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# Instability Threshold and Peculiar Solutions of Hartree–Fock Equations

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**Abstracts**

Perturbation theory in the vicinity of an RHF closed-shell instability threshold is developed. Equations determining the appearance of new solutions are formulated solely in terms of the electron interaction operator.

Une théorie des perturbations au voisinage d'une instabilité d'une fonction RHF pour une couche fermée a été developpée. Des équations, qui déterminent l'apparition des nouvelles solutions sont formulées entièrement en termes de l'opérateur de l'interaction électronique.

Eine Störungstheorie für die Nachbarschaft einer Instabilität der RHF-Funktion für eine abgeschlossene Schale wird entwickelt. Gleichungen, die das Auftreten neuer Lösungen bestimmen, werden ausschliesslich durch den Elektronenwechselwirkungsoperator formuliert.

## 1. Introduction

The Hartree-Fock (HF) equations nonlinearity, which results from electron interaction, leads to a self-consistent method of their solution. Sometimes this tedious procedure hides physically more interesting peculiarities connected with the nonlinearity. Such a problem is the appearance of additional solutions of the HF equations caused by an increase in their power as compared to a linear problem. These new solutions, which are impossible in principle if the electron interaction is neglected, may reveal collective features of electronic movement. The most successful progress in searching the additional solutions of the HF equations has been achieved in MO LCAO approximation [1–10].

It seems that the density matrix technique may be applied as a convenient tool for the investigation of this problem. In terms of the residual charge-bond-order involutive matrix $Y$ the HF problem looks like

$$Y^2 = I \tag{1}$$

$$[F, Y] = 0, \qquad F = H + G(Y) \tag{2}$$

Here $H$ is the screened core energy matrix and $G(Y)$ is the electron interaction matrix which is a linear function of $Y$ elements:

$$G_{pq}(Y) = \sum_{s,t=1}^{m} Y_{ts}\Gamma_{ts,pq}, \quad \Gamma_{ts,pq} = \langle ps|qt\rangle - \tfrac{1}{2}\langle ps|tq\rangle \tag{3}$$

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The requirement of conservation of electron number $N = 2n$ is

$$\mathrm{Sp}\, Y = N - m \tag{4}$$

where $m$ is the basis dimension. It should be emphasized that Eqs. (1), (2), and (4) do not determine unambiguously the matrix $Y$ as a consequence of nonlinearity of (1) even in the absence of $G$ term in Eq. (2). They have as many as $\binom{m}{n}$ solutions for $Y$ [7]. This ambiguity is quite natural because the HF equations are necessary but not sufficient conditions of the energy minimum:

$$E = \tfrac{1}{2}\mathrm{Sp}(I + Y)(2H + G(Y - I)) \tag{5}$$

They guarantee only the first $E$ variation to vanish. Any solution of Eqs. (1), (2), and (4) corresponds to some distribution of $n$ units among $m$ eigenvalues of $Y$, which are equal to $\pm 1$ according to Eq. (1). In other words, it means a certain choice of $n$ eigenvectors filled in the ground state. In principle, this choice should be concretized after calculation of $E$ from Eq. (5) for every of $\binom{m}{n}$ possible solutions.

After these preliminaries it should be noted that we are interested here not in the variety of solutions mentioned but just in the additional solutions that appear as a result of inclusion of the $G$ term in Eq. (2) and that have been defined above as "peculiar." It seems that the first paper in which the ambiguity of solutions of the HF equations was emphasized was Slater's work [1], where it has been shown that for a large separation of nuclei in hydrogen molecule two types of solutions exist. In the first case the electrons are symmetrically distributed between the nuclei and in the second electrons are concentrated in the vicinity of one nucleus. This problem for two-electron molecules has also been considered by Coulson and Fisher [2] and especially by Fukutome [3]. Slater's idea, in fact, has been developed by Stanton [4], who calculated the number of possible solutions of the HF equations when the system falls into different regions described by nonoverlapped orbitals. Additional solutions in the four-electron $\pi$ system of butadiene molecule have been considered by Chirgwin [5] and Hall [6] in terms of the charge-bond-order matrix. But as it was shown in Ref. 7 (see also Ref. 8) new solutions obtained by Hall are due to the redistribution of electrons between the empty and filled orbitals and do not belong to the type we are concerned with. The condition that guarantees the existence of additional solutions caused by electron interaction in butadiene has been formulated in Ref. 7. The investigation of the problem in larger molecules is restricted to the benzene molecule where Cizek and Paldus discovered the bond-order wave-type solution [9].

The same authors have connected the appearance of a new solution to the instability problem and have shown that, if the system is unstable, a new solution appears, which violates some space or spin symmetry [10]. For example, spin density waves do exist in the infinite polyenes as a result of triplet instability, as has been demonstrated by Fukutome [11]. In the Hubbard approximation the solutions of the spin density wave type in long polyenes have been obtained in the explicit form by Ovchinnicov and Misurkin [12]. Overhauser, without using the

LCAO approximation, has discovered in the electron gas the low-lying Hartree–Fock state in the form of helical spin polarization waves [13].

However, it should be noted that all the solution types just mentioned are not in the framework of the restricted HF method, violating the double occupancy of orbitals. In the present paper we shall confine ourselves only to the restricted HF scheme in order not to deal with the complications of $\hat{S}^2$ problem. Therefore, it is worthwhile to mention that the example of butadiene [14] confirms the appearance of totally symmetric additional solutions simultaneously with the vanishing of one of the internal instability frequencies, as well as in the case of destroyed symmetry. Thus the appearance of HF peculiar solutions, defined above, at the instability threshold may be considered as their characteristic feature. Fukutome's important work [15] is devoted to the detailed general investigation of the unrestricted HF solution behavior in the vicinity of the instability threshold. We shall consider a similar problem for the restricted HF method using quite a different technique. It should be mentioned that in Ref. 15 the order of some small quantities has not been taken into account very strictly. Therefore, our final results differ somewhat from those of Ref. 15. We shall demonstrate that the emergence of a new solution is directly conditioned by the presence of the Coulomb-exchange term in the HF equations (2).

For these reasons we consider here the solution branching conditions together with the restricted HF perturbation theory in the vicinity of the instability threshold. The branching equation will be formulated solely in terms of the $G$ operator. According to the terminology proposed [16] only the internal instabilities may give rise to a new solution of a given method, whereas external instabilities may lead to solutions of some more general scheme.

## 2. Perturbation Theory

The convenience of matrix $Y(1)$ is that it allows one to separate in any matrix $A$ two components: $A_+$, which commutes with $Y$, and $A_-$, which anticommutes with it. Suitable components of two arbitrary matrices are mutually orthogonal

$$A = A_+ + A_-, \qquad A_\pm = \tfrac{1}{2}(A \pm YAY), \qquad \mathrm{Sp}\, A_+ B_- = 0 \tag{6}$$

Because of this property it is not difficult to calculate the energy (5) variations:

$$\delta E = \mathrm{Sp}\, F\delta Y = 0, \qquad \delta^2 E = \tfrac{1}{2}\mathrm{Sp}\, \delta Y \Lambda(\delta Y) \tag{7}$$

where the matrix operator $\Lambda$ is defined according to

$$\Lambda(D) = -[N, D]_+ + 2G_-(D), \quad N = FY \tag{8}$$

Its eigenvalues $\lambda$

$$\Lambda(D) = \lambda D \tag{9}$$

indicate whether the corresponding solution $Y$ is stable (all $\lambda > 0$), or unstable (some $\lambda < 0$) or belongs to the threshold (some $\lambda = 0$).

From the properties of the integrals (3) it can be shown that $\Lambda$ is Hermitian operator

$$\mathrm{Sp}\, A^{+}\Lambda(B) = \mathrm{Sp}\, \Lambda^{+}(A)B \tag{10}$$

which acts so that

$$\Lambda^{+}(A) = \Lambda(A^{+}) \tag{10'}$$

As a consequence of Eq. (10') the classification of solutions $D$ of Eq. (9) on Hermitian and skew-Hermitian ones is possible. Since according to Eq. (1) $[\delta Y, Y]_{+} = 0$, it is natural to subject the solutions of Eq. (9) to the condition

$$[D, Y]_{+} = 0 \tag{11}$$

which leads to

$$\mathrm{Sp}\, DF = 0 \tag{12}$$

There are as many as $n(m-n)$ Hermitian solutions and the same number of skew-Hermitian ones which obey Eqs. (11) and (12). Both the solution sets are complete in suitable subspaces. Therefore an arbitrary matrix $K_{-}$ that fulfills Eq. (11), e.g., a Hermitian one, may be expanded over $D_s$ [17]

$$K_{-} = \sum_{s=1}^{n(m-n)} x_s D_s, \qquad x_s = \mathrm{Sp}\, D_s^{+} K_{-} \tag{13}$$

where $[K_{-}, Y]_{+} = 0$. The different solutions $D_s$, later supposed to be known, are orthonormal because of Eqs. (9) and (10):

$$\mathrm{Sp}\, D_s^{+} D_t = \delta_{st} \tag{14}$$

For our purposes it is convenient to separate from the "minus" subspace the part belonging to the threshold and denoted by $\|$. From Eq. (13)

$$K_{-} = K_{\|} + K_{\perp} \tag{13'}$$

where

$$\Lambda(K_{\|}) = 0, \qquad \text{i.e.,} \qquad [F, K_{\|}]_{-} + [G(K_{\|}), Y]_{-} = 0 \tag{15}$$

and $K_{\perp}$ belongs to the orthogonal to $\|$ subspace.

Following Fukutome [15] let us consider the behavior of a system under a small perturbation of its adiabatic parameters (i.e., elements of $H$ and $\langle ps|tq\rangle$) in the vicinity of the threshold. This requires a perturbation theory in Eq. (2) that differs essentially from the HF perturbation theory in the absence of threshold [17] as well as from the perturbation theory in the vicinity of a threshold, which neglects the electron interaction. The latter reduces in fact to the standard perturbation theory for a degenerate state. Actually, the matrix $\Lambda(D)$ does not change after substitution of $F$ by $F - \mu I$ where $\mu$ is an arbitrary constant. Therefore, if the levels of $H$ are filled without gaps, the matrix $-N$ may be considered as a positive definite one (the constant $\mu$ should be chosen between the highest occupied and the lowest unoccupied $H$ level). Then the system is stable

and all $\lambda > 0$. In the opposite case there always exist some $\lambda < 0$ and the system is unstable. The threshold ($\lambda = 0$) appears if the matrix $N$ has zero eigenvalue, which is possible when the highest occupied $H$ level is degenerate and only partly filled.

If the parameters of the system are perturbed, the matrices $Y$ and $F$ in Eq. (2) receive corrections $T$ and

$$U = A + G(T) + \Delta G(T), \qquad A = \Delta H + \Delta G(Y) \tag{16}$$

respectively, and Eq. (2) reduces to

$$[F, T]_- + [U, Y + T]_- = 0 \tag{17}$$

All the quantities that contain $\Delta$ are supposed to be of the first order. The main difference of the threshold perturbation theory from the usual approach is that $T$ is not of the first but of lower order, which is determined by the equations themselves. As a result the order of $U$ is less than unity. The distorted matrix $Y + T$ must obey an equation of type (1), which is identically fulfilled if $T$ has the form [17, p. 230]

$$T = T_+ + T_-, \qquad T_- = 2K(I + K^2)^{-1} = 2(K - K^3 + \cdots),$$
$$T_+ = -2YK^2(I + K^2)^{-1} = -2YK^2 + \cdots \tag{18}$$

where $K$ is an arbitrary "minus-type" matrix. Taking the commutator and anticommutator of Eq. (17) with $Y$, we can write it in projections into "+" and "−" subspaces:

$$[N, T_-]_+ - 2U_- + Y[U_+, T_-]_- + Y[U_-, T_+]_- = 0 \tag{19}$$

$$[N, T_+]_- + Y[U_+, T_+]_- + Y[U_-, T_-]_- = 0 \tag{20}$$

In Eqs. (19) and (20) it has been taken into account that $[Y, T]_+ = 2YT_+$, $[Y, T]_- = 2YT_-$. As it will be shown later only the first Eq. (19) is essential.

As it is clear from Eq. (15) the order of $K_\parallel$ is lower than that of $K_\perp$. Retaining in $T_\pm$ only lowest-order terms $T_- = 2(K_\parallel + K_\perp)$, $T_+ = -2YK_\parallel^2$ because of Eq. (15), we put Eqs. (19) and (20) in the form

$$2G_-(K_\parallel^2 Y) + 2Y[G_+(K_\parallel), K_\parallel]_- - \Lambda(K_\perp) = A_- \tag{21}$$

$$[F, K_\parallel^2]_- - 2Y[G_-(K_\parallel), K_\parallel]_- = 0 \tag{22}$$

From Eq. (21) it follows that $K_\perp$ is of first order and the order of $K_\parallel$ is $\frac{1}{2}$. Equation (22) is identically fulfilled because it is a commutator of $K_\parallel$ with threshold equation (15). After projection of Eq. (21) on $\perp$ and $\parallel$ subspaces we have

$$2G_\parallel(K_\parallel^2 Y) + 2\{Y[G_+(K_\parallel), K_\parallel]_-\}_\parallel = A_\parallel \tag{23}$$

$$\Lambda(K_\perp) = 2G_\perp(K_\parallel^2 Y) + 2\{Y[G_+(K_\parallel), K_\parallel]_-\}_\perp - A_\perp \tag{24}$$

since $\Lambda(K_\perp)$ according to Eqs. (9) and (13) belongs to the second subspace.

Equation (23), which determines the main contribution $2K_\parallel$ to the density matrix correction, contains only the second powers of $K_\parallel$. Generally, it has a variety of solutions; therefore, it may be defined as a branching equation. For each

of its solutions $K_\parallel$ Eq. (24), which is linear in $K_\perp$, determines suitable $K_\perp$, since in $\perp$ subspace the operator $\Lambda$ is nonsingular. The operator on the left-hand side of the branching equation (23) is built only of the Coulomb-exchange operator $G$ of Eq. (3). Consequently this equation cannot have any analog in the theory of noninteracting particles. Thus solutions emerging from the threshold are those additional solutions of HF equations which are due to the interelectronic interaction.

### 3. Branching Equation

In the case of nondegenerate threshold only one matrix $D_0$ in Eq. (9) belongs to zero eigenvalue of $\Lambda$. Therefore, $K_\parallel = xD_0$ and $A_\parallel = aD_0$, where $a = \mathrm{Sp}\, D_0 A_\parallel$. As a result of linearity of the $G$ operator, $G_\parallel(K_\parallel^2 Y) = gx^2 D_0$ where according to Eq. (13)

$$g = \mathrm{Sp}\, D_0 G(D_0^2 Y) \tag{25}$$

In a similar way we obtain $\{Y[G_+(K_\parallel), K_\parallel]_-\}_\parallel = 2x^2 g D_0$. Hence, Eq. (23) gives

$$6gx^2 = a, \qquad x = \pm(a/6g)^{1/2} \tag{26}$$

Expression (26) means that for allowed values of perturbation parameter $a$ (of the same sign as $g$) two solutions $Y \pm (a/6g)^{1/2} D_0$ emerge from the threshold $Y$, which corresponds to $a = 0$. The existence of the parameter $a$ domain, in which suitable solution is absent, is a characteristic feature showing that on the instability threshold only new solutions appear. The cases of butadiene [14, 17] and the heteropolar two-electron system [3] illustrate such a situation.

The energy increment in its extremum consists of the part

$$\Delta' E = \mathrm{Sp}\,(I + Y)(A - \tfrac{1}{2}\Delta G(I + Y))$$

independent of $T$ and of a part determined by $T$

$$\Delta E = \mathrm{Sp}\, T(F + A + \tfrac{1}{2}G(T) + \tfrac{1}{2}\Delta G(T)) \tag{27}$$

In the lowest order

$$\begin{aligned}\Delta E &= 2\mathrm{Sp}(K_\parallel + K_\perp - YK_\parallel^2 - Y[K_\parallel, K_\perp]_+)(F + A + \tfrac{1}{2}G(K_\parallel + K_\perp - YK_\parallel^2)) \\ &= \tfrac{4}{3}\mathrm{Sp}\, K_\parallel A_\parallel\end{aligned} \tag{28}$$

where the sequence of relations (18), (12), (15), (8), (10), and (23) has been used. For a nondegenerate threshold owing to Eqs. (25) and (26), we have

$$\Delta E = \pm\tfrac{4}{3} a (a/6g)^{1/2} \tag{29}$$

Thus, one of the obtained solutions is stable, the other is not.

More than two solutions may emerge from the threshold if it is degenerate. Here

$$K_\parallel = \sum_{u=1}^{s} x_u D_u \tag{30}$$

After substitution of this expansion into Eq. (23) and using the linear property of the operator $G$, we obtain for $x_u$ the homogeneous quadratic algebraic system with the right-hand part

$$\sum_{u,v=1}^{s} g_{iuv}x_u x_v = a_i, \qquad i = 1, 2, \ldots, s \tag{31}$$

where

$$g_{iuv} = g_{uv}^{(i)} + g_{vi}^{(u)} + g_{iu}^{(v)}, \qquad g_{uv}^{(i)} = \mathrm{Sp}\, D_i G([D_u, D_v]_+ Y), \qquad a_i = \mathrm{Sp}\, D_i A_{\|} \tag{32}$$

According to Eq. (32) the coefficients of Eq. (31) $g_{iuv}$ are invariant to any permutation of their subscripts $i$, $u$, $v$.

The twofold degenerate case will be considered in greater detail. In this case

$$g_1 x_1^2 + 2g_2 x_1 x_2 + g_3 x_2^2 = a_1, \qquad g_2 x_1^2 + 2g_3 x_1 x_2 + g_4 x_2^2 = a_2 \tag{31'}$$

where $g_1 = g_{111}$, $g_2 = g_{112}$, $g_3 = g_{122}$, $g_4 = g_{222}$.

The substitutions $x_1 = y_1 + y_2$, $x_2 = \alpha_1 y_1 + \alpha_2 y_2$, where $\alpha_1$ and $\alpha_2$ are the roots of equation $p\alpha^2 - q\alpha + r = 0$ and $p = g_3^2 - g_2 g_1$, $q = g_1 g_4 - g_2 g_3$, $r = g_2^2 - g_1 g_3$, $B = q^2 - 4pr$ allows one to write the system (31') in the form

$$By_1^2 = p(g_3 + \alpha_2 g_4)(a_1 + \alpha_1 a_2), \qquad By_2^2 = p(g_3 + \alpha_1 g_4)(q_1 + \alpha_2 a_2) \tag{33}$$

In the case $B > 0$ the solution exists in the plane $(a_1, a_2)$ only in one of four sectors which is bounded by the straight lines $a_1 + \alpha_1 a_2 = 0$ and $a_1 + \alpha_2 a_2 = 0$ and diverges from the coordinate origin. For any point $(a_1, a_2)$ from this sector there exist four solutions. In this case four branches converge in the threshold. If $B < 0$, then $y_2 = y_1^*$, $\alpha_2 = \alpha_1^*$, and there exist two real solutions for $x_1$, $x_2$ in the whole plane $(a_1, a_2)$. Here the threshold corresponds to the intersection of solutions in the point (0, 0) but not to the origin of them. It is clear that, if the degree of degeneracy increases, the situation becomes more complicated.

It is worthwhile to note that the situation characteristic of a nondegenerate threshold is repeated in the more complicated case of Eq. (31'): either the inhomogeneous system has a solution (if $g \neq 0$ and $B \neq 0$, respectively) or (if $g = 0$ and $B = 0$) the corresponding homogeneous system does not impose any restriction on the unknowns (except of particular cases $p = 0$ or $q = 0$). This is an essential difference of the nonlinear system (31) from a linear one. Such a nonusual situation ($g = 0$, $B = 0$) appears in alternant hydrocarbons. For these molecules all matrices are naturally divided into four blocks, e.g., in $Y$ only nondiagonal blocks are nonzero and matrices $D$ may be of two types. The first type has the same structure as $Y$ ("$-$ states" in Pariser's notation), the second type of matrices are quasidiagonal ("$+$ states") [17]. Since the operator $G$ does not change the block structures of its argument matrix, all $g_{iuv} = 0$ if the threshold belongs to "$+$ states" as it is seen from Eq. (32).

In the *special* case ($g_{iuv} = 0$), which we consider now, the inclusion of the next terms of perturbation series (18) may clarify the situation. However, here the

perturbation theory goes not "up" but "down." If we include the terms of type $K_{\|}^3$, it is evident that the order of the quantity $K_{\|}$ will not be $\frac{1}{2}$ but $\frac{1}{3}$. Then $K_{\perp}$ must contain two terms $K_{\perp} = L + M$, where $L$ is of order $\frac{2}{3}$ and $M$ is of the first order. Thus

$$T_- = 2(K_{\|} + L + M - K_{\|}^3), \qquad T_+ = -2(K_{\|}^2 + [K_{\|}, L]_+)Y \tag{34}$$

Substituting these expansions into Eqs. (19) and (20) and separating different orders we obtain the former Eq. (22) and the homogeneous analog of Eq. (21):

$$2G_-(K_{\|}^2 Y) + 2Y[G_+(K_{\|}), K_{\|}]_- - \Lambda(L) = 0 \tag{35}$$

and also

$$J(K_{\|}, L) - \Lambda(M) = A_- \tag{36}$$

$$[F, [K_{\|}, L]_+]_- + 2[G_+(K_{\|}), K_{\|}^2]_- + 2Y[G_-(K_{\|}^2 Y), K_{\|}]_- - 2Y[G_-(L), K_{\|}]_- - 2Y[G_-(K_{\|}), L]_- = 0 \tag{37}$$

where

$$J(K_{\|}, L) = \Lambda(K_{\|}^3) + 2\{G_-([K_{\|}, L]_+ Y) + Y[G_+(L), K_{\|}]_- + Y[G_+(K_{\|}), L]_- - Y[G_+(K_{\|}^2 Y), K_{\|}]_- + [G_-(K_{\|}), K_{\|}^2]_+\} \tag{38}$$

As before Eq. (37), which has been obtained from Eq. (20), is fulfilled identically: because of the threshold Eq. (15) it is an anticommutator of Eq. (35) with $K_{\|}$. After projection of Eqs. (35) and (36) on $\|$ and $\perp$ subspaces, we have

$$G_{\|}(K_{\|}^2 Y) + \{Y[G_+(K_{\|}), K_{\|}]_-\}_{\|} = 0 \tag{39a}$$

$$\Lambda(L) = 2G_{\perp}(K_{\|}^2 Y) + 2\{Y[G_+(K_{\|}), K_{\|}]_-\}_{\perp} \tag{39b}$$

$$2G_{\|}([K_{\|}, L]_+ Y) + 2\{Y[G_+(L - K_{\|}^2 Y), K_{\|}]_- + Y[G_+(K_{\|}), L]_- + [G_-(K_{\|}), K_{\|}^2]_+\}_{\|} = A_{\|} \tag{39c}$$

$$\Lambda(M) = A_{\perp} - J_{\perp}(K_{\|}, L) \tag{39d}$$

The system (39) in principle solves completely the problem in given order. Equation (39a) is fulfilled in a consequence of a *special* type of the threshold, since Eq. (23) has no solution. Equation (39b) allows one to express $L$ in terms of matrix $K_{\|}$. After substitution of this expression $L$ into Eq. (39c) the latter transforms in a homogeneous system for $K_{\|}$ of the third power with the right-hand part and here plays the role of the branching equation. Finally, Eq. (39d) determines suitable $M$ for every solution of $K_{\|}$.

We shall apply Eqs. (39) only to nondegenerate threshold. Here $K_{\|} = xD_0$, Eq. (25) gives $g = 0$ and guarantees to fulfill Eq. (39a) and (39c) leads to

$$x = \tfrac{1}{2}(a/h)^{1/3}, \qquad h = \tfrac{1}{2}[\mathrm{Sp}\, D_0(G(D_0^3) - D_0^2 Y G(D_0^2 Y)] + \sum_i \frac{g_{i00}^2}{4\lambda_i} \tag{40}$$

In Eq. (40) $g_{i00}$ should be defined according to Eq. (32), however, $D_i$ belongs not to the threshold but to eigenvalue $\lambda_i$ of $\Lambda$ of Eq. (9). Formula (40) reveals an

essential difference of the present case with Eq. (26). For all values of perturbation parameter $a$ there exists now a single $x$ which continues the solution on the threshold $Y+xD_0$ for perturbed system. New solutions do not appear. For example, in alternant hydrocarbons the threshold of Pariser's + type cannot give the origin of a new solution ($h \neq 0$ in contrast to $g$) in agreement with the consideration of individual molecules [17]. The vanishing of $\lambda$ only indicated weaker (of order $\frac{1}{3}$) influence of the perturbation on the matrix $Y$ than in a standard perturbation theory, where the correction is of the first order.

In the degenerate case the situation becomes highly complicated. The perturbation $A$ may be partly or completely attributed to the equations of higher perturbation theory orders by means of further separation of $\|$ subspace. The analysis becomes more and more difficult as a result of an increase in equation power for $K_\|$, and we shall not continue it. It is clear that the branching equation (23) remains the main condition determining the appearance of new solutions.

Note that Eq. (39c) as well as Eq. (23) loses its sense if the electron interaction is neglected ($G = 0$). In such a case the representation of $T$ as a power series (18) is impossible. However, in this case $K_\|$ and $H$ commute according to Eq. (15), and Eq. (11) shows that in the basis of $H$ eigenvectors $K_\|$ have only one nonzero diagonal block corresponding to the highest filled degenerate level of $H$. Therefore, Eq. (17) for the perturbed system reduces to the commutation of this block with a suitable block of $\Delta H$, and we return to the standard form of the perturbation theory which requires diagonalization of the mentioned block $\Delta H$, as this was to be expected in the degenerate case.

Finally, we shall discuss a much more *peculiar* situation which is characterized by $A_\perp = A_\| = 0$, i.e., $A_- = 0$. The results (39) are also useful for its analysis. In this case $A = A_+$ commutes with $Y$ and the variation of adiabatic parameters does not prevent $Y$ from satisfying the perturbed HF equations with operator $F + A$ (hence $T = 0$). This will be the case if $Y$ is completely determined by Eq. (1) and symmetry conditions only. To answer whether or not some additional solutions appear on the instability threshold in such a rare situation, Eqs. (35)–(39) should be only slightly modified. Taking into account that their derivation has been based solely on the assumption that the orders of $K_\|$, $L$, and $M$ are related as $1:2:3$, we see that in the homogeneous case ($A_- = 0$) they continue to be valid, but the order of $K_\|$ remains undetermined. If we suppose that it equals $\frac{1}{2}$, the single additional term from $U_+$ of Eq. (19), namely, $Y[A, K_\|]_-$, contributes to $J$ in Eq. (38). Thus, the considered peculiar situation ($A_- = 0$) is described by the same set (39) in which $A_\|$ and $A_\perp$ should be replaced by $-\{Y[A, K_\|]_-\}_\|$ and $-\{Y[A, K_\|]_-\}_\perp$, respectively. It always has the trivial solution $K_\| = L = M = 0$ corresponding to the initial invariant matrix $Y$ but in principle may lead to new solutions with $K_\|^2 \sim A$. It should be emphasized that new solutions may appear in the *peculiar* case if Eq. (39a) allows nonzero $K_\|$, i.e., only if this case is at the same time *special*. Any assumption about the order of $K_\|$ which is less than unity may not lead to the additional terms containing $A$ in quadratic equations (23), (24), or (39a) and (39b) if $A_- = 0$.

For nondegenerate threshold in the peculiar special case Eq. (39c) gives $8x^3h = 2xa_+$, where $a_+ = -\frac{1}{2}\mathrm{Sp}\, D_0 Y[A, D_0]_-$ and $h$ is the same as in Eq. (40). Hence the existence of the invariant $Y$ solution does not prevent two new solutions with

$$x = \pm\tfrac{1}{2}(a_+/h)^{1/2} \tag{41}$$

to appear as in case of Eq. (26). This highly specific situation is met in the homopolar two-electron system and in the infinite polyene chain [18].

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