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Abstract

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ON THE SPECTRUM OF AN ELECTRON IN A POLYMER CHAIN

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In the theory of ideal crystals it is shown that the set of eigenvalues of the problem of the motion of an electron in the periodic field of a lattice splits into bands, i.e., regions of energy in which the eigenvalues are situated very close to one another. These regions, generally speaking, are separated by intervals in which there are no eigenvalues at all. The presence of these forbidden bands is usually used to explain the existence of semiconductors and insulators.

There are known, however, numerous examples of substances that do not possess a periodic structure and at the same time are semiconductors or insulators. Therefore the existence of allowed and forbidden bands is apparently a consequence of certain more profound causes than the assumption of an ideal periodicity of the field in which the electron moves. In those cases where in a small neighborhood of almost every atom the periodicity is approximately preserved (short-range order), the existence of bands is a simple consequence of the fact that under small changes in the form of the operator and in the boundary conditions its spectrum changes rather little ([1]). In the present work, using a polymer as an example, it is shown that the spectrum may be band-like even in a completely isotropic body, when any ordering is absent even in small regions.

Usually ([2]) a polymer chain of N links is modeled by a set of N vectors of equal length: $\mathbf{l}_1, \mathbf{l}_2, \dots, \mathbf{l}_N$. In this case the vector $\mathbf{l}_{i+1}$ is obtained from the vector $\mathbf{l}_i$ by the transformation

$$\mathbf{l}_{i+1} = A_{i+1,i}\mathbf{l}_i, \tag{1}$$

where $A_{i+1,i}$ are matrices describing rotation. The vectors $\mathbf{l}_i$ are arranged in space so that the end of the vector $\mathbf{l}_i$ coincides with the beginning of the vector $\mathbf{l}_{i+1}$. Then the radius vector $\mathbf{R}_i$, connecting the beginning of the vector $\mathbf{l}_1$ with the beginning of the vector $\mathbf{l}_i$, is equal to

$$\mathbf{R}_i = \sum_{k=1}^{i-1} \mathbf{l}_k. \tag{2}$$

Thus, the matrices $A_{i+1,i}$ completely determine the chain.

To determine the character of the electron spectrum it is necessary to solve the Schrödinger equation with a potential describing the field of all the nuclei of the polymer and the self-consistent field of all the other electrons. The wave function of an electron in a polymer can be constructed in general form by the same method as is used in considering the motion of an electron in a crystalline lattice ([3],[4]). Namely, let $\Phi(\mathbf{r})$ be some function of the spatial coordinates. Define the functions $\Phi_i(\mathbf{r})$, $i = 1, 2, \dots, N$, by

$$\Phi_i(\mathbf{r}) = \Phi\left(A_{i,i-1} A_{i-1,i-2} \dots A_{21}\mathbf{r} + \mathbf{R}_i\right). \tag{3}$$

Without loss of generality the functions $\Phi_i(\mathbf{r})$ may be regarded as orthonormal. We shall seek the solution of the Schrödinger equation $H\psi = E\psi$ in the form of a li—

linear combination of the functions $\Phi_i(\mathbf{r})$. Then the eigenvalues are the roots of the secular equation

$$|H_{ik} - E\delta_{ik}| = 0, \tag{4}$$

where $H_{ik} = \int \Phi_i^* H \Phi_k \, dV$. According to Gershgorin' s theorem ([5]), the roots of equation (4) lie in the closed region formed by circles with radii

$$\rho_i(N) = \sum_{k=1}^{N}{}' |H_{ik}|, \tag{5}$$

where the prime indicates that in the summation the term $|H_{ii}|$ is omitted. The centers of these circles are located at the points H_{ii}. In the case under consideration the roots of equation (4) are real. Therefore the region in which all the roots are located is a segment of the real axis. Thus, the set of eigenvalues of the problem of electron motion in the field of a chain is bounded above and below, i.e., it forms a band.

The spectrum of an electron in an infinite chain is band-like when the limits exist:

$$\rho_i = \lim_{N\to\infty} \rho_i(N) = \sum_{k=1}^{\infty}{}' |H_{ik}|, \tag{6}$$

provided that the sequence of values H_{ii} is bounded above and below.

For both a finite and an infinite chain, the distribution of the density of levels over the band may be very different. In particular, within the band there may exist intervals in which there are no levels at all. Such splitting of bands may already occur when long-range order is destroyed ([1]).

More detailed information about the properties of the band can be obtained by assuming that the matrices $A_{i+1,i}$ are defined statistically and that the vectors $\mathbf{l}_1, \mathbf{l}_2, \ldots$ form a Markov chain.

The system of functions $\Phi_i(\mathbf{r})$ is not complete. Therefore, in order to find all solutions of the Schrödinger equation, one must start from several trial functions, chosen so that the totality of all solutions forms a complete system. Depending on whether the valence band is then separated from the conduction band by a more or less wide interval or overlaps with it, the polymer will be an insulator, a semiconductor, or a metal.

Thus, the band character of the spectrum is not a specific feature of periodic structures: under very general assumptions about the properties of the Hamiltonian and the wave functions, it turns out that in polymers, even those that do not possess even approximately periodic properties, the spectrum can be band-like. The concept of quasimomentum as a number, along with the energy, characterizing the state of an electron in a band can, of course, be introduced only in the case of periodic structures, when determinant (4) reduces to a cyclic determinant. The existence of bands in polymers is connected with the fact that the roots of the secular equation are grouped in some finite region not only for cyclic determinants, but also for a significantly broader class of secular equations.

The conditions (6) for the existence of bands are sufficient, but not necessary.

Numerous experimental data and theoretical considerations indicate that the electrical properties of a substance are determined mainly by short-range order ([1,6]). Here, electrical properties are understood as the entire set of characteristics of the medium that determine conductivity: the effective mass of the carriers, the width of the forbidden band, etc. The preceding arguments only indicate that, under certain conditions, the existence of forbidden bands is not connected

has no relation to any ideas about order. Therefore, the destruction of short-range order can radically change the electrical (and, in general, electronic) properties of a substance.

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