ELECTRONIC STRUCTURE OF KARBIN IN THE UNRESTRICTED HARTREE-FOCK APPROXIMATION

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We consider the electronic structure of a linear chain of carbon atoms in the π-electron approximation. We determine the values of the parameters for which different the values of the parameters for which different types of states with broken symmetry are the ground state. We compare our results with the results of other calculations and with experiment.

Recently various modifications of carbon have been obtained, many of which (see the review in [1]) are considered as crystals consisting of chains of carbon atoms of different lengths. In a number of cases [1], the differences between the modifications are connected with the difference between the polyyne structure $((-C\equiv)_N)$ and the cumulene structure $((=C=)_N)$, although such an interpretation is ambiguous.

The electronic structure of karbin as N → ∞ was calculated previously in different approximations [2-7]. Examination of this problem in the π-electron approximation in a simplified variant of the restricted Hartree-Fock (RHF) method [2, 3] led to the conclusion that there exists weak alternation of bond lengths in the chain. Calculations in the extended Hückel method (EHM) and CNDO/2 led to the same conclusions [5, 6].

In [4], the karbin molecule was considered in the π-electron approximation in terms of the unrestricted Hartree-Fock (UHF) method, taking into account the interaction of electrons found on the same carbon atom. It turned out that the state corresponding to alternation of the spin density in the cumulene case (as in the polyacetylene case) lies lower in energy than the RHF state. The possibility of alternation of bond lengths was not considered in [4]. Therefore the question concerning the type of ground state remains open. In polyene $(CH)_N$ with N → ∞, taking into account the interaction of electrons found on adjacent carbon atoms (the parameter γ_1 in formula (1)) leads to the need to consider states with alternating bond order (BOW) or alternating charge densities (CDW). States of the CDW type in karbin were considered in [7] in terms of a nonempirical calculations in a minimal basis. Let us consider a chain of N carbon atoms with cyclic boundary conditions in the π approximation with the Hamiltonian

$$\begin{aligned} H = &-\sum_{n,\sigma}\beta_{n,n+1}\left(a^+_{n\sigma}a_{n+1\sigma}+b^+_{n\sigma}b_{n+1\sigma}+\text{H.c.}\right)+\\ &\gamma_0\sum_n\left[a^+_{n\alpha}a_{n\alpha}a^+_{n\beta}a_{n\beta}+b^+_{n\alpha}b_{n\alpha}b^+_{n\beta}b_{n\beta}\right]+\gamma_0'\sum_{n,\sigma,\sigma'}a^+_{n\sigma}a_{n\sigma}b^+_{n\sigma'}b_{n\sigma'}+\\ &+\frac{\gamma_0-\gamma_0'}{4}\left\{\sum_{n,\sigma}\left(a^+_{n\sigma}b_{n\sigma}a^+_{n-\sigma}b_{n-\sigma}+b^+_{n\sigma}a_{n\sigma}b^+_{n-\sigma}a_{n-\sigma}\right)+\right.\\ &\left.\sum_{n,\sigma,\sigma'}\left(a^+_{n\sigma}b_{n\sigma}b^+_{n\sigma'}a_{n\sigma'}+b^+_{n\sigma}a_{n\sigma}a^+_{n\sigma'}b_{n\sigma'}\right)\right\}+\gamma_1\sum_{n,\sigma,\sigma'}\left[a^+_{n\sigma}a_{n\sigma}\left(a^+_{n+1\sigma'}a_{n+1\sigma'}+\right.\right.\\ &\left.+a^+_{n-1\sigma'}a_{n-1\sigma'}\right)+b^+_{n\sigma}b_{n\sigma}\left(b^+_{n+1\sigma'}b_{n+1\sigma'}+b^+_{n-1\sigma'}b_{n-1\sigma'}\right)\Big]+\\ &\gamma_1'\sum_{n,\sigma,\sigma'}\Big[a^+_{n\sigma}a_{n\sigma}\left(b^+_{n+1\sigma'}b_{n+1\sigma'}+b^+_{n-1\sigma'}b_{n-1\sigma'}\right)+b^+_{n\sigma}b_{n\sigma}\left(a^+_{n+1\sigma'}a_{n+1\sigma'}+\right.\\ &\left.a^+_{n-1\sigma'}a_{n-1\sigma'}\right)\Big]-2\left(\gamma_1+\gamma_1'\right)\sum_{n,\sigma}\left(a^+_{n\sigma}a_{n\sigma}+b^+_{n\sigma}b_{n\sigma}\right)+\frac{K_\sigma}{2}\sum_n\xi^2_{n,n+1}. \end{aligned} \tag{1}$$

In approximation (1), $a_{n\sigma}$ and $b_{n\sigma}$ are the electron creation operators at C atom with number n, spin projections σ = α, β in a and b subsystems, consisting of respectively the $2p_x$ and $2p_y$ atomic orbitals (AO) of the carbon (the z axis coincides with the molecular axis of the

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karbin). The first term in (1) is the resonance interaction of electrons in subsystems a and b. The resonance integral $\beta_{n,n+1} = \beta_0 + \beta'\xi_{n,n+1}$ depends on $\xi_{n,n+1} = (-1)^n\xi$, the distortions in the C–C bond length and the β' derivative of the resonance integral with respect to the distance between the C atoms. The second and third terms describe the Coulomb repulsion of the electrons on the same atom in the same and in different subsystems respectively. The fourth term represents the exchange interaction of electrons of different subsystems on the same carbon atom. The fifth and sixth terms are the Coulomb interaction of electrons on adjacent atoms of the chain in the same and in different subsystems respectively. The next-to-last term describes attraction of electrons to the core of adjacent carbon atoms. The last term is the elastic energy of the σ core. In order to determine the eigenfunctions of Hamiltonian (1), let us make use of the equation of motion method [4, 8]. Let us take the averages over the ground state:

$$\begin{aligned}\langle a^+_{n\sigma}a_{n\sigma}\rangle &= \frac{1}{2} + (-1)^n\delta_{a\sigma},\\ \langle b^+_{n\sigma}b_{n\sigma}\rangle &= \frac{1}{2} + (-1)^n\delta_{b\sigma},\\ \langle a^+_{n\sigma}a_{n+1\sigma}\rangle &= P_{a\sigma} + (-1)^n\Delta_{a\sigma},\\ \langle b^+_{n\sigma}b_{n+1\sigma}\rangle &= P_{b\sigma} + (-1)^n\Delta_{b\sigma},\end{aligned} \tag{2}$$

where $\delta_{\lambda\sigma}$, $\Delta_{\lambda\sigma}$, $P_{\lambda\sigma}$ are the parameters of the density matrix. Such a form for the averages corresponds to doubling the period of the solutions, compared with the perod of the original chain. The spectrum of the one-particle states will be

$$\varepsilon_{\lambda\sigma}(k) = \frac{1}{4}(\gamma_0 + 5\gamma_0') \pm \sqrt{e^2_{\lambda\sigma} + 4b^2_{\lambda\sigma} - 4(b^2_{\lambda\sigma} - d^2_{\lambda\sigma})\sin^2 k}, \tag{3}$$

where λ = a, b is the subscript of the subsystems a and b,

$$\begin{aligned}e_{a\sigma} &= -\left[\gamma_0\delta_{a,-\sigma} + (\gamma_0' - 2\gamma_1')(\delta_{b\alpha} + \delta_{b\beta}) - \frac{\gamma_0 - \gamma_0'}{2}\delta_{b\beta} - 2\gamma_1(\delta_{a\alpha} + \delta_{a\beta})\right],\\ b_{a\sigma} &= \beta_0 + \gamma_1 P_{a\sigma},\\ d_{a\sigma} &= \beta'\xi + \gamma_1\Delta_{a\sigma}.\end{aligned} \tag{4}$$

The one-electron spectrum has a gap for $k = k_F = \pi/2$

$$\Delta E_{\lambda\sigma} = 2\sqrt{e^2_{\lambda\sigma} + 4d^2_{\lambda\sigma}}. \tag{5}$$

The expressions for subsystem b are obtained by interchanging the subscripts a and b.

The self-consistency conditions for the parameters of the density matrix (DM) introduced into (2) have the form

$$\begin{aligned}\delta_{\lambda\sigma} &= \frac{e_{\lambda\sigma}}{\pi\sqrt{e^2_{\lambda\sigma} + 4b^2_{\lambda\sigma}}}K(k_{\lambda\sigma}),\\ \Delta_{\lambda\sigma} &= \frac{2d_{\lambda\sigma}}{\pi\sqrt{e^2_{\lambda\sigma} + 4b^2_{\lambda\sigma}}}D(k_{\lambda\sigma}),\\ P_{\lambda\sigma} &= \frac{2b_{\lambda\sigma}}{\pi\sqrt{e^2_{\lambda\sigma} + 4b^2_{\lambda\sigma}}}(K(k_{\lambda\sigma}) - D(k_{\lambda\sigma})),\\ k^2_{\lambda\sigma} &= 4(b^2_{\lambda\sigma} - d^2_{\lambda\sigma})/(e^2_{\lambda\sigma} + 4b^2_{\lambda\sigma}),\end{aligned} \tag{6}$$

where K and D are the complete integrals of the first and third kind respectively.

The self-consistency cndition for ξ:

$$\xi = \frac{2\beta'}{K_\sigma}\sum_{\lambda\sigma}\Delta_{\lambda\sigma} \tag{7}$$

represents the "bond length–bond order" formula for karbin.

The trivial solution for the system of equations (6) and (7) (or the RHF solution for a chain of equal bonds) has the form:

$$P_{\lambda\sigma} = 1/\pi, \; \delta_{\lambda\sigma} = \Delta_{\lambda\sigma} = \xi = 0.$$

This solution, without a gap in the one-electron spectrum, coincides with the solution of the simple Hückel method: plane waves.

All the solutions to system (6) with doubled period of the chain can be separated into symmetric and antisymmetric solutions relative to rotation by $\pi/2$ about the molecular axis. In the symmetric solution case, the phases of the charge density waves (CDW), the spin density waves (SDW), and the bond order waves (BOW) coincide in subsystem a and b. We will designate these solutions as in-phase waves: SDW/+, CDW/+, BOW/+. In the antisymmetric solution case, the waves in subsystems a and b have opposite phases. We will designate such solutions as out-of-phase waves: SDW/–, CDW/–, BOW/–.

Let us consider the system of equations (6) and (7) for $\beta' = 0$. In this case, all the self-consistent solutions have identical wavelengths ($\xi = 0$). The energy of the karbin (here and later, calculated per electron) is determined by the expression

$$\begin{gathered}\varepsilon_0 = -\beta_0 \sum_{\lambda\sigma} P_{\lambda\sigma} + \frac{\gamma_0}{2}(\delta_{a\alpha}\delta_{a\beta} + \delta_{b\alpha}\delta_{b\beta}) + \frac{\gamma_0'}{2}(\delta_{a\alpha} + \delta_{a\beta})(\delta_{b\alpha} + \delta_{b\beta}) - \\ \frac{\gamma_0 - \gamma_0'}{4}(\delta_{a\alpha}\delta_{b\alpha} + \delta_{a\beta}\delta_{b\beta}) - \frac{\gamma_1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}^2 - \frac{\gamma_1}{2}\sum_{\lambda\sigma}\Delta_{\lambda\sigma}^2 - \\ \frac{\gamma_1}{2}[(\delta_{a\alpha} + \delta_{a\beta})^2 + (\delta_{b\alpha} + \delta_{b\beta})^2] - \gamma_1'(\delta_{a\alpha} + \delta_{a\beta})(\delta_{b\alpha} + \delta_{b\beta}) + \frac{\gamma_0}{4} + \frac{\gamma_0'}{2} + \frac{\gamma_0 - \gamma_0'}{8},\end{gathered} \tag{8}$$

where $\delta_{\lambda\sigma}$, $\Delta_{\lambda\sigma}$ and $P_{\lambda\sigma}$ are the solutions to the equations in (6). The expressions for the energy in different types of states will be

$$\begin{gathered}\varepsilon_0(\mathrm{SDW}/+) = \Gamma - \delta^2\left(\gamma_0 + \frac{\gamma_0 - \gamma_0'}{2}\right), \\ \varepsilon_0(\mathrm{SDW}/-) = \Gamma - \delta^2\left(\gamma_0 - \frac{\gamma_0 - \gamma_0'}{2}\right), \\ \varepsilon_0(\mathrm{CDW}/+) = \Gamma + \delta^2\left(\gamma_0 + 2\gamma_0' - \frac{\gamma_0 - \gamma_0'}{2} - 4\gamma_1 - 4\gamma_1'\right), \\ \varepsilon_0(\mathrm{CDW}/-) = \Gamma + \delta^2\left(\gamma_0 + 2\gamma_0' + \frac{\gamma_0 - \gamma_0'}{2} - 4\gamma_1 + 4\gamma_1'\right), \\ \varepsilon_0(\mathrm{BOW}/+) = \varepsilon_0(\mathrm{BOW}/-) = \Gamma - 2\gamma_1\Delta^2,\end{gathered} \tag{9}$$

where

$$\begin{gathered}P = P_{\lambda\sigma}, \quad \Delta = |\Delta_{\lambda\sigma}|, \quad \delta = |\delta_{\lambda\sigma}|, \\ \Gamma = -2\gamma_1 P^2 - 4\beta_0 P + \frac{3}{8}(\gamma_0 + \gamma_0').\end{gathered}$$

We will not consider here other solutions to system (6) (for example, in-phase and out-of-phase spin density waves for the bond order, or solutions with different types of ordering in different subsystems).

For $\beta' \neq 0$, we will have $\xi \neq 0$ and the energy of the karbin is is determined by the expression

$$\varepsilon = \varepsilon_0 - \beta'\xi\sum_{\lambda\sigma}\Delta_{\lambda\sigma} + \frac{K_\sigma}{4}\xi^2, \tag{10}$$

where ξ and $\Delta_{\lambda\sigma}$ are the solutions to the self-consistency equations (6) and (7), while ε_0 is determined by formula (8), in which the MP parameters are also determined from (6) and (7).

In [9, 10], it was shown that in large systems, as a result of electron correlation effects the interelectron interaction is renormalized so that the two-center Coulomb integrals $\gamma_{m,n}$ increase exponentially with the separation between the centers, going to the constant γ_{1N}.

If we take into account the fact that the PPP Hamiltonian allows for one more renormalization: $\gamma_0 = \gamma_{11} - \gamma_{1N}$, $\gamma_1 = \gamma_{12} - \gamma_{1,N}$, $\cdots$ [11], then, using the values of γ_{mn} from [10], we find that the one-center parameter γ_0 has the value 5.5 eV, while $\gamma_1 = \gamma_1' = 2.5$ eV. The resonance parameter β_0 was determined as in the PPP method: $\beta_0 = 2.371 \cdot S(1.30)/S(1.397) = 2.78$ eV, where S is the overlap integral for the π-AO's. The energies in the states with $\xi \neq 0$ are determined by the parameters β' and K_σ. Let us set $K_\sigma = 48$ eV/Å², which practically coincides with K_σ in polyacetylene. Such an approximation is reasonable, since first of all the parameters of the σ zones, determined from the Auger spectra, are close in polyacetylene and karbin [12]; and secondly, in the calculation of the structure of diacetylene by the Hückel-Lennard-Jones method with self-consistent determination of the bond orders and bond lengths we found [13] that the parameter $\omega = 2\beta'/K_\sigma = 0.15$, which is close to the corresponding value $\omega = 0.18$ in polyenes. Such a decrease in ω is not so great as assumed in [2], and corresponds to a decrease in β' down to the value $\beta' = 3.6$ eV/Å with unchanged K_σ.

Among the states with $\xi = 0$, the SDW/+ state has the lowest energy if $\gamma_0' > 4\gamma_1 - \gamma_0$. Otherwise, CDW/+ has this energy. As is evident from formula (5), all the states with alternation of spin density, charge density, or bond order have a gap in the one-electron spectrum. For $\gamma_0' = 4.65$ eV, the gap in the one-electron spectrum for the SDW/+ state is $\Delta E = 1.18$ eV. For $K_\sigma = 48$ eV/Å² and $\beta' = 3.6$ eV/Å², the energies of the BOW/+ states with $\xi \neq 0$ are lower than the energies of the SDW/+ states if $\gamma_1 > 2.0$ eV. For $\gamma_1 < 2.0$ eV, the conclusion in [4] that the ground state of cumulene is the SDW/+ state remains in force. For $\gamma_1 = 2.5$ eV, in the BOW/+ state the bond length length alternation parameter is $\xi = 0.06$ Å, and the size of the gap in the one-electron spectrum is equal to 1.91 eV, which is significantly greater than the experimental value of 1 eV [12]. The magnitude of the alternation parameter that we obtained is significantly smaller than in the nonempirical calculation in [7] ($\xi = 0.13 \pm 0.01$ Å), and in the all-valence CNDO/2 calculation in [6] ($\xi = 0.15$ Å). Despite the large difference from experiment, the size of the gap we obtained for the BOW/+ state is much closer to the correct value than the results in [6, 7] ($\Delta E = 14$ eV). The agreement between the calculated size of the gap for the SDW/+ state and experiment is not unambiguous evidence in favor of a SDW/+ ground state, since in our calculation we can find only a π-elecron gap, while the experimental value may be determined by ($\pi - \sigma^*$)-transitions [12].

The greater tendency of cumulene toward bond length alternation compared with polyene is explained by the fact that for practically identical contributions of elecron correlation to the total energy per electron in cumulene, containing two π bonds on each pair of C atom, the contribution form π electrons to the deformation energy ($-4\beta'\xi\Delta$) is two times greater than in polyene ($-2\beta'\xi\Delta$) with a single π bond on each pair of C atoms. Therefore, for the same value for the stiffness K_σ of the core, for cumulene the BOW/+ state has a greater gain than for polyene.

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