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POTENTIAL ENERGY SURFACE NEAR THE HARTREE–FOCK INSTABILITY THRESHOLD

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ABSTRACT

The existence of four types of the closed shell Hartree–Fock instability thresholds is established. The potential energy surface behaviour at the threshold is analyzed.

The nonlinearity of the Hartree–Fock (HF) equations is most distinctly revealed in the behaviour of their solutions near the instability threshold. It is exactly the point where additional to the linear problem solutions appear. The physical importance of such peculiar solutions of the HF problem has been emphasized by Slater [1] and Mott [2]. Additional solutions in the four-electron π-system of butadiene have been considered in refs. 3–6. It was shown in ref. 7 that the condition of their existence is equivalent to vanishing of one the instability frequences λ. Čižek and Paldus emphasized the nonanalytic behaviour of the solution at the branching point in the benzene molecule [8].

Further progress in the general investigation of the problem was achieved in the paper by Fukutome [9] who advanced the idea of the perturbation at the UHF-instability threshold. These results are also outlined on p. 988 of his review [10]. A similar idea was exploited within the RHF theory in matrix formulation (see ref. 11 where the relation of the approach used to the Fukutome technique has also been discussed). In the present note we report a complete description of the closed shell instability threshold types in the framework of the scheme of ref. 11. Further details may be found in ref. 12.

Our starting point is the closed shell HF equation $[\mathbf{F},\mathbf{Y}]_- = 0$ for the involutive counterpart $\mathbf{Y}$ of the Fock–Dirac density matrix: $\mathbf{Y}^2 = \mathbf{I}$. If the core Hamiltonian matrix $\mathbf{H}$ receives an increment $\mathbf{A}$ the corresponding change of $\mathbf{Y}$ is denoted by $\mathbf{P}$. The perturbation theory for the density matrix $\mathbf{Y}$ corrections

$$\mathbf{T} = \sum_{u=1}^{p} t_u \mathbf{D}_{(u)} \tag{1}$$

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near the p-fold degenerate instability threshold is based on the equations

$$[\mathbf{F},\mathbf{P}]_- + [\mathbf{A}+\mathbf{G}(\mathbf{P}),\mathbf{Y}+\mathbf{P}]_- = 0 \qquad (\mathbf{Y}+\mathbf{P})^2 = \mathbf{I} \tag{2}$$

Here $\mathbf{F} = \mathbf{H}+\mathbf{G}(\mathbf{I}+\mathbf{Y})$ is the Fock operator, $\mathbf{G}(\mathbf{X})$ is the averaged electron interaction operator depending on its argument density matrix $\mathbf{X}$. Matrix $\mathbf{Y}$ obeys the same system (2), in which perturbation is absent ($\mathbf{P} = 0$, $\mathbf{A} = 0$), and is supposed to be known. Correction $\mathbf{T}$ is that part of the whole perturbation $\mathbf{P}$ which is determined by the threshold properties. Its remaining part is built by means of the standard coupled Hartree–Fock perturbation theory [12]. Matrices $\mathbf{D}_{(u)}$ fulfill the threshold equation

$$\Lambda(\mathbf{D}_{(u)}) = 0 \tag{3}$$

and the condition

$$[\mathbf{D}_{(u)},\mathbf{Y}]_+ = 0 \tag{4}$$

Operator Λ is the same that is used in inhomogeneous equations of the coupled perturbation theory. It acts according to the rule

$$\Lambda(\mathbf{D}) = -[\mathbf{FY},\mathbf{D}]_+ + \mathbf{G}(\mathbf{D}) - \mathbf{YG}(\mathbf{D})\mathbf{Y} \tag{5}$$

Matrices $\mathbf{D}_{(u)}$ as well as $\mathbf{Y}$ are assumed to be known.

All the peculiarities of the threshold perturbation theory are contained in the nonlinear equations for coefficients t_u from eqn. (1). These follow from eqns. (2) and depend on the properties of the perturbation $\mathbf{A}$ and on the threshold nature.

If even one of the coefficients

$$a_u = \mathrm{Sp}\,\mathbf{AD}_{(u)} \qquad u = 1,2,\ldots,p \tag{6}$$

is nonzero, the equations for t_u are quadratic (case "a")

$$\sum_{v,w=1}^{p} g_{uvw} t_v t_w = 2\,a_u \qquad u = 1,2,\ldots,p \tag{7}$$

where the threshold parameters

$$g_{uvw} = 3\mathrm{Sym}(u,v,w)\,(\mathrm{Sp}\,\mathbf{D}_{(u)}\mathbf{G}([\mathbf{D}_{(w)},\mathbf{D}_{(v)}]_+\mathbf{Y})) \tag{8}$$

are symmetric in all subscripts u,v,w.

If all $a_u = 0$ the system is modified (case "b")

$$\sum_{v,w,=1}^{p} g_{uvw} t_v t_w + \sum_{v=1}^{p} b_{uv} t_v = b_u \tag{9}$$

The new perturbation parameters are

$$b_{uv} = a_{uv} - 4\sum_i g_{uvi}a_i/\lambda_i \qquad a_{uv} = \mathrm{SpA}[\mathbf{D}_{(u)},\mathbf{D}_{(v)}]_+\mathbf{Y}$$
$$b_u = 2\sum_i a_{ui}a_i/\lambda_i - 4\sum_{i,j} g_{uij}a_ia_j/(\lambda_i\lambda_j) \tag{10}$$

where $\mathbf{D}_{(i)}$, $\mathbf{D}_{(j)}$ in contrast to $\mathbf{D}_{(u)}$ from eqn. (3) belong to the nonzero eigenvalues λ_i, λ_j of Λ, and a_i, a_j are defined by means of eqn. (6) through $\mathbf{D}_{(i)}$, $\mathbf{D}_{(j)}$.

In special cases, when all the threshold parameters g_{uvw} are zero, the systems corresponding to eqns. (7) and (9) are

$$\sum_{v,w,x=1}^{p} h_{uvwx}t_vt_wt_x = a_u \qquad u = 1,2,...,p \tag{11}$$

$$\sum_{v,w,x=1}^{p} h_{uvwx}t_wt_vt_x + \tfrac{1}{2}\sum_{v=1}^{p} b_{uv}t_v = 0 \tag{12}$$

respectively, (cases "c" and "d"). The four-subscript values h_{uvwx} are defined by

$$h_{uvwx} = \mathrm{Sym}(u,v,w)\{\tfrac{1}{8}\mathrm{Sp}(\mathbf{G}(\mathbf{D}_x)[\mathbf{D}_{(u)},[\mathbf{D}_{(v)},\mathbf{D}_{(w)}]_+]_+ - \mathbf{Y}[\mathbf{D}_{(u)},\mathbf{D}_{(v)}]_+\mathbf{G}(\mathbf{Y}[\mathbf{D}_{(w)},\mathbf{D}_{(x)}]_+)) + \sum_i g_{iuv}g_{iwx}/\lambda_i \tag{13}$$

Systems "a"–"d" demonstrate explicitly that all peculiarities which follow from the nonlinearity of the HF-equations are conditioned solely by electron interaction since $g_{uvw} = 0$ as well as $h_{uvwx} = 0$ for $\mathbf{G} = 0$.

It can be shown [12] that the signs of increments of the total energy and the stability eigenvalue λ are opposite in all the cases "a"–"d". Thus the energy of the stable solution is decreased from the maximum on the threshold and that of the unstable one is increased from the minimum for the growing perturbation.

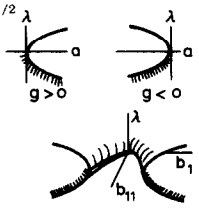
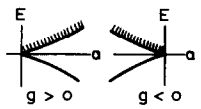
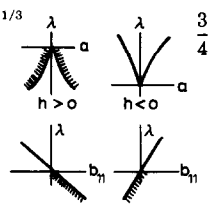
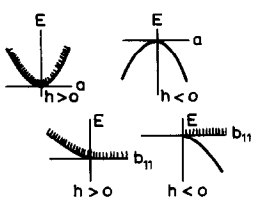
In the one-dimentional case ($p = 1$, $g = g_{111}$, $h = h_{1111}$, $a = a_1$) solutions of all equations are presented in Table 1.

In the first three cases "a"–"c" RHF solutions emerge from the threshold or have a cusp. In the fourth case "d" the pairs of degenerate new solutions branch out smoothly from the already existing solution which changes its stability type. For $h > 0$ initial and appeared (double-degenerate) solutions are unstable whereas nondegenerate solution becomes stable after the threshold. Such a situation is met in the case of core double vacancies [13]. Here the unstable solution formed is responsible for the observed decrease of the core ionization potential [14] and for the correct asymptotic behaviour of the wavefunction [13].

For $h < 0$ the initial and resulting degenerate solutions are stable whereas the nondegenerate solution is unstable after the threshold. The last mechanism is typical for the axial-spin (triplet) and complex instability and also for the appearance of new solutions of the "allowed" type (according the Pariser's

TABLE 1

Parameters for nondegenerate threshold

	Threshold type		
	t	λ	E
Emergence			
a	$\pm\left(\frac{2a}{g}\right)^{1/2}$	$\pm(8ga)^{1/2}$ 	$\pm\frac{1}{3}\left(\frac{8a^3}{g}\right)^{1/2}$ 
b	$\frac{-(b_{11}\pm(b_{11}^2+4gb_1)^{1/2})}{2g}$	$\pm(b_{11}^2+4gb_1)^{1/2}$	$E_c-\frac{1}{24g^2}(\lambda^3+b_{11}\lambda^2+2gb_1b_{11})$
Branching ($g=0$)			
c	$\left(\frac{a}{h}\right)^{1/3}$	$-6(hd^2)^{1/3}$ 	$\frac{3}{4}\left(\frac{a^4}{h}\right)^{1/3}$ 
d	$0,\pm\left(\frac{b_{11}}{h}\right)^{1/2}$	$-b_{11},2b_{11}$	$E_c,E_c+\frac{b_{11}^2}{16h}$

[a]Notation: ////// unstable, ——— stable solution.

classification) in alternant hydrocarbons. Space unsymmetrical solutions also branch out from the symmetric one if the threshold matrix $\mathbf{D}_{(1)}$ belongs to the one-dimensional but not the identity representation of the symmetry group [12]. However in the latter case, e.g. in butadiene, and in asymmetric systems, e.g. heteronuclear diatomic molecule [15] the new solution emerges "from the air" according to eqn. (7).

Near the two-dimensional threshold the latter type of behaviour may lead to a rather complicated structure of the potential energy surface (see for example, Fig. 1).

If the perturbation is characterized by more than one degree of freedom, e.g. by symmetric and antisymmetric combinations of nuclear displacements, the threshold on the two-dimensional potential surface is the origin of the Whithey fold (Fig. 2, point T).

The pictures corresponding to cases "d" and "c", respectively are observed in two orthogonal sections passing through the threshold T while in the dis-

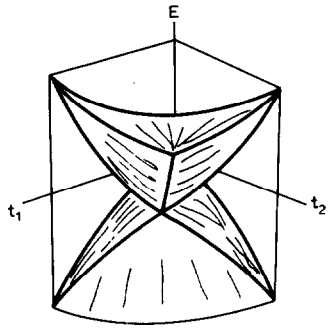


Fig. 1. The potential energy surface at the double-degenerate emergence point.

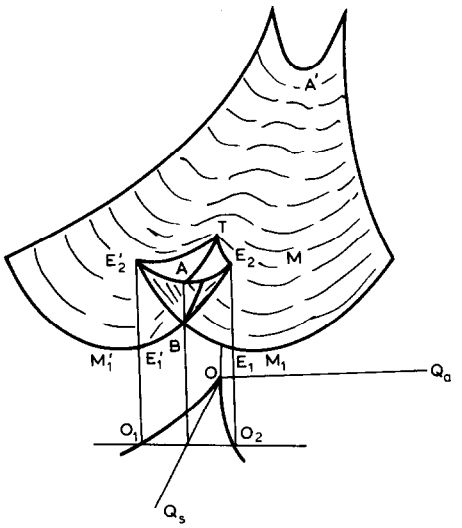


Fig. 2. The threshold on the two-dimensional energy surface.

placed sections (where $g \neq 0$) we have pictures corresponding to case "a". The upper unstable sheet contains the symmetric minimum, and the lower degenerate stable minimum is situated on the self-intersection line of the potential surface. The dynamic instability, which means the potential surface negative curvature (in a section $Q_s = \text{const}$)

$$k = k_0 - 2 \sum_i a_i^2/\lambda_i \qquad \text{Sp} \frac{\partial \mathbf{F}}{\partial Q_a} \mathbf{D}_{(i)} = a_i \tag{14}$$

appears in the point A′ which precedes the threshold T when going along a symmetric coordinate towards the instability region.

The parameters which determine the position of the potential surface characteristic points are expressed through the threshold parameters h, a

$$n = \text{Sp}\, \mathbf{D}_1^2 \mathbf{Y} \frac{\partial \mathbf{F}}{\partial Q_s} - 4 \sum_s g_{oos} a_s/\lambda_s \tag{15}$$

and through the displacement $Q_s > 0$ of the considered cross section from the threshold along the symmetric coordinate. The heights of the points E_2, E_1 and B relative to A are approximately, $-n^2Q_s^2/48h, n^2Q_s^2/6h, n^2Q_s^2/16h$. The slopes of the curves E_2BE_1' and $E_2'BE_1$ at E_2, E_2' and at B are $\pm(-nQ_s/6h)^{\frac{1}{2}}a/4$ and $\pm(-nQ_s/2h)^{\frac{1}{2}}a$, respectively $(h<0)$. The curvature of $E_2'AE_2$ is decreased by $\frac{5}{4}a^2/nQ_s$ when going from A to E_2.

It is worthwhile noting that positions of the unstable A and stable point B and the slope at B may be obtained by means of a standard calculation of the HF potential energy surface without any use of the threshold theory. Then varying the symmetric coordinate x (space scale factor) and repeating calculation of the quantities mentioned for several values of x we can determine the threshold parameter combinations n^2/h, and a^2/n and its distance Q_s from the considered points A, B if the x-dependence of $E_A - E_B$ is approximated by a suitable parabola: $E_A - E_B = -n^2/16h(x-Q_s)^2$. After this we can build the curve $0_1 00_2$ in the (Q_s, Q_a)-plane: $Q_s = \kappa Q_a^{\frac{3}{2}}$, where $\kappa = -3(2ha^2)^{\frac{1}{2}}/n = -3(2a^2/n{:}n^2/h)^{\frac{1}{2}}$ and reconstruct the positions of the points E_2, E_2' which cannot be found by means of a standard calculation. The displacement of the minima M_1 from that in the $Q_s = 0$ plane (M) can be also calculated: energy lowering is $4a^2nQ_s/9hk$.

The space-projected HF solution, i.e. the arithmetic mean of the two HF wavefunctions existing in the point B, lowers the position of the point B and smooths the curve E_1BE_1'. This lowering $(-n\Delta/8h)Q_s$ is linearly increased and may exceed that of M_1 if the energy of singlet excitation at the threshold Δ is greater than $\frac{32}{9}a^2/k$.

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