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J. Čížek, and J. Paldus



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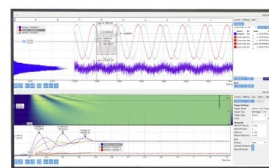
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by one another plus any short-range correlations after the shielding is taken into account.⁷

There are two corrections to the basic approach. First, even when $V_{\pi\pi^c}$ is dominant there are corrections to the time-dependent Hartree method. These corrections may be obtained by using the method of Green's functions for two coupled systems, or by Schwinger's method.⁸ When $V_{\pi\pi^c}$ becomes important,

⁷ Y. Öhrn and J. Linderberg, *Phys. Rev.* **139**, A1063 (1965).

⁸ J. Schwinger, *Proc. Natl. Acad. Sci. U.S.* **37**, 452, 455 (1951); *J. Math. Phys.* **2**, 407 (1961).

though weak, the method of Green's functions provides a way of doing perturbation theory about $V_{\pi\pi^c}$.

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A portion of these ideas were developed in discussions with M. Karplus. V. McKoy has told me that he has applied the random-phase approximation to ethylene. Much of this work was written while I was on leave at the James Franck Institute at the University of Chicago. I wish to thank S. Rice for his hospitality.

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Stability Conditions for the Solutions of the Hartree-Fock Equations for Atomic and Molecular Systems. Application to the Pi-Electron Model of Cyclic Polyenes

J. ČÍŽEK AND J. PALDUS

Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague 2, Máchova 7, Czechoslovakia

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The stability conditions which ensure that the Hartree-Fock determinant minimizes the energy expectation value are rederived using the language familiar in quantum chemistry. These stability conditions are then specified for the case of closed-shell electronic systems which allow additional simplification of the conditions as well as a certain classification of the instabilities.

Examples of the instabilities of different types are presented and the case of the so-called singlet instabilities—most interesting from the physical point of view—is studied in detail for the pi-electron model of cyclic polyenes.

I. INTRODUCTION

Let us recall that the Hartree-Fock (HF) equations guarantee that the first variation of the functional $E(\Phi) = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle$ is equal to zero for the Slater determinant of HF orbitals. In other words, the HF determinant represents a point of the respective functional space in which the functional $E(\Phi)$ is stationary. In order to find out whether this stationary point represents a minimum, a maximum, or a stationary point of a more complicated nature, we have to examine the second variation.

In the following, the HF solution which corresponds to the local minimum of the functional $E(\Phi)$ is referred to as the *stable* solution.

Until 1960 almost no attention was paid to the possibility that the HF solutions obtained by an ordinary SCF procedure, and above all the HF solutions which follow directly from the symmetry of the given problem, might be unstable in the above defined sense. The real importance of this problem was realized only after Overhauser¹ published an alternative solution of the HF equations for the linear infinite system of fermions interacting through a two-body delta-function-type potential which gives a lower expectation energy value than the ordinary plane-wave solution. Thereupon, the general conditions for the stability of the

HF solutions were formulated by Thouless,² who showed also how this problem was related to the problem of the stability of collective modes of motion of many-body systems.

Almost at the same time, Sawada and Fukuda³ used directly the relationship between the stabilities of the HF solutions and of the collective motions to study the stability of the plane-wave solutions of the three-dimensional Fermi gas with a delta-function type interaction as well as the stability of the HF determinant for the BCS-Bogoljubov Hamiltonian.

In the field of atomic and molecular electronic structure, only a few papers, namely those by Adams,⁴ Löwdin,⁵ Koutecký,⁶ and Lefebvre and Smeyers,⁷ dealing with the problem from different points of view, were published.

In the paper by Adams⁴ the stability conditions were rederived using the density matrix formalism and applied to the study of the stability of the HF solutions for LiH molecule and for the electron gas.

² D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

³ K. Sawada and N. Fukuda, *Progr. Theoret. Phys. (Kyoto)* **25**, 653 (1961).

⁴ W. H. Adams, *Phys. Rev.* **127**, 1650 (1962).

⁵ P.-O. Löwdin, *Rev. Mod. Phys.* **35**, 496 (1963).

⁶ J. Koutecký, *J. Chem. Phys.* **46**, 2443 (1967).

⁷ R. Lefebvre and Y. G. Smeyers, *Intern. J. Quantum Chem.* **1**, 403 (1967). We are indebted to Dr. Lefebvre for the Preprint of this paper.

¹ A. W. Overhauser, *Phys. Rev. Letters* **4**, 415, 466 (1960).

The general aspects of the stability problem were discussed by Löwdin,⁵ while Koutecký⁶ has shown recently that for some closed-shell pi-electronic systems the unrestricted HF method yields lower ground-state energy than the ordinary HF method.

In the present work, the Thouless' stability conditions are first rederived using the formalism which is familiar in quantum chemistry. These conditions are further specified for the closed-shell electronic systems. In this case the elimination of the spin variables results in an additional simplification and, at the same time, enables a certain classification of the instabilities. From the physical point of view, the most interesting instabilities are those which we call the singlet type instabilities, for which the respective varied wavefunction remains a pure singlet function. The instabilities of this type are then studied for the pi-electron model of the cyclic polyenes $C_{4\nu+2}H_{4\nu+2}$.

II. STABILITY CONDITIONS FOR THE HARTREE-FOCK SOLUTIONS

Let us consider a system of N electrons moving in a field of fixed nuclei. The Hamiltonian for such a system is

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

where \hat{z}_i is the kinetic energy and the nuclear framework potential energy one-particle operator of the i th electron and \hat{v}_{ij} is the two-particle operator of the Coulomb repulsion between the electrons i and j .

In deriving the stability conditions for the HF wavefunction we use a similar formalism as used by Lefebvre⁸ for the derivation of the self-consistency conditions. Suppose $|A_i\rangle$, $i=1, 2, \dots, \infty$ is a complete orthonormal set of spin orbitals and assume, further, that these spin orbitals are arranged in some definite order.

Let $|\Phi_0\rangle$ be a Slater determinant of first N spin orbitals $|A_i\rangle$, $i=1, 2, \dots, N$. Then an arbitrary Slater determinant $|\Phi\rangle$, which is not orthogonal to $|\Phi_0\rangle$, may be constructed in such a way that the spin orbital $|A_i\rangle$ of $|\Phi_0\rangle$ is replaced by the spin orbital $|\tilde{A}_i\rangle$,

$$|\tilde{A}_i\rangle = |A_i\rangle + \sum_{m=N+1}^{\infty} c_i^m |A_m\rangle, \quad (2)$$

$$i=1, 2, \dots, N.$$

Therefore, the determinant $|\Phi\rangle$ may be written in the following form

$$|\Phi\rangle = |\Phi_0\rangle + \sum_{i=1}^N |\Phi_i\rangle, \quad (3)$$

where

$$|\Phi_i\rangle = i!^{-1} \sum_{U_1, U_2, \dots, U_i} \left(\prod_{j=1}^i d_{U_j} \right) |U_1, U_2, \dots, U_i\rangle. \quad (4)$$

The symbol U_j in the last formula represents a pair of

spin orbitals $|A_{k_j}\rangle$ and $|A_{l_j}\rangle$, and is written symbolically as

$$U_j = \begin{pmatrix} A_{l_j} \\ A_{k_j} \end{pmatrix}, \quad (5)$$

where, at the same time, $k_j \leq N$ and $l_j > N$. Further, for the sake of simplicity, we define

$$d_{U_j} = c_{k_j}^{l_j}. \quad (6)$$

The symbol $|U_1, U_2, \dots, U_i\rangle$ stands for the determinant which is obtained from $|\Phi_0\rangle$ if the spin orbital $|A_{k_j}\rangle$ of $|\Phi_0\rangle$ is replaced by the spin orbital $|A_{l_j}\rangle$, $j=1, 2, \dots, i$.

In the following derivations we deal with those functions $|\Phi\rangle$ which lie in an infinitesimal neighborhood of the function $|\Phi_0\rangle$ of the respective functional space. In such a case the coefficients d_{U_i} may be regarded as infinitesimal quantities as well, so that in the expansion (3) it will be sufficient, for our purposes, to retain only the first- and the second-order terms in the coefficients d_{U_i} ,

$$|\Phi\rangle \cong |\Phi_0\rangle + |\Phi_1\rangle + |\Phi_2\rangle. \quad (7)$$

Let us now examine how the expectation value $E(\Phi)$,

$$E(\Phi) = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}, \quad (8)$$

is changed, if we go over from the function $|\Phi_0\rangle$ to some other function $|\Phi\rangle$ lying in an infinitesimal neighborhood of $|\Phi_0\rangle$. If we again neglect all terms higher than the second order in the coefficients d_{U_i} we obtain for this change the following expression

$$\Delta E = E(\Phi) - E(\Phi_0) \cong \langle \Phi_0 | \hat{Q} | \Phi_1 \rangle + \langle \Phi_1 | Q | \Phi_0 \rangle + \langle \Phi_1 | Q | \Phi_1 \rangle + \langle \Phi_2 | \hat{Q} | \Phi_0 \rangle + \langle \Phi_0 | Q | \Phi_2 \rangle, \quad (9)$$

where

$$\hat{Q} = \hat{H} - E(\Phi_0). \quad (10)$$

Thus far, the determinant function $|\Phi_0\rangle$ of spin orbitals $|A_i\rangle$, $i=1, 2, \dots, N$, is free of any restrictions. Let us now suppose that $|\Phi_0\rangle$ is a HF determinant. Then, on the basis of the Brillouin theorem, the first-order terms in the coefficients d_{U_i} on the right-hand side of Eq. (9) are equal to zero. Therefore, the expression for ΔE may be written in the following form

$$\Delta E = \sum_{U_1, U_2} \{ a_{U_1, U_2} \tilde{d}_{U_1} d_{U_2} + \frac{1}{2} b_{U_1, U_2} \tilde{d}_{U_1} \tilde{d}_{U_2} + \frac{1}{2} \tilde{b}_{U_1, U_2} d_{U_1} d_{U_2} \}, \quad (11)$$

where the coefficients a_{U_1, U_2} and b_{U_1, U_2} are given by the well-known formulas for the matrix elements of the Hamiltonian (1) between the monoexcited states and between the ground state and biexcited states (cf. for

⁸ R. Lefebvre, *Cahiers Phys.* **13**, 369 (1959).

example⁹)

$$a_{U_1, U_2} = \langle U_1 | \hat{Q} | U_2 \rangle \\ = \langle l_1 | \hat{f} | l_2 \rangle \langle k_1 | k_2 \rangle - \langle k_2 | \hat{f} | k_1 \rangle \langle l_1 | l_2 \rangle \\ + \langle l_1, k_2 | \hat{v} | k_1, l_2 \rangle_A, \quad (12)$$

$$b_{U_1, U_2} = \langle U_1, U_2 | \hat{Q} | \Phi_0 \rangle = \langle l_1, l_2 | \hat{v} | k_1, k_2 \rangle_A,$$

where

$$\langle i | f | j \rangle = \langle A_i | \hat{f} | A_j \rangle + \sum_{k \leq N} \langle i, k | \hat{v} | j, k \rangle_A.$$

Further, we have defined

$$\langle i, j | \hat{v} | k, l \rangle_A = \langle A_i, A_j | \hat{v} | A_k, A_l \rangle - \langle A_i, A_j | \hat{v} | A_l, A_k \rangle,$$

and

$$\langle i | j \rangle = \langle A_i | A_j \rangle.$$

The expression (11) for ΔE represents a quadratic form in the coefficients d_{U_i} . This quadratic form may be written symbolically as follows:

$$\Delta E = \frac{1}{2} \begin{pmatrix} D \\ \bar{D} \end{pmatrix}^+ \begin{pmatrix} A & B \\ \bar{B} & \bar{A} \end{pmatrix} \begin{pmatrix} D \\ \bar{D} \end{pmatrix}, \quad (13)$$

where D is a column vector of coefficients d_{U_i} and the matrix elements a_{U_1, U_2} and b_{U_1, U_2} of the matrices A and B , respectively, are defined by formulae (12). Further, \bar{X} represents a complex conjugate matrix to the matrix X while X^+ stands for a matrix which is Hermitian conjugate to the matrix X . Observe that $A^+ = A$ and $B^+ = \bar{B}$, so that the quadratic form (13) is Hermitian.

We are now ready to formulate the stability conditions for the HF determinant to minimize the expectation value $E(\Phi)$: In order that the HF determinant be stable it is necessary and sufficient that the quadratic form (13) be positive definite.

It is well known that the Hermitian quadratic form is positive definite if and only if all the eigenvalues of the matrix of this quadratic form are positive. Therefore, the desired stability condition requires all the eigenvalues of the following characteristic problem

$$\begin{pmatrix} A & B \\ \bar{B} & \bar{A} \end{pmatrix} \begin{pmatrix} D \\ \bar{D} \end{pmatrix} = \lambda \begin{pmatrix} D \\ \bar{D} \end{pmatrix} \quad (14)$$

to be positive quantities. This stability condition has been already derived by Thouless² using the formalism of the second quantization.

A negative eigenvalue of the characteristic problem (14) indicates the instability of the corresponding HF solution $|\Phi_0\rangle$. This means that another HF solution $|\Phi'\rangle$ with a lower expectation value $E(\Phi')$ must exist. In order to find this solution of the HF equations we may proceed as indicated below.

Let $|\Phi_{\lambda \text{ neg}}(\kappa)\rangle$ designates the determinantal function (3) in which the coefficients d_{U_i} are replaced by the products $\kappa d_{U_i}^{\lambda \text{ neg}}$ of a dimensionless parameter κ with the components $d_{U_i}^{\lambda \text{ neg}}$ of the eigenvector $D_{\lambda \text{ neg}}$ corresponding to the negative eigenvalue λ_{neg} of the characteristic problem (14). Obviously, we have

$$|\Phi_{\lambda \text{ neg}}(\kappa)\rangle|_{\kappa=0} = |\Phi_0\rangle. \quad (15)$$

At the same time we suppose that the eigenvector $D_{\lambda \text{ neg}}$ is normalized as follows

$$\begin{pmatrix} D_{\lambda \text{ neg}} \\ \bar{D}_{\lambda \text{ neg}} \end{pmatrix}^+ \begin{pmatrix} D_{\lambda \text{ neg}} \\ \bar{D}_{\lambda \text{ neg}} \end{pmatrix} = 1. \quad (16)$$

Let us further designate by $E_{\lambda \text{ neg}}(\kappa)$ the expectation value (8) for the wavefunction $|\Phi_{\lambda \text{ neg}}(\kappa)\rangle$. We obtain immediately for the first and the second derivatives of the expectation value functional $E_{\lambda \text{ neg}}(\kappa)$ with respect to the parameter κ in the point $|\Phi_0\rangle$:

$$\left. \frac{dE_{\lambda \text{ neg}}(\kappa)}{d\kappa} \right|_{\kappa=0} = 0, \quad \left. \frac{d^2E_{\lambda \text{ neg}}(\kappa)}{d\kappa^2} \right|_{\kappa=0} = \lambda_{\text{neg}}. \quad (17)$$

Since it is obvious that the expectation value $E_{\lambda \text{ neg}}(\kappa)$ will be greater than $E_{\lambda \text{ neg}}(\kappa)|_{\kappa=0} = E(\Phi_0)$ for κ large enough, equations (17) ensure the existence of a minimum of $E_{\lambda \text{ neg}}(\kappa)$ as a function of κ for some $\kappa \neq 0$.

If now κ_0 denotes the value of the parameter κ which minimizes the expectation value functional $E_{\lambda \text{ neg}}(\kappa)$, we can use the determinantal function $|\Phi_{\lambda \text{ neg}}(\kappa_0)\rangle$ as a starting point of the ordinary SCF iterative procedure, which will hopefully converge to a new HF solution with a lower energy than $|\Phi_0\rangle$.

Moreover, it is very convenient, when carrying out the SCF calculations, to represent the HF operator in the basis of the HF molecular orbitals of the unstable solution $|\Phi_0\rangle$ instead of using the usual atomic orbital representation. Due to this representation, the SCF eigenvalue problem factorizes usually into a number of mutually coupled characteristic problems of a very low order.

In Part IV all the above mentioned ideas are illustrated by actual computations concerning the pi-electron model of cyclic polyenes.

III. SINGLET AND TRIPLET INSTABILITIES

Let us now specify the stability conditions (14) for the closed-shell systems. In this case a unitary transformation may be found which makes the explicit consideration of spin variables unnecessary and makes it possible, therefore, to proceed from the spin orbital formulation to the orbital one.

Let us observe that with the excitation from the orbital $|a_k\rangle$ to the orbital $|a_l\rangle$ four different spin orbital excitations are associated, namely the excitations from the spin orbitals $|a_k\alpha\rangle$, $|a_k\beta\rangle$ to the spin orbitals $|a_l\alpha\rangle$, $|a_l\beta\rangle$. Introducing the following notation for the

⁹ J. Čížek, Theoret. Chim. Acta 6, 292 (1966).

spin orbital excitations

$$\begin{aligned} U^1 &= \begin{pmatrix} a_l \alpha \\ a_k \alpha \end{pmatrix}, & U^2 &= \begin{pmatrix} a_l \beta \\ a_k \beta \end{pmatrix}, \\ U^3 &= \begin{pmatrix} a_l \beta \\ a_k \alpha \end{pmatrix}, & U^4 &= \begin{pmatrix} a_l \alpha \\ a_k \beta \end{pmatrix}, \end{aligned} \quad (18)$$

the unitary transformation mentioned above may be defined as follows:

$$\begin{aligned} d_u^s &= (1/\sqrt{2}) (d_{U^1} + d_{U^2}), \\ d_u^{t1} &= (1/\sqrt{2}) (d_{U^1} - d_{U^2}), \\ d_u^{t2} &= (1/\sqrt{2}) (d_{U^3} + d_{U^4}), \\ d_u^{t3} &= (i/\sqrt{2}) (d_{U^3} - d_{U^4}), \end{aligned} \quad (19)$$

where u represents corresponding orbital excitation

$$u = \begin{pmatrix} a_l \\ a_k \end{pmatrix}. \quad (20)$$

One can now easily verify that the unitary trans-

formation (19) factorizes the eigenvalue problem (14) into four subproblems, three of which, corresponding to the eigenvectors with components d_u^{t1} , d_u^{t2} , and d_u^{t3} , are identical. Therefore, it is sufficient to consider only one of these subproblems and define

$$d_u^{t1} = d_u^{t2} = d_u^{t3} = d_u^t. \quad (21)$$

The three identical subproblems correspond to triplet type excitations, while the remaining subproblem is associated with excitations of the singlet type.

In the case of the singlet type excitations the resulting determinant remains a singlet function, while the determinant resulting from the triplet type excitations is not an eigenfunction of \hat{S}^2 any more and represents, in fact, a linear combination of different multiplets.

The two relevant eigenvalue subproblems into which (14) factorizes are

$$\begin{pmatrix} A^x & B^x \\ \bar{B}^x & \bar{A}^x \end{pmatrix} \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix} = \lambda \begin{pmatrix} D^x \\ \bar{D}^x \end{pmatrix}, \quad (22)$$

where $x=s, t$. The corresponding matrix elements have the following form

$$\begin{aligned} a_{u1,u2}^s &= \langle l_1 | \hat{f} | l_2 \rangle \langle k_1 | k_2 \rangle - \langle k_2 | \hat{f} | k_1 \rangle \langle l_1 | l_2 \rangle + 2 \langle l_1, k_2 | \hat{v} | k_1, l_2 \rangle - \langle l_1, k_2 | \hat{v} | l_2, k_1 \rangle, \\ b_{u1,u2}^s &= 2 \langle l_1, l_2 | \hat{v} | k_1, k_2 \rangle - \langle l_1, l_2 | \hat{v} | k_2, k_1 \rangle, \\ a_{u1,u2}^{t1} &= \langle l_1 | \hat{f} | l_2 \rangle \langle k_1 | k_2 \rangle - \langle k_2 | \hat{f} | k_1 \rangle \langle l_1 | l_2 \rangle - \langle l_1, k_2 | \hat{v} | l_2, k_1 \rangle, \\ b_{u1,u2}^{t1} &= -\langle l_1, l_2 | \hat{v} | k_2, k_1 \rangle, \end{aligned} \quad (23)$$

where

$$u_1 = \begin{pmatrix} a_{l1} \\ a_{k1} \end{pmatrix}, \quad u_2 = \begin{pmatrix} a_{l2} \\ a_{k2} \end{pmatrix}.$$

Further, we have denoted

$$\langle i | \hat{f} | j \rangle = \langle a_i | \hat{f} | a_j \rangle + \sum_{k(\text{occ})} \{ 2 \langle i, k | \hat{v} | j, k \rangle - \langle i, k | \hat{v} | k, j \rangle \}, \quad (24)$$

where $\sum_{k(\text{occ})}$ means that the summation extends over the occupied orbitals only. Furthermore, we have designated

$$\langle i, j | \hat{v} | k, l \rangle = \langle a_i, a_j | \hat{v} | a_k, a_l \rangle, \quad (25)$$

and

$$\langle i | j \rangle = \langle a_i | a_j \rangle.$$

Let us now remark that if the matrices A^x , B^x , $x=s, t$, are real matrices—which is the case in most of the practical computations—a further simplification of the stability conditions (22) is feasible. Indeed, the eigenvalue problem (22) factorizes in such a case into two characteristic problems of the half order

$$\begin{aligned} [A^x + (-1)^y B^x] E^{x,y} &= \lambda E^{x,y}, \\ x &= s, t; \quad y = 0, 1; \end{aligned} \quad (26)$$

and, at the same time, we have

$$D^x = E^{x,0} \quad \text{for } y=0,$$

or, eventually,

$$D^x = i E^{x,1} \quad \text{for } y=1; x=s, t,$$

where $E^{x,y}$ are *real* column vectors.

We shall now discuss a classification of the instabilities of the HF solutions suggested by the form of the above derived stability conditions (22) and (26).

For the sake of brevity, the instabilities which are related to the triplet type monoexcitations are referred to as the *triplet instabilities*, while the term *singlet instabilities* is used for the instabilities associated with the stability conditions (22) or (26) for $x=s$, which are obviously connected with the monoexcitations of the singlet type. The latter are of special interest from the physical point of view, since they indicate directly the existence of another HF solution with a lower energy which is at the same time a pure singlet eigenfunction of the operator \hat{S}^2 .

The triplet instabilities have been studied by several authors. For instance, the instabilities found by Overhauser are of this type.

For molecular systems a problem closely related to the problem of triplet instabilities has been recently

studied by Koutecký,⁶ who calculated the unrestricted Hartree-Fock (UHF) energies of a number of closed-shell pi-electronic systems using the standard approximations of current semiempirical methods of the Pariser-Parr-Pople type.

Koutecký found that in some cases the UHF method yielded a lower energy than the restricted Hartree-Fock (RHF) method, while the same result was obtained with either method otherwise. As expected, these results are strongly dependent on the parameterization used for the Coulomb two-center electron repulsion integrals γ_{ij} . For instance, in the case of the benzene molecule, Koutecký found that the UHF energy was lower than the RHF energy if the Mataga and Nishimoto parameterization¹⁰ (further M parameterization) of the γ integrals was used, while the same energy was obtained with the parameterization due to Pariser and Parr.¹¹

In the special case of the ethylene molecule Koutecký found the explicit conditions for an UHF energy to be lower than the RHF energy as a function of the parameterization used.

Let us now recall that the conditions (26) for $x=t$ enable us to predict *a priori* the instability of the RHF solution with respect to the triplet-type excitations for any molecule. For any triplet unstable RHF solution an UHF solution with a lower energy must exist.

On the other hand, we have to stress that a stability of the RHF solution does not preclude the existence of an UHF solution with a lower energy.

From this point of view it is interesting that in the case of the RHF solution of the benzene molecule the eigenvalue problem (26) for $x=t$ has one negative eigenvalue for M parameterization while all the eigenvalues are positive when using the Pariser-Parr parameterization. As already mentioned above, Koutecký has indeed found an UHF solution lower in energy than the RHF solution for M parameterization.

Similarly, in the case of the ethylene molecule, the condition for a triplet instability of the RHF solution as a function of the parameterization, which results from equation (26), $x=t$, is identical with the above mentioned condition found by Koutecký.

While there are several papers dealing with or related to the problem of triplet instabilities, almost no attention has been paid to the singlet instabilities.

The only paper related to this problem which we are aware of was published by Ooshika.¹² It deals with the benzene molecule and with an infinite polyene using the SCF-MO-LCAO method and the pi-electron approximation.

For the case of an infinite polyene, using the parameterization in which the resonance integrals β and Coulomb repulsion integrals γ were nonzero for nearest

neighbors only, Ooshika found a new HF solution having a lower energy than the usual HF solution, the molecular orbitals of which are identical with the Hückel molecular orbitals.

Using our terminology we can state that the existence of this additional HF solution is a consequence of the singlet instability of the Hückel-type HF solution.

We have observed that the cyclic polyenes present a very nice example of the singlet-type instabilities. The study of these instabilities using two different parameterizations is presented in the next section. In cases for which the usual HF solution is unstable we have found a new singlet HF solution having a lower energy.

IV. SINGLET INSTABILITIES FOR CYCLIC POLYENES

Let us investigate a planar model of cyclic polyenes C_NH_N , where

$$N=2n=4\nu+2; \quad \nu=1, 2, \dots, \quad (27)$$

which belong to the symmetry groups D_{Nh} .

In our calculations we use systematically the pi-electron approximation. The C-C bond length is 1.4 Å throughout. The one- and two-particle integrals over the carbon $2p_z$ atomic orbitals are determined using both the "theoretical" parameterization introduced by Pauncz, de Heer, and Löwdin¹³ and the parameterization suggested by Mataga and Nishimoto.¹⁰

The "theoretical" parameterization (further T parameterization) uses for one-particle integrals the values suggested by Ruedenberg¹⁴ (the Coulomb integral $\alpha = -6.20667$ eV, the resonance integral $\beta = -3.71631$ eV for nearest neighbors and zero otherwise) while for the two-particle electron repulsion integrals the Mulliken approximation is used. The resulting two-center Coulomb integrals $\gamma_{\mu\nu}$ over the Slater orbitals with an effective nuclear charge $Z=3.2358$ suggested by Ruedenberg¹⁴ are then calculated exactly using Roothaan's formulas.¹⁵ The overlap integrals $S_{\mu\nu}$ are considered for nearest neighbors only ($S_{12}=0.2468$).

On the other hand, the parameterization due to Mataga and Nishimoto¹⁰ (further M parameterization) uses a zero differential overlap approximation. The one-particle integrals are determined semiempirically ($\alpha=0$ since the energy differences are independent of α due to the zero differential overlap approximation and $\beta = -2.388$ eV). In a zero differential overlap approximation the only nonvanishing electron repulsion integrals are those of the Coulomb type $\gamma_{\mu\nu}$, which are approximated by the relation

$$\gamma_{\mu\nu} = e^2 / (a + r_{\mu\nu}). \quad (28)$$

¹⁰ N. Mataga and K. Nishimoto, Z. Physik. Chem. (Frankfurt) **13**, 140 (1957).

¹¹ R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

¹² Y. Ooshika, J. Phys. Soc. Japan **12**, 1246 (1957).

¹³ R. Pauncz, J. de Heer, and P.-O. Löwdin, J. Chem. Phys. **36**, 2247, 2257 (1962). J. de Heer and R. Pauncz, J. Mol. Spectry. **5**, 326 (1960).

¹⁴ K. Ruedenberg, J. Chem. Phys. **34**, 1861, 1878 (1961).

¹⁵ C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

The constant $\alpha=1.328$ is chosen in such a way that for $r_{\mu\nu}=0$, relation (28) gives the semiempirical value of γ_{00} approximated by the difference between the carbon valence state ionization potential and electron affinity.

Let us recall that the basis orbitals of the semiempirical theories using a zero differential overlap approximation are not the original atomic orbitals but proper linear combinations of these obtained by the symmetric orthogonalization of Löwdin.¹⁶ Bearing this in mind we observe that the only essential difference between the two parameterizations just mentioned consists in the effective weakening of the Coulomb interelectronic repulsion, especially for small interelectronic distances, in the M parameterization. As a matter of fact, the γ_{00} integral in the T parameterization is equal to 17.229 eV, while in the M parameterization its value is only 10.840 eV.

Having described the parameterizations used, we proceed now to the problem of stability of the usual HF solution.

For our model of cyclic polyenes C_NH_N the molecular orbitals a_j of the usual HF solution are given by the symmetry of the problem

$$a_j = K_j \sum_{\mu=0}^{N-1} \exp\left(-\frac{2\pi i j \mu}{N}\right) \chi_{\mu}; \quad (29)$$

$$j=0, 1, \dots, (N-1);$$

where $\chi_{\mu}, \mu=0, 1, \dots, (N-1)$, are basis atomic orbitals used and K_j is a normalization factor.

In solving the eigenvalue problems (26) it is very convenient to use the high symmetry of our model. It is well known that the indices j of the molecular orbitals a_j are closely associated with the quasimomentum of the given molecular orbital which, in turn, may be used conveniently to label the irreducible representations of the point group C_N . In order to use the symmetry properties of this subgroup first, we consider the quasimomentum transfer corresponding to the monoexcitation

$$u = \begin{pmatrix} a_l \\ a_k \end{pmatrix}$$

which is equal to $p_u = (l-k) \bmod N$.

We now observe that the matrix A^s or A^t of (26), which is in fact identical with the matrix of the configuration interaction among the monoexcited states, factorizes into $(N-1)$ submatrices, each of which corresponds to a different quasimomentum transfer p_u . Indeed, the matrix elements a_{u_1, u_2}^x of A^x , $x=s, t$, defined by formulas (23), are different from zero only if $p_{u_1} = p_{u_2}$.

On the other hand, the matrix elements b_{u_1, u_2}^x of the matrices B^x , $x=s, t$, have nonzero values if

$p_{u_1} + p_{u_2} = N$. Therefore, the matrix elements of B^x will couple together those submatrices of A^x with quasimomentum transfers p_{u_1} and p_{u_2} for which $p_{u_1} + p_{u_2} = N$, so that the eigenvalue problem (26) factorizes into only $(2\nu+1)$ subproblems. We label these subproblems by the minimal quasimomentum transfer p , $p = \min(p_{u_1}, p_{u_2})$. With this definition of the quasimomentum transfer p we can conveniently characterize the monoexcitation u

$$u = \begin{pmatrix} a_l \\ a_k \end{pmatrix} \equiv \begin{bmatrix} l \\ k \end{bmatrix} = \begin{bmatrix} (k+p_u) \bmod N \\ k \end{bmatrix}, \quad (30)$$

by the quasimomentum k of the occupied molecular orbital a_k and by the quasimomentum transfer $p = \min(p_u, N-p_u)$.

If we introduce the following notation for the components of the eigenvectors $E^{x,y}$ of equations (26):

$$e_{k,p}^{x,y} = e_u^{x,y},$$

$$y=0, 1; \quad x=s, t,$$

then the unitary transformation, factorizing each of the eigenvalue problems (26) into the $(2\nu+1)$ subproblems according to the quasimomentum transfer p , may be written as follows

$$\begin{aligned} {}^{\pm}f_{k,p}^{x,y} &= (1/\sqrt{2}) (d_{k,p}^{x,y} \pm d_{(N-k) \bmod N, (N-p) \bmod N}^{x,y}), \\ {}^{\pm}f_{0,n}^{x,y} &= d_{0,n}^{x,y}, \quad x=s, t; y=0, 1, \end{aligned} \quad (31)$$

where simultaneously $k \neq 0$, $p \neq n$ for each x and y . Let us note, further, that for the M parameterization an additional factorization is possible using the alternant properties of the molecular orbitals (29).

Using all the symmetry properties indicated the eigenvalue problems (26) factorize into a number of subproblems of a relatively very low order.

Having in mind the structure of the configuration interaction matrix A^s , we observe that the lowest lying eigenvalue of the characteristic problems (26), $x=s$, $y=0, 1$, will be found in the subproblem corresponding to the maximal quasimomentum transfer $p=n=2\nu+1$.

First of all, we present the results of numerical computations for the T parameterization.

The lowest lying eigenvalues and corresponding eigenvectors of the characteristic problems (26), $x=s$, $y=0, 1$ are given in Table I for the first five polyenes. We see immediately that the usual solution (29) of the HF equations, which is given by the symmetry of the problem, is singlet stable for the six- and ten-membered rings while it is singlet unstable for larger polyenes than $C_{10}H_{10}$.

Therefore, a new HF solution which is lower in energy may be found for cyclic polyenes with $N \geq 14$ using the T parameterization. For the sake of complete-

¹⁶ P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

ness let us mention that the lowest-lying eigenvalue of the characteristic problem (26) for $x=t$ is negative already for C_6H_6 and, with an increasing size of the polyene, it further decreases.

In order to find out a new HF solution just men-

tioned, we carry out the prescription following equation (14) of the second chapter.

Let us write the ground state HF determinant $|\Phi_0\rangle$ of C_NH_N for a usual symmetric solution (29) in the form:

$$|\Phi_0\rangle = \det\{a_0\alpha, a_0\beta, a_1\alpha, a_1\beta, a_{N-1}\alpha, a_{N-1}\beta, a_2\alpha, \dots, a_{N-\nu}\alpha, a_{N-\nu}\beta\}. \quad (32)$$

Then the determinantal function $|\Phi_{\lambda \text{ neg}}(\kappa)\rangle$ will have an analogous form

$$|\Phi_{\lambda \text{ neg}}(\kappa)\rangle = \det\{b_0\alpha, b_0\beta, b_1\alpha, b_1\beta, b_{N-1}\alpha, b_{N-1}\beta, b_2\alpha, \dots, b_{N-\nu}\alpha, b_{N-\nu}\beta\}. \quad (33)$$

Due to the fact that the lowest-lying root $\lambda_{\text{neg}} = \lambda_1^-$ of the characteristic problems (26) is obtained from the subproblem for which $x=s$, $y=1$ and $p=n$, so that the eigenvector $D_{\lambda_1^-}$ of (22) is given by the relation $D_{\lambda_1^-} = iE_{\lambda_1^-} a_{i,n}$, we get for the molecular orbitals b_i of (33) the following relations

$$\begin{aligned} b_0 &= a_0, \\ b_l &= a_l + ike_{l,n} a_{l+n}, \\ b_{N-l} &= a_{N-l} - ike_{l,n} a_{n-l}; \quad l=1, 2, \dots, \nu. \end{aligned} \quad (34)$$

The dependence of the energy expectation value $E_{\lambda_1^-}(\kappa)$ corresponding to the function (33) on the parameter κ is shown in Fig. 1 for the case of the cyclic polyene with $N=18$.

It is obvious that we could easily find a value κ_0 of the parameter κ corresponding to the minimum of the $E_{\lambda_1^-}(\kappa)$ as accurately as desired. However, this would be useless since we are solving the HF equations using the iterative SCF procedure and we use $|\Phi_{\lambda_1^-}(\kappa_0)\rangle$ only as a starting point. Therefore, we can use any value of κ lying in the "neighborhood" of κ_0 and expect

that the SCF procedure will converge to the desired HF solution.

In actual computations we have calculated $E_{\lambda_1^-}(\kappa)$ for κ increasing by a rather large step $\Delta\kappa$ until we found κ' such that

$$E_{\lambda_1^-}(\kappa') \leq E_{\lambda_1^-}(\kappa' + \Delta\kappa).$$

The molecular orbitals of the function $|\Phi_{\lambda_1^-}(\kappa')\rangle$ were then used as an initial iteration.

Following further the procedure suggested in the second section, we use in solving the HF equations the representation of the molecular orbitals of an unstable HF solution. In our case the factorization of the SCF eigenvalue problem due to this representation is very effective.

Indeed, using the molecular orbitals (29) as a basis for the representation of the HF operator, the respective SCF eigenvalue problem factorizes into the $N/2$ mutually coupled subproblems of the second order, since the only nonzero matrix elements of the HF operator are those between the molecular orbitals a_i and a_{i+n} . Assuming the following form of the new SCF molecular orbitals

$$c_l = \alpha_l a_l + i\beta_l a_{(l+n) \bmod N}, \quad (35)$$

$$l=0, 1, \dots, \nu \quad \text{and} \quad l=N-\nu, \dots, N-1;$$

where

$$\begin{aligned} \alpha_0 &= 1, & \beta_0 &= 0, \\ \alpha_{N-l} &= \alpha_l, & \beta_{N-l} &= -\beta_l, \\ l &= 1, 2, \dots, \nu; \end{aligned}$$

we get for the nonzero matrix elements of the HF operator \hat{f} in our representation the following formulas

$$\begin{aligned} \langle a_k | \hat{f} | a_k \rangle &= \langle a_{N-k} | \hat{f} | a_{N-k} \rangle \\ &= \langle a_k | \hat{z} | a_k \rangle + \sum_{l \in \omega} \{ 2 \langle a_k, a_l | \hat{v} | a_k, a_l \rangle - \alpha_l^2 \langle a_k, a_l | \hat{v} | a_l, a_k \rangle - \beta_l^2 \langle a_k, a_{l+n} | \hat{v} | a_{l+n}, a_k \rangle \}, \\ \langle a_k | \hat{f} | a_{k+n} \rangle &= - \langle a_{N-k} | \hat{f} | a_{n-k} \rangle \\ &= i \sum_{l \in \omega} \alpha_l \beta_l \{ \langle a_k, a_{l+n} | \hat{v} | a_l, a_{k+n} \rangle - \langle a_k, a_l | \hat{v} | a_{l+n}, a_{k+n} \rangle \}; \quad k=0, 1, \dots, \nu, \end{aligned} \quad (36)$$

where ω designates a set of indices l of the occupied molecular orbitals: $l=0, 1, \dots, \nu$ and $l=N-\nu, \dots, N-1$.

It is perhaps worth mentioning that in the actual numerical computations the convergency of the usual SCF iterative procedure was rather slow. In order to speed it up, we extrapolated new molecular orbitals after every third iteration, assuming that the differences of the extrapolated molecular-orbital coefficients and of the molecular-orbital coefficients of the i th iteration form a geometric series.

The resulting molecular orbitals representing a new solution of the HF equations are given in Table II together with the differences between the new HF energy and the energy of the unstable HF solution, as well as their one- and two-particle components.

Let us note that the Coulombic part of the electronic repulsion energy is invariant with respect to the transformation (34) or (35) and, consequently, identical for

TABLE I. The lowest lying eigenvalues λ_1^- (in electron volts) of the characteristic problem (26) for $x=s$, $y=1$ and corresponding eigenvectors $-F_{n,s,1}$ with the components $-f_{i,n,s,1}$ defined by the equation (31) for the first five cyclic polyenes C_NH_N , $N=4\nu+2=2n$, calculated using the T parameterization. Furthermore, $-f_{0,n,s,1}=0$ and the eigenvectors $-F_{n,s,1}$ are normalized to $\frac{1}{2}$.

ν N	1 6	2 10	3 14	4 18	5 22
λ_1^-	2.823	0.190	-0.889	-1.463	-1.814
$-f_{1,n,s,1}$	0.70711	0.14263	0.06812	0.04183	0.02904
$-f_{2,n,s,1}$...	0.69257	0.19764	0.10372	0.06688
$-f_{3,n,s,1}$	0.67550	0.22951	0.12786
$-f_{4,n,s,1}$	0.65941	0.25059
$-f_{5,n,s,1}$	0.64462

both HF solutions. Therefore, the two-particle component of the difference between the new and the original HF energies is solely due to the exchange part.

At this point we should remark that the HF determinant formed from the new SCF molecular orbitals has lower symmetry than the pertinent Hamiltonian. This will become immediately apparent from the bond orderlike quantities $p_{\mu\nu}$ of two neighboring bonds of our polyene, defined similarly as Coulson's bond orders

$$p_{\mu\nu} = 2 \sum_{l \in \omega} \bar{d}_{l\mu} d_{l\nu}, \quad (37)$$

where $d_{k\mu}$ is a coefficient at the atomic orbital χ_μ in the molecular orbital \bar{c}_k ,

$$\bar{c}_k = \tau c_k = \sum_{\mu=0}^{N-1} d_{k\mu} \chi_\mu, \quad (38)$$

with the coefficient τ chosen in such a way that it holds

$$\sum_{\mu=0}^{N-1} \bar{d}_{k\mu} d_{k\mu} = 1, \quad (39)$$

TABLE II. The energy differences ΔE between the new and the usual symmetric HF energies as well as their one- and two-electron components, ΔE_1 and ΔE_2 , respectively, $\Delta E = \Delta E_1 + \Delta E_2$, (all in electron volts); the bond orderlike quantities $p_{\mu\nu}$ for two neighboring bonds; and the coefficients β_i of the new SCF molecular orbitals (35) with $\alpha_i = (1 - \beta_i^2)^{1/2}$ obtained with the T parameterization for the first five cyclic polyenes C_NH_N , $N=2n=4\nu+2$. The coefficients β_i describe the degree of mixing of the unoccupied molecular orbitals (29) in the new HF molecular orbitals (35).

ν N	1 6	2 10	3 14	4 18	5 22
ΔE_1	0.0	0.0	1.147	1.813	2.290
ΔE_2	0.0	0.0	-1.361	-2.442	-3.347
ΔE	0.0	0.0	-0.214	-0.629	-1.057
$p_{i-1,i}$	0.6667	0.6472	0.3972	0.3615	0.3518
$p_{i,i+1}$	0.6667	0.6472	0.8507	0.8739	0.8800
β_1	0.0	0.0	0.03446	0.02906	0.02399
β_2	...	0.0	0.10114	0.07295	0.05584
β_3	0.32937	0.16372	0.10846
β_4	0.42656	0.21470
β_5	0.48060

Evidently, the bond-order-like quantities $p_{\mu\nu}$ represent the standard bond orders, if the basis set atomic orbitals χ_μ are orthonormal.

In our case, with the normalized SCF molecular orbitals of the form (35), we get an explicit expression for $p_{\mu\nu}$ of two neighboring bonds

$$p_{\mu,\mu\pm 1} = n^{-1} \sum_{l \in \omega} [(\alpha_l^2 - \beta_l^2) \cos(\pi l/n) \pm 2\alpha_l \beta_l \sin(\pi l/n)], \quad (40)$$

where μ is an even integer. The numerical values of these quantities are given in Table II and clearly demonstrate that the new HF determinant has a lower spatial symmetry than the Hamiltonian used. Indeed, the new HF determinant for cyclic polyenes with $N \geq 14$ has only the symmetry of the point group

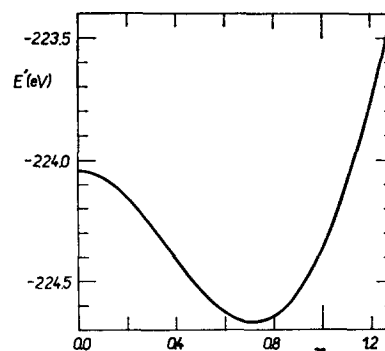


FIG. 1. The dependence of the energy expectation value $E_{\lambda_1^-}(\kappa)$ on the mixing parameter κ for the cyclic polyene $C_{18}H_{18}$ using the T parameterization. In this figure, the actually plotted quantity E' is the sum of the one-electron energy and of the two-electron exchange energy. The total energy expectation value $E_{\lambda_1^-}(\kappa)$ is obtained from E' by adding a two-electron Coulomb energy, which is independent of κ , so that $E_{\lambda_1^-}(\kappa) = E' + E_{Coul}$ where $E_{Coul} = 643.581$ eV.

TABLE III. The lowest lying eigenvalues λ_1^- (in electron volts) of the characteristic problem (26) for $x=s$, $y=1$, calculated using the M parameterization, for the first six cyclic polyenes C_NH_N , $N=4\nu+2$.

ν	1	2	3	4	5	6
λ_1^-	4.179	1.943	0.950	0.395	0.043	-0.198

D_{nh} , while the symmetry group of the Hamiltonian is D_{Nh} .

We now turn our attention to the results of similar calculations which were obtained using the M parameterization.

In this case, the lowest-lying eigenvalues of the characteristic problems (26), $x=s$, which are given in Table III, indicate that the instability of the usual symmetric solution (29) does not occur until $N=26$ is reached. This result might have been expected since in the M parameterization the interelectronic repulsion was weakened at short interelectronic distances as compared with the T parameterization.

In order to demonstrate the dependence of the stability of the HF solutions on the relative importance of the one- and two-electron parts of the Hamiltonian we carried out the calculations of the "benzene molecule" ($N=6$) for different values of the resonance integral β , while using the M parameterization for the electron repulsion integrals. This is a suitable model for an illustration of the studied effects, though it has no direct physical sense. Nevertheless, roughly speaking, decreasing the resonance integral β has the same effect as increasing of the size of the cyclic polyene. An additional advantage of the benzene molecule for such a study is that the minimum of the function $|\Phi_{\lambda_1^-}(\kappa)\rangle$ represents directly the HF determinant of the new solution.

The results of these calculations are summarized in Fig. 2, where the dependence of the energy expectation value $E_{\lambda_1^-}(\kappa)$ is plotted as a function of κ for different values of the resonance integral β . It is immediately evident from this figure that for an extremely small absolute values of the resonance integral β the usual symmetric HF solution (29) becomes singlet unstable while being perfectly stable for $|\beta| > +0.3$ eV.

V. CONCLUSIONS

In the correlation energy calculations for the atomic and molecular closed-shell systems, the HF determinant serves usually as a convenient starting point in both perturbative¹⁷ and nonperturbative¹⁸ theories. If the

HF solution is unstable with respect to the singlet type monoexcitations (2), then the one-particle approximation is not adequate, and thus the pertinent HF determinant does not represent a significant component of the exact wavefunction.

Let us now briefly mention the two possible conclusions one can make under these circumstances.

The first is a purely formal conclusion: since a singlet unstable HF determinant does not represent a good starting point for the calculations of the exact wavefunction, a superior approximation of the ground-state wavefunction should be used instead.

One of the possibilities which offers itself would be to use the new stable HF solution, the existence of which as well as a possible way of construction have been demonstrated in this paper. Since the new HF determinant represents usually a linear combination of functions belonging to different irreducible representations of the symmetry group of the Hamiltonian it

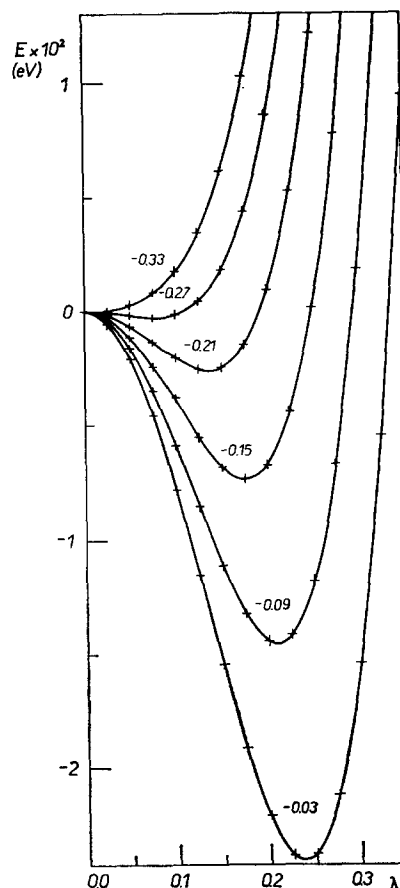


FIG. 2. The dependence of the energy expectation value $E_{\lambda_1^-}(\lambda)$ as a function of the mixing parameter λ for the model of the benzene molecule, using the M parameterization for the electron repulsion integrals and different values of the resonance integral β (in electron volts) given at each curve. The parameter λ is connected with the parameter κ of Eq. (34) by the relationship $\kappa = \sqrt{2}\lambda/(1-\lambda^2)^{1/2}$ and represents directly the normalized mixing coefficient at the excited molecular orbitals a_{i+n} .

¹⁷ J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957). H. P. Kelly, Phys. Rev. **136**, B896 (1964).

¹⁸ O. Sinanoğlu, Advan. Chem. Phys. **6**, 315 (1963). R. K. Nesbet, Advan. Chem. Phys. **9**, 321 (1965). J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

cannot be used directly. Nevertheless, a suitable starting function for most of the closed-shell systems may be obtained by projecting the new HF determinant onto a subspace of totally symmetric functions of the pertinent representation space.

The second conclusion has a rather hypothetical character. Namely, one can presume that the nuclear configuration used in the Hamiltonian does not represent a minimum of a potential hypersurface, so that the actual molecular structure corresponds to another nuclear configuration of lower symmetry. The experimental evidence of bond lengths alternation in long polyenes supports this hypothesis in the case of our model of cyclic polyenes.

In addition, let us remark that the assumption of bond lengths alternation increases the energy gap between the highest occupied and lowest unoccupied one-electron energy levels. Consequently, we can expect in this case that the one-particle approximation is more suitable than in the case of the symmetric Hamiltonian so that the HF determinant is stable and, therefore, represents a good starting point for the calculation of the exact wavefunction.

We are deliberately restricting ourselves to the above comments since a more detailed discussion would require consideration of a number of complex problems, e.g., the problem of the adequacy of the adiabatic approximation.

In any event, the present paper leaves no doubt that the stability of the HF solutions has serious implications as far as the usefulness of the HF determinant in the calculations of the exact wavefunction is concerned.

Note added in proof: (I) Let us make a comment concerning the unitary transformation (19) in order to avoid eventual misunderstanding. In carrying out this transformation it is important to realize that both eigenvalue problems,

$$\begin{pmatrix} a & b \\ \bar{b} & \bar{a} \end{pmatrix} \begin{pmatrix} x \\ \bar{x} \end{pmatrix} = \lambda \begin{pmatrix} x \\ \bar{x} \end{pmatrix}$$

and

$$\begin{pmatrix} a & -b \\ -\bar{b} & \bar{a} \end{pmatrix} \begin{pmatrix} y \\ \bar{y} \end{pmatrix} = \lambda \begin{pmatrix} y \\ \bar{y} \end{pmatrix}$$

have identical eigenvalue spectra. This is immediately clear if we make the substitution $y = ix$.

Bearing this in mind, it would not be necessary to have an imaginary unit in the last equation of the transformation (19). (II) We would like to draw at-

tention to some further papers dealing with problems closely related to the stability problem considered in this paper:

(A) First we quote a paper of Slater¹⁹ in which, for perhaps the first time, it was noticed that the energetically-best HF solution is not necessarily symmetry adapted.²⁰ An excellent account of the present status of the achievements in this respect has recently been given by Löwdin.²¹

(B) Further, a very interesting paper by Coulson²² has appeared in which the pertinent phenomena are studied for the case of the He atom. His older paper²³ concerning the hydrogen molecule is very interesting in this respect, too.

(C) Finally, in a recent paper by Kaplan and Kleiner,²⁴ some related stability problems are considered for one-center systems.

Let us stress that, using the terminology of this paper, the instabilities discussed in all the papers just mentioned are of the *triplet type*.

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¹⁹ J. C. Slater, Phys. Rev. **35**, 509 (1930).

²⁰ We would like to thank Prof. P.-O. Löwdin for pointing this out to us.

²¹ P.-O. Löwdin, "The Projected Hartree-Fock Method: An Extension of the Independent-Particle Scheme," *Quantum Theory of Atoms, Molecules, and the Solid State, A Tribute to John C. Slater*, P.-O. Löwdin, Ed. (Academic Press Inc., New York, 1966), p. 601.

²² Ref. 21, C. A. Coulson, "Note on the Saddle-Point Character of Hartree and Hartree-Fock Wave Functions," p. 97.

²³ C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 (1949).

²⁴ T. A. Kaplan and W. H. Kleiner, Phys. Rev. **156**, 1 (1967). We would like to thank Prof. W. H. Adams for bringing this paper to our attention.