

ON THE DIFFERENT TYPES OF STATES OF A ONE DIMENSIONAL SYSTEM OF
ELECTRONS IN THE HARTREE-FOCK METHOD

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We consider the different types of ground states of one-dimensional lattice gas of electrons. Interactions between electrons on the same lattice point and on neighboring lattice points are taken into account. The treatment is based on Hartree-Fock approximation for an unbounded system. Regions of the parameter space of the electron-electron interaction are found corresponding to the existence of mixed solutions (i.e., diagonal and nondiagonal long-range order are present simultaneously). It is shown that the ground state of the system always corresponds to one of the pure types of order (only diagonal or only nondiagonal long-range order) and that diagonal order is present in the ground state. Conditions for the stability of the pure solutions against various perturbations are found.

A natural strategy for the study of the properties of quasi-one-dimensional dipole-acceptor crystals or polymer materials is as follows. Instead of looking for possibly more exact solutions of the problem for one-dimensional structure (sheets of molecules, polymer chains), one attempts to provide an adequate description of the interaction between sheets or chains, where each sheet or chain is assumed to be in a certain ordered state. For example, the antiferromagnetic state in Bechgard salts has been treated in terms of sheets of molecules in the spin-density-wave state [1]. Resonant interactions between sheets were taken into account and the transition temperature of the crystal into the antiferromagnetic state was estimated. The molecules of a polymer with continuous conjugation in the main chain and with free radical substituents form a state with a large spin proportional to the number of substituents. It is only because of resonant interactions between chains that these molecules (considered as a single system) can transform into the ferromagnetic state, i.e., form an organic ferromagnet [2]. As for the accuracy required in the description of the separate chains or sheets, it turns out that in quasi one-dimensional problems an adequate approximation for the theoretical treatment of one-dimensional structures [1, 2] and for the interpretation of experimental data (see [3], for example) is the one-particle representation and the states characteristic for one-dimensional problems in the self-consistent field approximation (Hartree-Fock method for an infinite system). The different types of states are: spin-density-wave states (SW), charge-density-wave states (CW), and bond-ordering-wave states (BOW). In spite of much effort [4-6], the problem of describing the different types of states of a one-dimensional structure in the Hartree-Fock approximation is still far from completely solved. For example, the existence of the mixed states SW-BOW and CW-BOW was correctly established in [6] but the regions of the parameter space corresponding to these states were determined incorrectly.

In the present paper we give a general method for determining the different types of states in one-dimensional systems in the Hartree-Fock approximation and we study the stability of these states.

ONE-ELECTRON DENSITY MATRIX FOR POLYENE WITH BROKEN SYMMETRY OF
THE DOUBLE PERIOD TYPE

We consider the example of cyclic polyene $(CH)_N$ (N is even) in the π -electron approximation. The electronic structure of the ground state in the Hartree-Fock approximation is, in the second quantization formalism

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$$\Phi = \prod_{|k| < k_F} \hat{f}_{k\beta}^{\dagger} \hat{f}_{k\alpha}^{\dagger} |0\rangle, \quad k = 2\pi j/N, \quad -N/2 \leq j \leq N/2, \quad k_F = \pi/2, \quad (1)$$

where the operators

$$\hat{f}_{k\sigma} = x_{k\sigma} a_{k\sigma} + y_{k\sigma} a_{\bar{k}\sigma}, \quad \bar{k} = k + 2k_F, \quad (2)$$

correspond to filled molecular orbitals and the operators

$$\tilde{f}_{k\sigma} = -y_{k\sigma}^* a_{k\sigma} + x_{k\sigma}^* a_{\bar{k}\sigma}. \quad (3)$$

correspond to free molecular orbitals. In (2) and (3) $a_{k\sigma}$ is the destruction operator of an electron in state with quasimomentum k and spin projection σ

$$a_{k\sigma} = N^{-1/2} \sum_n \exp(-ikn) c_{n\sigma}, \quad (4)$$

where $c_{n\sigma}$ is the destruction operator of an electron with spin projection σ on atom n . The coefficients $x_{k\sigma}$ and $y_{k\sigma}$ satisfy the condition

$$|x_{k\sigma}|^2 + |y_{k\sigma}|^2 = 1$$

and can be expressed in terms of the real parameters $\theta_{k\sigma}$ and $\varphi_{k\sigma}$

$$x_{k\sigma} = \cos \theta_{k\sigma}, \quad y_{k\sigma} = \sin \theta_{k\sigma} \exp(i\varphi_{k\sigma}). \quad (5)$$

The operators $\hat{f}_{k\sigma}$ and $c_{n\sigma}$ are related by

$$\hat{f}_{k\sigma} = N^{-1/2} \sum_n (x_{k\sigma} + (-1)^n y_{k\sigma}) \exp(-ikn) c_{n\sigma}. \quad (6)$$

The elements of the one-particle density matrix in the node representation have the form

$$\langle c_{n\sigma}^{\dagger} c_{m\sigma} \rangle = 1/2 + (-1)^n N^{-1} \sum_{|k| < k_F} (y_{k\sigma}^* x_{k\sigma} + x_{k\sigma}^* y_{k\sigma}), \quad (7)$$

$$\langle c_{n\sigma}^{\dagger} c_{m\sigma} \rangle = N^{-1} \sum_{|k| < k_F} \exp[ik(n-m)] \{ |x_{k\sigma}|^2 - |y_{k\sigma}|^2 + (-1)^n (x_{k\sigma}^* y_{k\sigma} - y_{k\sigma}^* x_{k\sigma}) \},$$

where the expectation value $\langle \dots \rangle$ is evaluated using (1).

According to (7), the elements of the density matrix corresponding to a symmetry breaking of the double period type can be represented in the form

$$\langle c_{n\sigma}^{\dagger} c_{n\sigma} \rangle = 1/2 + (-1)^n \delta_{\sigma}, \quad \langle c_{n\sigma}^{\dagger} c_{n+1\sigma} \rangle = P_{\sigma} + (-1)^n \Delta_{\sigma}. \quad (8)$$

Assuming that the elements of the density matrix are real, we obtain from (5), (7), and (8)

$$\theta_{-k\sigma} = \theta_{k\sigma}, \quad \varphi_{-k\sigma} = -\varphi_{k\sigma}$$

and

$$\delta_{\sigma} = N^{-1} \sum_{|k| < k_F} \sin 2\theta_{k\sigma} \cos \varphi_{k\sigma}, \quad P_{\sigma} = N^{-1} \sum_{|k| < k_F} \cos k \cos 2\theta_{k\sigma},$$

$$\Delta_{\sigma} = N^{-1} \sum_{|k| < k_F} \sin k \sin 2\theta_{k\sigma} \sin \varphi_{k\sigma}. \quad (9)$$

Analysis of (8) and (9) shows that a pure charge-density-wave state (or pure spin-density-wave state) corresponds to $\varphi_{k\sigma} = 0$ and a pure bond-ordering-wave state corresponds to $\varphi_{k\sigma} = \pi/2$.

MIXED STATES IN THE HARTREE-FOCK APPROXIMATION WITH EXPANDED HUBBARD HAMILTONIAN

As the simplest model taking into account the effects of Coulomb interactions, we consider the expanded Hubbard Hamiltonian for polyene with identical bond lengths

$$H = -\beta \sum_{n,\sigma} (c_{n\sigma}^{\dagger} c_{n+1\sigma} + c_{n+1\sigma}^{\dagger} c_{n\sigma}) + \gamma_0 \sum_n c_{n\alpha}^{\dagger} c_{n\alpha} c_{n\beta}^{\dagger} c_{n\beta} +$$

$$+ \gamma_1 \sum_{n,\sigma,\rho} c_{n\sigma}^{\dagger} c_{n\sigma} (c_{n+1\rho}^{\dagger} c_{n+1\rho} + c_{n-1\rho}^{\dagger} c_{n-1\rho}) - 2\gamma_1 \sum_{n,\sigma} c_{n\sigma}^{\dagger} c_{n\sigma} + N\gamma_1, \quad (10)$$

where $\beta > 0$ is the resonance integral; γ_0 and γ_1 are the parameters of the Coulomb interaction between electrons on one atom and electrons on neighboring atoms, respectively; the final term

in (10) takes into account the repulsion between positive ions of the σ -skeleton and the next-to-last term takes into account the attraction of electrons to the neighboring ions of the σ -skeleton.

The equations of motion of the operators $c_{n\sigma}$ have been discussed in [4, 7], for example. Linearization of these equations with the use of (7), which corresponds to the Hartree-Fock approximation for an unbounded system, gives for the molecular-orbital energy

$$E_{k\sigma} = \gamma_0/2 \pm R_{k\sigma}, \quad R_{k\sigma} = [e_\sigma^2 + 4b_\sigma^2 - 4(b_\sigma^2 - d_\sigma^2) \sin^2 k]^{1/2} \quad (11)$$

and the molecular orbitals themselves, according to (5) and (6), are given by the relations

$$\sin 2\theta_{k\sigma} \cos \varphi_{k\sigma} = e_\sigma/R_{k\sigma}, \quad \sin 2\theta_{k\sigma} \sin \varphi_{k\sigma} = 2d_\sigma \sin k/R_{k\sigma}, \quad (12)$$

were

$$e_\sigma = 2\gamma_1(\delta_\alpha + \delta_\beta) - \gamma_0\delta_{-\sigma}, \quad b_\sigma = \beta + \gamma_1 P_\sigma, \quad d_\sigma = \gamma_1 \Delta_\sigma. \quad (13)$$

From (11) the gap in the energy spectrum of the molecular orbitals at $k = k_F$ is given by

$$\Delta E_\sigma = 2(e_\sigma^2 + 4d_\sigma^2)^{1/2}. \quad (14)$$

Substituting (12) into (9) and changing from a sum to an integral, we obtain the self-consistency conditions (equations for δ_σ , Δ_σ , P_σ)

$$\begin{aligned} \delta_\sigma &= (e_\sigma/Q_\sigma) K(k_\sigma), \quad \Delta_\sigma = (2d_\sigma/Q_\sigma) D(k_\sigma), \\ P_\sigma &= (2b_\sigma/Q_\sigma) [K(k_\sigma) - D(k_\sigma)], \end{aligned} \quad (15)$$

where

$$Q_\sigma = \pi(e_\sigma^2 + 4b_\sigma^2)^{1/2}, \quad k_\sigma^2 = 4(b_\sigma^2 - d_\sigma^2)/(4b_\sigma^2 + e_\sigma^2),$$

and K and D are the complete elliptic integrals of the first and third kinds, respectively.

The system of equations (15) was used in [6] and it was found that in the approximation of a weak interaction ($\gamma_0/\beta \ll 1$, $\gamma_1/\beta \ll 1$) there exist only solutions of the "pure" type: SW ($\delta_\alpha = -\delta_\beta = \delta$, $\Delta_\sigma = 0$), CW ($\delta_\alpha = \delta_\beta = \delta$, $\Delta_\sigma = 0$), and BOW ($\delta_\sigma = 0$, $\Delta_\alpha = \Delta_\beta = \Delta$). It follows from (15) that for arbitrary values of the parameters

$$U_0 = \gamma_0/\beta, \quad U_1 = \gamma_1/\beta \quad (16)$$

there exist solutions which are asymmetric in the spin indices and correspond to bond ordering α spin density waves (BOWSW α) or bond ordering β spin density waves (BOWSW β)

$$\begin{aligned} \delta_\sigma &= 0, \quad \Delta_\alpha \neq 0, \quad \Delta_\beta = 0, \quad \text{BOWSW}\alpha; \\ \delta_\sigma &= 0, \quad \Delta_\alpha = 0, \quad \Delta_\beta \neq 0, \quad \text{BOWSW}\beta. \end{aligned}$$

The states BOWSW $\alpha(\beta)$ are always higher in energy than states with both the amplitudes Δ_σ non-zero. The solution of (15) with bond ordering spin density waves (BOSW) [6]

$$\delta_\sigma = 0, \quad \Delta_\alpha = -\Delta_\beta = \Delta \quad (\text{BOSW})$$

corresponds to the same energy as the state BOW ($\delta_\sigma = 0$, $\Delta_\alpha = \Delta_\beta = \Delta$), because the square of the parameter Δ_σ appears in the expression for the energy of the chain.

We find the regions of the parameter space (16) where solutions of the mixed type (SW-BOW or CW-BOW) can exist. The following conditions must be satisfied for the SW-BOW state:

$$\delta_\alpha = -\delta_\beta = \delta, \quad \Delta_\alpha = \Delta_\beta = \Delta, \quad P_\alpha = P_\beta = P. \quad (17)$$

Using (16) and (17) we obtain the solution of (15) in the form

$$P = (2U_1 - U_0)/2U_1(U_0 - U_1), \quad (18)$$

$$\delta^2 = \pi^{-2} [K^2(k) - \pi^2/(U_0 - U_1)^2], \quad (19)$$

$$\Delta^2 = \pi^{-2} (U_0^2/4U_1^2) [\pi^2/(U_0 - U_1)^2 - k^2 K^2(k)], \quad (20)$$

where k is determined by the transcendental equation

$$K(k)/D(k) = 2U_1/U_0. \quad (21)$$

From (21) and the inequality $1 \leq K(k)/D(k) \leq 2$ we find a restriction on the parameters U_0 and U_1 :

$$U_0/2 \leq U_1 \leq U_0 \quad (22)$$

Detailed information on the region corresponding to the SW-BOW state is found by analyzing the system of Cauchy-Bunyakovskii inequalities for the elements of the density matrix (8)

$$0 < \delta^2 < 1/4, \quad \Delta^2 > 0, \quad -1 \leq P \pm \Delta \leq 1. \quad (23)$$

The conditions (23) replace the inexact conditions for P , Δ , δ given in [6].

The region of the parameter space (U_0, U_1) for which the conditions (22) and (23) are satisfied corresponds to a narrow band on the phase diagram (U_0, U_1) which goes along the line $U_1 = U_0/2$ for $U_0, U_1 \ll 1$ and approaches the line $U_0 = U_1$ for $U_0, U_1 \gg 1$. This is established by solving (19)-(21) with the conditions (22) and (23) numerically and is supported by the analytical method in the region $U_0, U_1 \ll 1$. It is evident from the condition (22) that the SW-BOW state can exist only in the region $(U_0/2 \leq U_1)$ where the CW state exists (and is the ground state) [5-7]. Numerical calculations have shown that the energy of the SW-BOW state is higher than that of the CW state in the entire region where the SW-BOW state exists.

A similar situation takes place for the CW-BOW state

$$\delta_\alpha = \delta_\beta = \delta, \quad \Delta_\alpha = \Delta_\beta = \Delta, \quad P_\alpha = P_\beta = P. \quad (24)$$

It exists only in the region

$$U_0/3 \leq U_1 \leq U_0/2 \quad (25)$$

(which is strongly restricted by the conditions (23)), where the SW state is the ground state of the system. Using (16), and (24), we find the solution of (15) for the CW-BOW state

$$P = (U_0 - 2U_1)/2U_1(3U_1 - U_0), \quad (26)$$

$$\delta^2 = \pi^{-2} [K^2(k) - \pi^2/(3U_1 - U_0)^2], \quad (27)$$

$$\Delta^2 = \pi^{-2} [(4U_1 - U_0)^2/4U_1^2] [\pi^2/(3U_1 - U_0)^2 - k^2K^2(k)], \quad (28)$$

and k is given by

$$K(k)/D(k) = 2U_1/(4U_1 - U_0). \quad (29)$$

Numerical analysis of (26)-(29) and (23) shows that the CW-BOW state exists only inside a narrow region of the space (U_0, U_1) which extends along the line $U_1 = U_0/2$ for $U_0, U_1 \ll 1$ and approaches the line $U_1 = U_0/3$ as $U_0, U_1 \gg 1$. Analytical expressions for the region of existence of the SW-BOW state can be obtained in the limit of a weak interaction ($U_0, U_1 \ll 1$). In this case we expand the elliptic integrals K and D and keep terms proportional to $k'^2 = 1 - k^2$. Then, in contrast to [3], we obtain an exponentially narrow region corresponding to existence of the mixed SW-BOW state: $U_A \leq U_0 \leq 2U_1$, where $U_A = 2U_1[1 - (4U_1/\pi e^4)\exp(-2\pi/U_1)]$. We note that in the approximation of a weak interaction it is not possible to find mixed states in which SW and CW co-exist (i.e., states with $|\delta_\alpha| \neq |\delta_\beta| \neq 0$).

STABILITY OF THE DIFFERENT TYPES OF STATES

We discuss the stability of a given type of state against a transition into a state of a different type. We consider the total energy ε of the system per electron (in units of β) as a function of the independent parameters $e_\sigma, d_\sigma, b_\sigma$ determining the type of state. An expression for ε can be obtained in terms of the parameters of the self-consistent density matrix:

$$\varepsilon = -2 \sum_{\sigma} P_{\sigma} + U_0/4 - U_1 \sum_{\sigma} P_{\sigma}^2 + U_0 \delta_{\alpha} \delta_{\beta} - U_1 (\delta_{\alpha} + \delta_{\beta})^2 - U_1 \sum_{\sigma} \Delta_{\sigma}^2, \quad (30)$$

and then with the help of the self-consistency conditions (15) the energy can be written in terms of the variables $e_\sigma, d_\sigma, b_\sigma$, which are the natural variables of the Hartree-Fock self-consistent field approximation for an unbounded system. The physical meaning of the parameters $e_\sigma, d_\sigma, b_\sigma$ follows from their connection (13) with the parameters of the self-consistent density matrix.

The different types of solutions correspond to different stationary points $(e_\alpha, e_\beta, d_\alpha, d_\beta, b_\alpha, b_\beta)$ on the energy surface $\varepsilon(e_\sigma, d_\sigma, b_\sigma)$ as follows:

$$\text{SW} \quad (e, -e, 0, 0, b, b), \quad (31)$$

$$\text{CW} \quad (e, e, 0, 0, b, b), \quad (32)$$

$$\text{BOW} \quad (0, 0, d, d, b, b). \quad (33)$$

The stability of the SW solution against a transition into the BOW state is determined by the sign of the coefficient \mathfrak{D}_{SW} in an expansion of (30) about the point (31)

$$\varepsilon(e_\sigma, d_\sigma, b_\sigma) = \varepsilon_{\text{SW}} + \mathfrak{D}_{\text{SW}} d^2/2 + \dots$$

The stability of the CW state against a BOW perturbation of the density matrix is analyzed by expanding (30) about the point (32)

$$\varepsilon(e_\sigma, d_\sigma, b_\sigma) = \varepsilon_{\text{CW}} + \mathfrak{D}_{\text{CW}} d^2/2 + \dots$$

and the stability of the BOW state to a transition into the SW or CW state is studied by expanding (30) about the point (33)

$$\varepsilon(e_\sigma, d_\sigma, b_\sigma) = \varepsilon_{\text{BOW}} + \mathfrak{E}_{\text{SW}} e^2/2 + \dots,$$

$$\varepsilon(e_\sigma, d_\sigma, b_\sigma) = \varepsilon_{\text{BOW}} + \mathfrak{E}_{\text{CW}} e^2/2 + \dots$$

In these expansions

$$\mathfrak{D}_{\text{SW}} = \frac{1}{4b^2 + e^2} \left[\frac{4}{\pi} \frac{\sqrt{4b^2 + e^2}}{b} (2D - K) + \frac{8U_1}{\pi^2} (2D - K)(K - D) + \frac{4U_0}{\pi^2} K(K - D) - \frac{8U_1}{\pi^2} D^2 \right] \quad (34)$$

where the elliptic integrals are evaluated at the point

$$k^2 = 4b^2/(4b^2 + e^2),$$

and the expression for \mathfrak{D}_{CW} is obtained from (34) with the substitutions $U_0 \rightarrow 4U_1 - U_0$;

$$\mathfrak{E}_{\text{SW}} = \frac{1}{4b^2} \left\{ \frac{2}{\pi} D + \frac{2U_1}{\pi^2} D(K - D) - \frac{U_0}{\pi^2} K^2 + \frac{U_1 d^2}{\pi^2 b^2} \left[D^2 + 2 \left(\frac{K - D}{1 - k^2} - D \right) \right] \right\}. \quad (35)$$

The elliptic integrals in (35) are evaluated at the point $k^2 = 1 - d^2/b^2$, and \mathfrak{E}_{CW} is obtained from (35) with the substitution $U_0 \rightarrow 4U_1 - U_0$. Study of the signs of the expressions \mathfrak{D}_{SW} and \mathfrak{E}_{CW} in the limit $U_0, U_1 \ll 1$ shows that in the region corresponding to the SW state ($U_1 \leq U_0/2$) this state is stable against a transition into the BOW state and in the region corresponding to the CW state ($U_1 \geq U_0/2$) the SW state is unstable against a transition into the BOW state. In the same way, in the region corresponding to the CW state ($U_1 \geq U_0/2$), this state is stable against the BOW state, while in the region corresponding to the SW state ($U_1 \leq U_0/2$) the CW state is unstable against a transition into the BOW state. A study of the signs of \mathfrak{E}_{SW} and \mathfrak{E}_{CW} shows that the BOW state is always unstable; in the SW region it is unstable against a transition into the SW state and in the CW region it is unstable against a transition into the CW state. We did not analyze the stability of the mixed states SW-BOW and CW-BOW. We established only that they are always higher in energy than the SW or CW states, which are the ground states in the corresponding regions of the parameter space (U_0, U_1).

It would not be correct to assume that only the stable states with the lowest energies are of interest and can be compared with experiment. The minimum-energy principle for an isolated cyclic chain leads to a high-symmetry exact solution of little interest. The diversity of the properties of real systems (states with spin density waves, charge density waves, and so on) is due to additional interactions (the effects of the ends, substituents, and neighboring molecules; interactions between molecules belonging to the same chain, and so on). Certain types of such external periodic fields can be taken into account in the Hartree-Fock approximation for an unbounded system by means of a self-consistent perturbation of a certain symmetry and type. Therefore, the types of solution in the Hartree-Fock approximation for an unbounded system provide a basis for more complicated theories and for the interpretation of the experimental data [1-3].

Study of the stability of pure states in the Hartree-Fock approximation against different types of perturbations of the density matrix shows that near the boundary of the SW-CW transition the pure states are unstable against a BOW perturbation in the limit $U_0, U_1 \ll 1$. In real systems a perturbation of the BOW type is always carried in by the ends: at the ends of a polyene chain bond ordering is always higher than the average value in the chain. Hence even when $U_0, U_1 \sim 1$ [8], the real state is mixed near the ends.

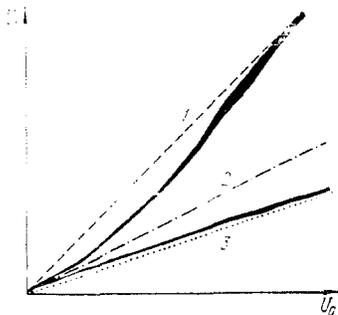


Fig. 1. Regions in the (U_0, U_1) plane corresponding to the existence of solutions of the equations of the Hartree-Fock method with mixed types of long-range order: 1) $U_1 = U_0$; 2) $U_1 = U_0/2$; 3) $U_1 = U_0/3$; the narrow shaded regions correspond to mixed solutions: SW-BOW for $U_1 > U_0/2$ and CW-BOW for $U_1 < U_0/2$.

We have also established that near the SW-CW boundary use of the leading logarithmic terms in the expansions of the elliptic integrals in (15) does not give a correct description of the solutions in the Hartree-Fock approximation for $U_0, U_1 \ll 1$ and higher order terms in the expansions must be taken into account. Hence a small external perturbation can strongly affect the type of state. Only when the higher-order terms are included are the mixed states SW-BOW and CW-BOW observed near this boundary; the energies of these mixed states approach the energies of the pure SW and CW states in the region $U_0, U_1 \rightarrow 0$. When $U_0, U_1 > 1$ the region corresponding to these mixed states is also very narrow and their energies become much higher than the energies of the pure states, which also shows up in the numerical calculations described above.

The existence of a narrow region near the SW-CW boundary implies that there are convergence problems with the self-consistency procedure in the Hartree-Fock approximation (see [7]). Such a region showed up near the boundary $U_1 = U_0/2$ in a Monte-Carlo study [9] of the phase diagram of a short ($N = 32$) chain using a Hubbard expanded Hamiltonian. It was shown in [9] that for small U_0, U_1 the transition SW \rightarrow CW is smooth with respect to the parameters U_0 and U_1 , whereas the transition becomes sharp for large U_0, U_1 . For large U_0 and U_1 (Fig. 1) there are no mixed states close in energy in the Hartree-Fock method near the boundary $U_1 = U_0/2$. Their existence in the region $U_1, U_0 \ll 1$ is explained by the fact that spin ordering in [9] persists above the boundary $U_1 = U_0/2$ into the CW region.

Finally, we note the effect of bond length alternation on certain types of solutions in the Hartree-Fock method. For example, in the case of polyene the energy per electron takes the form [4]

$$\varepsilon = \varepsilon_0 - \beta' \xi \sum_{\sigma} \Delta_{\sigma} + K_{\sigma} \xi^2/2, \quad (36)$$

where $\xi > 0$ is the displacement of the nucleus from its initial equibonded position, $\beta' = |\partial\beta/\partial\xi| > 0$, K_{σ} is the elastic constant of the σ -skeleton, and the quantity ε_0 is given by (30). It follows from (36) that bond length alternation removes the degeneracy of the BOW and SWBO states: the energy of the SWBO state ($\Delta_{\alpha} = -\Delta_{\beta}$) obtains a purely positive correction $K_{\sigma}\xi^2/2$, while the energy of the BOW state obtains the negative correction $-2\beta'\Delta\xi$.

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SPECTRAL AND SPIN DIFFUSION IN STATIONARY SATURATION OF ESR SPECTRA
OF PARAMAGNETIC CENTERS

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Theoretical and experimental approaches have been taken in a study of the feasibility of using the method of stationary saturation of ESR spectra in studying processes of dipole relaxation of paramagnetic centers in magnetically dilute solids. In the example of a system consisting of two kinds of paramagnetic centers, relaxation characteristics have been formulated by the stationary saturation method and the electron spin-echo method. It has been established that, with certain limitations and the use of a correct workup of the experiment, the stationary saturation method can be applied successfully in determining the relaxation characteristics of paramagnetic centers and features of their spatial position. Results obtained by this method are discussed in the example of systems in which electron-nucleus interaction makes a substantial contribution to the phase relaxation process.

In electron paramagnetic resonance (electron spin resonance, ESR), both stationary and pulse methods are used in measuring the relaxation characteristics of paramagnetic centers [1-4]. Among the stationary methods, extensive use has been made of the stationary saturation method, in which measurements are made of some particular characteristic of an ESR line Γ (area, amplitude, or amplitude of first or second derivative) as a function of the strength of the SHF (microwave) field H_1 in the resonator of the spectrometer. The relaxation parameters of the spin system are determined by subsequent treatment of the saturation curve $\Gamma(H_1)$. Methods for working up the saturation curves, based on a model of non-interacting spin packets of the Lorentz form [5], were developed in [6, 7]. As a result of processing the curves, the transverse and longitudinal relaxation times are found.

The sources responsible for transverse and longitudinal relaxation in magnetically dilute solids have been investigated in considerable detail [8-10]. Among these sources are spin-lattice coupling, modulation of dipole-dipole (d-d) coupling between electron spins by random turnovers due to spin-lattice coupling or mutual flip-flops (spectral diffusion SD in "type T_1 " or "type T_2 " specimens [8]), random modulation of electron-nucleus spin-spin coupling due to spin diffusion in the system of nuclear spins, and transfer of spin excitation between electron spins (SpD). In stationary saturation, each of these processes is assumed to be characterized by a single phenomenological parameter, i.e., the corresponding relaxation time; and the overall rate (reciprocal time) of transverse or longitudinal relaxation is taken as the sum of the rates of the individual processes.

In application to a pulse experiment, the model of noninteracting spin packets assumes an exponential law of decay of longitudinal and transverse magnetism: $\exp(-t/T_1)$ and $\exp(-t/T_2)$. However, studies of relaxation processes in magnetically dilute solids [10] have shown that by no means all of the processes giving rise to transverse and longitudinal relaxation will lead to an exponential law of decay. Therefore, a problem arises in describing correctly the

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