MULTIDIMENSIONAL QUANTUM DESCRIPTION OF ORGANIC CONDUCTORS*

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In this paper usefulness of Kaluza–Klein-like description of charge carriers in some condensed matter systems is suggested. Application for description of polarons and bipolarons in some synthetic metals is proposed. Connection between this approach and the more standard, one-dimensional one, is shown. The multidimensional description is relativistic, applies multidimensional Dirac or Klein–Gordon equation. The one-dimensional description applies Schrödinger or Dirac equation with appropriate periodic potential. Physical consequences for the "multidimensional" mechanism of conductivity in synthetic metals are discussed and comparison with experiments is given.

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1. Introduction

There is a believe among theoretical physicists that the fundamental interactions have geometrical nature and can be described in purely geometrical terms. The first example of a succesful theory of this type is Einstein's general relativity describing gravitational interactions by curvature of the space-time considered as a pseudo-Riemannian manifold. In the time of originating the Einstein's theory only one more interaction was known, namely the electromagnetic interaction. The first attempt towards geometric unification of the two interactions made Kaluza in 1919 (published in 1921 [1]). He used the principal bundle picture with the 4-dimensional space-time being a pseudo-Riemannian manifold, like in general relativity, and

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with 5-dimensional total space, the fibers of which were identified with circles diffeomorphic to the U(1) manifold. The action of the theory was taken to be the action of 5-dimensional general relativity, with the Lagrangian equal to the 5-dimensional scalar curvature. Interpreting appropriately the components of the 5-dimensional metric tensor as the combinations of the 4-dimensional metric tensor, and of the electromagnetic potential, one arrives (in an ansätz where the Brans–Dicke scalar is constant) at the unified theory of gravity and electromagnetism. The first objection against this unification was made by Einstein, who questioned the theory which is not 5-dimensionally generally covariant. Nevertheless, from these times many theories of the Kaluza-Klein type were proposed for unification of gravity with not only electromagnetism but also with weak and strong interactions [2, 3], among them supergravity and superstring theories [4]. An important problem in the theories of this kind, interesting also for our further discussion, is the problem of introducing matter fields into the theory. If the multidimensional matter fields are massless, they usually become massive when considered limited to the external space. Therefore, for the operators of the field equations that split into a sum of operators acting on the external and internal space, the mass spectrum problem is equivalent to the eigenvalue problem for the internal space operator. As a result, typical masses obtained this way are inversely proportional to the characteristic size of the internal space.

Typical problem we meet in the usual theories of the Kaluza–Klein type is the size of the internal space is of the order of the Planck length. Therefore, the usual masses of particles in the theory are extremely large. This result causes one should look for some additional fields, but this complicates the theories, which we believed to be simple and fundamental. Another option is we can use similar picture of the space-time in other areas of theoretical physics, for example in some models of condensed matter. The model we introduced recently in description of conductivity in synthetic metals [5] is an example of such application. Here we remind the fundaments of the model, with special emphasis on the Kaluza–Klein like mechanism of getting masses by formerly massless quasiparticles. In our case the quasiparticles are charge carriers in the synthetic metals.

The crucial problem for further discussion is physical interpretation of these results. Our interpretation of the mass spectrum for polarons in synthetic metals of the type of polyaniline as the energy spectrum for these charge carriers found a support from experimental results [6–8]. We remind here also these results. Furthermore, we find some connection between this Kaluza-Klein like approach and the quantum mechanical approach, with appropriate potential.

The plan of the paper is as follows. Firstly, the Kaluza–Klein approach to description of charge carriers in synthetic metals is reminded. Secondly, the correspondence between the Kaluza–Klein approach to description of polarons and bipolarons and the one based on usual quantum mechanics, is introduced. Thirdly, the physical interpretation of the results and comparison with the experiments is given. Finally, conclusions on the future prospects for this approach are presented.

2. Kaluza–Klein type approach to description of charge carriers in synthetic metals

We begin with reminding our recently proposed approach [5] to description of charge carriers in synthetic metals, especially of the polyaniline — like synthetic metals. The description is in terms of multidimensional Kaluza–Klein-like theory. In our model the external space, being the physical space, is flat. The internal space is treated as the space connected directly with the order parameter, in the mostly used picture it is the space where the order parameter takes its values. In the models we were considering to describe polarons in polyaniline, polypyrrole and polythiophene, we used SU(2) group manifold as the internal space. For bipolarons, on the other hand, the internal space can be different homogeneous manifold.

In our approach we are interested mainly in a proper description of energies and energy spectra of charge carriers in the synthetic metals. We start with some massless quasiparticles satisfying an appropriate multidimensional wave equation which is either the Dirac equation for polarons or the Klein–Gordon equation for bipolarons. Energy spectrum is obtained if we split the Dirac or the Klein–Gordon operator into parts corresponding to the internal and external spaces, then we consider the eigenvalue problem for the parts of the operators on the internal space, and interpret the results as the mass of the apropriate charge carrier. The usual mass-energy correspondence shows the energy spectrum is obtained this way.

As an example of application of this scheme let us discuss shortly the recently investigated case of polarons in some synthetic metals including polyaniline, polypyrrole and polythiophene, the classification being with respect to the ordering characteristics of these materials. We proposed [5], that due to the internal order in these nematic-like materials, the internal space is the SU(2) manifold. Polarons, which are fermions, are described by the multidimensional massless Dirac equation. The Dirac operator D splits into a sum of the Dirac operator on the exernal space D^{ext} and the Dirac operator on the internal space D^{int}: $D = D^{ext} + D^{int}$. According to the scheme sketched above we consider the eigenvalue problem for the Dirac operator on the internal space. In the case in which the internal space

is the SU(2) manifold, as we proposed, we have to find the eigenvalues for $D^{SU(2)}$, the Dirac operator on the SU(2) manifold, it means the constants λ satisfying:

$$D^{\mathrm{SU}(2)}\Psi = \lambda\Psi\,. \tag{1}$$

For this aim we identify the SU(2) manifold with the 3-dimensional sphere S^3 and apply the results on the spectrum of the Dirac operator on S^3, obtained by Trautman [9]. The resulting spectrum is

$$E_l = \left(l + \frac{3}{2}\right) E_0\,, \tag{2}$$

where E_0 is a constant, l are integers. From this form we can deduce that the energy spectrum of polarons in these materials should be of such form that consecutive energies of transitions are integer multiples of an energy unit. In the next section we discuss physical interpretation of this result and its comparison with experiments.

3. Bipolarons and polarons: connection of Kaluza–Klein approach with one dimensional potential approach

We discuss here shortly (recently found [10]) a connection between the Kaluza–Klein approach to description of charge carriers in synthetic metals and the more common approach using potentials. Let us begin with bipolarons. Let us postulate for a moment they are described by the Schrödinger equation with the potential of the type $(\sin x)^{-2}$, which is periodic as it should be since the chain is periodic and has infinite values on the ends of the chain's units. Then it reads

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{g^2}{sin^2 x}\right)\Psi = E\Psi\,. \tag{4}$$

This Schrödinger equation is discussed in the context of quantum integrable systems [11]. The ground state wave function is of the form $\Psi_0(x) = \sin^{\mu} x$, where μ satisfies the condition $g^2 = \frac{1}{2}\mu(\mu-1)\frac{\hbar^2}{m}$. The solutions of (3) are then numbered by integers l and are of the form $\Psi_l = \Psi_0\phi_l$. The functions ϕ_l satisfy the following equation:

$$-\frac{1}{2}\left[\frac{d^2}{dx^2} + 2\mu\cot x\frac{d}{dx} - \mu^2\right]\phi_l = \frac{m}{\hbar^2}E\phi_l\,. \tag{4}$$

Here the operator $B = \frac{d^2}{dx^2} + 2\mu\cot x\frac{d}{dx}$ is the radial Laplace–Beltrami operator on the n-dimensional sphere S^n for $\mu = \frac{(n-1)}{2}$. The eigenfunctions of this operator satisfy the equation (3) and they are zonal spherical

functions. Such form of the equation implies the energy spectrum of the form: $E_l = \frac{\hbar^2}{2m}(l+\mu)^2$. This energy spectrum is physically undistinguishable from the spectrum of the radial Laplace–Beltrami operator since they differ only by a constant. Since the Laplace–Bertrami operator is the part of the Klein–Gordon operator connected with the internal space, we have the desired correspondence with the relativistic multidimensional description of bipolarons.

The correspondence thus established for the particular case of the 3-dimensional sphere gives a correspondence with the case of the SU(2) manifold, and with polyaniline, polypyrrole and polythiophene.

Now along similar lines we would like to establish analogous connection for polarons. Polarons should be described by a spinorial wave function that satisfies the Dirac equation. Let us consider the Dirac operator on the SU(2) manifold, which is equivalent to the Dirac operator on the S^3 manifold. Let us consider the eigenproblem on this manifold. For this aim let us introduce on the S^3 spherical coordinates: χ, θ, ϕ, for convenience. Our eigenproblem reads:

$$\left[\gamma^1\left(\frac{\partial}{\partial\chi} + \cot\chi\right) + \gamma^2\frac{1}{\sin\chi}\left(\frac{\partial}{\partial\theta} + \frac{1}{2}\cot\theta\right) + \gamma^3\frac{1}{\sin\chi\sin\theta}\frac{\partial}{\partial\phi}\right]\psi = \lambda\psi\,.$$

As the next step let us use the fact that the free motion on a manifold is geodesic and introduce appropriate coordinates: $\theta = \theta_0$, $\phi = \phi_0$.

Then we split the ψ function to get the following form of the equation:

$$\psi = \begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{pmatrix} \quad \text{splits into} \quad \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}, \quad \begin{pmatrix}\psi_3\\ \psi_4\end{pmatrix}$$

$$\left[\gamma^1\left(\frac{d}{d\chi} + \cot\chi\right) + \gamma^2 V_0\right]\phi = \lambda\phi\,,$$

where

$$\phi = \begin{pmatrix}\psi_1\sin\chi\\ \psi_2\sin\chi\end{pmatrix} \quad \text{or} \quad \phi = \begin{pmatrix}\psi_3\sin\chi\\ \psi_4\sin\chi\end{pmatrix}$$

with

$$V_0 = \begin{cases}\infty & \text{for} \quad y \neq y_0 \quad \text{or} \quad z \neq z_0\\ \frac{\text{const}}{\sin\chi} & \text{for} \quad y = y_0 \quad \text{and} \quad z = z_0\,.\end{cases}$$

We interpret this form of the eigenvalue problem as the Dirac equation in one dimensional space with a potential of the $(\sin x)^{-1}$ type and this is the proposed connection of the two descriptions for polarons.

4. Physical interpretation and comparison with experiments

In this section we would like to compare our results with experiments and give them a physical interpretation. Let us remind the results on UV-Vis spectra for charge carriers in polyaniline, polypyrrole and polythiophene. Since there are a few kinds of charge carriers in these polymers: polarons, bipolarons, and in a sense solitons, it is difficult to discriminate the lines in the spectra which correspond to various carriers. Different experimental methods show that some of them are most likely of polaronic origin. These are: 1,2,3,4 eV for polyaniline, 0.7, 1.4, 2.1 eV for polypyrrole, and 0.6, 1.3, 1.5-1.8 eV for polythiophene. There are also some other lines connected with different charge carriers or with interchain hopping of charge carriers. All the other lines have energies of the similar order to the polaronic ones. Another observation is that the lines are not sharp but rather broad ones.

Our model is a single band model of conductivity of synthetic metals in which we assume additionally that charge carriers are highly delocalized. This delocalization of charge carriers causes they are influenced by the geometry of macromolecules. Let us now interpret physically the observations concerning the spectra. First observation, which we made some time ago [12, 5], is that the sequences of energies for the polymers are in such order that satisfies the formula (2). This fact supports our mathematical model of the Kaluza–Klein type. The problem that appears is that the energy unit is of the order of 1 eV (1 eV for polyaniline, 0.7 eV for polypyrrole, 0.6 eV for polythiophene). Materials for which the energy gaps are so big are expected to be isolators. The experience with semiconductors could suggest that dopants change the energy levels picture, by introducing additional levels inside the energy gap. However, this argument does not seem to be correct, since the UV-Vis spectra discussed below are taken for materials for which the dopants are already present. We suggest we should look for a different mechanism of conductivity in the synthetic metal. We suggest the following mechanism of conductivity in the class of synthetic metals: The sharp energy lines for charge carriers are broadened by interaction of the carriers with particular structures present in the polaronic chain. The charge carriers, either polarons or bipolarons, translate along the polymeric chains, with the energy being all the time inside the narrow band which originates from the energy level. We believe that conductivity for the case with high density of dopants is not described by a model similar to the one for polarons and bipolarons. We would expect rather solitons being formed as a result of a phase transition when the density of polarons or bipolarons is high.

5. Conclusions

In this paper we discussed possiblity of application of the Kaluza–Klein type description of space-time in physics of synthetic metals. We suggested, in similar scheme as the one used in our paper [5], that the proper description of charge carriers in synthetic metals could be one that deals with a multidimensional space-time of the type similar to the Kaluza–Klein theory. We discussed comparison of the theoretical form of energy spectra of polarons in synthetic metals like polyaniline, polypyrrole, polythiophene, with their experimental counterparts, that gives very good agreement. We proposed in this paper a new physical interpretation of these results. Namely, conductivity of synthetic metals could be not semiconductors-like with many additional energy levels inside the energy gap, because there is too big energy gap in synthetic metals; their energies measured in experiment are at the range of 1 eV. We would rather assign the conductivity in synthetic metals to narrow bands, that result from sharp energy lines discussed, by smearing of the energy levels connected with local interaction effects.

As a further perspective for our research we would like to find appropriate spectra for bipolarons by eigenvalue problems for the Laplace operators on internal spaces. It seems reasonable to look also for different internal spaces to include different synthetic metals. Such internal spaces could be either Lie groups or homogeneous spaces of the Lie groups. Next, the comparison with experimental data on energy spectra for various charge carriers and various synthetic metals is a necessary test of our theoretical considerations.

In the paper we were concerned also with a connection between two approaches to descriptions of charge carriers in synthetic metals of the type of polyaniline, the one using an internal space and free multidimensional carriers and the other using a potential of interaction with the polymer. We discussed recently found connection between the two approaches [10]. For bipolarons the potential is of the $(\sin x)^{-2}$ form, for polarons of the $(\sin x)^{-1}$ form. This problem still deserves further explanation, but the general conclusion is that if we accept anyone of the two approaches, this would mean we accept that internal geometry and not a detailed chemical structure of a synthetic metal is crucial for the mechanism of conductivity.

REFERENCES

[1] T. Kaluza, *Sitzungsber. Preuss. Akad. Wiss.* 966 (1921).
[2] J. Rayski, *Acta Phys. Polon.* **27**, 947 (1965).
[3] R. Kerner, *Ann. de l'Inst. H. Poincaré* **9**, 143 (1968).
[4] M.B. Green, J.H. Schwarz, E. Witten, *Superstring Theory*, Cambridge University Press, Cambridge 1987.

[5] H. Makaruk, *Mod. Phys. Lett.* **B9**, 543 (1995).
[6] A.O. Patil, A.J. Heeger, F. Wudl, *Chem. Rev.* **88**, 183 (1988).
[7] Y. Cao, P. Smith, A.J. Heeger,
[8] S. Stafström, B. Sjögren, J.L. Brédas, *Synthetic Metals* **29**, E219 (1989).
[9] A. Trautman, *Acta. Phys. Pol.* **B26**, 1283 (1995).
[10] H. Makaruk, submitted to Proc. XIV-th Workshop on Geometric Methods on Physics, Bialowieża, 9-15 July, 1995, ed. A. Strasburger.
[11] M.A. Olshanetsky, A.M. Perelomov, *Phys. Rep.* **96**, 313 (1983).
[12] H. Makaruk, *J. Tech. Phys.* **35**, 75 (1994).