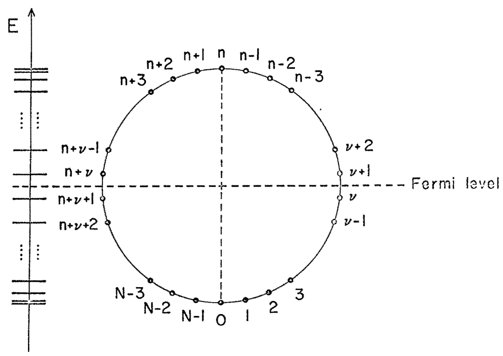

FIG. 1. Schematic representation of the orbital energies and corresponding molecular-orbital numbering.

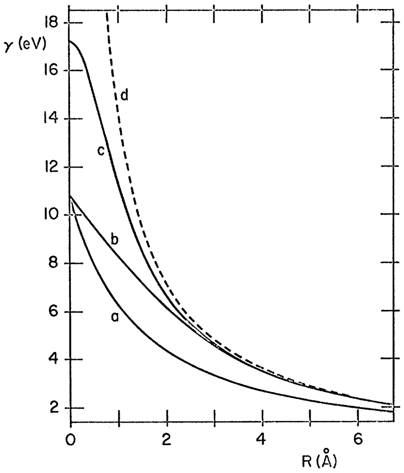

FIG. 2. Dependence of the two-electron Coulomb-repulsion integrals $\gamma_{\mu\nu} \equiv \langle \chi_\mu \chi_\nu | v | \chi_\mu \chi_\nu \rangle$, over the basic atomic orbitals χ_μ, on the internuclear distance R between the atomic sites μ and ν, using various approximations: (a) Matago-Nishimoto approximation; (b) Pariser-Parr approximation; (c) theoretical approximation; (d) point-charge (Pople) approximation.

$$\gamma(R) = e^2/(a+R) \ , \tag{24}$$

where $a = e^2/\gamma_{00}$. This approximation represents an "interpolation" between the finite γ value for $R=0$ and the point-charge Coulomb repulsion for $R \to \infty$.

c. Theoretical parametrization[30] (T). We use $\beta = -3.71631$ eV,[30] while γ integrals are calculated using the analytical expression for these integrals with the Slater $2p_z$ atomic orbitals,[31] with the effective nuclear charge $Z = 3.2358$.[30,32]

In this parametrization we also assume the orthogonality of the individual orbitals, unlike in Paper I, where overlap was considered explicitly. This simplifies significantly all calculations while having no effect on the basic conclusions we get with this parametrization, which we use in order to demonstrate the type of effects obtained when no correlation and σ-electron screening is included in the semiempirical values of the integrals, i.e., when the Coulomb interaction is not screened ($\gamma_{00} = 17.229$ eV as compared with $\gamma_{00} = 10.840$ eV in both PP and MN parametrizations).

The dependence of the Coulomb-repulsion integrals $\gamma_{ij}(R)$ on the internuclear separation R is illustrated in Fig. 2 for PP, MN, and T parametrizations. This figure shows the degree of screening in individual parametrizations. For comparison, the point-charge approximation is also included.

In all cases we take the C – C bond length $d = 1.4$ Å, so that we have

$$\gamma_{0\mu} = \gamma(R_{0\mu}) \ , \tag{25}$$

where

$$R_{0\mu} = d \frac{\sin(\pi\mu/N)}{\sin(\pi/N)} \ .$$

IV. APPLICATION OF STABILITY CONDITIONS TO THE CYCLIC POLYENES

The stability eigenvalue problem (3) or (10) for the symmetry-adapted HF solutions (18) of cyclic polyenes may be very effectively simplified using the high symmetry of our model, as shown already in Paper I.

Realizing that the numbers labeling molecular orbitals (18) are closely associated with the quasimomentum of these orbitals which, in turn, may be used to label the irreducible representations of the subgroup C_N of the point group D_{Nh}, we can associate with each monoexcitation

$$u_i \equiv \begin{pmatrix} l_i \\ k_i \end{pmatrix}$$

a corresponding quasimomentum transfer p_{u_i},

$$p_{u_i} = (l_i - k_i) \bmod N \ . \tag{26}$$

We find easily that the A matrix elements $\langle u_i | A^x | u_j \rangle$ (for both $x=s$ and $x=t$ cases) vanish unless $(p_{u_i} - p_{u_j}) \times \bmod N = 0$, so that the A matrix factors into $(N-1)$ submatrices, one for each quasimomentum transfer p, $p = 1, 2, \ldots, N-1$. However, B matrix elements $\langle u_i | B^x | u_j \rangle$ are nonzero only if $(p_{u_i} + p_{u_j}) \bmod N = 0$, so that they couple together corresponding submatrices of the A matrix. Altogether, we get factorization of the stability eigenvalue problem (10) into the $n = 2\nu + 1$ subproblems. It is convenient to label these subproblems by the corresponding minimal quasimomentum transfer p,

$$p = \min(p_{u_i}, \ p_{u_j}) \ , \tag{27}$$

of two subproblems coupled together by the B matrix elements. This definition enables us to characterize each monoexcitation u_i by the quasimomentum k_i of the occupied molecular orbital $|k_i\rangle$ and by the quasimomentum transfer p_{u_i}, $p_{u_i} = \min(p_{u_i}, N - p_{u_i})$,

$$u_i \equiv \begin{pmatrix} l_i \\ k_i \end{pmatrix} = \begin{pmatrix} (k_i + p_{u_i}) \bmod N \\ k_i \end{pmatrix} \ . \tag{28}$$

As indicated in Paper I, we can find easily that the lowest eigenvalue of the stability problem (10) may be expected in the subproblem, corresponding to the maximum possible quasimomentum transfer

$$p = n = 2\nu + 1 \ . \tag{29}$$

In the following we shall, therefore, consider only this subproblem,[33] which may be still further simplified, if we choose proper linear combinations of the degenerate monoexcitations. Since in this subproblem all monoexcitations have the same quasimomentum transfer $p=n$, we can label the individual monoexcitations only by the quasimomentum of the corresponding occupied molecular orbital. Using this convention, we can write the A matrix elements as follows:

$$\langle u_1|A^x|u_2\rangle \equiv \langle k_1|A^x|k_2\rangle , \quad x=s,t, \tag{30}$$

where

$$u_i \equiv \begin{pmatrix} (k_i+n)\,\mathrm{mod}N \\ k_i \end{pmatrix}, \quad i=1,2$$

and, similarly, for the B matrix elements. The $p=n$ subproblems of the stability problem (10) may then be written as follows:

$$\sum_{k'\in\omega} \langle k|A^x+(-1)^y B^x|k'\rangle e_{k'}^{x,y} = \lambda^{x,y} e_k^{x,y} ,$$
$$x=s,t, \quad y=0,1. \tag{31}$$

The unitary transformation, which further factors this subproblem into another two subproblems, may be defined as follows

$$\begin{aligned} e_{k^\pm}^{x,y} &= (e_k^{x,y} \pm e_{N-k}^{x,y})/\sqrt{2} , \quad k\neq 0 \\ e_{0^+}^{x,y} &= e_0^{x,y} . \end{aligned} \tag{32}$$

We find easily that all matrix elements of the type

$$\langle k^+|A\pm B|k'^-\rangle \tag{33}$$

always vanish, and the stability subproblem (31) of the nth order factors into two subproblems of the orders $(\nu+1)$ and ν for "+ states" and "− states," respectively.

Altogether, (31) represents four subproblems for each $x=s$ and $x=t$, which we can designate for simplicity as $(A+B)^+$, $(A+B)^-$, $(A-B)^+$, and $(A-B)^-$ subproblems. Clearly, $(A+B)$ and $(A-B)$ cases correspond to $y=0$ and $y=1$ cases, respectively, while the sign given as a superscript distinguishes "+" and "−" states, defined by the unitary transformation (32).

The explicit expressions for the necessary matrix elements of these four subproblems, both for singlet and nonsinglet case, are given in the Appendix A.

Let us now find out which of the above four subproblems are likely to yield singlet instability. This may be seen from the behavior of the lowest diagonal matrix element in each subproblem. Clearly, if this matrix element will approach zero or even will become negative for certain values of N, this will necessarily indicate the instability of the symmetry-adapted HF solution. Using the expressions of Appendix A, we find the following smallest diagonal matrix elements for the individual subproblems studied:

$$\begin{aligned} (A^s+B^s)^\pm &: \quad \Delta\beta+2K(n)\pm[4K(n)-K(n-1)-K(1)] , \\ (A^{s,t}-B^{s,t})^\pm &: \quad \Delta\beta\pm[K(1)-K(n-1)] , \\ (A^t+B^t)^\pm &: \quad \Delta\beta-2K(n)\mp[K(n-1)+K(1)] , \end{aligned} \tag{34}$$

where $\Delta\beta=-4\beta\cos(\pi\nu/n)$ is a positive number. Since $K(i)>K(j)$ as long as $i<j$, and since $K(n)\to 1/N$ as $N\to\infty$ while $K(0)\to(\ln N)/N$ as $N\to\infty$, we see immediately that the instability may occur in subproblems $(A+B)^+$ and $(A-B)^-$ (both in singlet and nonsinglet cases), while it is very unlikely to occur in the remaining two subproblems. In fact, it may be shown that instability of subproblems $(A+B)^-$ and $(A-B)^+$ would lead to the new HF solutions, having lower energy than the symmetry-adapted HF solution, which violate not only spatial (and, in case of nonsinglet instabilities, spin) symmetry, but also the time-reversal symmetry.[8,9]

These considerations are indeed confirmed by actual calculations. The dependence of the lowest eigenvalue for each of the four singlet subproblems considered above as a function of the size of the cyclic polyene N, using MN parametrization, is shown in Fig. 3 [for the nonsinglet case only the lowest root, obtained from the subproblem $(A^t+B^t)^+$, is given for comparison].

We see immediately that the lowest root of the singlet stability problem comes from the $(A^s-B^s)^-$ subproblem. However, the $(A^s+B^s)^+$ subproblem also yields negative eigenvalue, even though for larger N. An analogous situation is obtained for

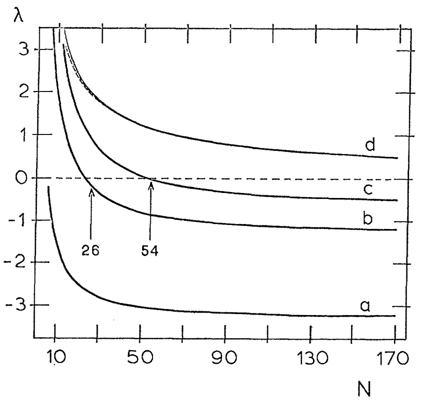

FIG. 3. Dependence of the lowest eigenvalue λ from various subproblems (listed below) of the stability problems (3) on the size of the cyclic polyenes C_NH_N, $N=4\nu+2$, given by the number of atomic sites N, plotted as a continous function. The results were obtained with MN parametrization. The lowest eigenvalues from the following subproblems are shown: (a): $(A^t+B^t)^+$; (b): $(A^{s,t}-B^{s,t})^-$; (c) $(A^s+B^s)^+$; (d) $(A^s+B^s)^-$; dashed (d): $(A^s-B^s)^+$. The triplet instability of the $(A^t+B^t)^+$type occurs already for $N=6$; the singlet instability of the $(A^s-B^s)^-$and $(A^s+B^s)^+$ type occurs first for the polyenes with $N=26$ and $N=54$, respectively, marked in the figure with vertical arrows (cf. Table I).

the other two parametrizations considered, and the critical size of the cyclic polyene, for which the singlet instability of either type appears for the first time, is given in Table I. Now, it is obvious (see also Paper I) that an instability of the symmetry-adapted restricted HF solution indicates the existence of another HF solution, having lower energy than the symmetry-adapted solution. This new HF solution will not be any more symmetry adapted and, in fact, will violate some conservation laws. In the case of singlet instability, we know that the spin symmetry is preserved, but space symmetry becomes violated. For the alternant π-electronic systems, there is also the possibility of violating the alternacy symmetry.

If we examine the type of variations of the symmetry-adapted HF solution, which leads to the instability, one can see immediately which conservation law will be violated by the new HF solution. As will be shown in Secs. V–VII in detail, the instability originating in the $(A^s - B^s)^-$ subproblem leads to the HF solutions violating space symmetry, while the second possible instability, originating from the $(A^s + B^s)^+$ subproblem, leads to a solution violating both space and alternacy symmetry. In the following, we shall find these nonsymmetry-adapted HF solutions and will examine their singlet stability.

V. SYMMETRY-NONADAPTED RESTRICTED HF SOLUTIONS

Let us now find the new restricted symmetry-nonadapted (broken symmetry) HF solutions, which we know must exist in cases when the symmetry-adapted HF solution is singlet-unstable. Clearly, we could find these with an ordinary SCF procedure selecting properly the initial approximation, so that the SCF procedure would not converge back to the symmetry-adapted HF solution. The choice of the starting approximation has been discussed in considerable detail in Paper II.

However, in the case of cyclic polyenes there is a great advantage, as compared with the general case discussed in Paper II, due to the high symmetry of this model. Namely, in any subproblem of the stability problem (3) each occupied orbital mixes together with only *one* virtual orbital. In this way the new molecular orbitals, obtained by occupied- and virtual-orbital mixing, remain orthogonal and all the difficulties of the general case, discussed in Paper II, are therefore avoided.

TABLE I. Minimal N values, for which the symmetry-adapted HF solutions of the cyclic polyenes C_NH_N become singlet-unstable with respect to the charge-density fluctuations of the diagonal (atomic charges) and of the off-diagonal (bond-order) type.

Parametrization	$(A^s - B^s)^-$ type instability (off-diagonal CDW's)	$(A^s + B^s)^+$ type instability (diagonal CDW's)
MN	26	54
PP	18	22
T	18	38

The ratios, in which we have to admix the virtual orbitals to the occupied HF orbitals in order to yield a variational wave function in the direction of the mean-energy steepest descent (slowest ascent), are determined by the eigenvector of the stability problem (3), corresponding to the lowest eigenvalue. Obviously, a similar rule applies to any eigenvalue and a corresponding eigenvector of the stability problem, each eigenvector yielding some direction in the variational space corresponding to the curvature given by the associated eigenvalue.

For the particular case of the maximal quasimomentum transfer subproblems, which contain the lowest-lying roots of the stability problem (3), orbital mixing, leading to the new HF molecular orbitals, may be written as follows:

$(A^s + B^s)^+$ case:

$$\begin{aligned} &|r^M\rangle = \alpha_r|r\rangle + \beta_r|(r+n)\,\mathrm{mod}N\rangle \ , \\ &\alpha_{N-r} = \alpha_r \ , \quad \beta_{N-r} = \beta_r \ , \end{aligned} \tag{35a}$$

$(A^s - B^s)^-$ case:

$$\begin{aligned} &|r^M\rangle = \alpha_r|r\rangle + i\beta_r|(r+n)\,\mathrm{mod}N\rangle \ , \\ &\alpha_0 = 1, \qquad \beta_0 = 0 \ , \\ &\alpha_{N-r} = \alpha_r \ , \quad \beta_{N-r} = -\beta_r \ , \end{aligned} \tag{35b}$$

$(A^t + B^t)^+$ case:

$$\begin{aligned} &|r^M\rangle = \alpha_r|r\rangle + \beta_r|(r+n)\,\mathrm{mod}N\rangle \quad \text{for } \alpha \text{ spins} \ , \\ &|r^M\rangle = \alpha_r|r\rangle - \beta_r|(r+n)\,\mathrm{mod}N\rangle \quad \text{for } \beta \text{ spins} \ , \\ &\alpha_{N-r} = \alpha_r \ , \quad \beta_{N-r} = \beta_r \ , \end{aligned} \tag{35c}$$

$(A^t - B^t)^-$ case:

$$\begin{aligned} &|r^M\rangle = \alpha_r|r\rangle + i\beta_r|(r+n)\,\mathrm{mod}N\rangle \quad \text{for } \alpha \text{ spins} \ , \\ &|r^M\rangle = \alpha_r|r\rangle - i\beta_r|(r+n)\,\mathrm{mod}N\rangle \quad \text{for } \beta \text{ spins} \ , \\ &\alpha_0 = 1, \qquad \beta_0 = 0 \ , \\ &\alpha_{N-r} = \alpha_r \ , \quad \beta_{N-r} = -\beta_r \ . \end{aligned} \tag{35d}$$

In these formulas we have denoted by $|r^M\rangle$ the molecular orbitals obtained by a proper mixing of the occupied and unoccupied orbitals as implied by the individual subproblems. Clearly, we can set

$$\alpha_r = \cos\lambda_r \ , \quad \beta_r = \sin\lambda_r \ , \tag{36}$$

ensuring the normalization of the new orbitals. The symmetry-adapted HF molecular orbitals then correspond to $\lambda_r = 0$ for all r.

Moreover, the additional advantage of the very limited orbital mixing (35a)–(35d), which occurs for cyclic polyenes, consists of a possibility of using the symmetry-adapted HF molecular orbitals $|r\rangle$ as a basis in calculating the symmetry-nonadapted solutions. Clearly, the HF problem will then factor into the n 2×2 subproblems, each determining one parameter λ_r above. Clearly, all n subproblems are coupled together through the HF operator.

This form of the SCF problem has been used in Paper I for the $(A^s - B^s)^-$ case. On the other hand, Fukutome[8] presented these equations for the $(A^s + B^s)^+$ case in the form of the BCS-Bogoliubov equations, as was done for the first time for the triplet instabilities by Shi.[15]

We shall, therefore, present here a unified formulation of these equations, for all four cases (35a)–(35d) associated with the maximal quasimomentum transfer, in the BCS-Bogoliubov form. We shall illustrate this for the $(A^s - B^s)^-$ case, described in Paper I with an ordinary formalism. A general 2×2 subproblem of the HF problem, spanned by the symmetry-adapted HF orbitals $|r\rangle$ and $|(r+n)\,\mathrm{mod}N\rangle$, may be written as follows:

$$\begin{aligned}
&\cos\lambda_r \langle r|f^M|r\rangle + i\sin\lambda_r \langle r|f^M|(r+n)\,\mathrm{mod}N\rangle = \epsilon^M \cos\lambda_r \ ,\\
&\cos\lambda_r \langle (r+n)\,\mathrm{mod}N|f^M|r\rangle + i\sin\lambda_r (r+n)\\
&\qquad \times \mathrm{mod}N|f^M|(r+n)\,\mathrm{mod}N\rangle = \epsilon^M i \sin\lambda_r \ ,
\end{aligned} \tag{37}$$

where f^M is the HF operator corresponding to the new symmetry-nonadapted solution

$$\begin{aligned}
\langle r_1|f^M|r_2\rangle = \langle r_1|\hat{z}|r_2\rangle + \sum_{r^M\in\omega^M} &(2\langle r_1 r^M|\hat{v}|r_2 r^M\rangle\\
&- \langle r_1 r^M|\hat{v}|r^M r_2\rangle) \ ,
\end{aligned} \tag{38}$$

where ω^M designates a set of occupied symmetry-nonadapted molecular orbitals. For the matrix elements appearing in (37) we get, in particular,

$$\begin{aligned}
\langle r|f^M|r\rangle &= \epsilon_r + \sum_{k\in\omega} \sin^2\lambda_k\\
&\qquad \times (\langle rk|\hat{v}|kr\rangle - \langle rk'|\hat{v}|k'r\rangle) \ ,\\
\langle r|f^M|r'\rangle &= i\sum_{k\in\omega} \sin\lambda_k \cos\lambda_k\\
&\qquad \times (\langle rk'|\hat{v}|kr'\rangle - \langle rk|\hat{v}|k'r'\rangle) \ ,
\end{aligned} \tag{39}$$

where we have made convention that $r' = (r+n)\,\mathrm{mod}N$ and, similarly $k' = (k+n)\,\mathrm{mod}N$.

Further $\epsilon_r = \langle r|f|r\rangle$ is the rth HF orbital energy of the symmetry-adapted solution and also ω designates a set of occupied symmetry-adapted HF orbitals. If we now define

$$\begin{aligned}
A_r &= \langle r'|f^M|r'\rangle - \langle r|f^M|r\rangle \ ,\\
B_r &= -2i\langle r|f^M|r'\rangle = 2i\langle r'|f^M|r\rangle = \bar{B}_r \ ,
\end{aligned} \tag{40}$$

we find from (37)

$$B_r/A_r = \tan(2\lambda_r) \ . \tag{41}$$

Further, using (39) the quantities A_r and B_r may be given the form

$$\begin{aligned}
A_r &= \Omega_r + 2\sum_{k\in\omega} \sin^2\lambda_k [K(r+n-k) - K(r-k)] \ ,\\
B_r &= 2\sum_{k\in\omega} \sin\lambda_k \cos\lambda_k [K(r-k) - K(r+n-k)] \ ,
\end{aligned} \tag{42}$$

where

$$\Omega_r = \langle (r+n)\,\mathrm{mod}N|f|(r+n)\,\mathrm{mod}N\rangle - \langle r|f|r\rangle = \epsilon_{r'} - \epsilon_r$$

and $K(r)$ is defined in (21).

Using (41) we can write

$$\begin{aligned}
2\sin^2\lambda_k &= 1 - A_k/(A_k^2 + B_k^2)^{1/2} \ ,\\
2\sin\lambda_k \cos\lambda_k &= B_k/(A_k^2 + B_k^2)^{1/2} \ ,
\end{aligned} \tag{43}$$

so that we finally get

$$\begin{aligned}
A_r &= \Omega_r + \sum_{k\in\omega} [K(r+n-k) - K(r-k)]\\
&\qquad \times [1 - A_k/(A_k^2 + B_k^2)^{1/2}] \ ,\\
B_r &= \sum_{k\in\omega} [K(r-k) - K(r+n-k)] B_k/(A_k^2 + B_k^2)^{1/2} \ .
\end{aligned} \tag{44}$$

An analogous derivation may be carried out for the remaining subproblems. The quantity A_r is always defined as in (40), but the definition of B_r must be changed accordingly,

$$\begin{aligned}
&(A^s + B^s)^+ \text{ case:} \quad B_r = -2\langle r|f^M|r'\rangle \ ;\\
&(A^t - B^t)^- \text{ case:} \quad B_r = -2i\langle r|f^M|r'\rangle \quad \text{for } \alpha \text{ spins} \ ,\\
&\qquad\qquad\qquad\quad\ B_r = 2i\langle r|f^M|r'\rangle \quad \text{for } \beta \text{ spins} \ ;\\
&(A^t + B^t)^+ \text{ case:} \quad B_r = -2\langle r|f^M|r'\rangle \quad \text{for } \alpha \text{ spins} \ ,\\
&\qquad\qquad\qquad\quad\ B_r = 2\langle r|f^M|r'\rangle \quad \text{for } \beta \text{ spins} \ .
\end{aligned} \tag{45}$$

Then the HF equations for the symmetry-nonadapted solutions may be given the following form:

$$\begin{aligned}
A_r &= \Omega_r + \sum_{k\in\omega} [K(r+n-k) - K(r-k)]\\
&\qquad \times [1 - A_k/(A_k^2 + B_k^2)^{1/2}] \ ,\\
B_r &= \sum_{k\in\omega} Q(r,k) B_k/(A_k^2 + B_k^2)^{1/2} \ ,
\end{aligned} \tag{46}$$

where

$$Q(r,k) = K(r+n-k) + K(r-k) - 4K(n) \qquad \text{for } (A^s + B^s)^+ \text{ case} \ ,$$

$$Q(r,k) = K(r-k) - K(r+n-k)$$

$$\text{for } (A^s-B^s)^- \text{ and } (A^t-B^t)^- \text{ cases},$$

$$Q(r,k)=K(r+n-k)+K(r-k)$$

$$\text{for } (A^t+B^t)^+ \text{ case}.$$

These equations may be easily iterated until the self-consistency is achieved, assuming an adequate initial approximation is used. Clearly, a trivial solution $A_r=\Omega_r$, $B_r\equiv 0$ corresponds to the symmetry-adapted solution.

The best choice for the initial approximation is to use the wave function corresponding to the minimal energy mean value in the direction of the energy's steepest descent, at the point corresponding to the symmetry-adapted solution, given by the appropriate eigenvector of the stability problem. The variational wave function corresponding to this direction is obtained by choosing

$$\tan\lambda_r \sim e_r^{x,y}\ , \tag{47}$$

where $e_r^{x,y}$ designates the rth component of the appropriate eigenvector of (10). Clearly, putting

$$\tan\lambda_r=\kappa e_r^{x,y}\ , \tag{48}$$

the energy minimum in this direction is easily determined from a one-parameter variational problem. The necessary formulas expressing the energy as a function of the parameter κ are given in Appendix B. Knowing the coefficients α_r^0 and β_r^0 corresponding to the initial approximation, it is easy to calculate the starting values of A_r and B_r from (36) and (42). On the other hand, after the self-consistency of the solution of the HF equations (46) is achieved, we can get the HF molecular orbitals in the form (35a)–(35d) using the following relationships:

$$\begin{aligned}\alpha_r&=[\tfrac{1}{2}(1+g_r)]^{1/2}\ ,\\ \beta_r&=\operatorname{sign}(B_k)\,[\tfrac{1}{2}(1-g_r)]^{1/2}\ ,\end{aligned} \tag{49}$$

where

$$g_r=[1+(B_r/A_r)^2]^{-1/2}\ .$$

The most striking properties of the new singlet HF solutions, corresponding to the $(A^s+B^s)^+$ and $(A^s-B^s)^-$ types of singlet instability, may be seen from the respective first-order density matrices.

Let us first consider the $(A^s+B^s)^+$ case. Using the molecular orbitals (35a), we can derive easily the following expressions for the matrix elements of the first-order density matrix in the representation of the atomic-orbital basis (i.e., so-called atomic-charge and bond-order matrix):

$$p_{0,\mu}=\frac{1}{n}\sum_{k\in\omega}(\alpha_k+\beta_k)^2\cos\frac{\pi k\mu}{n}\qquad(\mu\ even)\ ,$$

$$p_{0,\mu}=p_{1,(1+\mu)}=\frac{1}{n}\sum_{k\in\omega}(\alpha_k^2-\beta_k^2)\cos\frac{\pi k\mu}{n}\qquad(\mu\ odd)\ , \tag{50}$$

$$p_{1,(1+\mu)}=\frac{1}{n}\sum_{k\in\omega}(\alpha_k-\beta_k)^2\cos\frac{\pi k\mu}{n}\qquad(\mu\ even)\ .$$

All other matrix elements $p_{\mu,\nu}$ follow from those given above using the $D_{(N/2)h}$ symmetry of the new solutions. For atomic charges and nearest-neighbor bond orders we get, in particular, from the above formulas

$$\begin{aligned}&p_{00}=1+\delta\ ,\quad p_{11}=1-\delta\ ,\\ &p_{01}=p_{12}=p_{01}^0-\frac{2}{n}\sum_{k\in\omega}\beta_k^2\cos\frac{\pi k}{n}\ ,\end{aligned} \tag{51}$$

where

$$\delta=\frac{2}{n}\sum_{k\in\omega}\alpha_k\beta_k$$

and

$$p_{01}^0=\frac{1}{n}\sum_{k\in\omega}\cos\frac{\pi k}{n} \tag{52}$$

is the bond order between nearest neighbors for the symmetry-adapted solution.

We see, therefore, immediately that the new HF solutions of the $(A^s+B^s)^+$ type will violate both space and alternacy symmetry.

Let us consider now the $(A^s-B^s)^-$ case. With the molecular orbitals (35b) we get the following atomic charges and bond orders:

$$\begin{aligned}&p_{0,\mu}=p_{1,(1+\mu)}=\frac{2}{n}\left(\frac{1}{2}+\sum_{k=1}^{\nu}\cos\frac{\pi k\mu}{n}\right)\qquad(\mu\ even)\ ,\\ &\left.\begin{matrix}p_{0,\mu}\\ p_{1,(1+\mu)}\end{matrix}\right\}=\frac{1}{n}\left(1+2\sum_{k=1}^{\nu}\left[(\alpha_k^2-\beta_k^2)\cos\frac{\pi k\mu}{n}\pm 2\alpha_k\beta_k\sin\frac{\pi k\mu}{n}\right]\right)\qquad(\mu\ odd)\ .\end{aligned} \tag{53}$$

For even μ we get clearly

$$p_{\mu\mu}=1,\ p_{0,(2\mu)}=p_{1,(2\mu+1)}=0\ . \tag{54}$$

Finally, for the bond orders between nearest neighbors we get

$$\begin{aligned}p_{0,1}&=p_{0,1}^0+\delta^+\ ,\\ p_{1,2}&=p_{0,1}^0-\delta^-\ ,\end{aligned} \tag{55}$$

where

$$\delta^\pm=\frac{4}{n}\sum_{k=1}^{\nu}\beta_k\left(\pm\alpha_k\sin\frac{\pi k}{n}-\beta_k\cos\frac{\pi k}{n}\right)\ .$$

This result clearly indicates that the HF solutions of the $(A^s-B^s)^-$ type retain alternancy symmetry so that only space-symmetry conservation laws are violated.

VI. NUMERICAL RESULTS

The critical size of the cyclic polyene, for which the singlet instability of the given type appears for the first time, is given in Table I for each parametrization studied. Clearly, the symmetry-adapted HF solutions of larger cyclic polyenes than those listed in Table I are always singlet-unstable, so that the new symmetry-nonadapted HF solution must exist for them. Further, the $(A^s - B^s)^-$ type instability always precedes the $(A^s + B^s)^+$ type instability for all parametrizations studied. On the basis of the considerations of Sec. V, we can state that the $(A^s - B^s)^-$ type instability means instability to the bond-order alternation and, consequently, leads to the new HF solutions with alternating bond orders.

On the other hand, $(A^s + B^s)^+$ type instability means instability with respect to another kind of charge-density wave, namely, to the atomic-charge alternation, which yields new HF solutions with alternating atomic charges.

Indeed, the properties of the first-order density matrix in the atomic-orbital representation (atomic-charge and bond-order matrix) of the new states or HF solutions clearly show that different types of singlet instabilities yield different types of charge-density waves. In fact, for large enough cyclic polyenes we could find still other types of HF solutions, having lower energy than the symmetry-adapted one, and displaying more complicated CDW's than simple atomic-charge or bond-order alternation. These would correspond to the singlet-instability subproblems with lower than maximal quasimomentum transfer, as will be mentioned in greater detail in Sec. VII.

Restricting ourselves to the maximum quasimomentum transfer $(A^s + B^s)^+$ and $(A^s - B^s)^-$ types of singlet instabilities, and having in mind the form of the first-order density matrix of the new solutions implied by these instabilities, we can refer to the atomic-charge alternating solutions as the solutions displaying *diagonal charge-density waves* (CDW's) while the bond-order alternating ones yield *off-diagonal CDW*'s.

Clearly, this terminology refers only to the most important elements of the density matrix, namely, to the atomic charges and nearest-neighbor bond orders. In fact, as formulas (50) clearly show, in the $(A^s + B^s)^+$ case not only the atomic charges, but also the bond orders between starred (and between unstarred) atomic sites, alternate.

However, the latter correspond to the matrix elements, which vanish in the symmetry-adapted case or in the nearest-neighbor bond-order alternating case, when the alternancy symmetry is preserved. Moreover, even in the atomic-charge alternating case they are small in comparison with the bond orders between starred and unstarred atoms and alternate around the zero value (i.e., their absolute value is constant for a given type of the "bond").

Adopting this terminology, we can state, for example, for any parametrization studied, that if the symmetry-adapted HF solution, of a given cyclic polyene, is unstable with respect to the diagonal CDW's, it is also unstable to the off-diagonal CDW's.

Indeed, we find generally that the lowest root of the $(A^s - B^s)^-$ stability subproblem is always below the lowest root of the $(A^s + B^s)^+$ subproblem. This indicates that, at least initially in the infinitesimal neighborhood of the symmetry-adapted solution, the bond-order alternating states will have lower energy than the atomic-charge alternating ones. We shall see that this is also true for the actual diagonal or off-diagonal CDW HF solutions, which we consider next.

The broken-symmetry, atomic-charge, and bond-order alternating HF solutions were calculated by solving iterationally the HF equations (46), using the initial approximation described in Appendix B. Generally, not more than 40 iterations were required to reach the self-consistency to 8 decimals.

The energy decrease per electron of the new HF solutions with respect to the symmetry-adapted ones is plotted (as a positive quantity) in Fig. 4 as a function of the size of the cyclic polyene considered. Clearly, this decrease is always larger for bond-order alternating HF solutions than for the atomic-charge alternating ones.

The bond orders and atomic charges of these new HF solutions are given in Figs. 5–7 for all three parametrizations studied. Clearly, the atomic charges p_{kk} and $p_{k+1,k+1}$ correspond to the atomic-charge alternating HF solutions (diagonal CDW's) while nearest-neighbor bond orders $p_{k,k+1}$ and $p_{k,k-1}$, to the respective bond-order alternating HF solutions (off-diagonal CDW's).

Further, Fig. 8 shows the dependence of the mixing parameter β_k [Eqs. (35)] as a function of the quasimomentum k for both diagonal and off-diagonal CDW HF solutions for the largest cyclic polyene considered having 170 carbon atoms (i.e., $N = 170$, $\nu = 42$). Since this case represents practically the limiting case of infinite cyclic polyene, the mixing parameter β_k is actually plotted as a continuous function of the wave number q,

$$q = 2\pi k/N , \quad q \in \langle -\tfrac{1}{2}\pi, \tfrac{1}{2}\pi \rangle .$$

The values $q = \pm\frac{1}{2}\pi$ [or, $q = \pm\pi\nu/(2\nu+1)$] correspond to the Fermi level. Clearly, the largest mixing occurs around this level.

Finally, Fig. 9 illustrates the dispersion law for the largest cyclic polyene studied ($N = 170$) for both diagonal and off-diagonal CDW HF solutions as well

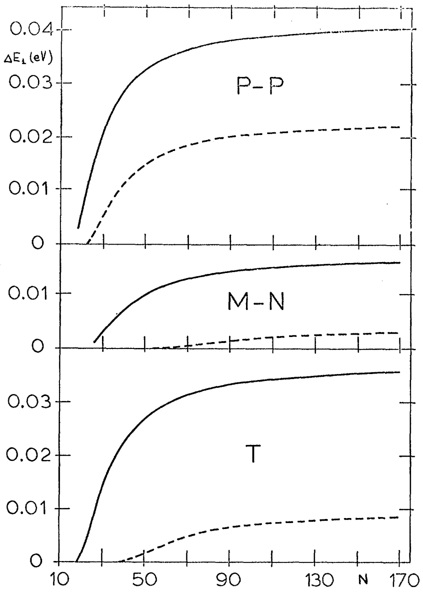

FIG. 4. Dependence of the energy decrease *per electron* ΔE_1, yielded in transition from the symmetry-adapted to the symmetry-nonadapted HF solution, on the size of the cyclic polyene C_NH_N, $N=4\nu+2$, plotted as a continuous positive quantity for three different parametrizations used (see text). *Full* lines correspond to the energy difference (per electron) between off-diagonal CDW (bond-order alternating) HF solution and symmetry-adapted HF solution, while *dashed* lines correspond to the energy difference (per electron) between diagonal CDW (atomic-charge alternating) HF solution and the symmetry-adapted one.

as for the symmetry-adapted HF solution.[34] In this figure we do not plot directly the single-particle energies but rather its differences corresponding to the elementary single excitations considered, namely,

$$\Delta\epsilon_k = \epsilon_{k+n} - \epsilon_k .$$

This figure clearly indicates the appearance of the energy gap for both diagonal and off-diagonal CDW HF solutions.

VII. DISCUSSION

In this paper we have studied in detail the singlet instability of the symmetry-adapted diamagnetic HF solutions of cyclic polyenes. It was found that considering the maximal quasimomentum-transfer excitations two basic types of singlet instabilities may occur, namely, the instability to the atomic-charge alternation or to the diagonal CDW's [originating from the $(A^s+B^s)^+$ subproblem] and the instability to the bond-order alternation or to the off-diagonal CDW's [from $(A^s-B^s)^-$ subproblem].

Let us first note that, in principle, we could find another type of singlet instabilities of the symmetry-adapted HF solution for cyclic polyenes, considering the stability subproblems corresponding to

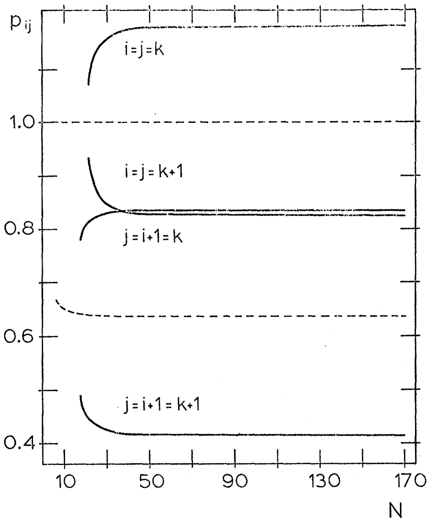

FIG. 5. Dependence of the atomic-charges and nearest-neighbor bond orders of the symmetry-nonadapted CDW HF solutions for cyclic polyenes C_NH_N, $N=4\nu+2$, obtained with PP approximation, as a continuous function of the size of the polyene N. The upper part of the figure gives the dependence of the atomic charges p_{ii} and $p_{i+1,\,i+1}$ of the atomic-charge alternating solution while the lower part of the figure gives the dependence of the bond orders $p_{i,\,i+1}$, $p_{i,i-1}$ of two neighboring bonds, while $p_{ii}=1$. Clearly, there are always two such solutions, so that if for one of them $i=k$, then for another $i=k+1$. The dashed lines give the value of the atomic-charge p_{ii} and nearest-neighbor bond order $p_{i,\,i+1}$ for the symmetry-adapted solution.

the quasimomentum transfer $p<n$, which would yield another type of CDW's (cf. also Ref. 35). Clearly, this type of instabilities will only occur for large enough cyclic polyenes and will be always

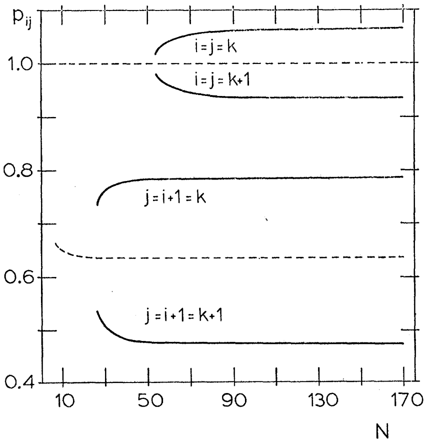

FIG. 6. Dependence of the atomic-charges and nearest-neighbor bond orders of the symmetry-nonadapted CDW HF solutions for cyclic polyenes C_NH_N obtained with MN approximation, as a function of the size of the polyene N. The same description as in Fig. 5. applies.

accompanied, at least for realistic Hamiltonians, by the instabilities of the studied type ($p=n$), which yield always the lowest eigenvalue of the stability problem. Further, the HF solutions corresponding to the singlet instabilities with $p<n$ will have generally still lower spatial symmetry than the solutions corresponding to $p=n$ and studied in this paper. We can also expect that their HF energies will be higher than the HF energies of the maximum quasimomentum-transfer solutions studied here, even though they will have lower energy than the symmetry-adapted HF solution.

Let us now discuss the properties of the new CDW HF solutions, which exist in the case of the singlet instability with respect to the atomic-charge or bond-order alternating fluctuations. Both the general considerations and the numerical calculations show that these solutions, which we call atomic-charge alternating and bond-order alternating solutions, or diagonal and off-diagonal CDW solutions, respectively, have lower energy than the corresponding singlet-unstable symmetry-adapted HF solutions. Both these new solutions violate the space-symmetry conservation laws and belong to the $D_{(N/2)h}$ point group. However, they represent different $D_{(N/2)h}$ subgroups of the original D_{Nh} point group of the Hamiltonian, since the two-fold symmetry axes pass through the atomic sites in case of the atomic-charge alternating solutions, while they pass through the C–C bond centers for the bond-order alternating solutions. Clearly, there are always two such solutions. Finally, the bond-order alternating solutions always have lower energy than the respective atomic-charge alternating ones for all three parametrizations studied. To reverse this order would require a rather unrealistic interelectronic interaction potential.

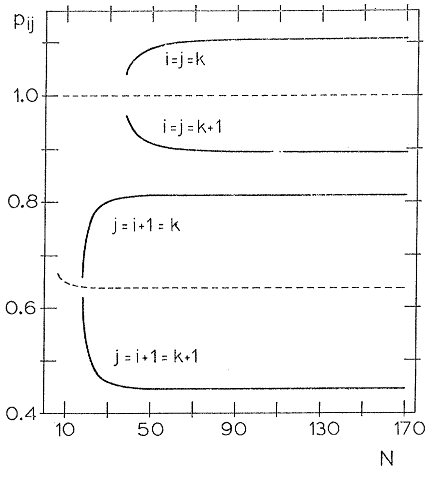

FIG. 7. Dependence of the atomic charges and nearest-neighbor bond orders of the symmetry-nonadapted CDW HF solutions for cyclic polyenes C_NH_N obtained with T approximation, as a function of the size of the polyene N. The same description as in Fig. 5 applies.

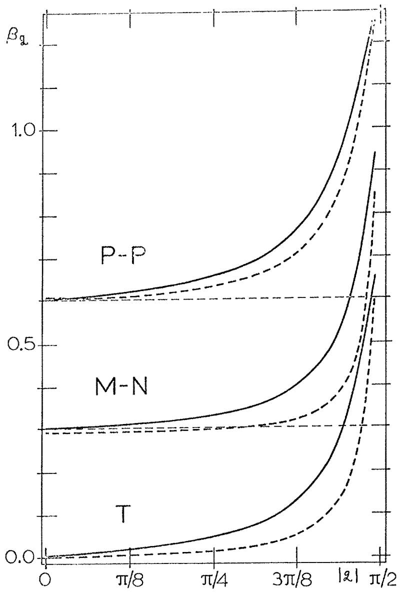

FIG. 8. Admixture of the symmetry-adapted virtual HF orbitals in the symmetry-nonadapted occupied HF orbitals, given by the normalized mixing coefficient β_k in Eq. (35), is plotted as a continuous function of the quasimomentum q, $q=2\pi k/N$, $q\epsilon\langle-\frac{1}{2}\pi, \frac{1}{2}\pi\rangle$, for the cyclic polyene with 170 atomic sites ($C_{170}H_{170}$), for three different parametrization schemes. The dependences for the MN and PP parametrizations are shifted on the abscissa axis by 0.3 and 0.6, respectively, to avoid overlap. The *full* lines correspond to the off-diagonal CDW (bond-order alternating) HF solutions while the *dashed* lines correspond to the diagonal CDW (atomic-charge alternating) HF solutions.

It is appropriate to mention in this place that, in an analogous way, we can obtain the diagonal and off-diagonal spin-density-wave (SDW) unrestricted HF solutions, depending on whether the nonsinglet instability of the symmetry-adapted HF solution originates from the $(A^t+B^t)^+$ or $(A^t-B^t)^-$ subproblems, respectively. However, in this case the diagonal SDW solution has the lower energy than the off-diagonal one, contrary to the CDW case. Further, the HF equations, as well as the HF energies, of the off-diagonal CDW and SDW solutions are identical, even though the corresponding wave functions have different spin-symmetry properties.

Furthermore, the individual α-spin and β-spin probability densities will alternate even in the CDW solutions, in contrast to the symmetry-adapted solution. However, these α- and β-spin "probability-density waves" will be in phase, yielding zero spin density (i.e., no SDW's). On the other hand, in the SDW solutions, α- and β-spin probability-density waves have an opposite phase, so that the deficiency of the α density in one place is compensated by the excess of the β density, and vice versa, so that the total density is constant and, consequently, no CDW exists. This "out-of-phase" shift of the individual α- and β-spin probability waves cause the energy decrease in the diagonal case [i.e., $(A^t+B^t)^+$ versus $(A^s+B^s)^+$], while in the off-diagonal case $[(A^{s,t}-B^{s,t})^-]$ the energy is invariant to this phase shift. These problems will be described in greater detail elsewhere, when the study of other than singlet instabilities are concluded.

Finally, let us mention that the distinction of the diagonal and off-diagonal SDW's and CDW's is due to the space inhomogenity of our model.

The question now arises whether or not these broken-symmetry HF solutions correspond to a local minimum of the energy hypersurface in a variational space of singlet one-determinantal functions. Clearly, this may be easily answered if we examine the singlet stability of these new HF solutions. In doing so we can use again extensively the $D_{(N/2)h}$ symmetry of these solutions to factor the stability problem. Generally, the resulting subproblems have a dimension twice as large as the corresponding subproblems for the symmetry-adapted case.

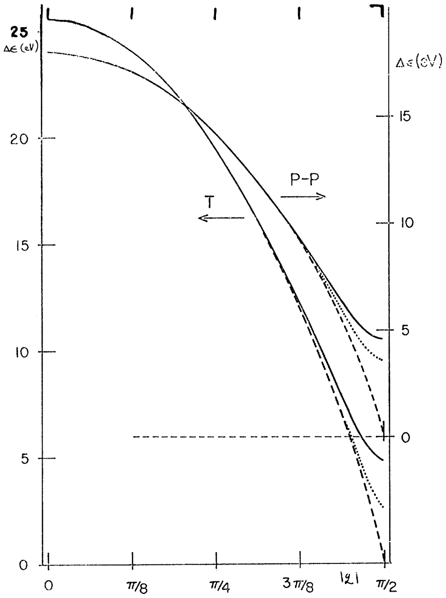

FIG. 9. Dispersion law (see the text) for the symmetry-adapted and nonadapted HF solutions for the cyclic polyene with $N=170$, obtained with PP and T parametrizations. (The MN parametrization yields very similar results as the PP parametrization.) The left-hand-side energy scale corresponds to the results for the T parametrization while the right-hand-side scale is associated with the PP parametrization results, as arrows indicate. The *full* lines correspond to the off-diagonal CDW (bond-order alternating) HF solution, the *dotted* lines to the diagonal CDW (atomic-charge alternating) HF solution and, finally, the *dashed* line corresponds to the symmetry-adapted HF solution, which exhibits no energy gap.

From these calculations we find that for all three parametrizations used the atomic-charge alternating (diagonal CDW) HF solutions are *always singlet-unstable* and, therefore, represent a saddle point on the mean-energy hypersurface. On the other hand, the bond-order alternating (off-diagonal CDW) HF solutions are *singlet-stable* and do represent a true minimum with respect to the variations preserving the singlet character of the trial wave function. Needless to say, both these solutions will likely be unstable to the spin-density fluctuations (triplet or nonsinglet instability) as is the original symmetry-adapted solution.

Furthermore, if we proceed in the direction of steepest descent, given by the lowest root of the stability problem for the atomic-charge alternating HF solution, and iterate to the new HF solution, we arrive at the stable bond-order alternating solution found earlier.

Finally, we would like to recall the important implications of the instabilities of the symmetry-adapted HF solutions. Generally, we can state that the instability indicates the inadequacy of the independent-particle picture for the studied system. This is clearly demonstrated by the convergency difficulties, which are encountered in the coupled-pair many-electron theory[36] when the singlet-unstable HF solution is used as an initial approximation.

Similarly, using the singlet- (triplet) unstable HF molecular orbitals as a basis of the exact first-order random-phase approximation (RPA) approach[22,37,38] to calculate the singlet-to-singlet (triplet) excitation energies, the imaginary values result for these excitation energies, as is well known.

In all these cases the independent-particle picture is inadequate, and we have to choose a better initial approximation to take the proper account of the collective phenomena.

This better approximation is suggested by the form of the stable HF solution, which may be found in case the symmetry-adapted HF solution is unstable. Unfortunately, this new HF solution, which is still a pure-singlet function with doubly occupied spatial orbitals, cannot be used directly, since it is not symmetry-adapted anymore. However, we can project out the symmetry-adapted component and obtain a multideterminantal wave function, which should be an adequate initial approximation for correlation-energy calculations.

ACKNOWLEDGMENTS

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APPENDIX A: STABILITY-PROBLEM MATRIX ELEMENTS

Using the definitions of the main text, we can derive the following explicit expressions for the matrix elements of the singlet- and nonsinglet-stability subproblems, corresponding to the maximum quasimomentum transfer $p=n$. For convenience, we first define

$$\Omega_{kl}=(\epsilon_{(k+n)\,\mathrm{mod}N}-\epsilon_k)\,\delta_{kl}\ , \tag{A1}$$

where ϵ_k is the HF orbital energy given by the formula (22). Then we have

(a) $(A^s+B^s)^\pm$ cases:

$$\begin{aligned}\langle k^\pm|A^s+B^s|j^\pm\rangle &= \Omega_{kj}+(4\pm4)K(n)-K(k+n-j)\\ &\quad -K(k-j)\mp[K(k+n+j)+K(k+j)]\ ,\\ \langle 0|A^s+B^s|k^+\rangle &= \sqrt{2}\,[4K(n)-K(k+n)-K(k)]\ ,\\ \langle 0|A^s+B^s|0\rangle &= \Omega_{00}+3K(n)-K(0)\ ,\end{aligned}$$

(b) $(A^s-B^s)^\pm$ cases:

$$\begin{aligned}\langle k^\pm|A^s-B^s|j^\pm\rangle &= \Omega_{kj}+K(k+n-j)-K(k-j)\\ &\quad \pm[K(k+n+j)-K(k+j)]\ ,\\ \langle 0|A^s-B^s|k^+\rangle &= \sqrt{2}\,[K(k+n)-K(k)]\ ,\\ \langle 0|A^s-B^s|0\rangle &= \Omega_{00}+K(n)-K(0)\ ,\end{aligned}$$

(c) $(A^t+B^t)^\pm$ cases:

$$\begin{aligned}\langle k^\pm|A^t+B^t|j^\pm\rangle &= \Omega_{kj}-K(k+n-j)-K(k-j)\\ &\quad \mp[K(k+n+j)+K(k+j)],\\ \langle 0|A^t+B^t|k^+\rangle &= -\sqrt{2}\,[K(n-k)+K(k)]\ ,\\ \langle 0|A^t+B^t|0\rangle &= \Omega_{00}-K(n)-K(0)\ ,\end{aligned}$$

(d) $(A^t-B^t)^\pm$ cases have identical matrix elements as $(A^s-B^s)^\pm$ cases. In all cases we have

$$\begin{aligned}\langle k^\pm|A^{s,t}\pm B^{s,t}|j^\mp\rangle &= 0\ ,\\ \langle 0|A^{s,t}\pm B^{s,t}|j^-\rangle &= 0\ .\end{aligned}$$

Finally, it is interesting to note that

$$\langle k^-|A^s+B^s|j^-\rangle=\langle k^-|A^t+B^t|j^-\rangle\ .$$

APPENDIX B: INITIAL APPROXIMATION FOR THE SYMMETRY-NONADAPTED HF SOLUTION

As explained in the main text and Paper II, the best choice of the initial approximation is the wave function corresponding to the energy minimum in the direction of the energy's steepest descent at the symmetry-adapted HF solution, given by the appropriate eigenvector of the stability problem. Unfortunately, this leads in general to the nonorthogonal basis. However, this difficulty is avoided for cyclic polyenes due to their high symmetry and, consequently, rather limited orbital mixing.

Consider first the $(A^s+B^s)^+$ case. Designating by d_r the rth component of the stability-problem eigenvector, belonging to the lowest eigenvalue of the $(A^s+B^s)^+$ subproblem, which corresponds to the monoexcitation u_r,

$$u_r\equiv\begin{pmatrix}(r+n)\,\mathrm{mod}N\\ r\end{pmatrix}\ , \tag{B1}$$

we can write the molecular orbitals of the form (35a) which, moreover, correspond to the appropriate direction of the variational space given by the above-mentioned eigenvector, as follows:

$$|\tilde{r}\rangle=n_r[\,|r\rangle+\kappa d_r|(r+n)\,\mathrm{mod}N\rangle]\ , \tag{B2}$$

where

$$n_r=(1+\kappa^2d_r^2)^{-1/2}\ , \tag{B3}$$

$$d_r=d_{N-r}\ . \tag{B4}$$

In order to find an initial approximation we have to determine the optimal value of the parameter κ, yielding the lowest energy mean value. This is easily achieved provided we know the functional dependence of the energy mean value $E(\kappa)$ on the parameter κ, which may be expressed as follows:

$$E(\kappa)=E_1(\kappa)+E_2(\kappa)\ , \tag{B5}$$

$$E_1(\kappa)=4\beta\sum_{k\in\omega}\frac{1-(d_k')^2}{1+(d_k')^2}\cos\frac{\pi k}{n}\ , \tag{B6}$$

$$\begin{aligned}E_2(\kappa)&=n(2n-1)K(0)+4K(n)\sum_{k\in\omega}N_k(1-N_k)\\ &\quad+\sum_{k,j\in\omega}{}'\,N_kN_j[8d_k'd_j'K(n)-(1+d_k'd_j')^2K(k-j)\\ &\quad-(d_k'+d_j')^2K(k+n-j)]\ ,\end{aligned} \tag{B7}$$

where

$$d_k'=\kappa d_k\ \text{ and }\ N_k=n_k^2\ . \tag{B8}$$

Similarly, for the $(A^s-B^s)^-$ case, the molecular orbitals have the form

$$|\tilde{r}\rangle=n_r[\,|r\rangle+i\kappa d_r|(r+n)\,\mathrm{mod}N\rangle]\ , \tag{B9}$$

where

$$d_{N-r}=d_r,\quad d_0=0\ , \tag{B10}$$

and n_r is defined again by (B3). The energy dependence on the variational parameter κ may be again expressed in the form (B5) with $E_1(\kappa)$ defined by (B6) and $E_2(\kappa)$ as follows:

$$\begin{aligned}E_2(\kappa)&=n(2n-1)K(0)\\ &\quad-\sum_{k,j\in\omega}{}'\,N_kN_j[(1+d_k'd_j')^2K(k-j)\\ &\quad+(d_k'-d_j')^2K(k+n-j)]\ .\end{aligned}$$

It is now easy to find the optimal value of κ which minimizes the above energy expressions and use the corresponding molecular orbitals as an initial approximation.

*Part V: Phys. Rev. A (to be published).

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