PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOL. 3, NO. 2 FEBRUARY 1971

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

The Nonanalytic Behavior of the Broken-Symmetry Solutions at the Branching Point†

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(Received 12 August 1970)

It is shown that both the energy and the wave function of the stable Hartree-Fock solution are nonanalytic functions of the coupling constant at the branching point, dividing the symmetry-adapted and the broken-symmetry solutions. The π-electronic model of benzene is used to illustrate this fact for the case of the Hartree-Fock singlet instability. It is indicated that the same type of nonanalytical behavior is found in other types of instabilities, i.e., nonsinglet (triplet) instabilities for closed shells and doublet instabilities for simple open shells. This nonanalyticity persists even after the projection on the totally symmetric subspace is carried out, and can only be avoided by projecting before the variational principle is applied.

As is well known,[1] the energy difference between normal and superconducting states depends on the *nonanalytic* function of the coupling constant. This was the main reason for the failure of the early attempts to explain the superconductivity phenomenon using the perturbation theory. Consequently, this problem has received considerable attention in the theory of superconductivity.

We would like to point out in this paper that a very similar nonanalytical behavior may occur in the Hartree-Fock (HF) problems of the electronic structure of the atomic and molecular systems, when currently used quantum-chemical methods are applied. Indeed, the HF solutions, describing the electronic structure of the atomic and molecular systems, may display various types of instabilities[2] with respect to the charge and spin-density fluctuations, leading to different broken-symmetry HF solutions. These instabilities are, formally, not unlike the instabilities leading to the violation of particle-number conservation laws,[3] which are essential in the BCS-Bogoliubov theory of superconductivity.

In previous papers[2] of this series, we have rederived the Thouless's stability conditions for the solutions of the HF equations and specified them to the closed-shell (Paper I) and the simple open-shell (Paper II) electronic systems with spin-independent Hamiltonian. This enabled a useful classification of the instabilities on the singlet and nonsinglet (triplet) ones in the closed-shell case, and on the doublet and nondoublet ones in the simple open-shell case. Moreover, various cases of the instabilities of the symmetry-adapted HF solutions for the π-electronic systems, described by the Pariser-Parr-Pople–type model Hamiltonian, have been demonstrated (Papers I, III, IV, and VI). Finally, simple rules have been formulated (Papers III and IV) for the π-electronic-model systems, based on the symmetry properties of the pertinent Kekulé structures, which determine whether the given symmetry-adapted HF solution will be always singlet stable or whether it may become singlet unstable. In the latter case we find, generally, that while the symmetry-adapted HF solution may be stable for small enough coupling constant λ, it will become unstable when the coupling constant is sufficiently increased. In this case, one can always determine the critical values λ_0 of the coupling constant λ, such that the symmetry-adapted HF solution is singlet stable for $\lambda < \lambda_0$ and unstable when $\lambda > \lambda_0$. Analogously, the critical values λ_0' may be determined for other than singlet instabilities. Clearly, in the instability region $\lambda > \lambda_0$, another HF solution(s), violating some conservation law, while having lower energy than the symmetry-adapted HF solution, exist(s). We will show in this paper that both the energy and the wave function (or density matrix) of the *stable* HF solution are nonanalytic functions of the coupling constant λ at the branching point $\lambda = \lambda_0$, corresponding to the onset of the instability of the symmetry-adapted HF solution.

In other words, we will show that the broken-symmetry HF solutions, which constitute the ground state of the system in the instability region $\lambda > \lambda_0$, do not represent an analytical continuation of the symmetry-adapted HF solutions, constituting the ground state in the stable region $\lambda < \lambda_0$.

We shall illustrate this phenomenon on the simplest possible model case, namely the singlet instability of the benzene π-electronic model, for which the energy and the density matrices may be expressed in a closed form. We have shown in Paper I, that this simple model will display the singlet instability if a large enough coupling constant is chosen.

The model Hamiltonian used in these calculations as well as various parametrization schemes for this model have been described in detail in previous papers, as well as in the subsequent Paper VI. We shall, therefore, limit ourselves here to merely giving the model Hamiltonian for our special case of the alternant nonheterocyclic π-electronic systems, in a tight-binding approximation. This Hamiltonian may be conveniently written, in the second-quantized form, as follows:

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

where $a^{\dagger}_{\mu\sigma}$ and $a_{\mu\sigma}$ are the creation and the annihilation operators, respectively, defined on the basis of Löwdin orthonormalized carbon $2p_z$ atomic orbitals, β is the nearest-neighbor resonance integral, and $\gamma_{\mu\nu}$ are the Coulomb repulsion integrals

$$\gamma_{\mu\nu} = \langle \mu\nu | e^2/r_{12} | \mu\nu \rangle .$$

The prime on the first summation symbol means that only the terms for which μ and ν are nearest neighbors are included.

Numbering the benzene atomic orbitals along the cycle from 1 to 6, and realizing that the pertinent Hamiltonian is invariant with respect to the operations of the point group D_{6h}, we can define conveniently the coupling constant λ as follows:

$$\lambda = \tfrac{1}{6}(\gamma_{12} - \gamma_{14})/|\beta| .$$

The singlet-stability condition for the symmetry-adapted HF solution, which is given fully by the symmetry of this simple model, gives[4] $\lambda < 1$. Consequently, in the instability region $\lambda > 1$, the broken- (space) symmetry solution, having lower energy than the symmetry-adapted solution, must exist. Clearly, the branching point, dividing the stability and instability regions, corresponds to $\lambda = 1$. The difference ΔE between the energy E_B of the broken-symmetry HF solution and the energy E_S of the symmetry-adapted HF solution $\Delta E = E_B - E_S$ may be expressed through the coupling constant λ as follows:

$$\Delta E(\lambda) = 2 - \lambda - 1/\lambda, \quad \lambda \geq 1$$

$$\Delta E(\lambda) = 0, \quad \lambda < 1 .$$

In this expression, the energy difference $\Delta E(\lambda)$ is expressed in terms of $|\beta|$ units. The graphical representation of this dependence is shown in Fig. 1, where we have also indicated the physically meaningless part for $\lambda < 1$ by the dashed line. Clearly, the symmetry-adapted HF solution represents the stable ground state in the region $\lambda < 1$, while the broken-symmetry HF solution(s) represent the stable ground state for $\lambda > 1$.

We now observe that while the energy difference $\Delta E(\lambda)$, as well as its first derivative $d(\Delta E)/d\lambda$, are continuous functions of λ, the higher derivatives are not, having the discontinuity at the branching point $\lambda = 1$. Indeed, calculating the second derivative at the point $\lambda = 1$, as a limit from the left-hand side and from the right-hand side, we obtain

$$d^2(\Delta E)/d\lambda^2 |_{\lambda = 1(+0)} = -2,$$

while

$$d^2(\Delta E)/d\lambda^2 |_{\lambda = 1(-0)} = 0.$$

Consequently, there is a nonanalyticity of $\Delta E(\lambda)$ at

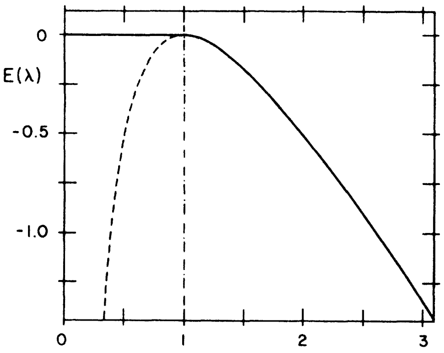

FIG. 1. Dependence of the energy E (in units of the resonance integral $|\beta|$) of the stable-restricted HF solution for the π-electronic model of benzene on the coupling constant λ (defined in the text). The dashed line corresponds to the physically meaningless continuation of the energy of the broken- (space) symmetry solution into the region, where the symmetry-adapted solution is stable and represents the ground state of the system.

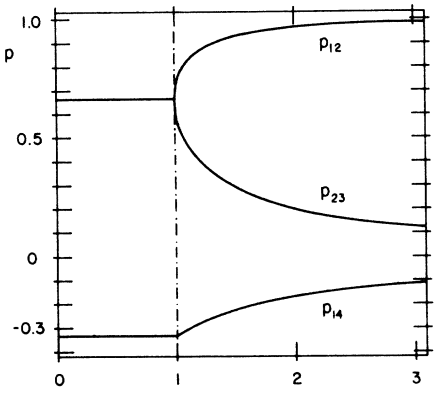

FIG. 2. Dependence of the first-order density (bond-order) matrix elements p_{12}, p_{23}, and p_{14} of the stable-restricted HF solutions of the π-electronic model of benzene as a function of the coupling constant λ (defined in the text).

$\lambda = 1$ so that $\Delta E(\lambda)$ is not an entire function of λ.

Let us now examine the behavior of the first-order density matrix in the atomic-orbital representation (i.e., the so-called atomic-charge and bond-order matrix) as a function of the coupling constant. Since we consider only alternant solutions, we shall always have

$$p_{\mu\mu} = 1, \qquad p_{\mu,\mu+2\nu} = 0.$$

Consequently, it is sufficient to consider the elements $p_{\mu\nu}$, where μ and ν differ by 1 or 3 (modulo 6). In the stable region $\lambda < 1$, these are well-known benzene-bond orders

$$p_{12} = p_{23} = \tfrac{2}{3}, \quad p_{14} = -\tfrac{1}{3}.$$

However, in the unstable region we get

$$\left.\begin{matrix} p_{12} \\ p_{23} \end{matrix}\right\} = \tfrac{1}{6}\{1 + 3\lambda \pm 3[(\lambda - 1)(\lambda + \tfrac{1}{3})]^{1/2}\}/\lambda \,,$$

$$p_{14} = -\tfrac{1}{3}/\lambda; \;\; \lambda \geqslant 1.$$

These results are shown in Fig. 2. We find immediately from the above relations that already the first derivative is discontinuous at $\lambda = 1$, since

$$\left.\frac{dp_{12}}{d\lambda}\right|_{\lambda=1(+0)} = +\infty; \qquad \left.\frac{dp_{23}}{d\lambda}\right|_{\lambda=1(+0)} = -\infty \,,$$

and

$$\left.\frac{dp_{14}}{d\lambda}\right|_{\lambda=1(+0)} = \frac{1}{3},$$

while

$$\left.\frac{dp_{\mu\nu}}{d\lambda}\right|_{\lambda=1(-0)} = 0.$$

Finally, it is interesting to notice the behavior of the broken-symmetry solution for $\lambda \to \infty$. The above relationships yield

$$\lim_{\lambda\to\infty} p_{12} = 1, \quad \lim_{\lambda\to\infty} p_{23} = \lim_{\lambda\to\infty} p_{14} = 0,$$

which means that the stable solution for $\lambda \to \infty$ corresponds to the three separated "ethylene" molecules.

The same type of the nonanalytical behavior may also be found in cases of other-type instabilities, namely in the case of nonsinglet (triplet) and doublet instabilities,[2] as may be easily illustrated in very much the same way as above on the simple π-electronic models of the ethylene molecule and the allyl radical, respectively. Indeed, using the analytical expressions given in Paper IV, one can easily verify the same type of the nonanalytical behavior for allyl radical, as already apparent from Fig. 3 of Paper IV.

In conclusion we can state that the nonanalytical behavior of the broken-symmetry HF solution indicates that this solution is not suitable as a starting point for a calculation of the correlation effects.

Moreover, it is not difficult to see that also the symmetry-adapted component, which may be projected out of the broken-symmetry HF solution, will display the same type of nonanalytical properties. Consequently, the only way to avoid this difficulty is to perform the projection prior to the application of the variational procedure, i.e., to use the multiconfigurational self-consistent-field (SCF) wave function. In this case the nonanalyticity disappears, and the resulting wave function represents an appropriate starting point for the calculations going further beyond the independent-particle picture.

This work has been supported by the National Research Council of Canada, by the Department of University Affairs of Ontario, and by the University of Waterloo Research Committee grants, which we hereby gratefully acknowledge.

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*For the previous Papers I–IV, see Ref. 2.

†Quantum Theory Group article No. M-110.

[1] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, New York, 1959).

[2] J. Čížek and J. Paldus, J. Chem Phys. 47, 3976 (1967), Paper I; J. Paldus and J. Čížek, Chem. Phys. Letters 3, 1 (1969), J. Chem. Phys. 52, 2919 (1970), Paper II; J. Čížek and J. Paldus, *ibid.*, 53, 821 (1970), Paper III; J. Paldus and J. Čížek, *ibid.* (to be published), Paper IV; Phys. Rev. (to be published), (Paper VI).

[3] J. Paldus and J. Čížek, J. Polymer Sci. C 29, 199 (1970).

[4] Note that this is equivalent with the condition given in Paper III, Eq. (15).