

IMPOSSIBILITY OF ANTIFERROMAGNETIC ORDERING IN ONE-DIMENSIONAL AND TWO-DIMENSIONAL MOLECULES WITH CONJUGATED BONDS

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To explain the gap in the spectrum of π electrons of large molecules with conjugated bonds (polyenes, polyacenes), the authors of [1,2] used the Hamiltonian

$$H = \beta \sum_{\ell, p, \sigma} a_{\ell\sigma}^{\dagger} a_{\ell+p, \sigma} + \frac{1}{2} \sum_{\ell, \ell'} F(\ell, \ell') n_{\ell} n_{\ell'} \quad (1)$$

$$n_{\ell} = \sum_{\sigma} n_{\ell\sigma}, \quad n_{\ell\sigma} = a_{\ell\sigma}^{\dagger} a_{\ell\sigma}$$

where β is the π -electron integral, $F(\ell, \ell')$ the Coulomb repulsion of the π electrons from the carbon nuclei ℓ and ℓ' , the summation with respect to p is made over the nearest neighbors of ℓ , and the number of π electrons N is equal to the number of carbon atoms in the conjugation bonds. It is shown in [1,2] that, starting with a certain number N , the ground state with antiferromagnetic ordering is lower in energy than the usual approximate Pariser-Parr-Pople solution. Together with the antiferromagnetic ordering, the authors obtained in the ground state a gap in the spectrum of the single-electron excitations, proportional to the modulus s of the average value of the spin of the π electron on the carbon atoms.

Using, as in [3], the Bogolyubov inequality, we shall show that antiferromagnetic ordering is impossible at a temperature $T \neq 0$ in infinite one-dimensional and two-dimensional systems described by the Hamiltonian (1) [4,5].

Determining the mean value of the spin on the atom in the presence of an arbitrarily weak field h violating the symmetry (1), we add to the Hamiltonian the term

$$\frac{1}{2} \sum_{\ell} h e^{iQ\ell} (a_{\ell+1}^{\dagger} a_{\ell+1} - a_{\ell,-1}^{\dagger} a_{\ell,-1}) \quad (2)$$

with $\exp(iQ\ell) = 1$ for the first sublattice and $\exp(iQ\ell) = -1$ for the second. In polymers we have simply $\exp(iQ\ell) = (-1)^{\ell}$.

We define the operators A and C in the Bogolyubov inequality

$$\frac{1}{2} \langle \{A, A^{\dagger}\} \rangle \langle \{[C, H], C^{\dagger}\} \rangle \geq kT |\langle [C, A] \rangle|^2 \quad (3)$$

in the following manner:

$$A = \sum_{\ell} e^{i(Q-Q)\ell} a_{\ell,-1}^{\dagger} a_{\ell,+1}, \quad (4)$$

$$C = \sum_{\ell} e^{iQ\ell} a_{\ell+1}^{\dagger} a_{\ell,-1}.$$

From (1), (2), and (4) we obtain for the quantities contained in (3)

$$\begin{aligned} \langle [C, A] \rangle &= \sum e^{iQ\ell} \langle (n_{\ell,+1} - n_{\ell,-1}) \rangle = 2NS, \\ \langle [[C, H], C^+] \rangle &= -\beta \sum_{\ell, p, \sigma} (1 - e^{-iQp}) \langle a_{\ell, \sigma}^{\dagger} a_{\ell+p, \sigma} \rangle + \\ &+ hs = \epsilon f(Q) + hs, \end{aligned} \quad (5)$$

$$f(Q) = \sum_p (1 - e^{-iQp}), \quad \epsilon = -\beta \sum_{\sigma} \langle a_{\ell, \sigma}^{\dagger} a_{\ell+p, \sigma} \rangle$$

and ϵ is the mean value of the kinetic energy per pair of atoms and is a finite quantity. Further,

$$\begin{aligned} \langle \{A, A^+\} \rangle &= \sum_{\ell, \ell'} \exp[i(Q-\ell-\ell')] \langle a_{\ell, -1}^{\dagger} a_{\ell+1} a_{\ell'+1}^{\dagger} a_{\ell'-1} + \\ &+ a_{\ell+1}^{\dagger} a_{\ell, -1} a_{\ell'+1}^{\dagger} a_{\ell'+1} \rangle. \end{aligned} \quad (6)$$

Using (3), (5), and (6), we obtain the inequality

$$\langle \{A, A^+\} \rangle \geq \frac{4Ns^2 kT}{\epsilon f(Q) + hs}. \quad (7)$$

Summing both parts of (7) over the momenta q in the first Brillouin zone, we obtain with allowance for (6)

$$\langle (n_{\ell,+1} - n_{\ell,-1})^2 \rangle \geq 4s^2 kT \frac{1}{N} \sum_q \frac{1}{\epsilon f(q) + hs}, \quad (8)$$

which goes over as $N \rightarrow \infty$ into

$$\langle (n_{\ell,+1} - n_{\ell,-1})^2 \rangle \geq 4s^2 kT \int \frac{dq}{\epsilon f(q) + hs}. \quad (9)$$

The left side of (9) does not exceed unity, and in the right side we can confine ourselves to summation over the region $q^2 \lesssim 1$. Then, recognizing that $f(q) \lesssim aq^2$, where a is a number on the order of unity, we get from (9)

$$1 \geq 4\pi s^{3/2} \frac{kT}{\sqrt{ha\epsilon}} \operatorname{arctg} \sqrt{\frac{a\epsilon}{hs}}, \quad (10)$$

$$1 \geq 4s^2 \frac{kT}{a\epsilon} \ln \left| 1 + \frac{a\epsilon}{hs} \right| \quad (11)$$

for one-dimensional (10) and two-dimensional (11) lattices. In both cases we obtain $s \rightarrow 0$ as $h \rightarrow 0$.

It was shown in [6] that the ground state of molecules with Hamiltonian (1) can be

described with the aid of a spin Hamiltonian of the Heisenberg type, since the ground state is quasi-homopolar. For this Hamiltonian they proved in [3] the equivalent statement, that the mean value of the spin vanishes at sites of one- and two-dimensional lattices when $h \rightarrow 0$ and $T \neq 0$.

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E R R A T A

Article by V. D. Borman et al., Vol. 6, No. 11.

The ordinates of Figs. 2 and 3 on pp. 363 and 364 are marked " $\epsilon_{\sim} \times 10^{-4}$ rel. un." They should read " $\epsilon_{\sim} \times 10^4$ rel. un."

Article by A. A. Chaban, Vol. 6, No. 12.

On page 382, top line, " $\omega_c = \delta/\epsilon \dots$ " should read " $\omega_c = \sigma/\epsilon$, σ - conductivity..."

On page 382, line 5 from bottom, " $|\kappa|/5 \sim 10 \text{ cm}^{-1} \dots$ " should read " $|\kappa|/s \sim 10 \text{ cm}^{-1} \dots$ "