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TWO-DIMENSIONAL ELECTRON–HOLE SYSTEM INTERACTING WITH QUANTUM POINT VORTICES IN THE FRAME OF THE CHERN–SIMONS THEORY

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Abstract

The Chern–Simons (C–S) theory developed by Jackiw and Pi [1] and widely used in the theory of the fractional quantum Hall effects (FQHEs) was applied to describe a two-dimensional coplanar electron–hole system in a perpendicular magnetic field interacting with quantum point vortices. The Hamiltonian of free bare conduction and valence electrons in the periodic lattice potential and the respective wave functions were subjected to the C–S unitary transformation leading to the new Schrodinger equations describing the dressed quasiparticles composed of bare electrons and holes with attached quantum point vortices. It was shown that the numbers of the attached point quantum vortices to each conduction electron and to each hole are the same. In contrast to a one-component two-dimensional electron gas, where the FQHEs were revealed, in the electron–hole system, the C–S vector potential is created together by the electron quantum vortices and by the hole quantum vortices and depends on the difference of the density operators of the two subsystems. In the mean-field approximation, the C–S vector potential and the effective magnetic field generated by it vanish if the average densities of the conduction electrons and holes coincide. Nevertheless, even in this case, the quantum fluctuation of the C–S field will lead to new branches of the collective elementary excitations.

1. Introduction

In [1], Jackiw and Pi have elaborated the classical and quantum nonrelativistic Chern–Simons (C–S) theory. The dynamics of the $N$ particles moving on the plane and interacting with each other through the mediation of the U(1) gauge field with C–S singular phase and kinetic action was described. The aim of our study is to apply the C–S theory to the system of two-dimensional (2D) coplanar electron–hole (e–h) gas subjected to the action of a strong magnetic field perpendicular to the surface of the layer, which together with the Coulomb e–h interaction gives rise to the formation of the 2D magnetoexcitons. The quantum point vortices arising in the e–h gas and described by the C–S field influence on the structure of the 2D magnetoexcitons and this influence is the topic of our paper. The quantum point vortices, as will be seen below, generate C–S vector potential $\vec{a}(\vec{r})$, which does exist supplementary to vector potential $\vec{A}(\vec{r})$ of the external magnetic field. Even if $\vec{a}(\vec{r})$ vanishes in the mean-field approximation, the quantum fluctuations generated by it will lead to new effects in the physics of 2D magnetoexcitons. Following completely the explanations of the [1], we will show that the C–S field alters the statistics of the e–h system and gives rise to dynamical interactions in it, exactly as in the case of
2D many body system considered in [1]. The paper is organized as follows. In Section 2, the main statements of the C–S theory are reviewed on the basis of [1]. In Section 3, the mathematical methods demonstrated in the case of the one-component electron system with only kinetic energy were used to describe the 2D e–h system in the field of the periodic lattice potential and of the external magnetic field taking into account the Landau quantization effects and the Coulomb interaction between the electrons and the holes. In Section 4, the required information concerning the point classical and quantum vortices is gathered from the literature. In Section 5, the C–S vector potential in the case of 2D electron–hole system is calculated. Section 6 is dedicated to the conclusions.

2. The Main Statements of the C–S Theory

C–S vector potential \( \hat{a}(\vec{r}) \) appears as the \( \vec{r} \) gradient of phase operator \( \hat{\omega}(\vec{r}) \) determined as follows:

\[
\hat{\omega}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2 r' \theta (\vec{r} - \vec{r}') \hat{\rho}(\vec{r}') \\
\hat{a}(\vec{r}) = \nabla \cdot \hat{\omega}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2 r' \nabla' \theta (\vec{r} - \vec{r}') \hat{\rho}(\vec{r}').
\]

(1)

Here, \( \phi \) is an integer number correlated with filling factor \( \nu \) in the case of the fractional quantum Hall effect (FQHE), \( \phi = \frac{1}{\nu} \), \( \alpha \) is the fine structure constant, \( \alpha = \frac{e^2}{\hbar c} = \frac{1}{137} \), and the charge of electron is \(-e\). Angle \( \theta (\vec{r} - \vec{r}') \) is formed by vector \( \vec{r} - \vec{r}' \) and the \( x \) axis. It is determined analytically as a multivalued function:

\[
\theta (\vec{r} - \vec{r}') = \arctan \left( \frac{y - y'}{x - x'} \right), \quad \theta (\vec{r}' - \vec{r}) = \theta (\vec{r} - \vec{r}') + \pi.
\]

(2)

The last relation in (2) represents the fact that the angle formed with the \( x \) axis by vector \( \vec{r}' - \vec{r} \) differs by \( \pi \) in comparison with the vector of opposite direction. This fact was taken into account in [1] and led to very important consequences concerning the statistics of the field operators in the presence of the Hamiltonian transformed with unitary transformation \( \hat{U}(\vec{r}) \) depending on phase \( \omega(\vec{r}) \) as follows:

\[
\hat{U}(\vec{r}) = e^{\frac{i e}{\hbar c} \omega(\vec{r})}, \quad \hat{U}(\vec{r})\hat{U}^* (\vec{r}) = 1; \quad \hat{\omega}^*(\vec{r}) = \hat{\omega}(\vec{r}).
\]

(3)

Bare electron field operators \( \hat{\psi}^+_e(\vec{r}) \) and \( \hat{\psi}_e(\vec{r}) \) obey the Fermi commutation relations

\[
\hat{\psi}_e(\vec{r})\hat{\psi}^+_e(\vec{r}') + \hat{\psi}^+_e(\vec{r}')\hat{\psi}_e(\vec{r}) = \delta^2 (\vec{r} - \vec{r}'),
\]

(4)

\[
\hat{\psi}_e(\vec{r})\hat{\psi}_e(\vec{r}') + \hat{\psi}_e(\vec{r}')\hat{\psi}_e(\vec{r}) = 0.
\]

In the presence of the C–S gauge field, new dressed or composite field operators \( \hat{\psi}^+(\vec{r}) \) and \( \hat{\psi}(\vec{r}) \) are introduced by the relations

\[
\hat{\psi}_e(\vec{r}) = \hat{\psi}^+(\vec{r}) = e^{\frac{i e}{\hbar c} \phi(\vec{r})}, \quad \hat{\psi}^+_e(\vec{r}) = \hat{\psi}^+(\vec{r})\hat{\psi}^+_e(\vec{r}) = \hat{\psi}^+ (\vec{r}) e^{\frac{i e}{\hbar c} \phi(\vec{r})}.
\]

(5)

\[
\hat{\rho}_e(\vec{r}) = \hat{\psi}_e(\vec{r})\hat{\psi}_e(\vec{r}) = \hat{\rho}(\vec{r}) = \hat{\psi}^+(\vec{r})\hat{\psi}(\vec{r}) = \hat{\rho}_e(\vec{r}) = \hat{\rho}^+(\vec{r}).
\]
The properties of density operators $\hat{\rho}_r(\vec{r}) = \hat{\rho}(r)$ determine the structure of phase operator $\hat{\omega}(r) = \omega^* (\vec{r})$. The new field operators will obey the Bose or Fermi statistics depending on the value of factor $\phi$ in formulas (1); however, their commutation relations with the density operators will be the same in the both cases:

\[
\begin{align*}
[\psi_r(\vec{r}), \hat{\rho}_r(\vec{r})] &= \delta^2 (\vec{r} - \vec{r}') \psi_r(\vec{r}'); \\
[\psi(\vec{r}), \hat{\rho}(\vec{r})] &= \delta^2 (\vec{r} - \vec{r}') \psi(\vec{r}'); \\
[\hat{\psi}(\vec{r}), \hat{\rho}_r(\vec{r})] &= -\delta^2 (\vec{r} - \vec{r}') \hat{\psi}_r(\vec{r}'); \\
[\hat{\psi}(\vec{r}), \hat{\rho}(\vec{r})] &= -\delta^2 (\vec{r} - \vec{r}') \hat{\psi}(\vec{r}'); \\
[\hat{\rho}(\vec{r}), \hat{\rho}(\vec{r})] &= 0; \\
[\hat{\rho}(\vec{r}), \hat{a}(\vec{r})] &= 0; \\
[\hat{\omega}(\vec{r}), \hat{a}(\vec{r})] &= 0; \\
\hat{\rho}(r)\hat{\rho}(r) &= \hat{\rho}(r)\hat{\omega}(r) = \hat{\omega}(r)\hat{\rho}(r). 
\end{align*}
\]

(6)

On the basis of these commutation relations, one can determine eigenfunctions $|\psi(\vec{r})\rangle$ and eigenvalues $\delta^2 (\vec{r} - \vec{r}')$ of density operator $\hat{\rho}(r)$ in the way

\[
\begin{align*}
|\psi_r(\vec{r})\rangle &= \psi_r(\vec{r})|0\rangle; \\
\hat{\rho}_r(\vec{r})|\psi_r(\vec{r})\rangle &= \delta^2 (\vec{r} - \vec{r}')|\psi_r(\vec{r})\rangle; \\
|\psi(\vec{r})\rangle &= \psi(\vec{r})|0\rangle; \\
\hat{\rho}(\vec{r})|\psi(\vec{r})\rangle &= \delta^2 (\vec{r} - \vec{r}')|\psi(\vec{r})\rangle.
\end{align*}
\]

(7)

Here, $|0\rangle$ is the ground state of the system. As was mentioned in [1], in the nonrelativistic quantum mechanics, the particles are points and matter density operator $\hat{\rho}(r)$ is localized in these points being a superposition of $\delta-$functions. This fact plays a crucial role in the calculations involving the C–S gauge field. For example it permits to interchange the integration and the differentiation in the definition (1) of C–S vector potential $\hat{a}(\vec{r})$.

Otherwise, as was underlined in [1], it would be impossible to move the gradient with respect to $\vec{r}$ out of the integral on variable $\vec{r}'$. In a general case, operators (1) are singular because $\theta(\vec{r} - \vec{r}')$ is a multivalued function and the integration over 2D $\vec{r}'$ plane requires specifying of the cut in $\vec{r}'$ beginning in $\vec{r}$. However, in our case, the presence of density operator $\hat{\rho}(\vec{r})$ in the integral with $\delta-$function eigenvalues leads to an exceptional situation when the $\vec{r}$ gradient can be moved outside the integral with impunity [1].

There are other peculiarities related with the 2D space and with function $\theta(\vec{r} - \vec{r}')$, whose derivatives are ill defined at the origin and whose regularization was proposed in [1].

As was mentioned in [1], in the 2D plane the curl of vector $\vec{V}$ is a scalar $S$, and the curl of scalar $S$ is a vector. These and other needed derivatives are recalled below

\[
\begin{align*}
curl \vec{V} &= \vec{\nabla} \times \vec{V} = \hat{\epsilon}_x \frac{\partial}{\partial x} V_y - \hat{\epsilon}_y \frac{\partial}{\partial y} V_x = S \\
(curl S)_i &= (\nabla \times S)_i = \hat{\epsilon}_i \frac{\partial}{\partial \theta} S, \quad \delta^{12} = -\delta^{21} = 1; \quad \delta^{11} = \delta^{22} = 0 \\
\vec{V} &= \vec{\epsilon}_x \frac{\partial}{\partial x} + \vec{\epsilon}_y \frac{\partial}{\partial y} = \vec{\epsilon}_r \frac{\partial}{\partial r} + \vec{\epsilon}_\theta \frac{\partial}{\partial \theta} \\
\partial_b(\vec{r}) &= \frac{-\hat{\epsilon}_x y + \hat{\epsilon}_y x}{r}, \quad \vec{e}_r = \frac{\hat{r}}{r}.
\end{align*}
\]

(8)
Here, \( \vec{e}_x \) and \( \vec{e}_y \); \( \vec{\partial}_b (r) \) and \( \vec{\partial}_y \) are unit 2D vectors in Descartes and in polar coordinates, respectively:

\[
\frac{\partial}{\partial x} \theta(\vec{r} - \vec{r}^\prime) = \frac{\partial}{\partial y} \ln |\vec{r} - \vec{r}^\prime| = -\frac{(y-y^\prime)}{|\vec{r} - \vec{r}^\prime|};
\]

\[
\frac{\partial}{\partial y} \theta(\vec{r} - \vec{r}^\prime) = \frac{\partial}{\partial x} \ln |\vec{r} - \vec{r}^\prime| = -\frac{(x-x^\prime)}{|\vec{r} - \vec{r}^\prime|};
\]

\[
\vec{\nabla} \theta(\vec{r} - \vec{r}^\prime) = -\vec{\nabla} \times \ln |\vec{r} - \vec{r}^\prime| = \frac{-\vec{e}_x (y-y^\prime) + \vec{e}_y (x-x^\prime)}{|\vec{r} - \vec{r}^\prime|^2} + \vec{\partial}_b (\vec{r} - \vec{r}^\prime),
\]

\[
\vec{\nabla} \times \theta(\vec{r} - \vec{r}^\prime) = \vec{\nabla} \ln |\vec{r} - \vec{r}^\prime|,
\]

\[
\frac{\partial^2}{\partial x^2} \theta(\vec{r}) = \frac{2xy}{r^4}; \quad \frac{\partial^2}{\partial y^2} \theta(\vec{r}) = -\frac{2xy}{r^4}; \quad \Delta \theta(\vec{r}) = 0;
\]

\[
\frac{\partial^2}{\partial x \partial y} \ln r = \frac{x^2 - y^2}{r^4}; \quad \frac{\partial^2}{\partial y^2} \ln r = \frac{x^2 - y^2}{r^4}; \quad \Delta \ln r = 0, \ r \neq 0
\]

\[
\Delta \theta(\vec{r} - \vec{r}^\prime) = 0; \quad \Delta \ln |\vec{r} - \vec{r}^\prime| = 2\pi \delta^2 (\vec{r} - \vec{r}^\prime);
\]

\[
\vec{\nabla} \theta(\vec{r} - \vec{r}^\prime) \bigg|_{r=r^\prime} = 0; \quad \theta(\vec{r} - \vec{r}^\prime) \bigg|_{r=r^\prime} = \theta(0).
\]

Here, it is underlined that function \( \frac{1}{2\pi} \ln r \) is a Green’s function of the Laplacian in the 2D space.

The regularization of the derivative \( \vec{\nabla} \theta(\vec{r} - \vec{r}^\prime) \bigg|_{r=r^\prime} \) proposed in [1] in the origin prescribes to consider it equal to zero. We can add the proposal to consider \( \theta(0) = 0 \).

Relations (6) make it possible to deduce the commutation relations of the field operators with phase operator \( \vec{\partial}_b (\vec{r}) \) and unitary transformation operator \( \hat{U} (\vec{r}) \) in the way...
\[
\left[\hat{\psi}_\alpha (\vec{r}'), \hat{\omega} (\vec{r}') \right] = -\frac{i e}{\hbar c} \int d^3 \vec{r}'' \theta (\vec{r}' - \vec{r}'') \left[ \hat{\psi}_\alpha (r), \hat{\rho} (\vec{r}'') \right] = -\frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \hat{\psi}_\alpha (r);
\]
\[
\left[\hat{\psi} (\vec{r}), \hat{\omega} (\vec{r}') \right] = -\frac{i e}{\hbar c} \int d^3 \vec{r}' \theta (\vec{r}' - \vec{r}') \hat{\psi} (\vec{r}) = -\frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \hat{\psi} (\vec{r});
\]
\[
\left[\psi^+ (\vec{r}), \hat{\omega} (\vec{r}') \right] = \frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \psi^+ (\vec{r}); \left[\hat{\psi}^+_\alpha (\vec{r}), \hat{\omega} (\vec{r}') \right] = \frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \hat{\psi}^+_\alpha (\vec{r});
\]
\[
\hat{\psi} (\vec{r}) \hat{\omega}^n (\vec{r}') = \left[ \hat{\omega} (\vec{r}') - \frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \right]^n \psi^+ (\vec{r});
\]
\[
\psi^+ (\vec{r}) \hat{\omega}^n (\vec{r}') = \left[ \hat{\omega} (\vec{r}') + \frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \right]^n \psi (\vec{r}); \tag{10}
\]
\[
\hat{\psi} (\vec{r}) e^{i e \phi (\vec{r}) \hbar / c} = \sum_{n=0}^{\infty} \left( \frac{i e}{\hbar c} \right)^n \frac{1}{n!} \hat{\psi} (\vec{r}) \hat{\omega}^n (\vec{r}') =
\]
\[
= \sum_{n=0}^{\infty} \left( \frac{i e}{\hbar c} \right)^n \frac{1}{n!} \left[ \hat{\omega} (\vec{r}') - \frac{i e}{\hbar c} \theta (\vec{r}' - \vec{r}) \right]^n \psi (\vec{r}) = e^{-i \phi (\vec{r}' - \vec{r}) / \hbar c} e^{i e \phi (\vec{r}) \hbar / c} \hat{\psi} (\vec{r});
\]
\[
\hat{\psi} (\vec{r}) \cdot e^{i e \phi (\vec{r} - \vec{r}') \hbar / c} = e^{i e \phi (\vec{r}' - \vec{r}) \hbar / c} e^{i e \phi (\vec{r}) \hbar / c} \psi^+ (\vec{r}).
\]

In the same way, one can obtain
\[
\psi^+ (\vec{r}) \hat{U}^+ (\vec{r}') = e^{i \phi (\vec{r}' - \vec{r})} \hat{U}^+ (\vec{r}') \psi^+ (\vec{r});
\]
\[
\hat{U} (\vec{r}) \psi^+_\alpha (\vec{r}') = e^{-i \phi (\vec{r}' - \vec{r})} \hat{U} (\vec{r}) \psi^+_\alpha (\vec{r}'); \tag{11}
\]
\[
\hat{\psi} (\vec{r}) \hat{U} (\vec{r}) = e^{-i \phi (0)} \hat{U} (\vec{r}) \hat{\psi} (\vec{r}); \theta (\vec{r}' - \vec{r}) \big|_{\vec{r} = \vec{r}'} = \theta (0).
\]

The statistical properties of the dressed field operators are the consequences of the previous commutation relations and can be revealed starting with the definitions
\[
\hat{\psi} (\vec{r}) = \hat{U}^+ (\vec{r}) \hat{\psi}_\alpha (\vec{r}) = \psi^+_\alpha (\vec{r}) \hat{U}^+ (\vec{r}) e^{-i \phi (0)};
\]
\[
\psi^+ (\vec{r}) = \psi^+_\alpha (\vec{r}) \hat{U} (\vec{r}) = \hat{U} (\vec{r}) \psi^+_\alpha (r) e^{i \phi (0)}. \tag{12}
\]

As mentioned above, bare Fermi field operators \( \hat{\psi}^+_\alpha (\vec{r}) \) and \( \hat{\psi}_\alpha (\vec{r}) \) obey the same commutation relations with density operator (6) as the dressed field operators. To obey the Fermi or Bose statistics, the dressed field operators must satisfy the following requirements:
\[
\hat{\psi} (\vec{r}) \psi^+ (\vec{r}') \pm \psi^+ (\vec{r}') \hat{\psi} (\vec{r}) = \delta^2 (\vec{r} - \vec{r}'); \tag{13}
\]
\[
\hat{\psi} (\vec{r}) \psi^+ (\vec{r}') \pm \psi^+ (\vec{r}') \hat{\psi} (\vec{r}) = 0,
\]
where the upper and lower signs \pm concern the Fermi and Bose statistics, respectively.

Substituting operators (12) in the first equation (13), we will obtain...
\[
\hat{U}^+(\vec{r}') \hat{\psi}_e(\vec{r}') \hat{\psi}_e^+(\vec{r}') \hat{U}(\vec{r}') \pm \hat{\psi}_e^+(\vec{r}') \hat{U}^+(\vec{r}') \hat{\psi}_e^+(\vec{r}') =
\]
\[
= e^{i\phi(0)} \left[ \hat{U}^+(\vec{r}) \hat{\psi}_e(\vec{r}) \hat{U}(\vec{r}) \hat{\psi}_e^+(\vec{r}) \pm \hat{U}(\vec{r}) \hat{\psi}_e^+(\vec{r}) U^+(\vec{r}) \hat{\psi}_e(\vec{r}) \right] =
\]
\[
= e^{i\phi(0)} \left[ e^{-i\phi(\vec{r} - \vec{r}')} \hat{U}^+(\vec{r}) \hat{\psi}_e(\vec{r}) \hat{\psi}_e^+(\vec{r}') \right] \pm
\]
\[
\pm e^{-i\phi(\vec{r} - \vec{r}')} \hat{U}(\vec{r}') \hat{\psi}_e^+(\vec{r}') \hat{\psi}_e(\vec{r}) = \delta^2(\vec{r} - \vec{r}').
\]

Taking into account relations \(\hat{U}(\vec{r}') \hat{U}^+(\vec{r}) = \hat{U}^+(\vec{r}) \hat{U}(\vec{r}')\) and \(\theta(\vec{r} - \vec{r}') = \theta(\vec{r}' - \vec{r}) - \pi\), as was established in formula (2), we can transcribe (14) in the form
\[
\hat{\psi}_e^+(\vec{r}) \hat{\psi}_e^+(\vec{r}') \pm \hat{\psi}_e^+(\vec{r}') \hat{\psi}_e(\vec{r}) = e^{i\phi(0) - \theta(\vec{r} - \vec{r}')}) \hat{U}^+(\vec{r}) \hat{U}(\vec{r}') \times
\]
\[
\times \left[ \hat{\psi}_e(\vec{r}) \hat{\psi}_e^+(\vec{r}') \pm \hat{e}^{i\phi} \hat{\psi}_e^+(\vec{r}') \hat{\psi}_e(\vec{r}) \right] = \delta^2(\vec{r} - \vec{r}').
\]

These requirements can be satisfied when
\[
\pm e^{i\phi} = 1. \tag{16}
\]

It means that unitary transformation \(\hat{U}(\vec{r})\) with even integer values of \(\phi = 0, 2, 4, \ldots\) leads to dressed field operators \(\hat{\psi}_e^+(\vec{r}), \hat{\psi}_e(\vec{r})\) obeying the statistic Fermi, whereas in the case of the odd integer values \(\phi = 1, 3, 5, \ldots\) the dressed field operators will obey the Bose statistics. The same requirement on the values of factor \(\phi\) appears from the second equation (13) as follows:
\[
\hat{U}^+(\vec{r}) \hat{\psi}_e(\vec{r}) \hat{U}(\vec{r}) \hat{\psi}_e^+(\vec{r}') \pm \hat{U}(\vec{r}) \hat{\psi}_e^+(\vec{r}') \hat{U}^+(\vec{r}') \hat{\psi}_e(\vec{r}) =
\]
\[
= \hat{U}^+(\vec{r}) \hat{U}(\vec{r}') e^{i\phi(\vec{r} - \vec{r}') \hat{\psi}_e(\vec{r}') \hat{\psi}_e(\vec{r}) (1 + e^{-i\phi}) = 0; \quad (1 + e^{-i\phi}) = 0. \tag{17}
\]

As was established in the many basic papers dedicated to the FQHE [4–16], the dressed field operators describe composite Fermi and Bose particles composed of 2D electrons and attached point quantum vortices. In our case, the dressed electrons belong to the conduction and valence bands. All of them are dressed in an equal manner with the same number of the attached point quantum vortices. Because the description of the valence electron operators is substituted by the description of the holes filed operators, in our case, the introduction of the C–S gauge field means the attachment of \(\phi\) point quantum vortices to each electron and to each hole of the system.

The time derivative of the unitary transformation operator \(\frac{d}{dt} \hat{U}(\vec{r}) = \frac{d}{dt} e^{ie\phi(\vec{r})}\) needs a special explanation because phase operator derivative \(\frac{d}{dt} \hat{\phi}(\vec{r})\) does not commute with the same operator \(\hat{\phi}(\vec{r})\).

Below, we will determine derivative \(\frac{d}{dt} \hat{\phi}(\vec{r})\) using the commutation of operator \(\hat{\phi}(\vec{r})\) with the Hamiltonian and will obtain the formulas
\[
\left[ \frac{d}{dt} \hat{\phi}(\vec{r}), \hat{\phi}(\vec{r}) \right] = \dot{\hat{L}}(\vec{r}), \left[ \dot{\hat{L}}(\vec{r}), \hat{\phi}(\vec{r}) \right] = 0. \tag{18}
\]

On their basis, it is possible to derive the needed derivative
\[
\frac{d}{dt} \hat{U}(\vec{r}) = \frac{d}{dt} e^{\frac{ie\phi(\vec{r})}{\hbar c}} = \sum_{n=0}^{\infty} \left( \frac{ie}{\hbar c} \right)^n \frac{1}{n!} \frac{d}{dt} \hat{\phi}^n(\vec{r}). \tag{19}
\]
Starting with relations (18), we can write
\[
\frac{d\hat{\omega}^2(\vec{r})}{dt} = \frac{d\hat{\omega}(\vec{r})}{dt} \hat{\omega} + \hat{\omega}(\vec{r}) \frac{d\hat{\omega}}{dt} = 2\hat{\omega}(\vec{r}) \frac{d\hat{\omega}}{dt} + \hat{L}(\vec{r}),
\]
\[
\frac{d\hat{\omega}^3(\vec{r})}{dt} = 3\hat{\omega}^2(\vec{r}) \frac{d\hat{\omega}(\vec{r})}{dt} + 3\hat{L}(\vec{r}) \hat{\omega}(\vec{r}),
\]
\[
\frac{d\hat{\omega}^n(\vec{r})}{dt} = n\hat{\omega}^{n-1}(\vec{r}) \frac{d\hat{\omega}(\vec{r})}{dt} + X_n \hat{\omega}^{n-2}(\vec{r}) \hat{L}(\vec{r}), \quad n \geq 2.
\]  
(20)

The recurrent formula was found out to be
\[
X_n = (n-1) + X_{n-1} = \frac{n(n-1)}{2}, \quad n \geq 1.
\]  
(21)

After the substitution of derivatives (20) in series (19), we will obtain
\[
\frac{d}{dt} e^{\frac{ie}{\hbar c}(\vec{r})} = e^{\frac{ie}{\hbar c}(\vec{r})} \left[ \left( \frac{ie}{\hbar c} \right) \frac{d\hat{\omega}(\vec{r})}{dt} + \frac{1}{2} \left( \frac{ie}{\hbar c} \right)^2 \hat{L}(\vec{r}) \right] =
\]
\[
= \left[ \frac{ie}{\hbar c} \frac{d\hat{\omega}}{dt} - \frac{1}{2} \left( \frac{ie}{\hbar c} \right)^2 \hat{L}(\vec{r}) \right] e^{\frac{ie}{\hbar c}(\vec{r})},
\]
\[
\frac{\frac{ie}{\hbar c}(\vec{r})}{\hat{\omega}(\vec{r})} \frac{d\hat{\omega}(\vec{r})}{dt} = \frac{d\hat{\omega}(\vec{r})}{dt} e^{\frac{ie}{\hbar c}(\vec{r})} - \left( \frac{ie}{\hbar c} \right) \hat{L}(\vec{r}) e^{\frac{ie}{\hbar c}(\vec{r})}.
\]  
(22)

Taking into account the equality
\[
\frac{X_{m+2}}{(m+1)(m+2)} = \frac{1}{2}, \quad m \geq 0,
\]  
(23)

we can write
\[
\frac{d}{dt} e^{\frac{ie}{\hbar c}(\vec{r})} = e^{\frac{ie}{\hbar c}(\vec{r})} \left[ \left( \frac{ie}{\hbar c} \right) \frac{d\hat{\omega}(\vec{r})}{dt} + \frac{1}{2} \left( \frac{ie}{\hbar c} \right)^2 \hat{L}(\vec{r}) \right] =
\]
\[
= \left[ \frac{ie}{\hbar c} \frac{d\hat{\omega}}{dt} - \frac{1}{2} \left( \frac{ie}{\hbar c} \right)^2 \hat{L}(\vec{r}) \right] e^{\frac{ie}{\hbar c}(\vec{r})},
\]
\[
\frac{\frac{ie}{\hbar c}(\vec{r})}{\hat{\omega}(\vec{r})} \frac{d\hat{\omega}(\vec{r})}{dt} = \frac{d\hat{\omega}(\vec{r})}{dt} e^{\frac{ie}{\hbar c}(\vec{r})} - \left( \frac{ie}{\hbar c} \right) \hat{L}(\vec{r}) e^{\frac{ie}{\hbar c}(\vec{r})}.
\]  
(24)

3. Equations of Motion for Electron Field Operators

The Hamiltonian of the bare proper 2D electrons in the semiconductor layer existing under the influence of crystal lattice periodic potential \( V_{per}(\vec{r}) \) of the external magnetic field \( \vec{B} \) perpendicular to the surface of the layer, as well as interacting between themselves by the Coulomb potential \( V_{Coul}(\vec{r}) \), has the form
\[
H = \frac{\hbar^2}{2m_0} \int d^2\vec{r}^\prime \psi_+^\ast(\vec{r}^\prime) \left( -i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r}^\prime) \right)^2 \psi_+(\vec{r}^\prime) +
\]
\[
+ \int d^2\vec{r}^\prime \psi_+^\ast(\vec{r}^\prime) V_{per}(\vec{r}^\prime) \psi_+(\vec{r}^\prime) + \frac{1}{2} \int d^2\vec{r}^\prime \int d^2\vec{r}^\prime' \psi_+^\ast(\vec{r}^\prime) \psi_+(\vec{r}^\prime') \psi_+^\ast(\vec{r}^\prime') \psi_+(\vec{r}^\prime')
\]
\[
= \frac{\hbar^2}{2m_0} \int d^2\vec{r}^\prime \psi_+^\ast(\vec{r}^\prime) \left( -i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r}^\prime) \right)^2 \psi_+(\vec{r}^\prime) +
\]
\[
+ \int d^2\vec{r}^\prime \psi_+^\ast(\vec{r}^\prime) V_{per}(\vec{r}^\prime) \psi_+(\vec{r}^\prime) + \frac{1}{2} \int d^2\vec{r}^\prime \int d^2\vec{r}^\prime' \psi_+^\ast(\vec{r}^\prime) \psi_+(\vec{r}^\prime') \psi_+^\ast(\vec{r}^\prime') \psi_+(\vec{r}^\prime')
\]
\[
V_{Coul}(\vec{r}^\prime-\vec{r}^\prime') \psi_+(\vec{r}^\prime') \psi_+(\vec{r}^\prime').
\]  
(25)
Here, $m_0$ is the bare electron mass, $e$ is the absolute value of the electron charge, $\vec{A}(\vec{r})$ is the vector potential value of the external magnetic field, which in the Landau gauge equals to $\vec{A}(\vec{r})=(-By,0,0)$. The bare electron field operators $\hat{\psi}_e(\vec{r})$ and $\hat{\psi}_e^+(\vec{r})$ obey the Fermi commutation relations (3). Their equation of motions looks as follows:

$$i\hbar \frac{d\hat{\psi}_e(\vec{r})}{dt} = \left[\hat{\psi}_e(\vec{r}), \hat{H}\right] = \frac{\hbar^2}{2m_0} \left(-i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r})\right)^2 \hat{\psi}_e(\vec{r}) +$$

$$+V_{\text{per}}(\vec{r})\hat{\psi}_e(\vec{r}) + \int d^2\vec{r}' V_{\text{coul}}(\vec{r}-\vec{r}') \hat{\rho}(\vec{r}')\hat{\psi}_e^+(\vec{r}')\vec{\nabla} \cdot \vec{A}(\vec{r}) = 0;$$

$$i\hbar \frac{d\hat{\psi}_e^+(\vec{r})}{dt} = \left[\hat{\psi}_e^+(\vec{r}), \hat{H}\right] = -\frac{\hbar^2}{2m_0} \left(i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r})\right)^2 \hat{\psi}_e^+(\vec{r}) -$$

$$-V_{\text{per}}(\vec{r})\hat{\psi}_e^+(\vec{r}) - \int d^2\vec{r}' V_{\text{coul}}(\vec{r}-\vec{r}') \hat{\rho}(\vec{r}')\hat{\psi}_e^+(\vec{r})\hat{\rho}_e(r');$$

$$\hat{\rho}_e(\vec{r}) = \hat{\rho}_e^+(\vec{r}) = \hat{\psi}_e^+(\vec{r})\hat{\psi}_e(\vec{r}).$$

The continuity equation for density operators $\hat{\rho}_e(\vec{r})$ has the form

$$\frac{d\hat{\rho}_e(\vec{r})}{dt} = \frac{1}{i\hbar} \left[\hat{\rho}_e(\vec{r}), \hat{H}\right] = -\vec{\nabla} \cdot \hat{J}_e(\vec{r})$$

$$\hat{J}_e(\vec{r}) = \frac{\hbar}{2m_0} \left(\hat{\psi}_e^+(\vec{r})\vec{\nabla} \hat{\psi}_e(\vec{r}) - \vec{\nabla} \cdot \hat{\psi}_e^+(\vec{r})\hat{\psi}_e(\vec{r})\right) +$$

$$+\frac{e}{m_0c} \vec{A}(\vec{r})\hat{\rho}_e(\vec{r});\quad \vec{\nabla} \cdot \vec{A}(\vec{r}) = 0.$$

The equations of motion for dressed electron field operators $\hat{\psi}(\vec{r})=\hat{U}^+(\vec{r})\hat{\psi}_e(\vec{r})$ and $\hat{\psi}^+(\vec{r})=\hat{\psi}_e^+(r)\hat{U}(r)$ were obtained on the basis of the previous equations of motion (26) using the properties of the unitary transformation operator $\hat{U}(\vec{r})$ (3) and (24). They are

$$i\hbar \frac{d\hat{\psi}(\vec{r})}{dt} = i\hbar \frac{d\hat{U}^+(\vec{r})}{dt} \hat{\psi}_e(\vec{r}) + \hat{U}^+(\vec{r})i\hbar \frac{d\hat{\psi}_e(\vec{r})}{dt};$$

$$\frac{d\hat{U}^+(\vec{r})}{dt} = \hat{U}^+(\vec{r}) \left[-ie \frac{d\hat{\omega}(\vec{r})}{dt} + \frac{e^2}{2\hbar^2 c^2} \hat{L}(r)\right];$$

$$i\hbar \frac{d\hat{\psi}(\vec{r})}{dt} = \frac{\hbar^2}{2m_0} \left(-i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r}) + \frac{e}{\hbar c} \vec{a}(\vec{r})\right)^2 \hat{\psi}(\vec{r}) +$$

$$+V_{\text{per}}(\vec{r})\hat{\psi}^+(\vec{r}) + \int d^2\vec{r}' V_{\text{coul}}(\vec{r}-\vec{r}') \hat{\rho}(\vec{r}')\hat{\psi}(\vec{r}) +$$

$$+\frac{e}{c} \frac{d\hat{\omega}(\vec{r})}{dt} \hat{\psi}(\vec{r}) + \frac{e^2}{2\hbar^2 c^2} i\hat{L}(\vec{r})\hat{\psi}(\vec{r})$$

$$i\hbar \frac{d\hat{\psi}^+(\vec{r})}{dt} = -\frac{\hbar^2}{2m_0} \left(i\vec{\nabla} + \frac{e}{\hbar c} \vec{A}(\vec{r}) + \frac{e}{\hbar c} \vec{a}(\vec{r})\right)^2 \hat{\psi}^+(\vec{r}) - V_{\text{per}}(\vec{r})\hat{\psi}^+(\vec{r}) -$$

$$-\int d^2\vec{r}' V_{\text{coul}}(\vec{r}-\vec{r}')\hat{\psi}^+(\vec{r}')\hat{\rho}(\vec{r}') - \frac{e}{c} \frac{d\hat{\omega}(\vec{r})}{dt} \hat{\psi}^+(\vec{r}) - \frac{e^2}{2\hbar^2 c^2} \left(i\hat{L}(r)\right)^2.$$
In this deduction, the following properties were taken into account:

\[ \hat{a}(\vec{r}) = \hat{a}(\vec{r}); \quad \hat{\omega}(\vec{r}) = \hat{\omega}(r); \quad \rho(\vec{r}) = \rho^*(\vec{r}); \]

\[ \nabla \hat{a}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2\vec{r}' \Delta \theta(\vec{r} - \vec{r}') \hat{\rho}(r') = 0; \quad \Delta \theta(\vec{r} - \vec{r}') = 0; \]

\[ \nabla \times \hat{a}(\vec{r}) = \nabla \times \frac{\phi e}{\alpha} \int d^2\vec{r}' \hat{\rho}(r') \nabla \ln |\vec{r} - \vec{r}'| = \frac{\phi e}{\alpha} \int d^2r' \hat{\rho}(r') \Delta \ln |\vec{r} - \vec{r}'| = \]

\[ = \frac{2\pi\phi e}{\alpha} \int d^2\vec{r}' \hat{\rho}(r') \delta^2(\vec{r} - \vec{r}') = \frac{2\pi\phi e}{\alpha} \hat{\rho}(r); \]

\[ \left[ \hat{a}(r), \psi(\vec{r}) \right] = 0; \quad \left[ \hat{\omega}(\vec{r}), \psi^*(\vec{r}) \right] = 0; \quad \nabla \theta(\vec{r} - \vec{r}') \bigg|_{\vec{r} = \vec{r}'} = 0; \]

\[ \left[ \hat{a}(\vec{r}), \hat{\rho}(\vec{r}) \right] = 0; \quad \left[ \hat{\omega}(\vec{r}'), \hat{U}(\vec{r}) \right] = 0; \quad \left[ \hat{a}(r), \hat{\omega}(r') \right] = 0. \]

The continuity equation for the dressed field operators being written in the dressed field operators looks as follows:

\[ \frac{d\hat{\rho}(\vec{r})}{dt} = -\nabla \cdot \hat{\mathbf{j}}(\vec{r}), \]

\[ \hat{\mathbf{j}}(\vec{r}) = \frac{\hbar}{2m_e} (\psi^*(\vec{r})\nabla \psi(\vec{r}) - \nabla \psi^*(\vec{r}) \cdot \psi(\vec{r}) + \frac{e}{m_e c} (\hat{A}(\vec{r}) + \hat{a}(r)) \hat{\rho}(\vec{r}); \]

\[ \frac{d\rho(\vec{r})}{dt} = \frac{d\hat{\rho}_e(\vec{r})}{dt} = -\nabla \cdot \hat{\mathbf{j}}_e(\vec{r}) = -\nabla \cdot \hat{\mathbf{j}}(r). \]

In spite of equalities \( \hat{\rho}(\vec{r}) = \hat{\rho}_e(\vec{r}) \) and \( \hat{\mathbf{j}}_e(\vec{r}) = \hat{\mathbf{j}}(\vec{r}) \), continuity equations (27) and (30) look different because the gradients of the bare and of the dressed field operators differ as follows:

\[ \nabla \psi(\vec{r}) = \nabla \hat{U}^*(r) \cdot \hat{\psi}_e(r) + \hat{U}^*(\vec{r}) \nabla \hat{\psi}_e(\vec{r}) = \]

\[ = -\frac{i\epsilon}{\hbar c} \hat{a}(\vec{r}) \hat{\psi}(\vec{r}) + \hat{U}^*(\vec{r}) \nabla \hat{\psi}_e(\vec{r}); \quad \hat{a}(\vec{r}) = \nabla \hat{\omega}(\vec{r}) \]

\[ \nabla \hat{U}^*(\vec{r}) = -\frac{i\epsilon}{\hbar c} \hat{a}(r) \hat{U}^*(\vec{r}). \]

Equations (26)–(30) give the possibility to determine operator \( \hat{L}(\vec{r}) \), which was introduced above in formula (18) in the way.
\[
\hat{L}(\vec{r}) = \left[ \frac{d\hat{o}(\vec{r})}{dt}, \hat{o}(\vec{r}) \right] = \left( \frac{\phi_e}{\alpha} \right)^2 \int d^2\vec{r} \int d^2\vec{r}' \theta(\vec{r} - \vec{r}'') \times
\]
\[
\times \left[ \frac{d\hat{\rho}_e(\vec{r}')}{dt}, \hat{\rho}_e(\vec{r}'') \right] = \left( \frac{\phi_e}{\alpha} \right)^2 \int d^2\vec{r}' \int d^2\vec{r}'' \theta(\vec{r}' - \vec{r}'') \times \theta(\vec{r} - \vec{r}'') \times
\]
\[
\times \left[ \vec{\nabla}' \cdot \hat{\mathbf{J}}_e(\vec{r}'), \hat{\rho}_e(\vec{r}'') \right] = \left( \frac{\phi_e}{\alpha} \right)^2 \int d^2\vec{r}' \int d^2\vec{r}'' \vec{\nabla}' \cdot \theta(\vec{r}' - \vec{r}'') \times \theta(\vec{r} - \vec{r}'') \times
\]
\[
\left[ \frac{\phi_e}{\alpha} \right]^2 \int d^2\vec{r}' \int d^2\vec{r}'' \vec{\nabla}' \cdot \theta(\vec{r}' - \vec{r}'') \times \theta(\vec{r} - \vec{r}'') \times
\]
\[
\theta(\vec{r} - \vec{r}'') \left[ \hat{\psi}_e^+(\vec{r}') \vec{\nabla}' \hat{\psi}_e^+(\vec{r}''), \hat{\rho}_e(\vec{r}'') \right] - \left[ \vec{\nabla}' \hat{\psi}_e^+(\vec{r}') \cdot \hat{\psi}_e^+(\vec{r}''), \hat{\rho}_e(\vec{r}'') \right].
\]

Taking into account commutation relations (5), we can write
\[
\left[ \hat{\psi}_e^+(\vec{r}') \vec{\nabla}' \hat{\psi}_e^+(\vec{r}''), \hat{\rho}_e(\vec{r}'') \right] = \hat{\psi}_e^+(\vec{r}') \vec{\nabla}'(\delta^2(\vec{r}' - \vec{r}'') \hat{\psi}_e(\vec{r}'')) -
\]
\[
- \delta^2(\vec{r}' - \vec{r}'') \hat{\psi}_e^+(\vec{r}'') \vec{\nabla}' \hat{\psi}_e(\vec{r}'),
\]
\[
\left[ \vec{\nabla}' \hat{\psi}_e^+(\vec{r}') \cdot \hat{\psi}_e^+(\vec{r}''), \hat{\rho}_e(\vec{r}'') \right] = \delta^2(\vec{r}' - \vec{r}'') \vec{\nabla}' \hat{\psi}_e^+(\vec{r}') \cdot \hat{\psi}_e(\vec{r}'') -
\]
\[
- \vec{\nabla}' \delta^2(\vec{r}' - \vec{r}'') \hat{\psi}_e^+(\vec{r}'') \cdot \hat{\psi}_e(\vec{r}').
\]

Substituting expressions (32) into equation (31), we obtain
\[
\left[ \frac{d\hat{o}(\vec{r})}{dt}, \hat{o}(\vec{r}) \right] = \hat{L}(\vec{r}) = \frac{\hbar}{m_i} \left( \frac{\phi_e}{\alpha} \right)^2 \int d^2\vec{r}' \left( \vec{\nabla}' \theta(\vec{r}' - \vec{r}'') \right)^2 \hat{\rho}_e(\vec{r}').
\]
\[
= \frac{\hbar}{m_i} \left( \frac{\phi_e}{\alpha} \right)^2 \int d^2\vec{r}', \hat{\rho}_e(\vec{r}') \right| \vec{r} - \vec{r}'; \left\{ \hat{L}(\vec{r}), \hat{o}(\vec{r}) \right\} = 0,
\]
\[
\left( i\hat{L}(\vec{r}) \right)^+ = i\hat{L}(\vec{r}),
\]
\[
\frac{i}{2} \frac{e^2}{\hbar c^2} \hat{L}(\vec{r}) = \frac{\hbar^2}{2m_0} \phi^2 \int d^2\vec{r}', \hat{\rho}_e(\vec{r}') \left| \vec{r} - \vec{r}' \right|^2.
\]

The supplementary energy terms in the equation of motion (28) are related with the C–S gauge field. Operator \( i\hat{L}(\vec{r}) \) describes the kinetic energy created by the vortices, whereas the term \( \frac{e}{c} \frac{d\hat{o}}{dt}(\vec{r}) \) determines the electric potential created by them.

As was shown in (29), \( \text{curl } \vec{a}(\vec{r}) \) gives rise to a supplementary effective magnetic field.

### 4. Two-Dimensional Classical and Quantum Point Vortices

Multivalued function \( \theta(\vec{r} - \vec{r}') \) determines the singular properties of phase \( \hat{o}(\vec{r}) \) and vector potential \( \vec{a}(\vec{r}) \) operators in the C–S field theory. Function \( \theta(\vec{r}) \) being considered alone without density operator \( \hat{\rho}(\vec{r}) \) can give rise to the velocity field and the hydrodynamics of a classical 2D field composed of particles with mass \( m \).
Velocity field \( V(\vec{r}) \) with the potential flow in the region of \( \vec{r} \neq 0 \) determined by function \( \theta(\vec{r}) \) looks as follows:

\[
\vec{V}(\vec{r}) = \vec{\nabla} \phi(\vec{r}); \quad \phi(\vec{r}) = \frac{k}{2\pi} \theta(\vec{r});
\]

\[
\vec{V}(\vec{r}) = \frac{k}{2\pi} \vec{\nabla} \theta(\vec{r}) = -\frac{k}{2\pi} \vec{\nabla} \ln r = \frac{k}{2\pi} \frac{-\hat{e}_y \hat{e}_x + \hat{e}_x \hat{e}_y}{r^2} = \frac{k}{2\pi} \frac{\delta_\theta}{r}.
\]

Vorticity \( \Omega(\vec{r}) \) of the velocity field is determined in the way

\[
\Omega(\vec{r}) = \vec{\nabla} \times \vec{V}(\vec{r}) = \sum_{i,j} \partial_i \partial_j V_j(\vec{r}) = \frac{k}{2\pi} \ln r = k \delta^2(\vec{r}).
\]

The potential flow and the irrotational behavior of the velocity field take place almost on the entire 2D plane, except for one point with \( \vec{r} = 0 \). The surface of the vortex equals to zero, and we have to deal with the point 2D vortex with a singular vorticity \( k \cdot \delta^2(\vec{r}) \). Nonetheless, the total vorticity on the entire plane, as well as the circulation of the 2D point vortex, are finite as follows:

\[
k = \int d^2 r \Omega(\vec{r}) = \lim_{x \to \infty} \int \vec{V}(\vec{r}) d\vec{l} \cdot d\vec{l} = rd\theta \cdot \delta_\theta,
\]

where \( k \) is the strength of the vortex. Kinetic energy \( E \) of the 2D point vortex equals to

\[
E = \int \frac{m_\Delta^2}{2} d^2 \vec{r} = \frac{mk^2}{4\pi} \ln \frac{R}{a},
\]

where \( R \) is the radius of the entire system and \( a \) is the vortex core radius. The kinetic energy of a single point 2D vortex has an extensive value in the case of \( R \to \infty \).

In physical fluids, the vorticity is localized in small areas. Outside the vortices, most of the fluid is irrotational. In a 3D liquid, the vortex is a tube with strength \( k \).

In contrast to the classical 2D vortex with arbitrary value of \( k \), the vorticity of the quantum 2D vortex has discrete values. The existence of quantum vortices was suggested for the first time by Onsager [11], who proposed that the circulation in superfluid \( HeII \) is quantized with the quantum of circulation \( \frac{h}{m} \). The influence of quantum vortices on the superfluidity of \( HeII \) was underlined by Feynman [12]. The existence of the quantized lines in the 3D superfluid \( HeII \) was revealed by Vinen [13]. The details on this topics can be found in the candidatus scientiarum theses of Enger [14] and Myklebast [15] as well as in the review articles [16, 17]. The quantization of the vorticity in \( HeII \) was explained in terms of the Ginzburg–Landau theory [18].

The velocity field of the superfluid described by the wave functions

\[
\psi = \sqrt{\rho} e^{i\phi}; \quad \phi(r, \theta) = f(r) e^{i\theta}
\]

can be written correspondingly as

\[
\vec{V} = \frac{\hbar}{m} \vec{\nabla} S; \quad \vec{\nabla} = \frac{\hbar}{mr} \hat{e}_\theta.
\]

The circulation around a close path \( C \) in the case of wave function \( \psi \) equals to

\[
k = \int \vec{V} d\vec{l} = \frac{\hbar}{m} \int \vec{\nabla} S \cdot d\vec{l} = \frac{\hbar}{m} \delta S,
\]
where $\delta S$ is the change in the phase of the wave function, as one moves around close path $C$. However, wave function $\psi$ must be single-valued. By this reason, $\delta S$ must be integer multiple of $2\pi$. It means that

$$k = \frac{\hbar}{m} \cdot 2\pi s, \; s = 0, \pm 1, \pm 2... \tag{41}$$

The vorticity of the quantum vortex has discrete values with quantum $\frac{\hbar}{m}$. In the case of the rotational invariant wave function $\phi(\vec{r}, \theta)$ written in the polar coordinates, phase $S$ equals to $S = s\theta$. It produces the same velocity filed as the classical point vortex (39). The kinetic energy of the quantum 2D vortex is expressed in terms of coherence length $\xi$ instead of core radius $a$ in the way

$$E = \frac{\pi \hbar^2}{m} \xi^2 \ln \left( \frac{R}{\xi} \right). \tag{42}$$

The cutoff at $\xi$ is used to avoid the logarithmic divergence near the vortex core.

In spite of multivalued function $\theta(\vec{r} - \vec{r}')$ and of the singular properties of the phase operator $\hat{a}(\vec{r})$ in the case of C–S unitary transformation $U(\vec{r}) = e^{i\theta(\vec{r})}$, the dressed field operators $\hat{\psi}^*(\vec{r})$ and $\hat{\psi}(\vec{r})$ are single valued in the same way as bare field operators $\psi^*(\vec{r})$ and $\psi(\vec{r})$ due to the integer values of factor $\phi = \frac{1}{U}$ which have the physical sense only under the condition of fractional filing factors. The vortices in superconductors and superfluid $\text{HeII}$ were discussed in [19, 20].

### 5. Vector Potential and Effective Magnetic Field in the C–S Theory

To determine vector potential $\hat{a}(\vec{r})$ and the effective magnetic field generated in the presence of quantum point vortices, the density operator of the electron field $\hat{\rho}(\vec{r})$ in the spinless 2D e–h system introduced in [21–22] was used. The spinless 2D electrons and holes subjected to the action of an external perpendicular magnetic field are supposed to be on their lowest Landau levels ($\text{LLL}_s$). These states in the Landau gauge are described by two quantum numbers. One of them is a unidimensional wave vector $t$ of the free motion in one in-plane direction and the second is a discrete quantum number of the Landau quantized oscillations in another in-plane direction perpendicular to the previous one. Due to the fact that only the $\text{LLL}_s$ are discussed, the label describing the second quantum number is omitted. Density operator $\hat{\rho}(\vec{r})$ and its Fourier transforms $\hat{\rho}(\vec{Q})$ were determined in [21–22] as follows:

$$\hat{\rho}(\vec{r}) = \frac{1}{(2\pi)^2} \int d^2\vec{Q} \hat{\rho}(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}}, \quad \hat{\rho}(\vec{Q}) = \int d^2\vec{r} \hat{\rho}(\vec{r}) e^{i\vec{Q}\cdot\vec{r}}, \quad \hat{\rho}(\vec{Q}) = \hat{\rho}_e(\vec{Q}) - \hat{\rho}_h(\vec{Q}). \tag{43}$$

In the approximation of the $\text{LLL}_s$, plasmon operators $\hat{\rho}_e(\vec{Q})$ and $\hat{\rho}_h(\vec{Q})$ look as follows:

$$\hat{\rho}_e(\vec{Q}) = e^{-\frac{\hbar^2Q^2}{2m^2}} \sum_{t} e^{iQ_t\frac{a_t}{2}} a_t^+ a_t; \quad \hat{\rho}_h(\vec{Q}) = e^{-\frac{\hbar^2Q^2}{2m^2}} \sum_{t} e^{-iQ_t\frac{b_t}{2}} b_t^+ b_t, \tag{44}$$
where \( a^\dagger, a \) and \( b^\dagger, b \) are the creation and annihilation operators of the electrons and holes, respectively. The conduction and valence bands considered below are supposed to be simple; the densities of the electrons and holes in the momentum representation are denoted as \( \hat{\rho}_e(\vec{Q}) \) and \( \hat{\rho}_h(\vec{Q}) \), respectively. These expressions were used to determine vector potential \( \vec{a}(\vec{r}) \) introduced in formula (1). It can be transformed in the way

\[
\vec{a}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2 \vec{r} \phi(\vec{r}) \int d^2 \vec{r}' \hat{\rho}(\vec{r}') \frac{(-\vec{e}_x(y-y') + \vec{e}_y(x-x'))}{|\vec{r} - \vec{r}'|^2} =
\]

\[
= -\frac{\phi e}{\alpha} \int d^2 \vec{Q} \hat{\rho}(\vec{Q}) \int d^2 \vec{r}' e^{-i\vec{Q}\cdot\vec{r}'} \frac{(-\vec{e}_x(y-y') + \vec{e}_y(x-x'))}{|\vec{r} - \vec{r}'|^2} =
\]

\[
= -\frac{\phi e}{\alpha} \int d^2 \vec{Q} \hat{\rho}(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}} \int d\rho \int d\omega e^{i\rho \sin(\phi - \theta + \frac{\pi}{2})} (-\vec{e}_x \sin \varphi + \vec{e}_y \cos \varphi). \tag{45}
\]

The representations \( \hat{\rho} = \rho(\cos \varphi, \sin \varphi) \) and \( \vec{Q} = Q(\cos \theta, \sin \theta) \), and the formulas from [23] were used as follows:

\[
e^{i\varphi z} = J_0(z) + 2 \sum_{n=1}^{\infty} [J_{2n}(z) \cos 2nt + iJ_{2n-1}(z) \sin(2n-1)t];
\]

\[
\int_0^{2\pi} d\varphi e^{i\rho \sin(\varphi - \theta + \frac{\pi}{2})} z(-\vec{e}_x \sin \varphi + \vec{e}_y \cos \varphi) = 2\pi i J_1(Q \rho) (-\vec{e}_x \sin \theta + \vec{e}_y \cos \theta) = 2\pi i J_1(Q \rho) \frac{\hat{z} \times \vec{Q}}{|\vec{Q}|}, \tag{46}
\]

where \( \hat{z} \) is the unit vector perpendicular to the plane of the layer and \( J_1(x) \) is the Bessel function of the first order.

Taking into account the integral [24]

\[
\int_0^\infty d\rho J_1(\rho \Omega) = \frac{1}{\Omega}, \tag{47}
\]

one can write

\[
\hat{a}(\vec{r}) = -\frac{i \phi e}{2\pi \alpha} \int d^2 \vec{Q} e^{-i\vec{Q}\cdot\vec{r}} \hat{\rho}(\vec{Q}) \frac{\hat{z} \times \vec{Q}}{Q^2}; \quad \hat{\rho}_e(\vec{Q}) = \hat{\rho}(-\vec{Q}); \quad \hat{a}^\dagger(\vec{r}) = \hat{a}(\vec{r}). \tag{48}
\]

Vector potential \( \vec{a}(\vec{r}) \) leads to the existence of an effective magnetic field determined as follows:

\[
\vec{b}(r) = \text{curl}\hat{a}(\vec{r}) = (\vec{e}_x \frac{\partial}{\partial y} - \vec{e}_y \frac{\partial}{\partial x}) \hat{a}(\vec{r}) = \frac{\phi e}{2\pi \alpha} \int d^2 \vec{Q} \hat{\rho}(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}} =
\]

\[
= \frac{\phi e}{2\pi \alpha} \int d^2 \vec{Q} (\hat{\rho}_e(\vec{Q}) - \hat{\rho}_h(\vec{Q})) e^{-i\vec{Q}\cdot\vec{r}} = \frac{2\pi \phi e}{\alpha} \hat{\rho}(\vec{r}). \tag{49}
\]

As one can see, the effective magnetic field created by the point 2D vortices in the mean-field approximation vanishes, when the following condition is fulfilled:

\[
\left\langle \hat{\rho}(\vec{Q}) \right\rangle = \left\langle \hat{\rho}_e(\vec{Q}) \right\rangle - \left\langle \hat{\rho}_h(\vec{Q}) \right\rangle = 0, \quad \left\langle \hat{b}(\vec{r}) \right\rangle = 0. \tag{50}
\]

Nevertheless, the quantum fluctuations of the vector potential and the effective magnetic field will lead to the appearance of the new branches of the collective elementary excitations in the system. It is necessary to mention that the inclusion only of the \( \text{LLL}_z \) in the definition of the
electron and hole plasmon operators (44) without the participation of excited Landau levels \( (ELL) \) leads to an incomplete expression of density operator \( \hat{\rho}(\vec{r}) \), which can be denoted as \( \hat{\rho}(\vec{r}) \). Although the complete operators \( \hat{\rho}(\vec{r}) \) and \( \hat{\rho}(\vec{r}') \) obey commutation relation (6) \([\hat{\rho}(\vec{r}), \rho(\vec{r}')] = 0\), the incomplete operators \( \hat{\rho}(\vec{r}) \) and \( \hat{\rho}(\vec{r}') \) do not satisfy it exactly. The possibility to satisfy it approximately can be demonstrated in the way

\[
\left[ \hat{\rho}(\vec{r}), \hat{\rho}(\vec{r}') \right] = \frac{1}{(2\pi)^2} \int d^2 \vec{Q} \frac{1}{(2\pi)^2} \int d^2 \vec{P} e^{-i\vec{Q} \cdot \vec{r}' - i\vec{P} \cdot \vec{r}} \left[ \hat{\rho}(\vec{Q}), \hat{\rho}(\vec{P}) \right] =
\]

\[
= -2i \frac{1}{(2\pi)^2} \int d^2 \vec{Q} \frac{1}{(2\pi)^2} \int d^2 \vec{P} e^{-i\vec{Q} \cdot \vec{r}' - i\vec{P} \cdot \vec{r}} \sin \left( \frac{[\vec{P} \times \vec{Q}, \vec{l}_0^2]}{2} \right) \hat{\rho}(\vec{P} + \vec{Q}).
\]

It turns to be zero in the approximation

\[
\hat{\rho}(\vec{P} + \vec{Q}) \approx \hat{\rho}(0) \delta_{\vec{k}_0}(\vec{P} + \vec{Q}, 0).
\]

The commutation relations of plasmon operators \( \hat{\rho}(\vec{Q}), \hat{\rho}(\vec{P}) \) in the \( LLL \) approximation were deduced in [25].

In the theoretical–experimental investigations [26, 27], the striking features in the transverse laser beam patterns were observed. They look as a dark point in the transverse plane and appear as dark spots in the laser beam section. In these points, the real and imaginary parts of the laser electric field vanish; around the given point the modulus of the electric field rises from zero in the form of an inverted cone. If one performs a closed counterclockwise loop surrounding the point, the phase of the envelope of the electric field changes by a quantity referred to as topological charge \( \pm 2\pi m \), where \( m \) is a positive integer. The phase gradient circulation implies that the electric field phase is a multivalued function and the point is the singularity of the phase. As was underlined by the authors of these investigations [26, 27], the laser electric field plays the role of a complex-valued order parameter, whose phase singularities are mathematically described by the same analytical structure as of the two-dimensional pointlike vortices in hydrodynamics [28]. The order parameter in the C–S theory differs by a singular phase from the order parameters introduced in the Bogoliubov microscopic theory of superfluidity [29] and in the Ghinzburg–Landau phenomenological theory of superconductivity [18].

The results obtained in our papers will be used to investigate the transverse patterns of the polariton laser [30].

6. Conclusions

The C–S theory developed by Jackiw and Pi in [1–3] and widely used to describe the FQHEs [4–10] discovered in the one-component two-dimensional electron gas (2DEG) was applied to describe the system of 2D coplanar electrons and holes subjected to the action of a perpendicular magnetic field and interacting with the 2D quantum point vortices. This interaction was introduced into the Hamiltonian using the C–S unitary transformation, which transforms the electrons of the conduction and valence bands into dressed electrons and holes. They look as composite particles formed by bare electrons and holes with attached quantum point vortices. The numbers of the attached vortices to the conduction electron and to the valence electron are the same. Because the holes represent the absent electrons in the valence band, they inherit the number of attached vortices from them. In such a way, the numbers of the attached quantum
vortices to the conduction electrons and the holes are the same. In all points of the real space, where the charged particles do exist, the arising electron or hole point quantum vortices give rise to the resultant C–S vector potential and to the effective magnetic field generated by it. They exist simultaneously with the external magnetic field. The charged particles interact with both fields in the same manner, their interaction energies being proportional to the respective electric charges. It was shown that the C–S vector potential and the effective magnetic field vanish in the mean-field approximation, when the average values of the density operators describing the conduction electrons and the holes in the valence band coincide. It means that the C–S vector potentials created by electrons and holes in average compensate each other. However, even in this case, the quantum fluctuation of the C–S field will lead to the appearance of new branches of the collective elementary excitations.

References

METASTABLE BOUND STATES OF TWO-DIMENSIONAL MAGNETOEXCITONS IN
THE LOWEST LANDAU LEVELS APPROXIMATION

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Abstract

The possible existence of the two-dimensional bimagnetoexcitons and metastable bound
states formed by two magnetoexcitons with opposite in-plane wave vectors \( \vec{k} \) and \( -\vec{k} \) has been
studied. Magnetoexcitons taking part in the formation of molecules look as two electric dipoles
with the arms oriented in-plane perpendicular to the respective wave vectors and with the length
of the arms \( d = kl_0^2 \), where \( l_0 \) is the magnetic length. Two antiparallel dipoles moving with equal,
yet antiparallel, wave vectors have the possibility of moving with equal probability in any
direction of the plane, which is determined by the trial wave function of relative motion \( \varphi_n(\|\vec{k}\|) \)
depending on modulus \( k \). The magnetoexcitons are composed of electrons and holes situated on
the lowest Landau levels with the cyclotron energies greater than the binding energy of the 2D
Wannier–Mott exciton. The description has been made in Landau gauge. The spin states of two
electrons have been chosen in the form of antisymmetric or symmetric combinations with
parameter \( \eta = \pm 1 \). The effective spins of two heavy holes have been combined in the same
resultant spinor states as the spin of the electrons. Because the projections of the both spinor
states with \( \eta = \pm 1 \) are equal to zero, the influence of the Zeeman splitting effect vanishes. In the
case of trial wave function \( \varphi_2(k) = (8\alpha^3)^{1/2}k^2l_0^2e^{-\alpha k^2} \), the maximal density of the
magnetoexcitons in the momentum space is concentrated on the in-plane ring with radius
\( k_r = 1/(\sqrt{\alpha}l_0) \). In the approximation of the lowest Landau levels, when the influence of the
excited Landau levels is neglected, stable bound states of bimagnetoexcitons do not exist for both
spin orientations. Instead, in the case of \( \alpha = 0.5 \) and \( \eta = 1 \), a deep metastable bound state with
the activation barrier comparable with two magnetoexciton ionization potentials \( 2I_f \) has been
revealed. In the case of \( \eta = -1 \) and \( \alpha = 3.4 \), only a shallow metastable bound state can appear.

1. Introduction

The study of the biexciton formation in the presence of an external magnetic field was
initiated in [1, 3] using the theory of the hydrogen atom in a magnetic field [1, 4] and the theory
of the hydrogen molecule formation as a starting platform [5–7]. The authors of [1, 3] supposed
that the holes are sufficiently heavy so as to neglect their Landau quantization states.
At small magnetic fields, the ground state of the hydrogen-like biexciton with the molecular axis directed along the magnetic field corresponds to singlet term $1\Sigma_g^+$. With increasing magnetic field, at intermediary values, triplet state $3\Sigma_u^-$ becomes lower due to the interaction of the electron spins with the magnetic field. With a further increase in the magnetic field strength, triplet state $3\Pi_u^-$ comes into play and becomes the lowest tightly bound hydrogen molecular state [2, 3]. The authors of [1, 6, 7] suggested the possible existence of new bound complexes and chains at fairly high magnetic fields and electron–hole (e–h) densities. The binding energy per one e–h pair in these states may be higher than that in the exciton or excitonic molecule states.

According to [8, 9], the Coulomb exchange electron-hole interaction leads to the formation of para and ortho exciton states, which affect the binding energy of the biexciton. In the case of 2D magnetoexcitons, these aspects have not yet been studied because the main task in the creation of the bimagnetoexciton is the character of the spinless magnetoexciton–magnetoexciton interaction. Already in [10, 11, 12] it was established that the magnetoexcitons composed of electrons and holes lying on the lowest Landau levels (LLLs), being bound in the states with in-plane wave vectors $\vec{k}_i = 0$, form an ideal, noninteracting gas. This effect takes place because the 2D electron and the hole moving with resultant wave vector $\vec{k}_i = 0$ on the surface of a layer in a perpendicular magnetic field in the Landau gauge description are subjected to the Landau quantizations with the same gyration points. They have the quantum orbits with the same radii, which do not depend on the electron and hole masses and depend only on the magnetic length. These e–h pairs being bound by the direct Coulomb interaction and forming the bound states with wave vector $\vec{k}_i = 0$ look as completely neutral compound particles. These magnetoexcitons with $\vec{k}_i = 0$ cannot form bound states. Only two magnetoexcitons with opposite nonzero wave vectors $\vec{k}$ and $-\vec{k}$ can form bound states with the resultant wave vector equal to zero. This statement will be investigated in the present paper.

It is useful to remember that the interaction between two magnetoexcitons with wave vectors $\vec{k}_i = 0$ can appear, as was shown in [13], taking into account the influence of the excited Landau levels (ELLs) as well as the Rashba spin–orbit coupling (RSOC) generated by a perpendicular external electric field, parallel to the magnetic field. However, all interactions and bound states investigated below have nothing to do with these supplementary influences and are based exclusively on the direct Coulomb interactions of electrons and holes with arbitrary masses situated on their LLLs. The paper is organized as follows. In the second section, the Hamiltonian of the 2D electrons with spins and the heavy holes with effective spins lying on their LLLs and interacting through their Coulomb interactions is introduced. The necessary wave functions are proposed. In section three, the main analytical and numerical calculations are effectuated. Section four is dedicated to the discussions of the obtained results. The conclusions are formulated in section five.

### 2. The Hamiltonian of the e–h System and the Wave Functions of the Bound States of the Interacting Two-Dimensional Magnetoexcitons

The authors of [10–12, 14, 15] considered spinless 2D electrons and holes paying the main attention to the Landau quantization of their orbital motion on the surface of the layer subjected
to the action of an external perpendicular magnetic field. The description of their quantization is made in the Landau gauge, in which the charged particles have a free motion in one in-plane direction described by the plane waves with one-dimensional wave numbers \( p \) and \( q \) and undergo quantized oscillations around the gyration points in another in-plane direction perpendicular to the previous one.

The quantum numbers of the Landau quantized levels for electrons and holes are \( n_e \) and \( n_h \), which in our case are lowest \( n_e = n_h = 0 \). The creation and annihilation operators for electrons and for holes are denoted as \( a_{p,q,\sigma}^+, a_{p,\sigma} \) and \( b_{q,\sigma}^+, b_{q,\sigma} \), respectively. The operators have a supplementary spin label \( \sigma = \pm 1/2 \), which describes the spin projections of the conduction electrons and the effective spin of the heavy holes. In these denotations, a simple generalization of the Hamiltonian describing the Coulomb interaction of the 2D electrons and holes with spins situated on their LLLs, neglecting for simplicity the e–h exchange interaction leading to the formation of ortho and para magnetoexcitons, as well as the RSOC, has the form

\[
H_{\text{Coul}}^{\text{LLL}} = \frac{1}{2} \sum_{\mathbf{Q}} W(\mathbf{Q}) [\hat{\rho}(\mathbf{Q}) \hat{\rho}(-\mathbf{Q}) - \hat{N}_e - \hat{N}_h],
\]

\[
\hat{\rho}(\mathbf{Q}) = \hat{\rho}_e(\mathbf{Q}) - \hat{\rho}_h(\mathbf{Q}); W(\mathbf{Q}) = \frac{2\pi e^2}{\varepsilon_0 S} \left| \mathbf{Q} \right|^{-\frac{\varepsilon_0^2}{2}},
\]

\[
\hat{\rho}_e(\mathbf{Q}) = \sum_{i,\sigma} e^{iQ\cdot\mathbf{R}_i} a_{\mathbf{Q}+\mathbf{R}_i,\sigma}^+ a_{\mathbf{Q}+\mathbf{R}_i,\sigma}; \hat{N}_e = \hat{\rho}_e(0),
\]

\[
\hat{\rho}_h(\mathbf{Q}) = \sum_{i,\sigma} e^{-iQ\cdot\mathbf{R}_i} b_{\mathbf{Q}+\mathbf{R}_i,\sigma}^+ b_{\mathbf{Q}+\mathbf{R}_i,\sigma}; \hat{N}_h = \hat{\rho}_h(0),
\]

where \( \varepsilon_0 \) is the dielectric constant, \( S \) is the layer surface area, \( l_0 \) is the magnetic length, \( \hat{\rho}_e(\mathbf{Q}) \) and \( \hat{\rho}_h(\mathbf{Q}) \) are the electron and hole plasmon operators, respectively.

Hamiltonian (1) can be transcribed in the way

\[
\begin{align*}
H_{\text{Coul}}^{\text{LLL}} &= H_{e-e}^{\text{LLL}} + H_{h-h}^{\text{LLL}} + H_{e-h}^{\text{LLL}}, \\
H_{e-e}^{\text{LLL}} &= \frac{1}{2} \sum_{\mathbf{Q}} \sum_{p,q,\sigma,\sigma'} W(\mathbf{Q}) e^{iQ\cdot\mathbf{R}_{pq}} e^{iQ\cdot\mathbf{R}_{pq}} a_{p,\sigma}^+ a_{q,\sigma'}^+ a_{q,\sigma'} a_{p,\sigma}^+ , \\
H_{h-h}^{\text{LLL}} &= \frac{1}{2} \sum_{\mathbf{Q}} \sum_{p,q,\sigma,\sigma'} W(\mathbf{Q}) e^{-iQ\cdot\mathbf{R}_{pq}} e^{-iQ\cdot\mathbf{R}_{pq}} b_{p,\sigma}^+ b_{q,\sigma'}^+ b_{q,\sigma'} b_{p,\sigma}^+ , \\
H_{e-h}^{\text{LLL}} &= -\sum_{\mathbf{Q}} \sum_{p,q,\sigma,\sigma'} W(\mathbf{Q}) e^{iQ\cdot\mathbf{R}_{pq}} e^{iQ\cdot\mathbf{R}_{pq}} a_{p,\sigma}^+ b_{q,\sigma'}^+ b_{q,\sigma'} a_{p,\sigma}^+ .
\end{align*}
\]

The interaction coefficients depend only on the difference \( (p - q) \) in the case of the electron–electron \( (e-e) \) and hole–hole \( (h-h) \) interactions, and on the sum \( (p + q) \) in the case of the \( e-h \) interactions. The magnetoexciton creation operator introduced in [12] and later used in [13–15] with spin labels looks as follows:

\[
\psi_{e,h}(\mathbf{k},\Sigma_e,\Sigma_h) = \frac{1}{\sqrt{N}} \sum_{t} e^{-i\mathbf{k}\cdot\mathbf{R}_t} a_{\frac{1}{2}+\mathbf{k},\Sigma_e}^+ b_{\frac{1}{2}+\mathbf{k},\Sigma_h}^+ N = \frac{S}{2\pi l_0^2}; l_0 = \frac{\hbar c}{eB}.
\]

Here, \( \mathbf{k}(k_x,k_y) \) is the vector of the center of mass in-plane motion, \( t \) is the unidimensional
vector of the relative $e-h$ motion with the function of relative motion $e^{i\theta_i l_i^2}$ in the momentum representation, which leads to the $\delta(y-k_i l_i^2)$ function of the relative motion in the real space representation. $N$ is the degree of degeneracy of the Landau quantization levels. It is an extensive value proportional to $S$. $B$ is the magnetic field strength.

The wave function of the magnetoexciton looks as follows:

$$\left| \psi_{ex} \left( \vec{k}, \Sigma_e, \Sigma_h \right) \right\rangle = \hat{\psi}^+_{ex} \left( \vec{k}, \Sigma_e, \Sigma_h \right) |0\rangle; \quad a_{\alpha e} |0\rangle; \quad b_{\beta h} |0\rangle = 0,$$

where $|0\rangle$ is the ground state of the system. The 2D magnetoexciton with wave vector $\vec{k} \neq 0$ has the form of an electric dipole with arm $d = kl_0^2$ oriented perpendicular to wave vector $\vec{k}$. As was established in [10–12] and was mentioned above, two magnetoexcitons with wave vectors $\vec{k} = 0$ have no dipole moments, are similar with the neutral compound particles and do not interact with each other through the Coulomb forces. In contrast to them, two magnetoexcitons with nonzero wave vectors $\vec{k}_1$ and $\vec{k}_2$ do interact opening the possibility of forming bimagnetoexcitons. The wave function of two magnetoexcitons with quantum numbers $|\vec{k}, \Sigma_{e1}, \Sigma_{h1}\rangle$ and $|\vec{k}, \Sigma_{e2}, \Sigma_{h2}\rangle$ has the construction

$$\left| \psi_{ex,ex} \left( \vec{k}, \Sigma_{e1}, \Sigma_{h1}; -\vec{k}, \Sigma_{e2}, \Sigma_{h2} \right) \right\rangle = \frac{1}{N} \sum_{i,s} e^{i\theta_i (l_i^2 + i\epsilon)} a^+_s x_{\Sigma e, x_{\Sigma h}} a^*_s x_{\Sigma e, x_{\Sigma h}} b^+_s x_{\Sigma h, x_{\Sigma h}} b^*_s x_{\Sigma h, x_{\Sigma h}} |0\rangle. \quad (5)$$

The wave function of the bimagnetoexciton with wave vector $\vec{k} = 0$ as a bound state of two magnetoexcitons with wave vectors $\vec{k}$ and $-\vec{k}$ and spin quantum numbers $\Sigma_{e1}, \Sigma_{h1}, \Sigma_{e2}, \Sigma_{h2}$ can be constructed as a superposition of the wave functions (5) introducing wave function $\varphi_n(\vec{k})$ of relative motion, which can also play the role of the variational function determining the minimal energy of the bimagnetoexciton as well as the density $|\varphi_n(\vec{k})|^2$ of the magnetoexcitons taking part in the formation of the bound state. According to [8, 9], the spin configurations of the bound states depend essentially on the ratio between the ortho–para exciton splitting and the binding energy of the biexciton. In the presence of a strong magnetic field and magnetoexciton formation, these values are unknown; the present paper trends to determine one of them. We will construct symmetric and antisymmetric superpositions of two electron spin states and separately of two hole effective spin states in the form

$$\frac{1}{\sqrt{2}} \sum_{\Sigma = \frac{1}{2}}^{1/2} \left( \eta_e \right)^{\Sigma} a^*_p x_{\Sigma e} a^*_q x_{\Sigma h}; \quad \frac{1}{\sqrt{2}} \sum_{\Sigma = \frac{1}{2}}^{1/2} \left( \eta_h \right)^{\Sigma} b^*_p x_{\Sigma h} b^*_q x_{\Sigma h}; \quad \eta_e = \pm 1; \quad \eta_h = \pm 1; \quad (6)$$

because the e–h exchange interaction is neglected in the Hamiltonians (1) and (2). Below, we will suppose that both pairs of spins $(\Sigma_{e1}, \Sigma_{e2})$ and $(\Sigma_{h1}, \Sigma_{h2})$ are simultaneously in the states with the same $\eta_e = \eta_h = \eta = \pm 1$. The wave functions of the bimagnetoexcitons under these conditions look as follows:

$$\left| \psi_{\text{binex}} \left( 0, \eta, \varphi_n \right) \right\rangle = \frac{1}{2N^{1/2}} \sum_{\Sigma = \frac{1}{2}}^{1/2} \left( \eta \right)^{\Sigma} \sum_{k} \varphi_n(\vec{k}) \left( \eta \sum_{\Sigma} e^{i\theta_l l_k^2} a^+_n x_{\Sigma e} a^*_n x_{\Sigma h} b^+_n x_{\Sigma h} b^*_n x_{\Sigma h} \right) |0\rangle. \quad (7)$$

The chosen variational wave functions of the relative motion in the momentum and in the real
space representations \( \phi_n(\vec{k}) \) and \( \psi_n(\vec{r}) \), their normalization conditions and the main parameters are the followings:

\[
\phi_0(x) = (4\alpha)^{1/2} e^{-\alpha x^2}; \quad \phi_2(x) = (8\alpha^3)^{1/2} x^2 e^{-\alpha x^2}; \quad x = kl_0, \quad \frac{1}{N} \sum_k |\phi_n(\vec{k})|^2 = \int_0^\infty x dx |\phi_n(x)|^2 = 1, 
\]

\[
\psi_n(\vec{r}) = \int \phi_n(\vec{k}) e^{i\vec{k}\cdot\vec{r}} d^2\vec{k} = \int_0^\infty x dx \phi_n(x) J_0(x \cdot r/l_0), \quad \psi_0(r) = e^{-\frac{r^2}{4\alpha l_0^2}}; \quad \psi_2(r) \sim (1 - \frac{r^2}{4\alpha l_0^2}) e^{-\frac{r^2}{4\alpha l_0^2}).
\]

Here, \( J_0(z) \) is the Bessel function of the zeroth order. The selected trial wave functions depend only on modulus \( k = |\vec{k}| \). \( \phi_0(x) \) has the maximum at the point of \( x = 0 \), the middle value of \( x^2 = 1/(2\alpha) \), the radius of quantum state \( \psi_0(\vec{r}) \) equals to \( a = 2\sqrt{\alpha l_0} \). Function \( \phi_2(\vec{k}) \) has a maximum on the 2D ring with radius \( k_r = 1/(\sqrt{\alpha l_0}) \). In the real space, function \( \psi_2(r) \) has a maximum at the point of \( r_0 = 0 \), the positive values up till the point of \( r_1 = a_\eta \), where it changes the sign and achieves a minimum at the point of \( r_2 = 8\alpha l_0 \). The absolute value in the minimum is much smaller than in the maximum. In fact, function \( \psi_2(r) \) has the same radius \( a_\eta \); however, function \( \phi_2(x) \) has some preferential properties, when the normalization integral of the bimagnetoexciton wave function (7) is calculated. These calculations give rise to the overlapping integrals \( L_\eta(\alpha) \) as follows:

\[
\langle \phi_{\text{bimex}}(0,\eta,\phi_n) \psi_{\text{bimex}}(0,\eta,\phi_n) \rangle = 2(1 - \eta L_\eta(\alpha)),
\]

\[
L_\eta(\alpha) = \int_0^\infty x dx \int_0^\infty y dy \phi_n^*(x) \phi_n(y) J_0(xy); \quad L_0(\alpha) = \frac{1}{\alpha + \frac{1}{4\alpha}}; \quad L_2(\alpha) = \frac{2\alpha^2 - \frac{1}{\alpha}}{(\alpha + \frac{1}{4\alpha})^3}.
\]

The normalization integrals \( (1 - \eta L_\eta(\alpha)) \) are shown in Fig. 1. It is evident that the factor \( (1 - L_0(\alpha)) \) has the value zero at the point of \( \alpha = 1/2 \), which leads to a singularity in the inverse function. The inverse normalization integral \( (1 - L_2(\alpha))^{-1} \) is regular at any values of \( \alpha \).

Fig. 1. Normalization integrals as a function of parameter \( \alpha \): (a) the case of \( \eta = 1 \), (b) the case of \( \eta = -1 \).
3. Binding Energies of the Bound States of Two Interacting Magnetoexcitons

The expectation values of Hamiltonian (2) averaged with wave function (7) characterized by wave vector \( \vec{k} = 0 \), two values of \( \eta = \pm 1 \), and by trial wave functions \( \phi_n(\vec{k}) \) equal to

\[
E_{\text{bimex}}(0, \eta, \phi_n) = \frac{\langle \phi_{\text{bimex}}(0, \eta, \phi_n) | H_{\text{Coul}}^{\text{LLL}} | \phi_{\text{bimex}}(0, \eta, \phi_n) \rangle}{\langle \phi_{\text{bimex}}(0, \eta, \phi_n) | \phi_{\text{bimex}}(0, \eta, \phi_n) \rangle}. \tag{10}
\]

The average values of the partial Hamiltonians \( H_{e-e}^{\text{LLL}} \) and \( H_{h-h}^{\text{LLL}} \) calculated with the functions (7) are the same and equal to

\[
\langle \psi_{\text{bimex}}(0, \eta, \phi_n) | H_{e-e}^{\text{LLL}} | \psi_{\text{bimex}}(0, \eta, \phi_n) \rangle = \langle \psi_{\text{bimex}}(0, \eta, \phi_n) | H_{h-h}^{\text{LLL}} | \psi_{\text{bimex}}(0, \eta, \phi_n) \rangle = \frac{(2/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z}) e^{(\eta Q_0 - \eta Q_0') k_0^2}}{(2\eta/N^2) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z}) e^{(\eta Q_0 - \eta Q_0') k_0^2}}. \tag{11}
\]

In the polar coordinates representation, we can write

\[
\vec{k} = (k_x, k_y) = k (\cos \varphi, \sin \varphi); \quad \vec{k}_0 = \vec{z}, \quad k_0 = z;
\]

\[
\vec{Q} = (Q_x, Q_y) = Q (\cos \theta, \sin \theta); \quad \vec{Q}_0 = \vec{y}; \quad Q_0 = y;
\]

\[
\vec{z} = (z_x, z_y) = z (\cos \psi, \sin \psi); \quad \vec{z}_0 = \vec{x}; \quad z_0 = x;
\]

\[

(Q_x k_y - Q_y k_x) l_0^2 = Q k l_0^2 (\sin \varphi \cos \theta - \cos \varphi \sin \theta) = yz \sin (\varphi - \theta) = z_1 \sin t_1;
\]

\[

(x_x Q_y - x_y Q_x) l_0^2 = Q \vec{x}_0^2 (\sin \psi \cos \theta - \cos \psi \sin \theta) = xy \sin (\theta - \psi) = z_2 \sin t_2;
\]

\[

(k_x z_y - k_y z_x) l_0^2 = k z_0^2 (\sin \psi \cos \varphi - \cos \psi \sin \varphi) = xz \sin (\psi - \varphi) = z_3 \sin t_3.
\]

Here, we have introduced the denotations

\[
t_1 = \varphi - \theta; \quad t_2 = \theta - \psi; \quad t_3 = \psi - \varphi; \quad z_1 = yz; \quad z_2 = xy; \quad z_3 = xz.
\]

In these denotations, expression (11) looks as follows:

\[
\langle \psi_{\text{bimex}}(0, \eta, \phi_n) | H_{e-e}^{\text{LLL}} | \psi_{\text{bimex}}(0, \eta, \phi_n) \rangle = \frac{(2/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z}) e^{i z_2 \sin t_1}}{2 \eta/N^2 \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z}) e^{i z_2 \sin t_1}}. \tag{14}
\]

In the same denotations, the average e–h Hamiltonian looks as follows:

\[
\langle \psi_{\text{bimex}}(0, \eta, \phi_n) | H_{e-h}^{\text{LLL}} | \psi_{\text{bimex}}(0, \eta, \phi_n) \rangle = - \frac{(4/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})}{(4\eta/N^2) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})} - \frac{(4/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})}{(4\eta/N^2) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})} \tag{15}
\]

The average value of the full Coulomb interaction Hamiltonian (2) can be expressed as follows:

\[
\langle \psi_{\text{bimex}}(0, \eta, \phi_n) | H_{\text{Coul}}^{\text{LLL}} | \psi_{\text{bimex}}(0, \eta, \phi_n) \rangle = \frac{(4/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})}{(4\eta/N^2) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})} \times (e^{i z_2 \sin t_1} - 1) - \frac{(4/\sqrt{N}) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})}{(4\eta/N^2) \sum_r \sum_{Q \neq \vec{0}} W(\vec{Q}) \phi_n^*(\vec{z}) \phi_n(\vec{Q} - \vec{z})} \times \phi_n(\vec{Q} - \vec{z}) e^{i z_2 \sin t_1}.
\]
\[
\times \cos(z_2 \sin t_2) + (4\eta/N) \sum_{Q \neq k} \sum_{\tilde{k}} W(\tilde{Q}) \phi_n(\tilde{z}) \phi_n(\tilde{k}) \times \\
\times \left[ \cos(z_2 \sin t_2) \cos(z_3 \sin t_3) + \cos(z_1 \sin t_1) \cos(z_3 \sin t_3) - \\
- \exp(i z_1 \sin t_1 + i z_2 \sin t_2 + i z_3 \sin t_3) \right].
\]

To calculate these expressions, the relations below are required [16-17]:

\[
e^{iz_1 \sin t_1} = J_0(z) + 2 \sum_{k=1}^{\infty} J_{2k}(z) \cos(2kt) + i J_{2k-1}(z) \sin(2k-1)t; \\
e^{iz_2 \sin t_2} = I_0(z) + 2 \sum_{k=1}^{\infty} I_k(z) \cos kt,
\]

where \( J_\mu(z) \) and \( I_\mu(z) \) are the Bessel functions [16-17]. Taking into account that functions \( W(\tilde{Q}), \phi_n(\tilde{z}) \) and \( \phi_n(\tilde{k}) \) depend only on moduli \(|\tilde{Q}|, |\tilde{z}| \) and \(|\tilde{k}| \), respectively, the integrations on angles \( \varphi, \theta, \psi \) lead to the results

\[
\frac{1}{2\pi} \int_0^{2\pi} d\varphi \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy e^{iz_1 \sin t_1} e^{iz_2 \sin t_2} e^{iz_3 \sin t_3} = J_0(z_1) J_0(z_2) J_0(z_3) + 2 \sum_{k=1}^{\infty} J_{2k}(z_1) J_{2k}(z_2) J_{2k}(z_3); \\
\frac{1}{2\pi} \int_0^{2\pi} d\varphi \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy \cos(z_1 \sin t_1) \cos(z_3 \sin t_3) = J_0(z_1) J_0(z_3), \ i = 1, 2; \\
\frac{1}{2\pi} \int_0^{2\pi} d\varphi \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy \cos(z_2 \sin t_2) = J_0(z_2), \ i = 1, 2, 3; \\
\frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy e^{2\alpha xy \cos(\theta-\psi)} e^{i z_2 \sin(\theta-\psi)} = J_0(xy) I_0(2\alpha xy) + 2 \sum_{k=1}^{\infty} J_{2k}(xy) J_{2k}(2\alpha xy); \\
\frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy e^{2\alpha xy \cos(\theta-\psi)} = I_0(2\alpha xy).
\]

The angle integration excluding trial function \( \phi_n([\tilde{x} - \tilde{y}]) \) leads to the expression

\[
\langle \psi_{\text{bines}} (0, \eta, \varphi_n) | H_{\text{cos}} | \psi_{\text{bines}} (0, \eta, \varphi_n) \rangle = -4(e^2 / (\epsilon_0 \epsilon_0)) \int_0^{\infty} d\epsilon e^{-\epsilon^2/2} \times \\
\times \int_0^{\infty} dx |\phi_n(x)|^2 J_0(xy) + 4(e^2 / (\epsilon_0 \epsilon_0)) \int_0^{\infty} d\epsilon e^{-\epsilon^2/2} \int_0^{2\pi} d\theta \times \\
\times \int_0^{2\pi} d\psi \phi_n([\tilde{x} - \tilde{y}]) (e^{i \psi \sin(\theta-\psi)} - 1) + 4\eta e^2 / (\epsilon_0 \epsilon_0) \int_0^{\infty} d\epsilon e^{-\epsilon^2/2} \times \\
\times \int_0^{\infty} dx |\phi_n(x)|^2 \int_0^{\infty} dz \phi_n(z) (J_0(x \cdot y) J_0(x \cdot z) + J_0(x \cdot z) J_0(y \cdot z) - \\
- J_0(x \cdot y) J_0(x \cdot z) J_0(y \cdot z) - 2 \sum_{k=1}^{\infty} J_{2k}(x \cdot y) J_{2k}(x \cdot z) J_{2k}(y \cdot z)),
\]

where \(|\tilde{x} - \tilde{y}| = \sqrt{x^2 + y^2 - 2xy \cos(\theta-\psi)}\).

Trial wave function \( \phi_2(x) \) can be represented in the form

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\[ \varphi_2([\vec{x} - \vec{y}]) = \left(8\alpha^3\right)^{\frac{1}{2}} |\vec{x} - \vec{y}| e^{-a|x-y|} = \left(8\alpha^3\right)^{\frac{1}{2}} e^{-a(x^2+y^2)} \times \]
\[ \times \left[ x^2 + y^2 - 2xy \frac{\partial}{\partial(2\alpha xy)} \right] \left[ I_0(2\alpha xy) + 2\sum_{k=1}^{\infty} I_{2k}(2\alpha xy) \cos 2k(\theta - \varphi) \right]. \]

Using integrals (18), one can obtain the expression
\[ \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy \varphi_2([\vec{x} - \vec{y}]) \left( e^{i\alpha y \sin(\theta - \varphi)} - 1 \right) = \left(8\alpha^3\right)^{\frac{1}{2}} e^{-a(x^2+y^2)} \times \]
\[ \times \left\{ (x^2 + y^2) \left[ (J_0(xy) - 1)I_0(2\alpha xy) + \sum_{k=1}^{\infty} J_{2k}(xy)I_{2k}(2\alpha xy) \right] - \right. \]
\[ -2xy \left[ (J_0(xy) - 1)I_1(2\alpha xy) + \sum_{k=1}^{\infty} J_{2k}(xy)I_{2k+1}(2\alpha xy) \right] - \]
\[ \left. -\frac{2}{\alpha} \sum_{k=1}^{\infty} k \cdot J_{2k}(xy)I_{2k}(2\alpha xy) \right\}. \]

Here, the derivatives of Bessel functions \( I_n(z) \) and \( J_n(z) \) of the integer order were used [16, 18]:
\[ \frac{dI_n(z)}{dz} = -I_{n+1}(z), \quad \frac{dJ_n(z)}{dz} = J_{n+1}(z) - J_{n-1}(z). \]

Taking into account the integral (21), the second term in the right-hand side of the average value (19) can be transcribed in the following way
\[ \varepsilon_2 = 4 \left( \frac{e^2}{e_x^0} \right) \int_0^{\infty} dy \int_0^{\infty} dx \varphi_2(x) \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{1}{2\pi} \int_0^{2\pi} dy \times \]
\[ \times \varphi_2([\vec{x} - \vec{y}]) \left( e^{i\alpha y \sin(\theta - \varphi)} - 1 \right) = 4 \left( \frac{e^2}{e_x^0} \right) \left(8\alpha^3\right)^{\frac{1}{2}} \times \]
\[ \times \left\{ \int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} J_0(x,y)I_0(2\alpha xy) + \int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} J_0(x,y)I_0(2\alpha xy) - \right. \]
\[ -\int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} I_0(2\alpha xy) - 2\int_0^{\infty} dy \cdot ye^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} J_0(x,y)I_1(2\alpha xy) - \]
\[ -\int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} I_0(2\alpha xy) + 2\int_0^{\infty} dy \cdot ye^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} I_1(2\alpha xy) + \]
\[ +2\int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} \sum_{k=1}^{\infty} J_{2k}(xy)I_{2k}(2\alpha xy) - \]
\[ -4\int_0^{\infty} dy \cdot ye^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} \sum_{k=1}^{\infty} J_{2k}(xy)I_{2k+1}(2\alpha xy) + \]
\[ +2\int_0^{\infty} dy e^{-\frac{y^2}{2\alpha^2}} \int_0^{\infty} dx x^2 e^{-2\alpha x^2} \sum_{k=1}^{\infty} J_{2k}(xy)I_{2k}(2\alpha xy) - \]
\[
-\frac{4}{\alpha} \int_0^\infty \int d\gamma e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} \int d\mathbf{x} e^{-2\alpha x^2} \sum_{k=1}^{\infty} kJ_{2k}(xy)I_{2k}(2\alpha xy).
\]  

(23)

The third contribution to the average value (19) looks as follows:

\[
\varepsilon_3 = 4\eta \left(\frac{e^2}{\varepsilon_0\varepsilon_0}\right) \int_0^\infty \int d\gamma e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} x dx \varphi_2(x) \left(\int_0^\infty dz \varphi_2(z) \left[J_0(x \cdot y) J_0(x \cdot z) + J_0(x \cdot z) J_0(y \cdot z) - J_0(x \cdot y) J_0(x \cdot z) J_0(y \cdot z) - 2 \sum_{k=1}^{\infty} J_{2k}(xy) J_{2k}(xz) J_{2k}(yz)\right]\right) = 4\eta \left(\frac{e^2}{\varepsilon_0\varepsilon_0}\right) \left(8\alpha^2\right) \left(\int_0^\infty \int d\gamma e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} \int d\mathbf{x} e^{-\alpha x^2} \int d\mathbf{z} e^{-\alpha z^2} \left[J_0(x \cdot y) J_0(x \cdot z) + J_0(x \cdot z) J_0(y \cdot z) - J_0(x \cdot y) J_0(x \cdot z) J_0(y \cdot z) - 2 \sum_{k=1}^{\infty} J_{2k}(xy) J_{2k}(xz) J_{2k}(yz)\right]\right).
\]  

(24)

The first term in the average value (19), as well as the overlapping integrals \( L_n(\alpha) \), can be calculated analytically as follows:

\[
\varepsilon_1 = -4 \left(\frac{e^2}{\varepsilon_0\varepsilon_0}\right) \left(\frac{\pi}{2}\right) J_0(xy) = -4I_1 \frac{\sqrt{4\alpha}}{\sqrt{1+4\alpha}} \left[1 - \frac{1}{1+4\alpha} + \frac{3}{8} \frac{1}{(1+4\alpha)^2}\right];
\]  

\[
I_1 = \left(\frac{e^2}{\varepsilon_0\varepsilon_0}\right) \left(\frac{\pi}{2}\right); \quad L_2(\alpha) = \frac{2\alpha^2 - \frac{1}{2}}{\left(\alpha + \frac{1}{4\alpha}\right)^2}.
\]  

(25)

Here, \( I_1 \) is the ionization potential of the 2D magnetoexciton with wave vector \( k_\parallel = 0 \).

\[
\frac{E_1(\alpha)}{2I_1} = \frac{\varepsilon_1(\alpha)}{4I_1(1-\eta L_2(\alpha))} = -\frac{\sqrt{4\alpha}}{\sqrt{1+4\alpha}} \left[1 - \frac{1}{1+4\alpha} + \frac{3}{8} \frac{1}{(1+4\alpha)^2}\right] \left[1 - \eta(2\alpha^2 - 1/2)/\left(\alpha + 1/(4\alpha)^2\right)\right].
\]  

(26)

In expression \( \varepsilon_2 (23) \) there are three integrals containing only one modified Bessel function \( I_n(2\alpha xy) \) with \( \nu = 0, 1 \). They depend on parameter \( \alpha \) of variational wave function \( \varphi_2(x) \) in the way:

\[
I_1 = -\int_0^\infty \int d\gamma e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} \int d\mathbf{x} e^{-2\alpha x^2} I_0(2\alpha xy) = -\frac{\sqrt{2\pi}}{128\alpha^3} \frac{(8 + 24\alpha + 19\alpha^2)}{(1 + \alpha)^{3/2}},
\]  

\[
I_2 = -\int_0^\infty \int d\gamma y^2 e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} \int d\mathbf{x} e^{-2\alpha x^2} I_0(2\alpha xy) = -\frac{\sqrt{2\pi}}{32\alpha^2} \frac{(2 + 5\alpha)}{(1 + \alpha)^{3/2}},
\]  

\[
I_3 = 2\int_0^\infty \int d\gamma y e^{-\gamma \left(\frac{1}{2} + \alpha\right)^2} I_1(2\alpha xy) = \frac{\sqrt{2\pi}}{32\alpha^2} \frac{(4 + 7\alpha)}{(1 + \alpha)^{3/2}}.
\]  

(27)

In contrast to the first three integrals \( I_1, I_2, I_3 \) containing one modified Bessel function \( I_0(cx) \) or \( I_1(cx) \), the other three integrals contain the products of two Bessel functions of the
types $J_0(bx)I_0(cx)$ and $J_0(bx)I_1(cx)$, one of them being also a modified Bessel function.

Integrals $I_4$, $I_5$, and $I_6$ were calculated analytically exactly.

They have the expressions

$$I_4 = \int_0^\infty dy e^{-\frac{y}{2\alpha}} \int_0^\infty dx e^{-2\alpha x^2} J_0(xy) I_0(2\alpha xy) = \frac{1}{32\alpha^4} \left\{ 3I_0^{\frac{1}{2}}(q,c) + \frac{3}{8\alpha}(4\alpha^2 - 1)I_0^{\frac{3}{2}}(q,c) + \frac{(4\alpha^2 - 1)}{128\alpha^2}I_0^{\frac{5}{2}}(q,c) - \frac{7}{4}I_1^{\frac{1}{2}}(q,c) - \frac{4\alpha^2 - 1}{16\alpha}I_1^{\frac{3}{2}}(q,c) + \frac{1}{8}I_2^{\frac{1}{2}}(q,c) \right\},$$

$$I_5 = \int_0^\infty dy e^{-\frac{y}{2\alpha}} \int_0^\infty dx e^{-2\alpha x^2} J_0(xy) I_0(2\alpha xy) = \frac{1}{16\alpha^2} \left\{ I_0^{\frac{1}{2}}(q,c) + \frac{4\alpha^2 - 1}{8\alpha}I_0^{\frac{3}{2}}(q,c) - \frac{1}{2}I_1^{\frac{3}{2}}(q,c) \right\},$$

$$I_6 = -2\int_0^\infty dy e^{-\frac{y}{2\alpha}} \int_0^\infty dx e^{-2\alpha x^2} J_0(xy) I_1(2\alpha xy) = \frac{1}{16\alpha^3} \left\{ I_0^{\frac{1}{2}}(q,c) + \frac{4\alpha^2 - 1}{16\alpha}I_0^{\frac{3}{2}}(q,c) - \frac{1}{4}I_1^{\frac{3}{2}}(q,c) - \frac{3}{2}I_1^{\frac{1}{2}}(q,c) - \frac{4\alpha^2 - 1}{16\alpha}I_1^{\frac{3}{2}}(q,c) + \frac{1}{4}I_2^{\frac{1}{2}}(q,c) \right\}. \quad (28)$$

Here, the following denotations were used [18]:

$$I_0^{\frac{1}{2}}(q,c) = \frac{1}{(q^2 + c^2)^{\frac{1}{2}}}; \quad I_0^{\frac{3}{2}}(q,c) = \frac{q}{(q^2 + c^2)^{\frac{3}{2}}}; \quad I_1^{\frac{1}{2}}(q,c) = \frac{c}{(q^2 + c^2)^{\frac{3}{2}}}; \quad I_0^{\frac{5}{2}}(q,c) = 2\sqrt{\frac{1 - 2k^2}{\pi q}} K(k),$$

$$I_0^{\frac{3}{2}}(q,c) = \sqrt{\frac{1 - 2k^2}{\pi q^3}} \left[ 2E(k) - K(k) \right],$$

$$I_0^{\frac{5}{2}}(q,c) = \frac{1}{2} \sqrt{\frac{1 - 2k^2}{\pi q^3}} \left[ 8(1 - 2k^2)E(k) - (5 - 8k^2)K(k) \right],$$

$$I_1^{\frac{1}{2}}(q,c) = \frac{1}{k} \sqrt{\frac{1 - 2k^2}{\pi q^3(1 - k^2)}} \left[ (1 - k^2)K(k) - (1 - 2k^2)E(k) \right],$$

$$I_1^{\frac{3}{2}}(q,c) = \frac{1}{2k} \sqrt{\frac{1 - 2k^2}{\pi q^3(1 - k^2)}} \left[ (1 - k^2)(1 - 8k^2)K(k) - (1 - 16k^2 + 16k^4)E(k) \right],$$

$$I_1^{\frac{5}{2}}(q,c) = \frac{1}{2k^2(1 - k^2)} \sqrt{\frac{1 - 2k^2}{\pi q^3}} \left[ (2 + 5k^2 - 8k^4) \times \right.$$

$$\left. \times (1 - k^2)K(k) - 2(1 - 2k^2)(1 + 4k^2 - 4k^4)E(k) \right]. \quad (29)$$

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The complete elliptic integrals of the first and second orders $K(k)$ and $E(k)$ depend on modulus $k$, which in its turn depends on parameters $q$ and $c$ in the way

$$k = \frac{1}{\sqrt{2}} \left(1 - \frac{q}{\sqrt{q^2 + c^2}}\right)^{\frac{1}{2}}, \quad q = \frac{1 + 4\alpha + 4\alpha^2}{8\alpha}; \quad c = \frac{1}{2}. \quad (30)$$

In the range of small values of the modulus $k \ll 1$ the series expansions of functions $K(k)$ and $E(k)$ can be used:

$$K(k) \approx \frac{\pi}{2} \left(1 + \frac{k^2}{4} + \frac{9}{64} k^4\right); \quad E(k) \approx \frac{\pi}{2} \left(1 - \frac{k^2}{4} - \frac{3}{64} k^4\right). \quad (31)$$

In this limit, the apparent singular expressions in formulas (29) can be transformed in the regular forms as follows:

$$\frac{1}{k} \left[(1-k^2)K(k) - (1-2k^2)E(k)\right] \approx \frac{3}{4} \pi k \left(1 - \frac{3}{8} k^2\right);$$

$$\frac{1}{k} \left[(1-k^2)(1-8k^2)K(k) - (1-16k^2 + 16k^4)E(k)\right] \approx \frac{15}{4} \pi k \left(1 - \frac{15}{8} k^2\right);$$

$$\frac{1}{k^2} \left[(2+5k^2-8k^4)(1-k^2)K(k) - 2(1-2k^2)(1+4k^2-4k^4)E(k)\right] \approx \frac{105}{16} \pi k^2; \quad k \to 0. \quad (32)$$

Using these expressions, we can obtain the simplified formulas in the limit $k \to 0$

$$I_{1/2}^\alpha(q, c) = \frac{3}{4} \pi k \sqrt{\frac{1-2k^2}{\pi q^2}} \left(1 - \frac{3}{8} k^2\right); \quad I_{5/2}^\alpha(q, c) = \frac{15}{8} \pi k \sqrt{\frac{1-2k^2}{\pi q^5}} \left(1 - \frac{15}{8} k^2\right);$$

$$I_{5/2}^\alpha(q, c) = \frac{105}{32} \pi k^2 \left(1 - k^2\right) \sqrt{\frac{1-2k^2}{\pi q^5}}; \quad k \to 0. \quad (33)$$

The required table integrals $I_{p}^\beta$ as a function of parameter $\alpha$ in the case of parameters $q = (1+4\alpha + 4\alpha^2)/(8\alpha); \quad c = 1/2$ are shown in Fig. 2.

The next three integrals $I_7, I_8,$ and $I_9$ determine the third contribution $\delta_3$ described by the formulas (24). Some details of their calculations are the following. Integral $I_7$ equals to

$$I_7 = \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty d\gamma d\alpha d\beta \gamma^3 e^{-\gamma^2} \int_0^\infty \int_0^\infty x^3 e^{-\alpha x^2} \int_0^\infty \int_0^\infty z^3 e^{-\beta z^2} \left(J_0(\alpha x) J_0(\beta z) + J_0(\beta x) J_0(\alpha z)\right) =$$

$$= \frac{4\sqrt{\pi} (4\alpha^2 - 1)}{(4\alpha^2 + 1)^3} q^{1/2} q^{1/2} q^{1/2} q^{1/2} - \frac{2\alpha \sqrt{\pi} (4\alpha^2 - 3)}{(4\alpha^2 + 1)^4} q^{3/2} q^{3/2} q^{3/2} - \frac{3\alpha^2 \sqrt{\pi}}{4 (4\alpha^2 + 1)^4} q^{5/2} q^{5/2}. \quad (34)$$

It was calculated exactly taking into account that the product of two Bessel functions $J_0(\alpha x) J_0(\beta z)$ can be transformed into the expression $J_0(\alpha y) J_0(\beta z)$ by the interchange of the variables $x = z \cdot y$. The integral [18] was used:

$$\int_0^\infty dz e^{-\alpha^2 z^2} J_0(\beta z) = 1/(2\alpha) e^{-\alpha^2}. \quad (35)$$
Fig. 2. Table integrals $I_{\nu}^\beta$ as a function of indices $\nu$ and $\beta$, and parameters $q = \frac{4\alpha^2 + 4\alpha + 1}{8\alpha}, c = \frac{1}{2}$ in the cases (a–d) and parameters $q = \frac{1 + 4\alpha + 4\alpha^2}{2(1 + 4\alpha^2)}, c = \frac{1}{1 + 4\alpha^2}$ in the case (e). All of them are plotted as a function of parameter $\alpha$.

There are two integrals $I_8$ and $I_9$ containing three Bessel functions as follows:

$$I_8 = \int_0^\infty \int_0^\infty dx^2 e^{-ax^2} \int_0^\infty dz^2 e^{-az^2} J_0(xy) J_0(xz) J_0(yz),$$

and

$$I_9 = -2\sum_{n=1}^\infty \int_0^\infty \int_0^\infty dx^2 e^{-ax^2} \int_0^\infty dz^2 e^{-az^2} \cdot J_{2n}(xy) J_{2n}(xz) J_{2n}(yz).$$

The three steps in the deduction of integrals $I_8$, $I_9$ are based on the use of the formulas [17, 18]:

$$\int_0^\infty dz^2 e^{-az^2} J_0(xz) J_0(yz) = \frac{1}{2\alpha} e^{-\frac{(x^2 + y^2)}{4\alpha}} I_0\left(\frac{xy}{2\alpha}\right),$$

$$\int_0^\infty dx^2 e^{-ax^2} J_0(bx) I_0(cx) = \frac{1}{2p} \exp\left(-\frac{c^2 - b^2}{4p}\right) J_0\left(\frac{bc}{2p}\right),$$

$$\int_0^\infty \beta^2 e^{-\beta y} J_0(cx) = I_0^\beta(q, c).$$

The exact calculations of integrals (36) and (37) leads to cumbersome expressions listed in the
appendix. Expressions $I_{2n}^{1/2}(q,c)$ of the exact formulas (35)–(38), as well as of the appendix, are described in [18]. There are still four double integrals $I_{10} - I_{13}$ in the composition of expression (23). They were calculated analytically exactly below. In all of them the table integral [18]

$$Z_{2n}(p,b,c) = \int_0^\infty dx e^{-px^2} J_{2n}(bx) I_{2n}(cx) = \frac{1}{2p} e^{\frac{c^2-b^2}{4p}} J_{2n}\left(\frac{bc}{2p}\right)$$ (39)

and its derivatives were used as the first step:

$$-\frac{d}{dp} Z_{2n}(p,b,c) = \frac{1}{2p^2} \exp\left(\frac{c^2-b^2}{4p}\right) \left[2n+1 + \frac{c^2-b^2}{4p}\right] J_{2n}\left(\frac{bc}{2p}\right) -$$

$$- \frac{bc}{2p} J_{2n+1}\left(\frac{bc}{2p}\right) = \int_0^\infty dx e^{-px^2} J_{2n}(bx) I_{2n}(cx);$$

$$\frac{d^2}{dp^2} Z_{2n}(p,b,c) = \int_0^\infty dx e^{-px^2} J_{2n}(bx) I_{2n}(c,x) =$$

$$= \frac{1}{p^2} e^{\frac{c^2-b^2}{4p}} \left[ J_{2n}\left(\frac{bc}{2p}\right) \left[ 1 + n + \frac{c^2-b^2}{8p}\right] \left[ 1 + 2n + \frac{c^2-b^2}{4p}\right] + \frac{c^2-b^2}{8p} \right] -$$

$$- \frac{bc}{4p} \left[ 4n+5 + \frac{c^2-b^2}{2p}\right] J_{2n+1}\left(\frac{bc}{2p}\right) + \frac{b^2c^2}{8p} J_{2n+2}\left(\frac{bc}{2p}\right);$$

$$\left[ - \frac{\partial^2}{\partial p \partial c} + \frac{2n}{c} \frac{\partial}{\partial p} \right] Z_{2n}(p,b,c) = \int_0^\infty dx e^{-px^2} J_{2n}(bx) I_{2n+1}(cx) =$$

$$= \frac{1}{2p^2} e^{\frac{c^2-b^2}{4p}} \left\{ \frac{c}{2p} \left[ 2(n+1) + \frac{c^2-b^2}{4p}\right] J_{2n}\left(\frac{bc}{2p}\right) -$$

$$- \frac{bc^2}{4p^2} + \frac{b}{2p} \left[ 2n+3 + \frac{c^2-b^2}{4p}\right] J_{2n+1}\left(\frac{bc}{2p}\right) + \frac{b^2c^2}{4p^2} J_{2n+2}\left(\frac{bc}{2p}\right) \right\}. $$ (40)

In all these formulas, it is necessary to substitute parameters $p = 2x$, $b = y$, and $c = 2\alpha y$. They lead to expressions $(c^2-b^2)/(4p) = y^2(4\alpha^2-1)/(8\alpha)$, $(b c)^2/(2p^2) = y^2/(8\alpha)$; $(bc^2)/(4p^2) = y^3/4$, $(b c)/(4p^2) = y^3/(8\alpha)$, $1/(2p^2) = 1/(8\alpha^2)$. Formulas (40) permit to calculate the integral

$$\int_0^\infty dx e^{-2ax^2} J_{2n}(xy) I_{2n+1}(2\alpha xy) = \frac{1}{8\alpha^2} e^{\frac{(4\alpha^2-1)}{8\alpha}} x \times$$

$$\times \left\{ \frac{y}{2} \left[ 2(n+1) + \frac{(4\alpha^2-1)}{8\alpha} y^2\right] J_{2n}\left(\frac{y^2}{2}\right) - \left[ \frac{y}{4\alpha} \left( 2n+3 + \frac{(4\alpha^2-1)}{8\alpha} y^2\right) \right] \times$$

$$\times J_{2n+1}\left(\frac{y^2}{2}\right) + \frac{y^3}{8\alpha^2} J_{2n+2}\left(\frac{y^2}{2}\right) \right\}. $$ (41)
The following integration on variable $y$ using the table integral [18]

\[ \int_0^{\infty} z^{a-1} e^{-cz} J_a(cz) \, dz = I_a^{\infty}(q, c), \quad (42) \]

gives the possibility of exactly calculating the last four double integrals as follows:

\[
I_{10} = 2 \sum_{n=1}^{\infty} \int_0^{\infty} dy y^2 e^{-y^2(2+1/2\alpha^2)} \int_0^{\infty} dx x^3 e^{-2\alpha^2 x^2} J_{2n}(xy) I_{2n}(2\alpha xy) = \\
= \frac{1}{8\alpha^2} \sum_{n=1}^{\infty} \left[ (2n+1) \frac{\Gamma(\frac{3}{2})}{\Gamma(2n+1)} I_{2n}^{\infty}(q, c) + \frac{(4\alpha^2 - 1)}{8\alpha} I_{2n}^{\infty}(q, c) - \frac{1}{2} I_{2n+1}^{\infty}(q, c) \right],
\]

\[
I_{11} = -\frac{4}{\alpha} \sum_{n=1}^{\infty} \int_0^{\infty} dy e^{-y^2(1+1/2\alpha^2)} \int_0^{\infty} dx x^3 e^{-2\alpha^2 x^2} J_{2n}(xy) I_{2n}(2\alpha xy) = \\
= -\frac{1}{4\alpha^3} \sum_{n=1}^{\infty} \left[ (1+2n) \frac{\Gamma(\frac{3}{2})}{\Gamma(2n+1)} I_{2n}^{\infty}(q, c) + \frac{(4\alpha^2 - 1)}{8\alpha} I_{2n}^{\infty}(q, c) - \frac{1}{2} I_{2n+1}^{\infty}(q, c) \right];
\]

\[
I_{12} = 2 \sum_{n=1}^{\infty} \int_0^{\infty} dy e^{-y^2(2+1/2\alpha^2)} \int_0^{\infty} dx x^5 e^{-2\alpha^2 x^2} J_{2n}(xy) I_{2n}(2\alpha xy) = \\
= \frac{1}{8\alpha^2} \sum_{n=1}^{\infty} \left[ (1+n)(1+2n) \frac{\Gamma(\frac{3}{2})}{\Gamma(2n+1)} I_{2n}^{\infty}(q, c) + \frac{(4\alpha^2 - 1)}{8\alpha} I_{2n}^{\infty}(q, c) + \\
+ \frac{(4\alpha^2 - 1)^2}{128\alpha^2} I_{2n}^{\infty}(q, c) - \frac{4n+5}{4} I_{2n+1}^{\infty}(q, c) - \frac{(4\alpha^2 - 1)}{16\alpha} I_{2n+1}^{\infty}(q, c) + \frac{\alpha}{4} I_{2n+2}^{\infty}(q, c) \right];
\]

\[
I_{13} = -\sum_{n=1}^{\infty} \int_0^{\infty} dy e^{-y^2(2+1/2\alpha^2)} \int_0^{\infty} dx x^4 e^{-2\alpha^2 x^2} J_{2n}(xy) I_{2n+1}(2\alpha xy) = \\
= -\frac{1}{4\alpha^2} \sum_{n=1}^{\infty} \left[ (n+1) \frac{\Gamma(\frac{3}{2})}{\Gamma(2n+1)} I_{2n}^{\infty}(q, c) + \frac{(4\alpha^2 - 1)}{16\alpha} I_{2n+1}^{\infty}(q, c) - \frac{2n+3}{4\alpha} I_{2n+1}^{\infty}(q, c) - \left(1 + \frac{4\alpha^2 - 1}{32\alpha^2}\right) I_{2n+2}^{\infty}(q, c) + \\
+ \frac{1}{8\alpha} I_{2n+2}^{\infty}(q, c) \right];
\]

\[
q = \frac{1 + 4\alpha + 4\alpha^2}{8\alpha}, \quad c = \frac{1}{2}, \quad k = \frac{1}{\sqrt{2}} \left(1 - \frac{q}{\sqrt{q^2 + c^2}}\right)^{\frac{3}{2}}. \quad (43)
\]
The contributions to the energy spectrum expressed by integrals $I_1 - I_{13}$ are shown in Fig. 3 as the functions of parameter $\alpha$ of trial wave function $\varphi_2(k)$.

4. **The Electron Structure of the Bound States**

As was shown in the previous papers [10–12], the interaction of two 2D magnetoeexcitons with wave vectors $\vec{k} = 0$, which are composed of electrons and holes lying on the LLLs, vanishes because they look as two neutral compound particles. The interactions between them can appear
under the influence of the ELLs as well as the RSOC [13]. In the absence of the last interactions, only two magnetoexcitons with wave vectors \( \vec{k} \neq 0 \) can interact through the Coulomb forces and can take part in the formation of bound states. The 2D magnetoexcitons with \( \vec{k} \neq 0 \) look as electric dipoles whose the in-plane arms have a length of \( d = k l_0^2 \), where \( l_0 \) is the magnetic length. The arms are oriented perpendicular to the direction of wave vectors \( \vec{k} \). The molecule and the bound states can be formed by two magnetoexcitons with antiparallel wave vectors \( \vec{k} \) and \( -\vec{k} \). They have the structure of two antiparallel dipoles bound together. The possibility of their orientation as a whole in any direction of the layer plane with equal probability was supposed. This possibility is achieved via introducing the trial wave function of relative motion of two magnetoexcitons in the frame of bound state \( \varphi_n(\vec{k}) \), which depends on modulus \( k \).

![Graph](image)

**Fig. 4.** Total energies of two bound 2D magnetoexcitons with wave vectors \( \vec{k} \) and \( -\vec{k} \), with different spin structures \( \eta = \pm 1 \) and with trial wave function \( \varphi_2(k) \), as the functions of parameter \( \alpha \). (a) the case of \( \eta = 1 \), (b) the case of \( \eta = -1 \). The total energies are related to the value of \( 2I_f \), where \( I_f \) is the ionization potential of a free magnetoexciton with wave vector \( k = 0 \).
The numerical calculations effectuated in the case of the function 
\[
\varphi_2(\vec{k}) = (8\alpha^3)^{1/2} (k l_0)^2 e^{-\alpha(k l_0)^2}
\]
made it possible to obtain the full energies of the bound states as a function of parameter \(\alpha\) of the trial wave function in two cases with \(\eta = \pm 1\), corresponding to two electron and hole spin structures. In both spin configurations, the full energies of the bound states are greater than the value of \(-2I_i\) in the entire range of \(\alpha\). All these states are unstable as regards the dissociation in the form of two free magnetoexcitons with \(\vec{k} = 0\). Despite this fact, a deep metastable bound state with the activation barrier comparable to two magnetoexciton ionization potentials \(2I_i\) was revealed in the case of \(\eta = 1\) and \(\alpha = 0.5\). Only a shallow state was found in the case of \(\eta = -1\) and \(\alpha = 3.4\).

5. Conclusions

In the LLL approximation, when the influence of the ELLs is neglected, the bound states of two magnetoexcitons with opposite wave vectors \(\vec{k}\) and \(-\vec{k}\) have been studied. The electrons and the heavy holes are situated on the LLLs with the cyclotron energies greater than the binding energy of the 2D Wannier–Mott exciton. The spin states of two electrons and the effective spin states of two heavy holes have been combined so as to form symmetric or antisymmetric states separately, characterized by parameter \(\eta = \pm 1\). Each magnetoexciton with wave vector \(\vec{k} \neq 0\) looks as an electric dipole with the length of the arm between the electron and the hole equal to \(d = k l_0^2\), where \(l_0\) is the magnetic length. The arm is oriented in-plane perpendicular to wave vector \(\vec{k}\). It has been supposed that the bound states are formed by two dipoles with antiparallel arms and wave vectors, yet with the total wave vector equal to zero. The bound pair of two dipoles is oriented arbitrarily in the plane of the layer and characterized by the trial wave function of relative motion \(\varphi_n(\vec{k})\), which depends only on modulus \(|\vec{k}|\). The numerical calculations with trial wave function 
\[
\varphi_2(k) = (8\alpha^3)^{1/2} (k l_0)^2 e^{-\alpha(k l_0)^2}
\]
have demonstrated the absence of stable molecular bound states in both spin orientations \(\eta = \pm 1\). Instead of them, the metastable bound states have been revealed. One of them is a deep bound state. It does exist in the case of \(\eta = 1\) and \(\alpha = 0.5\) and is characterized by the activation barrier comparable to two magnetoexciton ionization potentials \(2I_i\). In the case of \(\eta = -1\) and \(\alpha = 3.4\), only a shallow metastable bound state can be formed.
Appendix

The exact values of integrals $I_8$ (36) and $I_9$ (37) are given below.

$$I_8 = \left[ -\sqrt{\frac{\pi}{2}} \left( \frac{32a^2}{(1+2a)^2(1+4a^2)^3} + \frac{16a}{(1+2a)^3(1+4a^2)^2} - ight. ight.$$ 

$$- \frac{4}{(1+2a)^2(1+4a^2)^3} + \frac{4}{(1+2a)^3(1+4a^2)^2} \right) \cdot \left( 2\sqrt{\frac{1}{(1+2a)^3(1+4a^2)^2}} \right) +$$ 

$$\sqrt{\frac{\pi}{2}} \left( \frac{4a}{(1+2a)^2(1+4a^2)^3} - \frac{2}{(1+2a)^3(1+4a^2)^2} \right) \cdot \frac{3^{3/2}}{4 \left( 1+2a \right)^3(1+4a^2)} \times \left[ \begin{array}{c} 2F_1[1/4,3/4,1,- \frac{4}{(1+2a)^4}] \\
\end{array} \right] +$$ 

$$+ \left\{ \frac{3}{2(1+2a)^5} \sqrt{\frac{1}{(1+2a)^3(1+4a^2)^2}} \right\} \cdot \left[ \begin{array}{c} 2F_1[5/4,7/4,2,- \frac{4}{(1+2a)^4}] \\
\end{array} \right] +$$ 

$$+ \left\{ \frac{6\sqrt{2\pi}}{(1+2a)^6} \right\} \times \left[ \begin{array}{c} 2F_1[5/4,7/4,2,- \frac{4}{(1+2a)^4}] \\
\end{array} \right] +$$ 

$$+ \left\{ \frac{10\sqrt{\frac{\pi}{2}}}{2(1+2a)^{10}} \right\} \times \left[ \begin{array}{c} 2F_1[9/4,11/4,3,- \frac{4}{(1+2a)^4}] \\
\end{array} \right]; \quad (A1)$$

Integral $I_9$ is a series expansion, whose terms are triple products of the Bessel functions of the orders $2n$ with $n = 1, 2, \ldots, \infty$. The first ten terms of the sum with $n=1, 2, \ldots, 10$ were taken into account explicitly. The negligible contributions of the next terms with $n \geq 11$ have been verified carefully.
\[
I_s = 2\sqrt{2}(\frac{1}{1+4a^2})^{3/2} \times \left( \frac{3\sqrt{\pi} F_1[\frac{5}{4}, \frac{7}{4}, \frac{3}{4}, -\frac{4}{(1+2a)^4}] - 8((1+2a)^2)^{3/2}}{128((1+2a)^2)^{3/2}} \right) + \\
\frac{35\sqrt{\pi} F_1[\frac{9}{4}, \frac{11}{4}, \frac{5}{4}, -\frac{4}{(1+2a)^4}]}{128((1+2a)^2)^{3/2}} - \frac{231\sqrt{\pi} F_1[\frac{13}{4}, \frac{15}{4}, \frac{7}{4}, -\frac{4}{(1+2a)^4}]}{1024((1+2a)^2)^{3/2}} + \\
\frac{6435\sqrt{\pi} F_1[\frac{17}{4}, \frac{19}{4}, \frac{9}{4}, -\frac{4}{(1+2a)^4}]}{32768((1+2a)^2)^{3/2}} - \frac{46189\sqrt{\pi} F_1[\frac{21}{4}, \frac{23}{4}, \frac{11}{4}, -\frac{4}{(1+2a)^4}]}{262144((1+2a)^2)^{1/2}} + \\
\frac{676039\sqrt{\pi} F_1[\frac{25}{4}, \frac{27}{4}, \frac{13}{4}, -\frac{4}{(1+2a)^4}]}{4194304(1+2a)^{3/2}} - \frac{5014575\sqrt{\pi} F_1[\frac{29}{4}, \frac{31}{4}, \frac{15}{4}, -\frac{4}{(1+2a)^4}]}{4179869184((1+2a)^2)^{3/2}} + \\
\frac{300540195\sqrt{\pi} F_1[\frac{33}{4}, \frac{35}{4}, \frac{17}{4}, -\frac{4}{(1+2a)^4}]}{2147483648((1+2a)^2)^{3/2}} - \frac{2268783825\sqrt{\pi} F_1[\frac{37}{4}, \frac{39}{4}, \frac{19}{4}, -\frac{4}{(1+2a)^4}]}{1719869184((1+2a)^2)^{3/2}} + \\
\frac{(34461632205\sqrt{\pi} F_1[\frac{41}{4}, \frac{43}{4}, \frac{21}{4}, -\frac{4}{(1+2a)^4}])}{(274877906944((1+2a)^2)^{3/2})} - \\
\frac{12\sqrt{2a^2}(\frac{1}{1+4a^2})^{3/2} \times \left( \frac{3\sqrt{\pi} F_1[\frac{5}{4}, \frac{7}{4}, \frac{3}{4}, -\frac{4}{(1+2a)^4}] - 8((1+2a)^2)^{3/2}}{128((1+2a)^2)^{3/2}} \right) + \\
\frac{35\sqrt{\pi} F_1[\frac{9}{4}, \frac{11}{4}, \frac{5}{4}, -\frac{4}{(1+2a)^4}]}{128((1+2a)^2)^{3/2}} - \frac{231\sqrt{\pi} F_1[\frac{13}{4}, \frac{15}{4}, \frac{7}{4}, -\frac{4}{(1+2a)^4}]}{1024((1+2a)^2)^{3/2}} + \\
\frac{6435\sqrt{\pi} F_1[\frac{17}{4}, \frac{19}{4}, \frac{9}{4}, -\frac{4}{(1+2a)^4}]}{32768((1+2a)^2)^{3/2}} - \frac{46189\sqrt{\pi} F_1[\frac{21}{4}, \frac{23}{4}, \frac{11}{4}, -\frac{4}{(1+2a)^4}]}{262144((1+2a)^2)^{1/2}} + \\
\frac{676039\sqrt{\pi} F_1[\frac{25}{4}, \frac{27}{4}, \frac{13}{4}, -\frac{4}{(1+2a)^4}]}{4194304(1+2a)^{3/2}} - \frac{5014575\sqrt{\pi} F_1[\frac{29}{4}, \frac{31}{4}, \frac{15}{4}, -\frac{4}{(1+2a)^4}]}{4179869184((1+2a)^2)^{3/2}} + \\
\frac{300540195\sqrt{\pi} F_1[\frac{33}{4}, \frac{35}{4}, \frac{17}{4}, -\frac{4}{(1+2a)^4}]}{2147483648((1+2a)^2)^{3/2}} - \frac{2268783825\sqrt{\pi} F_1[\frac{37}{4}, \frac{39}{4}, \frac{19}{4}, -\frac{4}{(1+2a)^4}]}{1719869184((1+2a)^2)^{3/2}} + \\
\frac{(34461632205\sqrt{\pi} F_1[\frac{41}{4}, \frac{43}{4}, \frac{21}{4}, -\frac{4}{(1+2a)^4}])}{(274877906944((1+2a)^2)^{3/2})} + \\
\frac{12\sqrt{2a^2}(\frac{1}{1+4a^2})^{3/2} \times \left( \frac{3\sqrt{\pi} F_1[\frac{5}{4}, \frac{7}{4}, \frac{3}{4}, -\frac{4}{(1+2a)^4}] - 8((1+2a)^2)^{3/2}}{128((1+2a)^2)^{3/2}} \right) + \\
\frac{35\sqrt{\pi} F_1[\frac{9}{4}, \frac{11}{4}, \frac{5}{4}, -\frac{4}{(1+2a)^4}]}{128((1+2a)^2)^{3/2}} - \frac{231\sqrt{\pi} F_1[\frac{13}{4}, \frac{15}{4}, \frac{7}{4}, -\frac{4}{(1+2a)^4}]}{1024((1+2a)^2)^{3/2}} + \\
\frac{6435\sqrt{\pi} F_1[\frac{17}{4}, \frac{19}{4}, \frac{9}{4}, -\frac{4}{(1+2a)^4}]}{32768((1+2a)^2)^{3/2}} - \frac{46189\sqrt{\pi} F_1[\frac{21}{4}, \frac{23}{4}, \frac{11}{4}, -\frac{4}{(1+2a)^4}]}{262144((1+2a)^2)^{1/2}} + \\
\frac{676039\sqrt{\pi} F_1[\frac{25}{4}, \frac{27}{4}, \frac{13}{4}, -\frac{4}{(1+2a)^4}]}{4194304(1+2a)^{3/2}} - \frac{5014575\sqrt{\pi} F_1[\frac{29}{4}, \frac{31}{4}, \frac{15}{4}, -\frac{4}{(1+2a)^4}]}{4179869184((1+2a)^2)^{3/2}} + \\
\frac{300540195\sqrt{\pi} F_1[\frac{33}{4}, \frac{35}{4}, \frac{17}{4}, -\frac{4}{(1+2a)^4}]}{2147483648((1+2a)^2)^{3/2}} - \frac{2268783825\sqrt{\pi} F_1[\frac{37}{4}, \frac{39}{4}, \frac{19}{4}, -\frac{4}{(1+2a)^4}]}{1719869184((1+2a)^2)^{3/2}} + \\
\frac{(34461632205\sqrt{\pi} F_1[\frac{41}{4}, \frac{43}{4}, \frac{21}{4}, -\frac{4}{(1+2a)^4}])}{(274877906944((1+2a)^2)^{3/2})} + \right)
\]
\[
4 \sqrt{2a} \left( \frac{1}{1 + 4a^2} \right)^{3/2} \times \left( - \frac{15(1 + 2a) \sqrt{\pi} F[Z_1, \frac{5}{4}, \frac{7}{4}, 3, - \frac{4}{(1 + 2a)^2}] + 35 \sqrt{\pi} F[Z_1, \frac{9}{4}, \frac{11}{4}, 4, - \frac{4}{(1 + 2a)^3}] - 128((1 + 2a)^3 (1 + 2a)^2)^{1/2} \right)
\]

\[
8(1 + 2a)^3 (1 + 2a)^2)^{5/2} - \frac{315(1 + 2a) \sqrt{\pi} F[Z_1, \frac{9}{4}, \frac{11}{4}, 5, - \frac{4}{(1 + 2a)^4}] + 1024((1 + 2a)^3 (1 + 2a)^2)^{3/2} \right) -
\]

\[
3003(1 + 2a) \sqrt{\pi} F[Z_1, \frac{13}{4}, \frac{15}{4}, 6, - \frac{4}{(1 + 2a)^5}] + 1024((1 + 2a)^3 (1 + 2a)^2)^{3/2} \right) \}
\]

\[
6435 \sqrt{\pi} F[Z_1, \frac{17}{4}, \frac{19}{4}, 8, - \frac{4}{(1 + 2a)^5}] - 307268((1 + 2a)^3 (1 + 2a)^2)^{9/2} \right) \}
\]

\[
230945 \sqrt{\pi} F[Z_1, \frac{21}{4}, \frac{23}{4}, 10, - \frac{4}{(1 + 2a)^5}] - 32768((1 + 2a)^3 (1 + 2a)^2)^{13/2} \right) \}
\]

\[
(969969(1 + 2a) \sqrt{\pi} F[Z_1, \frac{21}{4}, \frac{23}{4}, 11, - \frac{4}{(1 + 2a)^5}] + 2028117((1 + 2a)^3 (1 + 2a)^2)^{21/2} \right) \}
\]

\[
(16900975(1 + 2a) \sqrt{\pi} F[Z_1, \frac{25}{4}, \frac{27}{4}, 13, - \frac{4}{(1 + 2a)^5}] + 4917826435((1 + 2a)^3 (1 + 2a)^2)^{27/2} \right) \}
\]

\[
35102025 \sqrt{\pi} F[Z_1, \frac{29}{4}, \frac{31}{4}, 14, - \frac{4}{(1 + 2a)^5}] - 4194304((1 + 2a)^3 (1 + 2a)^2)^{25/2} \right) \}
\]

\[
(145422675(1 + 2a) \sqrt{\pi} F[Z_1, \frac{29}{4}, \frac{31}{4}, 15, - \frac{4}{(1 + 2a)^5}] + 33554432((1 + 2a)^3 (1 + 2a)^2)^{31/2} \right) \}
\]

\[
300540195 \sqrt{\pi} F[Z_1, \frac{33}{4}, \frac{35}{4}, 16, - \frac{4}{(1 + 2a)^5}] - 33554432((1 + 2a)^3 (1 + 2a)^2)^{29/2} \right) \}
\]

\[
(9917826435(1 + 2a) \sqrt{\pi} F[Z_1, \frac{33}{4}, \frac{35}{4}, 17, - \frac{4}{(1 + 2a)^5}] + 2147483648((1 + 2a)^3 (1 + 2a)^2)^{35/2} \right) \}
\]
\[
\begin{align*}
(20419054425\sqrt{\pi_2} F_i[\frac{37}{4}, \frac{39}{4}, -18, -4] / (2147483648(1+2a)^5((1+2a)^2)^{33/2}) - \\
(83945001525(1+2a)\sqrt{\pi_2} F_i[\frac{37}{4}, \frac{39}{4}, -19, -4] / (17179869184((1+2a)^2)^{39/2}) + \\
(17230816025\sqrt{\pi_2} F_i[\frac{41}{4}, \frac{43}{4}, -20, -4] / (17179869184((1+2a)^2)^{37/2}) - \\
(1412926920405(1+2a)\sqrt{\pi_2} F_i[\frac{41}{4}, \frac{43}{4}, -21, -4] / (274877906944((1+2a)^2)^{43/2}) + \\
(2893136075115\sqrt{\pi_2} F_i[\frac{45}{4}, \frac{47}{4}, -22, -4] / (274877906944((1+2a)^2)^{41/2}) - \\
\sqrt{2}\sqrt{\pi} F_i[\frac{5}{4}, \frac{7}{4}, -3, -4] / (1+2a)^2)^{7/2} - \\
175\sqrt{\pi_2} F_i[\frac{9}{4}, \frac{11}{4}, 5, -4] / (1+2a)^4((1+2a)^2)^{7/2} - \\
35\sqrt{\pi_2} F_i[\frac{9}{4}, \frac{11}{4}, 4, -4] / (1+2a)^6((1+2a)^2)^{5/2} + \\
2835\sqrt{\pi_2} F_i[\frac{13}{4}, \frac{15}{4}, 6, -4] / (1+2a)^8((1+2a)^2)^{5/2} - \\
6237\sqrt{\pi_2} F_i[\frac{13}{4}, \frac{15}{4}, 5, -4] / (1+2a)^{10}((1+2a)^2)^{5/2} + \\
64(1+2a)^4((1+2a)^2)^{11/2} - \\
39039\sqrt{\pi_2} F_i[\frac{13}{4}, \frac{15}{4}, 7, -4] / (1+2a)^{12}((1+2a)^2)^{5/2} + \\
1024((1+2a)^2)^{13/2} - \\
83655\sqrt{\pi_2} F_i[\frac{17}{4}, \frac{19}{4}, 8, -4] / (1+2a)^4((1+2a)^2)^{15/2} - \\
512((1+2a)^2)^{15/2} - \\
6435\sqrt{\pi_2} F_i[\frac{17}{4}, \frac{19}{4}, 8, -4] / (1+2a)^6((1+2a)^2)^{15/2} + \\
1859715(1+2a)^8((1+2a)^2)^{13/2} - \\
256((1+2a)^2)^{13/2} + \\
2078505\sqrt{\pi_2} F_i[\frac{21}{4}, \frac{23}{4}, 9, -4] / (1+2a)^{10}((1+2a)^2)^{13/2} + \\
3926065\sqrt{\pi_2} F_i[\frac{21}{4}, \frac{23}{4}, 10, -4] / (1+2a)^{10}((1+2a)^2)^{13/2} - \\
8192((1+2a)^2)^{13/2} - \\
230945\sqrt{\pi_2} F_i[\frac{21}{4}, \frac{23}{4}, 10, -4] / (1+2a)^6((1+2a)^2)^{17/2} + \\
8192((1+2a)^2)^{17/2}
\end{align*}
\]
\[
\begin{align*}
&20369349\sqrt{\pi} _2 F_1[\frac{21}{4}, \frac{23}{4}, 11, -\frac{4}{(1+2a)^3}] + 22309287\sqrt{\pi} _2 F_1[\frac{25}{4}, \frac{27}{4}, 11, -\frac{4}{(1+2a)^3}] + 262144((1+2a)^3)^{3/2} \\
&42590457\sqrt{\pi} _2 F_1[\frac{25}{4}, \frac{27}{4}, 12, -\frac{4}{(1+2a)^3}] - 2028117\sqrt{\pi} _2 F_1[\frac{25}{4}, \frac{27}{4}, 12, -\frac{4}{(1+2a)^3}] - 131072((1+2a)^3)^{3/2} \\
&422524375\sqrt{\pi} _2 F_1[\frac{25}{4}, \frac{27}{4}, 13, -\frac{4}{(1+2a)^3}] + 4194304((1+2a)^3)^{27/2} \\
&456326325\sqrt{\pi} _2 F_1[\frac{29}{4}, \frac{31}{4}, 13, -\frac{4}{(1+2a)^3}] - 877550625\sqrt{\pi} _2 F_1[\frac{29}{4}, \frac{31}{4}, 14, -\frac{4}{(1+2a)^3}] - 1048576(1+2a)^{10/2} \\
&35102025\sqrt{\pi} _2 F_1[\frac{29}{4}, \frac{31}{4}, 14, -\frac{4}{(1+2a)^3}] + 4217257575\sqrt{\pi} _2 F_1[\frac{29}{4}, \frac{31}{4}, 15, -\frac{4}{(1+2a)^3}] + 1048576((1+2a)^4)^{1/2} \\
&4508102925\sqrt{\pi} _2 F_1[\frac{33}{4}, \frac{35}{4}, 15, -\frac{4}{(1+2a)^3}] - 8388608(1+2a)^{10/2}((1+2a)^2)^{5/2} \\
&8715665655\sqrt{\pi} _2 F_1[\frac{33}{4}, \frac{35}{4}, 16, -\frac{4}{(1+2a)^4}] - 300540195\sqrt{\pi} _2 F_1[\frac{33}{4}, \frac{35}{4}, 16, -\frac{4}{(1+2a)^4}] - 16777216((1+2a)^4)^{3/2} \\
&20419054425\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 17, -\frac{4}{(1+2a)^5}] + 31059650625\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 18, -\frac{4}{(1+2a)^5}] + 8388608(1+2a)^{6/2}((1+2a)^2)^{3/2} \\
&(673828796025\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 18, -\frac{4}{(1+2a)^5}] + 536870912(1+2a)^{10/2}((1+2a)^2)^{29/2} - 541036958648((1+2a)^2)^{35/2})/327288272355 \\
&(347123925225\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 17, -\frac{4}{(1+2a)^5}] + 6375401957925\sqrt{\pi} _2 F_1[\frac{41}{4}, \frac{43}{4}, 19, -\frac{4}{(1+2a)^5}] + 4194304((1+2a)^3)^{27/2})/20419054425 \\
&(20419054425\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 18, -\frac{4}{(1+2a)^5}] + 31059650625\sqrt{\pi} _2 F_1[\frac{37}{4}, \frac{39}{4}, 19, -\frac{4}{(1+2a)^5}] + 300540195\sqrt{\pi} _2 F_1[\frac{33}{4}, \frac{35}{4}, 16, -\frac{4}{(1+2a)^4}])
\end{align*}
\]
\begin{align}
&\left(57930003736605\sqrt{\pi} \times 
\begin{array}{c}
2F_1\left[\frac{41}{4}, \frac{43}{4}, 21, -\frac{4}{(1+2a)^4}\right]/(274877906944((1+2a)^2)^{43/2}) + \\
(60755857577415\sqrt{\pi} \times 
2F_1\left[\frac{45}{4}, \frac{47}{4}, 21, -\frac{4}{(1+2a)^4}\right]/(68719476736(1+2a)^{10}((1+2a)^2)^{37/2}) - \\
(118618579079715\sqrt{\pi} \times 
2F_1\left[\frac{45}{4}, \frac{47}{4}, 22, -\frac{4}{(1+2a)^4}\right]/(137438953472(1+2a)^{10}((1+2a)^2)^{43/2}) - \\
(2893136075115\sqrt{\pi} \times 
2F_1\left[\frac{45}{4}, \frac{47}{4}, 22, -\frac{4}{(1+2a)^4}\right]/(68719476736(1+2a)^{10}((1+2a)^2)^{41/2}) + \\
(556271163533475\sqrt{\pi} \times 
2F_1\left[\frac{49}{4}, \frac{51}{4}, 23, -\frac{4}{(1+2a)^4}\right]/(549755813888(1+2a)^{10}((1+2a)^2)^{41/2})).
\end{array}
\right)
\end{align}

\textbf{References}

A TWO-DIMENSIONAL ELECTRON–HOLE SYSTEM IN TERMS OF THE CHERN–SIMONS THEORY: SLOWLY VARYING FIELD OPERATORS

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Abstract

In the previous paper [1], the conduction and the valence electrons of the two-dimensional (2D) semiconductor layer subjected to the action of an external perpendicular magnetic field and interacting with 2D quantum point vortices have been described in terms of the Chern–Simons (C–S) theory. The C–S unitary transformation introducing the vector and scalar potentials generated by the quantum point vortices into the Hamiltonian and transforming the conduction and valence electrons into composite particles attaching them equal numbers of 2D quantum point vortices has been used. In the present paper, slowly varying envelope-type field operators are introduced. The initial Hamiltonian containing the periodic lattice potential and bare electron mass $m_0$ is transformed into the form with effective electron and hole masses, which determine the cyclotron frequencies of the Landau quantization in the presence of a C–S field.

1. Introduction

In [1], the Chern–Simons (C–S) theory developed by Jackiw and Pi [2–4] was applied to describe the system of a coplanar electron–hole gas subjected to the action of a strong perpendicular magnetic field interacting with two-dimensional (2D) quantum point vortices. They generate the C–S vector and scalar potentials and effective magnetic and electric fields. Even if these fields vanish in the mean-field approximations in the case of electrons and holes with equal densities, the quantum fluctuations generated by these fields will lead to new effects in the physics of the 2D systems. Unitary transformation operator $\hat{U}(\vec{r})$ introduced in [1] and bare $\hat{\psi}_0^+(r), \hat{\psi}_0(r)$ and dressed $\hat{\psi}^+(r), \hat{\psi}(r)$ electron field operators look as follows:

$$
\hat{U}(r) = e^{\frac{i}{\hbar c}\vec{a}(r)}; \quad \hat{U}(\vec{r})\cdot U^+(\vec{r}) = 1 \quad \hat{\omega}^+(\vec{r}) = \omega(r)
$$

$$
\hat{\psi}_0(\vec{r}) = \hat{U}(\vec{r})\hat{\psi}(\vec{r}), \quad \hat{\psi}_0^+(\vec{r}) = \hat{\psi}^+(\vec{r})U^+(\vec{r})
$$

$$
\hat{\psi}(\vec{r}) = U^+(\vec{r})\hat{\psi}_0(\vec{r}), \quad \hat{\psi}^-(\vec{r}) = \hat{\psi}_0^+(r)\hat{U}(\vec{r})
$$

(1)

Singular phase operator $\hat{\omega}(\vec{r})$ and vector potential $\hat{a}(\vec{r})$ were determined in [1] by formulas (1) and are repeated below:
\[ \hat{o}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2 r' \theta(\vec{r} - \vec{r}') \hat{\rho}(r') \]
\[ \hat{a}(\vec{r}) = \vec{\nabla} \cdot \hat{o}(\vec{r}) = -\frac{\phi e}{\alpha} \int d^2 r' \nabla \cdot \theta(\vec{r} - \vec{r}') \hat{\rho}(r') \]
\[ \hat{\rho}(\vec{r}) = \psi^*_0(\vec{r}) \psi_0(\vec{r}) = \psi^+ (\vec{r}) \psi (\vec{r}) \]

Here, \( \phi \) is an integer number correlated with the filling factor \( \nu \) in the case of the fractional quantum Hall effect (FQHE), namely, \( \phi = \frac{1}{\nu} \); \( \alpha \) is the fine structure constant \( \alpha = \frac{1}{137} \) and the charge of the electron is \(-e = |e|\). The angle \( \theta(\vec{r} - \vec{r}') \) is formed by the vector \( \vec{r} - \vec{r}' \) with the \( x \) axis on the plane of the layer and is determined analytically by the multivalued function
\[ \theta(\vec{r} - \vec{r}') = \arctan \left( \frac{y-y'}{x-x'} \right), \quad \theta(\vec{r} - \vec{r}') = \theta(\vec{r}' - \vec{r}) + \pi \]  

The last relation in (3) represents the fact that the angle formed with the \( x \) axis by vector \( (\vec{r}' - \vec{r}) \) differs by \( \pi \) in comparison with vector \( (\vec{r} - \vec{r}') \). It was shown in [2] that unitary transformation \( \hat{U}(\vec{r}) \) changes the statistical properties of transformed operators \( \psi^+ (\vec{r}) \) and \( \psi (\vec{r}) \). This fact is well known in the conditions of the FQHE; it leads to the formation of composite particles predicted by Wilczek [5]. The composite particles look as bare electrons with an integer number \( \phi \) of the attached 2D quantum point vortices.

If bare electron field operators \( \psi^*_0(\vec{r}), \psi_0(\vec{r}) \) satisfy the Fermi commutation relations expressed by formulas (4) in [1], then dressed electron field operators \( \psi^+ (\vec{r}) \) and \( \psi (\vec{r}) \) obey the Fermi or to the Bose statistics as a function of integer number \( \phi \), which must satisfy the condition
\[ \pm e^{i\phi \pi} = 1 \]  

An even integer \( \phi = 0, 2, 4,... \) corresponds to the Fermi statistics, whereas the composite particles with odd integer numbers \( \phi = 1, 3, 5... \) of the vortices are bosons.

In [1], the equations of motion for the dressed electron field operators were deduced starting with initial Hamiltonian (25). It contains a periodic lattice potential; the effect of the external magnetic field and the Coulomb electron–electron interaction below the Coulomb electron–electron interaction will be dropped because the main task of the present paper is the introduction of slowly varying field operators instead of the full electron operators. We will determine the action of the C–S unitary transformation on the hole field operators instead of the valence electron ones. Another task is the excluding of the periodic lattice potential and the introduction of the effective electron and hole masses so as to simplify the description of the Landau quantization problem in the presence of the C–S vector potential. These questions will be solved in section 2 of the paper. Conclusions are made in section 3.

2. Equations of Motion for Dressed Electron Field Operators

The equations of motion described by formula (28) of [1] under stationary conditions neglecting the Coulomb electron–electron interaction look as follows:
Here, $\tilde{A}(\vec{r})$ is the vector potential of the external magnetic field; the following relationships were used [1]:

$$\hat{a}(\vec{r}) = \hat{a}(\vec{r})^+ + \hat{\omega}(\vec{r}) = \hat{\omega}(\vec{r}); \quad [\hat{a}(\vec{r}), \hat{\psi}(\vec{r})] = [\hat{a}(\vec{r}), \hat{\psi}^+(\vec{r})] = 0$$  \hspace{1cm} (6)

Operator $\frac{d\hat{a}(\vec{r})}{cdt}$ determines the scalar C–S potential, whereas the expression

$$iL(\vec{r}) = \frac{\hbar}{m_0} \left( \frac{\phi e}{a} \right)^2 \int d^2\vec{r} ' \left( \hat{\nabla} \cdot \theta (\vec{r} - \vec{r} ') \right)^2 \hat{\rho}(\vec{r} ') = \frac{\hbar}{m_0} \left( \frac{\phi e}{\alpha} \right)^2 \int d^2\vec{r} ' \hat{\rho}(\vec{r} ') \frac{1}{|\vec{r} - \vec{r} '|}$$  \hspace{1cm} (7)

describes the energy created by the vortices. It is useful to remember that curl $\hat{a}(\vec{r})$ gives rise to an effective magnetic field [1] generated by the vortices.

Schrödinger equations (5) contain a periodic crystal lattice potential $V_{\text{per}}(\vec{r})$, which is invariant under the translation on integer lattice vector $\vec{R}$ enumerating the lattice nodes: $V_{\text{per}}(\vec{r} + \vec{R}) = V_{\text{per}}(\vec{r})$. It was discussed in [6] that this property makes it possible to represent an arbitrary space vector $\vec{r}$ in the form $\vec{r} = \vec{R} + \vec{\rho}$, where $\vec{\rho}$ is a small vector changing inside the unit lattice cell with volume $V_0 = a_0^3$, where $a_0$ is the lattice constant. Due to this property, the electron Bloch wave functions can be represented as the products of periodic parts $U_{n,k}(\vec{\rho})$ quickly changing inside the electron shells of the atoms situated in the unit cells and depending only on variable $\vec{\rho}$ and envelope wave functions $\psi_{n,k}(\vec{R})$ slowly varying on variable $\vec{R}$. They almost do not depend on variable $\vec{\rho}$.

$$\psi_{nk}(\vec{r}) = U_{nk}(\vec{\rho}) \varphi_{n,k}(\vec{R})$$  \hspace{1cm} (8)

At the same time, the periodic parts quickly varying in space describe the semiconductor energy band structure quickly establishing in time, against the background of which the Landau quantization processes slowly varying in time take place. The dominance of the semiconductor energy band structure over other slowly varying processes makes it possible to introduce an adiabatic approximation and integrate over variable $\vec{\rho}$ as a method to exclude the quickly varying processes and concentrate the research on the physical processes slowly varying in space and time.

We are interested in these phenomena arising in a 2D electron–hole system and a 2D one-component electron gas.

The summation over the discrete lattice nodes of slowly varying envelope wave functions can be substituted by the integration over the surface area of the layer as follows:
\begin{equation}
\int d^2\tilde{r} = \sum_\mathbf{R} \int_{S_0} d^2\tilde{r} = \sum_\mathbf{R} a_0^2 \int_{S_0} d^2\tilde{r} = \int d^2\tilde{R} \cdot \frac{1}{V_0} \int d^3\tilde{\rho}\n\end{equation}

Here, the integration over surface area $S_0$ of the unit lattice cell was substituted by the integration over its volume $V_0$ because in reality 2D semiconductor structures have at least thickness $a_0$ of one atomic layer. Exactly following formula (11) of [6], vector potential $\tilde{A}(\tilde{r})$ of the external magnetic field and the required derivatives are shown below:

$$\tilde{A}(\tilde{r}) = \tilde{A}(\tilde{\rho}) + \tilde{A}(\tilde{R})$$

$$\frac{\partial}{\partial \tilde{r}} \psi(\tilde{\rho},\tilde{R}) = \frac{\partial}{\partial \tilde{\rho}} \psi(\tilde{\rho},\tilde{R}) + \frac{\partial}{\partial \tilde{R}} \psi(\tilde{\rho},\tilde{R}),$$

$$\hat{\tilde{p}}_r = \hat{\tilde{p}}_\rho + \hat{\tilde{p}}_R, \quad \tilde{B}(\tilde{\rho}) = \text{rot}_\rho \tilde{A}(\tilde{\rho}); \quad \tilde{B}(\tilde{R}) = \text{rot}_R \tilde{A}(\tilde{R})$$

It was mentioned in [6] that magnetic fields $\tilde{B}(\tilde{\rho})$ and $\tilde{B}(\tilde{R})$ are acting at different points of the real space: in the electron shell of the atoms situated inside the unit lattice cell giving rise to their Zeeman splitting effects and outside of it leading to the Landau quantization of the slowly moving electrons and holes.

In the two-band model of a semiconductor, using lattice variables $\tilde{\rho}$ and $\tilde{R}$, full electron field operators $\hat{\psi}(r)$ and $\hat{\psi}^+(\tilde{r})$ looks as follows:

$$\hat{\psi}(\tilde{r}) = \hat{\psi}(\tilde{\rho},\tilde{R}) = U_c(\tilde{\rho}) \hat{\phi}_c(\tilde{R}) + U_v(\tilde{\rho}) \hat{\phi}_v(\tilde{R})$$

$$\hat{\psi}^+(\tilde{r}) = \hat{\psi}^+(\tilde{\rho},\tilde{R}) = U_c^+(\tilde{\rho}) \hat{\phi}_c^+(\tilde{R}) + U_v^+(\tilde{\rho}) \hat{\phi}_v^+(\tilde{R})$$

where $U_c(\tilde{\rho})$ and $U_v(\tilde{\rho})$ are the periodic parts of the electron Bloch wave functions corresponding to the conduction and valence bands. They obey the normalization and orthogonality conditions:

$$\frac{1}{V_0} \int d^3\tilde{\rho} \left| U_c(\tilde{\rho}) \right|^2 = \frac{1}{V_0} \int d^3\tilde{\rho} \left| U_v(\tilde{\rho}) \right|^2 = 1$$

$$\frac{1}{V_0} \int d^3\tilde{\rho} U_c^+(\tilde{\rho}) U_v(\tilde{\rho}) = 0$$

$$\frac{1}{V_0} \int d^3\tilde{\rho} U_c^{+\ast}(\tilde{\rho}) \hat{\psi}(\tilde{\rho},\tilde{R}) = \hat{\phi}_c(\tilde{R})$$

$$\frac{1}{V_0} \int d^3\tilde{\rho} U_v^{+\ast}(\tilde{\rho}) \hat{\psi}(\tilde{\rho},\tilde{R}) = \hat{\phi}_v(\tilde{R})$$

Electron kinetic energy $\hat{\tilde{K}}(\tilde{r})$ in variables $\tilde{\rho}$ and $\tilde{R}$ has the form
\[ \hat{K}(\vec{r}) = \frac{\hbar^2}{2m_0} \hat{\Pi}(\vec{r})^2; \quad \hat{K}^+(\vec{r}) = \frac{\hbar^2}{2m_0} \hat{\Pi}^+(\vec{r})^2 \]

\[ \hat{\Pi}(\vec{r}) = -i\vec{\nabla}_{\vec{r}} + \frac{e}{\hbar c} \hat{A}(\vec{r}) + \frac{e}{\hbar c} \hat{\alpha}(\vec{r}) = -i\vec{\nabla}_{\vec{r}} + \frac{e}{\hbar c} \hat{A}(\vec{R}) + \frac{e}{\hbar c} \hat{\alpha}(\vec{R}) \]

\[ + \frac{e}{\hbar c} \hat{A}(\hat{\rho}) + \frac{e}{\hbar c} \hat{\alpha}(\vec{R}) = \hat{\Pi}(\vec{R}) + \hat{\Pi}(\hat{\rho}), \]

\[ \hat{\Pi}(\vec{R}) = -i\vec{\nabla}_{\vec{r}} + \frac{e}{\hbar c} \hat{A}(\vec{R}) + \frac{e}{\hbar c} \hat{\alpha}(\vec{R}), \quad \hat{\Pi}^+(\vec{R}) = i\vec{\nabla}_{\vec{r}} + \frac{e}{\hbar c} \hat{A}(\vec{R}) + \frac{e}{\hbar c} \hat{\alpha}(\vec{R}) \]

\[ K(\vec{r}) = \frac{\hbar^2}{2m_0} \left( \hat{\Pi}(\vec{R}) + \hat{\Pi}(\hat{\rho}) \right)^2 = \hat{K}(\vec{R}) + \hat{\Pi}(\hat{\rho}) + \frac{\hbar^2}{m_0} \hat{\Pi}(\vec{R}) \cdot \hat{\Pi}(\hat{\rho}) \]

\[ \hat{K}(\vec{R}) = \frac{\hbar^2}{2m_0} \hat{\Pi}(\vec{R})^2, \quad \hat{K}(\hat{\rho}) = \frac{\hbar^2}{2m_0} \hat{\Pi}(\hat{\rho})^2 \]

In these notations, Schrödinger equations (5) take the form

\[ E\psi(\hat{\rho}, \vec{R}) = \left[ H_0^{\hat{\rho}}(\hat{\rho}) + \hat{\Pi}(\vec{R}) + \frac{\hbar^2}{m_0} \hat{\Pi}(\vec{R}) \cdot \hat{\Pi}(\hat{\rho}) + \frac{e}{c} \frac{d\hat{\omega}(\vec{R})}{dt} + \frac{e^2}{2\hbar c^2} i\hat{L}(\vec{R}) \right] \psi(\hat{\rho}, \vec{R}). \]

\[ E\psi^+(\hat{\rho}, \vec{R}) = \left[ H_0^{\hat{\rho}}(\hat{\rho}) + \hat{\Pi}^+(\vec{R}) + \frac{\hbar^2}{m_0} \hat{\Pi}(\vec{R}) \cdot \hat{\Pi}(\hat{\rho}) \right] \psi^+(\hat{\rho}, \vec{R}) + \frac{e}{c} \psi^+(\hat{\rho}, \vec{R}) \frac{d\hat{\omega}(\vec{R})}{dt} + \frac{e^2}{2\hbar c^2} \psi^+(\hat{\rho}, \vec{R}) (i\hat{L}(\vec{R}))^+ \]

In the deduction of these equations, the following properties were taken into account:

\[ \vec{\nabla}_{\vec{r}} \cdot \hat{A}(\vec{R}) = \vec{\nabla}_{\vec{r}} \cdot \hat{A}(\hat{\rho}) = 0; \quad \vec{\nabla}_{\vec{r}} \cdot \hat{\alpha}(\vec{R}) = 0; \]

\[ [\hat{\alpha}(\vec{r}), \psi(\vec{r})] = 0; \quad \hat{\omega}(\vec{R}) = \hat{\omega}(\vec{R}) \]

\[ (15) \]

Operator \( H_0^{\hat{\rho}}(\hat{\rho}) \) consists of kinetic energy \( \hat{K}(\hat{\rho}) \) and periodic lattice potential \( V_{\text{per}}(\hat{\rho}) \) and determines the semiconductor band structure as follows:

\[ \hat{\Pi}_0(\hat{\rho}) = \hat{K}(\hat{\rho}) + V_{\text{per}}(\hat{\rho}) = \frac{\hbar^2}{2m_0} \left( -i\vec{\nabla}_{\hat{\rho}} + \frac{e}{\hbar c} \hat{A}(\hat{\rho}) \right)^2 + V_{\text{per}}(\hat{\rho}) \]

\[ \hat{\Pi}_0(\hat{\rho}) \cup_+(\hat{\rho}) = E_n U_n(\hat{\rho}), \quad \hat{\Pi}_0^+(\hat{\rho}) \cup_+(\hat{\rho}) = E_n^+ U_n^+(\hat{\rho}), \quad n = c, V, \quad E_c - E_V = E_g. \]

The \( E_c \) and \( E_V \) values determine the bottom of the conduction band and the top of the valence band, respectively. The difference equals to energy band gap \( E_g^0 \). Multiplying equations (14) from the left-hand side by functions \( U_c^+(\hat{\rho}) \) and \( U_V^+(\hat{\rho}) \) and integrating them over volume \( V_0 \) of the lattice cell, we will transform them into reduced Schrödinger equations. The averaging with quickly varying wave functions \( U_c(\rho) \) and \( U_V(\hat{\rho}) \) means the introduction of an adiabatic
approximation. In terms of this approximation, a semiconductor band structure is established. The remaining reduced Schrödinger equation describes only the slowly varying processes, such as the Landau quantization, that take place against the background of the already well established band structure. Relationships (16) lead to the following equalities:

\[ \frac{1}{\varepsilon_0} \int d^3 \rho U^* (\bar{\rho}) H_0 (\bar{\rho}) \psi (\bar{\rho}, \bar{R}) = E_c \phi_c (\bar{R}) \]

\[ \frac{1}{\varepsilon_0} \int d^3 \rho U^*_V (\bar{\rho}) H_0 (\bar{\rho}) \psi (\bar{\rho}, \bar{R}) = E_v \phi_v (\bar{R}) \]

\[ \frac{1}{\varepsilon_0} \int d^3 \rho U^*_V (\bar{\rho}) \hat{\Pi} (\bar{\rho}) \psi (\bar{\rho}, \bar{R}) = \tilde{\pi}_{c,V} \phi_v (\bar{R}) \]

\[ \frac{1}{\varepsilon_0} \int d^3 \rho U^*_V (\bar{\rho}) \hat{\Pi} (\bar{\rho}) \psi (\bar{\rho}, \bar{R}) = \tilde{\pi}_{v,c} \phi_c (\bar{R}) \]

where matrix elements \( \tilde{\pi}_{n,m} \) were introduced:

\[ \tilde{\pi}_{c,v} = \frac{1}{\varepsilon_0} \int d^3 \rho U^*_c (\bar{\rho}) \hat{\Pi} (\bar{\rho}) U_V (\bar{\rho}) = \tilde{\pi}_{v,c} = \tilde{\pi}_{v,v} = 0 \]  

(18)

The Schrödinger equations for slowly varying field operators \( \hat{\phi}_c (\bar{R}) \) and \( \hat{\phi}_v (\bar{R}) \) in the adiabatic approximation are as follows:

\[ E \hat{\phi}_c (\bar{R}) = E_c \hat{\phi}_c (\bar{R}) + \hat{K} (\bar{R}) \hat{\phi}_c (\bar{R}) + \frac{\hbar^2}{m_0} \hat{\Pi} (\bar{R}) \tilde{\pi}_{c,v} \hat{\phi}_v (\bar{R}) + \]

\[ + \frac{e}{c} \frac{d}{dt} \hat{\phi}_c (\bar{R}) + \frac{e^2}{2\hbar c^2} i \hat{L} (\bar{R}) \hat{\phi}_c (\bar{R}), \]  

(19)

\[ E \hat{\phi}_v (\bar{R}) = E_v \hat{\phi}_v (\bar{R}) + \hat{K} (\bar{R}) \hat{\phi}_v (\bar{R}) + \frac{\hbar^2}{m_0} \hat{\Pi} (\bar{R}) \tilde{\pi}_{v,c} \hat{\phi}_c (\bar{R}) + \]

\[ + \frac{e}{c} \frac{d}{dt} \hat{\phi}_v (\bar{R}) + \frac{e^2}{2\hbar c^2} i \hat{L} (\bar{R}) \hat{\phi}_v (\bar{R}). \]

Two equations (19) determine two slowly varying components \( \hat{\phi}_c (\bar{R}) \) and \( \hat{\phi}_v (\bar{R}) \) of field operator \( \hat{\psi} (\bar{\rho}, \bar{R}) \). Their solutions are completely different at different values of energy \( E \). In the range of \( E = E_c + \varepsilon_c \) with \( \varepsilon_c \ll E_c \), near the bottom of the conduction band, following the second equation (19), component \( \hat{\phi}_v (\bar{R}) \) is small in comparison with component \( \hat{\phi}_c (\bar{R}) \). Their relationship is as follows:

\[ \hat{\phi}_v (\bar{R}) = \frac{\hbar^2}{m_0 E_g} \hat{\Pi} (\bar{R}) \cdot \tilde{\pi}_{v,c} \hat{\phi}_c (\bar{R}), \]  

(20)

whereas component \( \hat{\phi}_c (\bar{R}) \) obeys the equation
\[ \varepsilon_c \hat{\phi}_c(R) = \left( \hat{K}(R) + \frac{\hbar^2}{m_e^0 E_g} \hat{\Pi}(\vec{R}) \cdot \vec{\pi}_{c,v} \cdot \hat{\Pi}(\vec{R}) \cdot \vec{\pi}_{c,v,c} \right) \hat{\phi}_c(R) + \]
\[ + \left( e \frac{d \hat{\omega}(\vec{R})}{dt} + \frac{e^2}{2 \hbar c} i \hat{L}(\vec{R}) \right) \hat{\phi}_c(R) \]

This procedure completely follows the method known as the envelope function approximation (EFA) developed by Winkler in his monograph [7]. After the simplification
\[ \hat{\Pi}(\vec{R}) \cdot \vec{\pi}_{c,v} \cdot \hat{\Pi}(\vec{R}) \approx \hat{\Pi}(\vec{R}) \cdot |\vec{\pi}_{c,v}|^2, \]
equation (21) takes the form
\[ \varepsilon_c \hat{\phi}_c(R) = \left[ \frac{\hbar^2}{2m_e} \hat{\Pi}(\vec{R})^2 + e \frac{d \hat{\omega}(\vec{R})}{dt} + \frac{e^2}{2 \hbar c^2} i \hat{L}(\vec{R}) \right] \hat{\phi}_c(R) \]
\[ \frac{m_0}{m_e} = \left( 1 + \frac{2 \hbar^2 |\vec{\pi}_{c,v}|^2}{m_0 E_g} \right) \]

If energy \( E \) lies near the top of the valence band \( E = E_{v'} + \varepsilon_{v'} \), with \( \varepsilon_{v'} \ll E_{v'} \), then the dressed or composite electrons coincide with the valence electrons. Now, the first equation (19) with \( E = E_{v'} \) gives rise to the relationship
\[ \hat{\phi}_{v'}(\vec{R}) = -\frac{\hbar^2}{m_e E_g} \hat{\Pi}(\vec{R}) \cdot \vec{\pi}_{c,v} \hat{\phi}_{v'}(\vec{R}), \]
whereas the second equation (19) looks as the reduced Schrödinger equation
\[ \varepsilon_{v'} \hat{\phi}_{v'}(\vec{R}) = \left[ \frac{\hbar^2}{2m_{v'}} \hat{\Pi}(\vec{R})^2 + e \frac{d \omega(\vec{R})}{dt} + \frac{e^2}{2 \hbar c^2} i \hat{L}(\vec{R}) \right] \hat{\phi}_{v'}(\vec{R}) \]
with \( m_{v'} \) determined by the formula
\[ \frac{m_0}{m_{v'}} = \left( 1 - \frac{2 \hbar^2 |\vec{\pi}_{v'}|^2}{m_0 E_g} \right) \]

Our intention is to introduce the notion of the hole instead of the valence electron. For this purpose, the equation for Hermitian conjugate operator \( \hat{\phi}_{v'}^*(\vec{R}) \) is required. It can be obtained starting from the second equation (5) for field operator \( \hat{\psi}^*(\vec{r}) \) or directly from equation (25) as follows:
\[ \varepsilon_{v'} \hat{\phi}_{v'}^*(\vec{R}) = \frac{\hbar^2}{2m_{v'}} \hat{\Pi}^*(\vec{R}) \cdot \hat{\phi}_{v'}(\vec{R}) + \frac{e d \omega(\vec{R})}{c dt} + \frac{e^2}{2 \hbar c^2} i \hat{L}(\vec{R}) \]

Here, the following relationships were used:
\[ \left[ \hat{a}(r), \hat{\psi}(\vec{r}) \right] = 0, \quad \omega^*(\vec{R}) = \omega(\vec{R}); \quad (i \hat{L}(\vec{R}))^+ = i \hat{L}(\vec{R}). \]

The hole has energy \( \varepsilon_h \), effective mass \( m_h \), and electrical charge \( q_h \) of the opposite signs compared with that of the valence electron. The creation and annihilation operators of it are
expressed through the Hermitian conjugate of the valence electrons, respectively. They are as follows:

$$\hat{\phi}_h^a(\vec{R}) = \varphi_v(\vec{R}), \quad \hat{\phi}_h^b(\vec{R}) = \varphi_v^*(\vec{R})$$

$$\varepsilon_h = -\varepsilon_v, \quad m_h = -m_v, \quad q_h = e$$

In these denotations, equation (27) looks as follows:

$$\varepsilon_h \hat{\phi}_h(\vec{R}) = \frac{\hbar^2}{2m_h} \left( -i\vec{\nabla}_R - \frac{e}{\hbar c} \vec{A}(\vec{R}) - \frac{e}{\hbar c} \hat{\mathbf{a}}(\vec{R}) \right)^2 \hat{\phi}_h(\vec{R}) -$$

$$-\hat{\phi}_h(\vec{R}) \left( \frac{e}{c} \frac{d\hat{\mathbf{a}}(\vec{R})}{dt} + \frac{e^2}{2\hbar c^2} \hat{i}\mathcal{L}(\vec{R}) \right)$$

(29)

One can observe that the sign of the electric charge both inside kinetic momentum $\hbar \hat{\mathbf{a}}(\vec{R})$ and in other terms of equation (29) is opposite to the one of the conduction electron.

Thus, we have shown that the reduced Schrödinger equations for slowly varying electron and hole field operators $\hat{\phi}_e(\vec{R}) = \hat{\phi}_e(\vec{R})$ and $\hat{\phi}_h(\vec{R}) = \hat{\phi}_h^v(\vec{R})$, which after unitary transformation (1) form composite particles with effective masses $m_e$ and $m_h$ and with electrical charges $\mp e$ look as follows:

$$\varepsilon_e \hat{\phi}_e(\vec{R}) = \frac{\hbar^2}{2m_e} \left( -i\vec{\nabla}_R + \frac{e}{\hbar c} \vec{A}(\vec{R}) + \frac{e}{\hbar c} \hat{\mathbf{a}}(\vec{R}) \right)^2 \hat{\phi}_e(\vec{R}) +$$

$$+ \left( \frac{e}{c} \frac{d\hat{\mathbf{a}}(\vec{R})}{dt} + \frac{e^2}{2\hbar c^2} \hat{i}\mathcal{L}(\vec{R}) \right) \hat{\phi}_e(\vec{R}),$$

$$\varepsilon_h \hat{\phi}_h(\vec{R}) = \frac{\hbar^2}{2m_h} \left( -i\vec{\nabla}_R - \frac{e}{\hbar c} \vec{A}(\vec{R}) - \frac{e}{\hbar c} \hat{\mathbf{a}}(\vec{R}) \right)^2 \hat{\phi}_h(\vec{R}) -$$

$$-\hat{\phi}_h(\vec{R}) \left( \frac{e}{c} \frac{d\hat{\mathbf{a}}(\vec{R})}{dt} + \frac{e^2}{2\hbar c^2} \hat{i}\mathcal{L}(\vec{R}) \right),$$

(30)

$$m_h = \left( 1 + \frac{2\hbar^2 |\vec{r}_{\text{ev}}|^2}{m_0 E_g^0} \right); \quad m_e = \left( 2\hbar^2 |\vec{r}_{\text{ev}}|^2 \right) \left\{ \frac{m_0 E_g^0}{m_0 E_g^0} - 1 \right\};$$

$$\hat{\phi}_e(\vec{R}) = \hat{\phi}_e^a(\vec{R}); \quad \hat{\phi}_h(\vec{R}) = \hat{\phi}_h^a(\vec{R})$$

Exactly the same equations can be obtained taking into account the Coulomb interactions between the electrons and the holes.

### 3. Conclusions

The paper is the continuation of the study published in the same issue [1], in which we have deduced the Schrödinger equations for the conduction and valence electrons of the 2D semiconductor layer subjected to the action of a perpendicular magnetic field and interacting with quantum point vortices in terms of the C–S theory. As new steps in this direction, the slowly varying electron and hole field operators in the adiabatic approximation have been introduced. To this end, the Schrödinger equations of [1] have been averaged using the periodic parts of the
electron Bloch wave functions and the reduced Schrödinger equation has been obtained. They are characterized by effective electron and hole masses and depend on the vector and scalar potentials created by the quantum point vortices in addition to the vector potential of the external magnetic field.

References

MAGNETIC PROPERTIES OF Fe-BASED AMORPHOUS MAGNETIC MICROWIRES

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Abstract

The magnetic characteristics of Fe-based cast amorphous glass-coated microwires (with a positive magnetostriction constant) have been studied. The residual stress distributions in this type of microwires determine the domain structures and the switching field behavior. These wires are characterized by a rectangular hysteresis loop and can be used in measuring and identification engineering. A mathematical model that describes the process of the reversal magnetization of an amorphous microwire with the help of a large Barkhausen jump has been proposed. The model has been estimated with regard to the optimization of the signal-to-noise ratio. Using nonlinear model, the physical factors that cause the fluctuations of the start field have been studied. The results obtained do not contradict the existing physical concepts concerning a domain wall motion and are more general and realistic in comparison with the previous model.

1. Introduction

Cast glass-coated amorphous micro- and nanowires (CGCAMNWs) with a positive magnetostriction are very interesting materials for the theoretical study and for the practical applications. Having a positive magnetostriction, their domain structure consists of two magnetized domains, and a magnetization process runs through a large Barkhausen jump (BJ) of a single domain wall (DW) along the entire microwire. An addition to the mathematical model of the potential-relief gradient developed in previous works [1–8] is proposed. The nonlinear equation of the DW motion in the process of a BJ is a necessary tool for solving this problem.

To qualitatively confirm the proposed model of the DW motion, the residual stresses and the theory of micromagnetism have been calculated. Quantitative estimates will be made in the subsequent works.

2. Theory Magnetization of Amorphous Microwires with Positive Magnetostriiction

It is known (see [2, 5–8]) that cast amorphous microwires with positive magnetostriction exhibit a rectangular hysteresis loop. Coercive forces $H_c$ can be regulated by both residual and external mechanical stresses [2, 5].

The dynamics of a DW is studied using the solution of the well-known Döring equation (see [1, 3, 4]):
\[ m\ddot{x} + \beta \dot{x} + F_i(x) = 2MH(t), \]  
\hspace{1cm} (1) 

where \( m \) is the effective mass of a DW; \( \beta \) is the phenomenological attenuation coefficient; \( x, \dot{x}, \ddot{x} \) are the generalized coordinate, velocity, and acceleration of a DW; and \( F_i(x) \) is the force function that characterizes the action of a magnetic matter on a DW. This force \( F_i(x) \) describes the gradient of the potential relief (GPR).

An external field with intensity \( H \) exerts a \( 2MH \) pressure on an 180° DW (\( M \) is the magnetization). The generalized coordinate \( x \) is the analog of the radial coordinate of a cylinder \( r \); however, by definition, the range of it can be formally extended from \( -\infty \) to \( +\infty \), which is determined by the correlation of the calculation data with the experimental results. According to [5, 6], it is assumed that \( F_i(x) \) appears primarily due to the residual stresses.

As noted earlier (see, [2, 5, 6]), the calculation of residual stresses and the simulation of the motion of a DW in a GPR using \( F_i(x) \) are carried out for the model in which the cross section is conventionally divided into some segments (see Fig. 1). Let us perform a micromagnetic foundation of the proposed approach to the dynamics of a DW. The dimensions for every segment of the microwire shown in Fig. 1 can be estimated (the residual stresses in these segments are calculated in [5]). According to this model, the process of the DW motion begins from the central region inside the cylinder within segment 3. So, there appears a magnetization reversal center.

![Fig. 1. Cross section of the microwire.](image)

In the scheme, the dependence of properties on radial coordinate \( r \) is used (see below).

At \( r = R_c \), we obtain the external radius of the glass envelope. At \( r = R_m \), we obtain the radius of the metal strand. At \( r = b \), we obtain the radius of the plastic deformation boundary.

The qualitative correspondence between the radial coordinate of the cylinder \( r \) and the generalized coordinate \( x \) (used in (1)) is shown in Fig. 2.

Let us present the function \( F_i(x) \) in a general form by the spline functions (SFs):
The force function $F_i(x)$ given by formula (1a) has two minima and a local maximum, as shown in Fig. 2.

$$F_i(x) = \begin{cases} 
1) -F_{m1} \frac{(x-c_k)^2}{(R-c_k)^2} + F_{m1} ; x < c_k ; \\
2) -\frac{2F_{m1}}{c_k^5} x^3 + \frac{3F_{m1}}{c_k^2} x^2 ; c_k \leq x < 0; \\
3) -\frac{2F_{m2}}{c_i^3} x^3 + \frac{3F_{m2}}{c_i^2} x^2 ; 0 \leq x \leq c_i; \\
4) -\frac{F_{m2}}{c_i} \frac{(x-c_i)^2}{(R-c_i)^2} + F_{m2} ; x > c_i. 
\end{cases}$$

(1a)

The magnetization reversal center, which appears in the initial region (segment 3 in Figs. 1 and 2), is described by (1a); the micromagnetic characteristics of it are calculated as follows in regions 3 and 2 (see Fig. 2).

The relationship between parameters $c_{i,k}$, $F_{m1,k}$ and residual stresses (see below) (as well as micromagnetic parameters, such as domain wall energy) will not be considered in this paper. We can only assume a qualitative correspondence between these parameters.

3. Residual Stresses in Microwires

(A, segment 2). In the first case, where $r \sim R_m$, this model gives [6–9]:

$$\sigma_r = \sigma_\varphi = P = \sigma_0 \frac{k_i x}{\left(\frac{k_i}{3} + 1\right)x + \frac{4}{3}}, \quad \sigma_z = P \frac{(k_i + 1)x + 2}{k_i x + 1}, \quad x = \left(\frac{R_c}{R_m}\right)^2 - 1,$$

(2)

where $R_m$ is the metallic core radius of the microwire and $R_c$ is the total radius of the microwire;
\[ \sigma_0 = \varepsilon Y_m, \]  
\[ k_i = \frac{Y_g}{Y_m}, \]  
\[ \varepsilon = (\alpha_m - \alpha_g)(T - T^*), \]  
where \( Y_m \) is the Young’s modulus of the metal and \( Y_g \) is the Young’s modulus of the glass; 
\[ \varepsilon = (\alpha_m - \alpha_g)(T - T^*), \]  
where \( \alpha_m \) and \( \alpha_g \) are the thermal expansion coefficients of the metal and the glass, respectively; \( T^* \) is the effective solidification temperature of the composite microwire (where both the metallic core and the glass coating are solidified); and \( T \) is the experimental temperature.

A more accurate model used for residual stresses at the microwires is provided below. The metallic core, segment 3, (see Fig. 1) preserves the liquid state from the cylinder axis up to a certain internal radius \( b \) (parameter \( b \) has a certain value depending on the defined metallic alloy composition and cooling rate), while from \( b \) up to \( R_m \), where only elastic residual stresses occur, the metallic surface, segment 2, (see Fig. 1) freezes earlier (see (2–4)).

\[ \sigma_{r(1)} \approx P \left[ 1 - \left( \frac{b}{r} \right)^2 \right], \quad \sigma_{\phi(1)} \approx P \left[ 1 + \left( \frac{b}{r} \right)^2 \right], \quad \sigma_{z(1)} \approx \nu (\sigma_{r(1)} + \sigma_{\phi(1)}), \]  
where \( P \) is the Poisson’s coefficient.

\[ \sigma_{r(2)} \approx 2K_2 \ln \left( \frac{r}{b} \right), \quad \sigma_{\phi(2)} \approx 2K_2 \left[ 1 + \ln \left( \frac{r}{b} \right) \right], \quad \sigma_{z(2)} \approx \nu (\sigma_{r(2)} + \sigma_{\phi(2)}), \]  
where \( K_2 \) is the thermoelastic constant of metal.

For simplification of formulas, constants of residual stress (independent of radius) are not written out.

Note that a rigorous solution should be obtained by lacing equations (2)–(6) (see [4–8]).

We note that parameter \( b \) corresponds to the zero value of the SFs given above (see Eq. (1a) and Fig. 2).

4. Initial Region of the DW Motion

In the model of a CGCAMNW, it is energetically more useful for the appearance of a DW in the region with \( r < b \) (\( b \sim 10^{-6} \) m is the radius of plastic deformations) where the anisotropy energy is smaller. Let us estimate the order of magnitudes of the DW dimensions \( \Delta_i \) (in different regions) that determine the values of \( c_i \) (see Eq. (1a)). The formula for the exchange interaction energy has a standard form, the same for all segments:

\[ W_A \approx \frac{A}{\Delta_i}, \]
where $A \sim 10^{-11} \text{ J/m}$ is the exchange energy constant and $i = 1,2,3$ is the index that characterizes the position of a DW in the scheme of the CGCAMNW cross section (see Fig. 1).

In the case of the known model in the Landau–Lifshitz (LL) theory, the anisotropy energy can be presented in the following form:

$$W_{\text{a(LL)}} \approx K\Delta_{\text{LL}},$$

where

$$K \sim \lambda \sigma,$$

here, $\lambda \sim (10^{-5} - 10^{-6})$ is the magnetostriction and $\sigma$ is the average value of the residual stresses.

Minimization of these competing energies is known and gives a classical result of the LL theory for the dimensions and energy of the DW:

$$\Delta_{\text{LL}} \approx (A / K)^{1/2} \sim 10^{-5} \text{ m},$$
$$W_{\text{LL}} \approx (AK)^{1/2} \sim 10^{-4} \text{ J/m}^2.$$

If, for the anisotropy energy, one uses the dependence on $\Delta_3$ (subscript 3 means the position of the DW, i.e., in the center of the CGCAMNW metal strand), which is obviously described by the residual stresses:

$$W_{a3} \approx \lambda Kb \times \ln\left(\frac{\Delta_3}{b}\right),$$

where $K \sim 10^8 \text{ Pa}$ is the constant of the plastic deformation stresses, then the minimization of the sum of (6) and (8) leads to a simple expression:

$$\Delta_3 \approx \frac{A}{\lambda Kb} \leq 10^{-7} \text{ m}.$$ (12)

The value of the DW dimensions is an order of magnitude less than the characteristic diameter of a CGCAMNW. This is important for an adjustment of our model because the DW dimensions could not be larger than the diameter of the microwire strand (use of the LL theory in this particular case is not suitable). We obtain the value of the energy density of the considered DW as follows:

$$W_3(\Delta_3) \approx \frac{A}{b} \leq 10^{-5} \text{ J/m}^2.$$ (13)

According to (13), the start field does not depend on anisotropy; it is governed by the technologic parameter $b$, which determines the magnitudes of the polynomial coefficients in the SFs (see Eq. (1a)). Using Eqs. (4), (5) and (6), it is also possible to estimate the dimension of the nucleation center of a cylinder DW that is generated in other amorphous materials as well. It follows that the energy estimations of the domain nucleation in the proposed model can differ markedly from the estimations in the LL theory giving smaller energies than those required to generate the magnetization reversal centers; this was observed experimentally.

If we return to Eq. (1), the DW motion is defined by force $F_i(x)$ that corresponds to a harmonic oscillation motion or a damped motion without oscillation. In fact, the damped form of motion describes a case when a DW is formed (initial region is located in segment 3 in Fig. 1). Note that the initial conditions for the DW motion are not very important in terms of the proposed model.
5. Middle Region of the DW Motion

Let us consider a case which is possible due to the peculiarity of the dependence of residual stresses on the radial coordinate of the wire. Let us describe the anisotropy energy in the following form:

\[ W_{a_2g} \approx K_{2g} \left( \frac{\Delta_g}{b} \right)^n, \]

where

\[ K_{2g} \approx \lambda Pb^2. \]  \hspace{1cm} (15)

For the value of a DW and the DW specific energy we obtain

\[ \Delta_g \approx b \left( \frac{A}{nK_{2g}} \right)^{1/(n+1)}, \]

\[ W_{a_2g} (\Delta_g) \approx k_{2g} \left( \frac{A}{nK_{2g}} \right)^{n/(n+1)}. \]  \hspace{1cm} \hspace{1cm} (16)

For the value of a DW and the DW specific energy we obtain

\[ \Delta_g \approx b \left( \frac{A}{nK_{2g}} \right)^{1/(n+1)}, \]

\[ W_{a_2g} (\Delta_g) \approx k_{2g} \left( \frac{A}{nK_{2g}} \right)^{n/(n+1)}. \]  \hspace{1cm} \hspace{1cm} (17)

Formulas (17) for a particular case \( n = 1 \) are the same as for the LL theory where the DW and the DW energy are known to be determined by the geometric means of two characteristic dimensions associated with the exchange interaction and anisotropy. On the base of physical considerations, \( n > 0 \) in (17); otherwise, there is no DW.

It should be noted that the simulation of the relaxation process in regions 3 and 2 (see Fig. 1) is the bottle neck for function \( F_i(x) \). In addition, the acceleration mechanism of the DW motion is simulated better than that of the relaxation mechanism even if we assume that the initial rate of the DW motion is zero. Thus, this is the reason to suggest that there is some accelerated motion of a DW in the case of the relaxation process.

6. Last Region of the DW Motion

Let us consider a case where a DW achieves the region close to the silicate glass junction, i.e., where the reversal magnetization process is over (end of segment 2 at the boundary with segment 1 in Fig. 1). In this case, the anisotropy energy is constant; it is defined by \( \sim \lambda P \). Thus, we assume that this quantity \( \sim \lambda P \) determines the constant terms of \( F_m \).

The quadratic term takes into account the fact that the DW dimension during motion increases due to the cylindrical shape. The following form of the anisotropy energy is considered:

\[ W_{a_{21}} \approx \lambda P \left( \frac{\Delta_{21}^2}{R_m} \right), \]

where \( R_m \) (radius of the CGCAMNW strand) is introduced to maintain the balance of dimensions of \( W_A \) and \( W_{a_{21}} \).

In this case, the size and energy of the DW will be defined as follows:
\[ \Delta_{21} = \left( \frac{AR_m}{\lambda P} \right)^{1/3} \approx 10^{-7} \text{m}, \quad (19) \]

\[ W_{21}(\Delta_{21}) = \left( \frac{A^2 \lambda P}{R_m} \right)^{1/3} \approx 10^{-4} \text{J/m}^2. \]

The start field \( H_{c21} \) (corresponding to \( W_{21} \)) is larger than the start field in the third region \( H_{c3} \) (corresponding to \( W_3 (\Delta_3) \)). The dependence of \( H_{c21} \) on the radius of the microwire strand \( R_m \) and the radius of the glass envelope \( R_c \), has the following form:

\[
H_{c21} \approx \sqrt[3]{\frac{\lambda k_1 x}{R_m \left[ \left( \frac{k_1}{3} + 1 \right) x + \frac{4}{3} \right]}},
\]

\[
k_1 \approx 0.3 - 0.5,
\]

\[
x = \left( \frac{R_c}{R_m} \right)^2 - 1. \quad (20)
\]

7. The “Head-To-Head” Model

Nowadays, when studying the reversal magnetization of a CGCAMNW, it is often supposed that one can use a model of the DW motion referred to as the “head-to-head” model (see Fig. 3).

For instance, a simplified version of this model can be considered as an extension of a spherical DW which is in a cylindrical amorphous magnetic matrix within the region where anisotropy differs from the anisotropy of the matrix.

If, as mentioned elsewhere, the energy corresponding to the anisotropy of a DW will change only due to an increase in the DW surface, then we will write this energy as a function of the DW width in the following form:

\[
W_{as} \approx K_s \left( \frac{\Delta_{21}^3}{R_s^2} \right), \quad (21)
\]
where multiplier $R_s^2$ ($R_s$ is the characteristic radius of the action of anisotropy close to the DW dimension) is used to maintain the balance of the dimensions of quantities $W_A$ and $W_{ex}$.

Minimization of the functional leads to the following formulas for the dimension and energy of a DW:

$$
\Delta_s = \left( \frac{AR_s^2}{K_s} \right)^{1/4} \approx (\Delta_{LL} R_s)^{1/2},
$$

$$
W_s(\Delta_s) \approx \frac{(W_{LL} A)^{1/2}}{(R_s)^{1/2}}.
$$

The DW dimension is here similar to the dimension of the domain in the LL theory with a “characteristic” sample length, the role of which in this case is played quantity $R_s$, i.e., the region where the anisotropy of the spherical inclusion considerably differs from the anisotropy of the matrix. The energy of a DW is proportional to the geometric mean of the DW energy in the LL model and the exchange energy; at the same time, it is inversely proportional to $(R_s)^{1/2}$. It should be noted that these domains exhibit “rigidity” and they are not easily suppressed by a magnetic field opposite to the anisotropy field of the spherical inclusion. The existence of these domains in a CGCAMNW, the reversal magnetization of which can considerably change the loop rectangularity, has not been observed experimentally.

The theory of micromagnetism allows us to justify the application of the SFs qualitatively, which was proposed above (see Eq. (1a) and Fig. 2). In the subsequent studies, the parameters of the SFs will be related to the estimates of the micromagnetic theory.

8. Conclusions

Using force function $F_i(x)$ with two minima shown in Fig. 2, it is possible to examine this bistable system for a case of the existence of a stochastic resonance with a quasi-static reversal magnetization of the magnetic micro/nanowires. The preliminary results of numerical calculations present a qualitative picture of the outlet increase in the signal/noise ratio at certain correlations of the monochromatic force frequency and the gradient function parameters. The range of these frequencies lies in the region of 10 KHz, which is of some interest to improve the operation of miniature magnetic field sensors.

The following conclusions should be outlined.

- We have analyzed the possibility of using the Döring equation applying the force fields described by a GPR with the help of the SFs proposed in the previous works [1–6]. These SFs, depending on the value of their parameters, can describe the relaxation and acceleration forms of the DW motion.
- The model of the phenomenological equation of the DW motion has been compared with the micromagnetic calculations. Thus, it is possible to substantiate the micromagnetic structure and the form of the SFs used for the study of the DW dynamics.
- The proposed version of the SFs for a GPR makes it possible to study the existence of a stochastic resonance in this system. An opportunity to observe experimentally the stochastic resonance for the phenomenon of the reversal magnetization is of a significant theoretical and practical importance. At present, there exist a rather limited number of systems in which a stochastic resonance appears.
- The proposed theory differs radically from the existing theories of the DW dynamics which are applicable to amorphous ribbons or films, yet do not take into
account the specific nature of microwires. In our opinion, this fact determines the scientific importance of this work. Note that amorphous wires produced by other technologies require other analytical models of the DW dynamics.

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**References**

IRON–LANTHANIDE SINGLE MOLECULE MAGNET COMPOUNDS

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Abstract

Over the last decades, interest of researchers in the preparation and study of heterometallic Fe–Ln organometallic compounds has increased due to their intriguing architectures and promising applications as single molecule magnets (SMMs) that exhibit magnetic hysteresis of purely molecular origin. SMMs are fundamentally different from conventional bulk magnets because a collective long-range magnetic ordering of magnetic moments is not necessary. It is expected that SMMs can be employed in the future as the smallest magnetic memory units or in quantum computational devices. This review examines synthetic strategies and magnetic properties of Fe–Ln SMM compounds published till July 2016.

1. Introduction

Single molecule magnets (SMMs) are coordination compounds with slow relaxation of their magnetisation at low temperatures. The first SMMs represent a dodecanuclear [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] manganese compound (Fig. 1a), which was first prepared by Lis in 1980 [1] and then studied in more detail by several research teams [2–5]. This Mn$_{12}$–Ac complex with an $S = 10$ ground state shows magnetization hysteresis and quantum tunnelling of magnetization (QTM). The term "single molecule magnet" was first employed by Christou in 1996, when his team studied the magnetic properties of distorted [Mn$^{IV}$Mn$^{III}_3$O$_3$X] (X = Cl, Br) cubane complexes [6].

Fig. 1. Structure of (a) [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] and (b) [Fe$_8$O$_{2}$(OH)$_{12}$(tacn)$_6$]$^{8+}$. Color definition: Mn, plum; Fe, green balls; N, blue; O, red; C, grey; and H, light grey sticks.
In 1984 Weighardt et al. prepared a \([\text{Fe}_8\text{O}_2\text{(OH)}_{12}\text{(tacn)}_6]\)Br_8(H_2O)_8·8H_2O (tacn =1,4,7-triazacyclononane) cluster [7] based on a \{Fe_8\} core (Fig. 1b), which was characterized as an SMM by Wernsdorfer in 2000 [8]. The Weighardt’s \{Fe_8\} compound showed a high spin ground state (S = 10), low anisotropy, and a hysteresis loop. This finding has given rise to intense development in this area of research. Since then, a large number of coordination compounds based on Mn [9–12], Fe [13–15] and, to a lesser extent, Ni [16–17] or Co [18–20] exhibiting an SMM behavior have been discovered. Hexanuclear \([\text{Mn}_6\text{O}_2\text{(L)}_6\text{(O}_2\text{CPh(Me)}_2)_2\text{(EtOH)}_6]\) (L=2-hydroxyphenylpropanone oxime) reported by Brechin showed a blocking temperature of ~4.5 K; this is the highest value of this parameter known to date [21].

Starting from the development of homometallic polynuclear d-block transition systems, the research moved to the discovery of f-based polynuclear complexes as promising candidates with SMM properties. The lanthanide centers have large magnetic moments and—what is most important—extremely high magnetic anisotropy owing to the orbital contribution that made them good candidates for construction of SMM materials. A contribution to this area was made by Kirin and his colleagues, when they first described the synthesis of phthalocyanine double-decker of lanthanides [\text{Pc}_2\text{Ln}] in 1965 [22]. In 1979, the structures of double-decker complexes of lanthanides were reported by Moskalev et al. [23]. Later, in 2003 [24] Ishikawa et al. studied the magnetic properties of the double-decker phthalocyanine (Pc) mononuclear complexes with Tb^{3+} or Dy^{3+} and composition [\text{Pc}_2\text{Tb}] and [\text{Pc}_2\text{Dy}] (Fig. 2) and showed slow magnetization relaxation as a single-molecular property; the temperature ranges in which the behavior was observed were higher than that in the 3d-cluster SMMs. Among lanthanide SMM systems that showed different magnetic behavior, some Ln complexes gave the highest energy barrier [25–28] or a prominent QTM effect in relaxation behavior below 3 K [29]; others showed a better single molecule behavior than that of the compounds of the same nuclearity [30–33]. Long and his colleagues reported a radical bridged diterbium complex exhibiting a magnetic hysteresis curve at 14 K. This hysteretic behavior occurs at the highest temperature recorded for any previous molecule known to date [34].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Structure of [\text{Pc}_2\text{Ln}]. Color definition: Ln, yellow balls; N, blue; C, gray; and H, light gray sticks.}
\end{figure}

Another advantageous approach to SMMs is based on the combination of different spin carriers as d-block metals with lanthanide ions into polyheterometallic assemblies. The
high spin-states of transition metals and the large predominately anisotropic—magnetic moment of some trivalent lanthanide ions can give 3d-4f SMM clusters with properties that differ from those of homometallic compounds. Furthermore, cluster that comprises a 3d–4f core can exhibit strong magnetic coupling of mixed-metals; there are possibilities of achieving a ferromagnetic interaction between these two types of metal ions. The development of the chemistry of d–f complexes originates in the early of 20th century, when a series of Ln[Co(CN)₆]·nH₂O [35] was reported. Since then, many transition metal–lanthanide compounds have been synthesized by various synthetic routes [36, 37]. Studies of SMM properties of 3d–Ln complexes began much later. The preparation of SMM complexes with high blocking temperatures has attracted much attention; many efforts have been made to find new approaches for obtaining these materials [38] after reporting the first 3d–Ln mixed SMM compound with a [Cu₂Tb₂] core by Matsumoto et al. in 2004 [39]. A survey of the literature shows that the researchers were mainly focused on Mn–Ln [40–47], Cu–Ln [48–61], Co–Ln [62], and Ni–Ln complexes [63–66] because integration of a high LnIII spin into 3d systems with a high-spin ground state can stimulate sufficient magnetic anisotropy to exhibit an SMM behavior. Fe–Ln clusters have also been documented, mainly for Dy and Tb [67–74]. Over the last decades, 417 structures of Fe–Ln compounds have been synthesized; however, only several of them have been characterized as SMMs [75–96]. This review reports a class of magnetic compounds based on Fe–Ln metals exhibiting single-molecule magnet properties. X-ray data of the described FeIII–LnIII SMM compounds have been searched in the CCDC database up to 2016 (version 5.37, updated on July 2016) [97].

2. Design and Preparation of Fe–Ln SMMs

To date, several approaches for the design and preparation of SMMs have been introduced; the most efficient and most widely used approach is the preparation of these materials via “serendipitous self-assembly.” The term “serendipitous self-assembly” in the chemistry literature was first introduced by Winpenny in “Serendipitous assembly of polynuclear cage compounds” [98]. A review of the methods of preparation of heterometallic clusters possessing SMMs has revealed that one of the frequently used techniques is "step-by-step" strategy, including preliminary preparation of a precursor, such as µ₃-oxo trinuclear transition metal carboxylates ([Fe₃O(benz)₆(H₂O)₃](benz) [99], [FeIII(bpca)₂]+ [100], [Fe₂BaO(tca)₆(thf)₆] [101], [Fe₆O(acet)₆(H₂O)₆]NO₃ [102], [Fe₆O(piv)₆(H₂O)₆](piv) [103], and [Fe₆O(cyan)₆(H₂O)₆](NO₃)·5H₂O [104] compounds (where benzH = benzoic acid, bpca = bis(2-pyridylcarbonylamine, tcaH = trichloroacetic acid, acetH = acetic acid, pivH = pivalic acid, cyanH = cyanoacetic acid) and salts of metals: Fe(NO₃)₃·9H₂O, FeCl₃·4H₂O, and Fe(ClO₄)₂·6H₂O. The reported Fe–Ln SMM compounds have been synthesized by several synthesis methods: reflux, microwave irradiation, liquid–liquid diffusion, hydro(solvo)thermal methods, stirring at room temperature, and recrystallization.

The N- and O-containing donor ligands have been frequently used to combine iron and a lanthanide ions in the same heterometallic cluster, because nitrogen atoms exhibit a strong tendency to coordinate with transition metal ions, while the oxygen atoms prefer to bond to the lanthanide metal ions.

Ligand selection strategy is an important stage in the design and preparation of SMMs. Carboxylate ligands are commonly involved in synthesis due to their ability to adopt many different coordination modes. Thus, carboxylate moieties are great candidates to synthesize heterometallic systems. The organic ligands used in the preparation of heterometallic SMMs are shown in Scheme 1.
Scheme 1. Ligands for the preparation of SMM compounds.

3. Fe$^{II/III}$–Ln$^{III}$ SMMs

The Fe–Ln SMMs era began in 2005 due to the paper of Christou et al. [75], who reported the $[\text{Fe}_2\text{Ho}_2(\mu_3-\text{OH})_2(\text{teaH})_2(\text{benz})_4(\text{NO}_3)_2]\cdot 4(\text{MeCN})\cdot 3(\text{H}_2\text{O})$ (1) and $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{benz})_6]$ (2) clusters (where teaH$^-$= triethanolamine) (Fig. 3a). Clusters 1 and 2 having an incomplete double cuban metallic core were prepared by the liquid–liquid diffusion method: two solutions $[\text{Fe}_3\text{O}(\text{benz})_6(\text{H}_2\text{O})_3](\text{benz})$ in acetonitrile and $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ (Ln = Ho, Dy) with teaH$^-$ in methanol/acetonitrile were mixed together and layered with diethyl ether. Single crystal X-ray diffraction analysis showed that 1 and 2 are isostructural, only two chelating NO$_3^-$ groups were replaced by chelating benzoate groups. Structure of 1 consists of a Fe$_2$Ho$_2$ core (Fig. 3a), in which $\mu_3$-OH$^-$ ligands bind two Fe$^{III}$ ions and one Dy$^{III}$ ion in a trinuclear $\{\text{Fe}_2\text{Ho}\}$ sub-unit. The teaH$^2$- and benz$^-$ ligands additionally bind the metal atoms in a Fe$_2$Ho sub unit to form three types of different O-bridges between the metal heteroatoms. The Fe...Ln distances are 3.3936(6) and 3.4026(8) Å; the Fe...Fe distance is 3.2430(8) Å. The temperature-dependent magnetic susceptibility data for 1 and 2 suggest predominantly antiferromagnetic exchange interactions within two complexes. The out-of-phase AC (alternating current) measurements displayed a hysteresis loop for 2 at 4 K and 1.1 K, whereas a hysteresis loop for 1 was observed with a very small coercivity at 0.3 K. In 2011, Powell et al. reported related $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{R-benz})_6]$ (3) (where R= para-CN (3a) and meta-CN (3b)) [76] compounds; both displayed out-of-phase ($\chi''$) signals establishing their SMM behavior.

In 2006, was reported a dinuclear $[\text{FeDy}(\text{b pca})(\mu-\text{b pca})(\text{NO}_3)_3]\cdot 4(\text{H}_2\text{O})$ (4) SMM compound [77] synthesized from the reaction of the $[\text{Fe}^{II}(\text{b pca})_2]^+$ building block (b pca$^-$ bis(2-pyridylcarbonylamine) with dysprosium(III) nitrate hydrate, where the b pca$^{−}$
acts as tridentante chelate N,N,N-ligand toward the $d$-ion and as a bidentate $O,O$-chelate towards the $f$-site. Cluster 4 crystallizes in the triclinic $P-1$ space group and comprises the Fe$^{III}$ and Dy$^{III}$ ions linked by a central bridging bpca$^-$ ligand (Fig. 3b). The second bpca$^-$ ligand coordinates in $NNN$-chelating manner to the Fe$^{III}$ ion and completes the coordination environment of Fe$^{III}$ ion up to octahedron. The coordination environment of Dy is completed by four NO$_3^-$ anions. The intra-cluster distance Fe…Dy is 5.730(2) Å. The AC measurements for 4 reveal a frequency-dependent signal $\chi''$ giving an energy barrier ($U_{eff}$) of 8.98 cm$^{-1}$ and relaxation time ($\tau_0$) of $7.77 \times 10^{-8}$ s.

![Fig. 3. Structure of (a) [Fe$_2$Ho$_2$(OH)$_2$(teaH)$_2$(benz)$_4$(NO$_3$)$_3$] (1) and (b) [Fe(bpca)(µ-bpca)Dy(NO$_3$)$_4$] (4).](image)

A year later, was reported a linear trinuclear [{Fe$^{II}$(bpca)$_2$}{Dy$^{III}$(hfac)$_3$}]$_2$·CHCl$_3$ (5) (hfac$^-$ = 1,1,1,5,5,5-hexafluoroacetylacetonate, see Scheme 1) cluster [78] obtained by interaction of [Dy(hfac)$_3$]·2(H$_2$O) and [Fe$^{III}$(bpca)$_2$]$^+$ precursors (Fig. 4a). Cluster 5 comprises two peripheral Dy$^{III}$ ions and one central Fe$^{II}$ ion. Two bpca ligands complete the N$_6$ octahedral environment of Fe$^{II}$ ion and bridge Dy$^{III}$ ions via $O,O$-chelate mode coordination. Three hfac$^-$ ligand coordinate chelating to each of the Dy centers. The Fe…Dy distances are 5.653(3) and 5.654(3) Å. The Dy centers have an O$_8$ coordination environment. In-phase ($\chi'$) and out-of-phase ($\chi''$) components of AC susceptibility of 5 were measured in a temperature range of 1.5–3.5 K. An energy barrier of 5 is $U_{eff} = 9.7$ K with a relaxation time of $\tau_0 = 8.71 \times 10^{-8}$ s.

![Fig. 4. (a) Structure of [{Fe(bpca)$_2$}{Dy(hfac)$_3$}]$_2$ (5) and (b) view of the structure of 5 under the different angles. Color definition: Fe, bright green; Ln, yellow; N, blue; O, red; F, violet; and C, grey spheres. H-atoms are omitted.](image)

In 2009, decanuclear [Fe$_7$Dy$_3$(µ$_4$-O)$_2$(µ$_3$-OH)$_2$(mdea)$_7$(benz)$_4$(N$_3$)$_6$]·7(MeOH)-2(H$_2$O) (6) [79], tetranuclear [Fe$_3$Tb(µ$_3$-O)$_2$(tea)$_8$(H$_2$O)(THF)$_3$]·THF (7) [80] and hexanuclear [Fe$_4$D$_2$(µ$_4$-O)$_2$(NO$_3$)$_2$(piv)$_6$(Hedte)$_2$]·x(CH$_3$CN)-y(CH$_2$Cl$_2$)-z(C$_6$H$_5$OH) (8) clusters [81] with SMM behavior were reported. The reaction of FeCl$_3$, DyCl$_3$, 6H$_2$O, benzoic acid, and sodium azide in the presence of methyldiethanolamine (mdeaH$_2$) yielded SMM cluster
[Fe₃Dy₃(μ₄-O)₂(μ₃-OH)₂(mdea)₇(benz)₈(N₃)₆] ·7(MeOH) ·2(H₂O) (6). The core of cluster 6 consists of seven Fe⁺³ and three Dy⁺³ ions bridged by two (μ₄-O)²⁻ and two (μ₃-OH)⁻ ligands (Fig. 5a). Each (μ₄-O)²⁻ ligand bridges two iron and two dysprosium ions to form {Fe₃Dy₂(μ₄-O)} units. Each (μ₃-OH)⁻ ligand links one Fe⁺³ center and two Dy⁺³ centers. Each of the seven mdea²⁻ ligands coordinates in tridentate η¹:η²:η³ – μ₁ chelate-bringing mode. Six azides coordinate to Fe ions and four benzoates bridge to the metal ions. The coordination sphere of the Fe center is a distorted cis-N₂O₄ octahedral environment, except for one (in the top of Fig. 5a) that has a NO₄ coordination environment. Three Dy centers are eight-coordinated and adopt a square-antiprismatic geometry. Magnetic susceptibility studies revealed dominant antiferromagnetic interactions between Fe⁺³ (S = 5/2) and Dy⁺³ (S = 5/2) ions. AC susceptibility data displayed the maximum in χ” at 4.4 K at a frequency of 1500 Hz. An effective energy barrier (U_eff) is 33.4 K at a relaxation time (τ₀) of 6.6 × 10⁻⁸ s. Magnetic measurements below a temperature of 1.8 K gave a hysteresis loop with a field sweep rate of 0.035 T/s. Later, this team reported a related dodecanuclear SMM compound with a Tb ion [Fe₃Tb₃(μ₄-O)₂(μ₃-OH)₂(mdea)₇(benz)₈]·4(MeCN)·H₂O (13) [86]. Clusters 6 and 13 are isostructural; however, they differ in solvate molecules in the outer sphere. Magnetic studies revealed that antiferromagnetic interactions within 13 are dominant. AC measurements of 13 showed a clear out-of-phase signal indicating that the cluster exhibits a slow relaxation of magnetization.

The interaction of iron–barium [Fe₂BaO(tca)₆(thf)₆] (tcaH=trichloroacetic acid, thf=tetrahydrofuran, see Scheme 1) with Tb(NO₃)₃·6H₂O resulted in a [Fe₃Tb(μ₃-O)₂(tca)₆(H₂O)(thf)] ·thf (7) cluster [80], which comprises a tetranuclear "butterfly"-type metallic core with two triangles sharing the Tb...Fe edge (Fig. 5b). The Tb³⁺ ion resides in the O₈ coordination environment, while three Fe centers adopt distorted O₆ octahedral geometries. The compound exhibits strong an intramolecular antiferromagnetic exchange between Fe ions. AC measurements revealed a weak out-of-phase signal.

![Fig. 5. Structure of [Ln₂Fe₇O₂(OH)₂(mdea)₇(benz)₈(N₃)₆] (Ln=Dy (6) and Tb (13)) (a) and [Fe₃TbO₂(tca)₆(H₂O)(thf)] (7) (b). Color definition: Fe, bright green; Ln, yellow; N, blue; O, red; Cl, green-yellow; and C, grey spheres.](image)

The [Fe₃Dy₂O₂(NO₃)₃₂(piv)₈(edteH)₂] ·x(CH₃CN) ·y(CH₃Cl₂) ·z(C₆H₅OH) (8) heterocluster (edteH⁺=N,N,N’,N’- tetraakis-(2-hydroxyethyl)ethylenediamine; pivH= pivalic acid) was obtained from the reaction of FeCl₃·4H₂O, Ln(NO₃)₃·H₂O, pivalic acid, edteH₄, and phenol in a mixture of acetonitrile and dichloromethane [81]. The central core of 8 consists of [Fe⁺³Dy₄(μ₄-O)₂]^{14+} with the four Fe⁺³ centers arranged in a butterfly shape (Fig. 6a). Three Fe ions and one Dy ion are connected via μ₄-O bridges to form one wing and two body-iron atoms. Fe...Dy distances in each of the Fe₃Dy wingtips are 3.3973(8)–3.8273(7) Å. Each of the Dy centers is coordinated by one NO₃⁻ and one pivalate group; the remaining four pivalic ligands coordinate in a syn,syn bridging fashion. The edteH⁻ ligand is triply coordinated and...
chelating to the iron center via two nitrogen and three \( \mu \)-alkoxo oxygen atoms and bridges two metal ions that are two iron metals and iron–dysprosium metals. The \( \text{Fe}_4\text{Dy}_2\text{O}_2 \) core characterized by antiferromagnetic \( \text{Fe}^{\text{III}} \) (wingtip)–\( \text{Fe}^{\text{III}} \) (body) and weaker \( \text{Fe}^{\text{III}} \) (body)–\( \text{Fe}^{\text{III}} \) (body) ferromagnetic interactions. AC magnetic susceptibility data showed the temperature dependence of AC susceptibility significantly depends on frequency below 6 K. The estimated energy barrier was \( U_{\text{eff}} = 30.85 \text{ K} \) with a relaxation time of \( \tau_0 = 3.7 \times 10^{-8} \text{ s} \) for 8.

The octanuclear \( [\text{Fe}_4\text{Dy}_2(\text{teaH})_8(\text{N}_3)_8(\text{H}_2\text{O})] \cdot 4(\text{CH}_3\text{CN})\cdot(\text{H}_2\text{O}) \) (9) compound is the first Fe-Ln cluster possessing a wheel-type architecture characterized as an SMM. It was prepared by the reaction of iron(III) chloride and dysprosium(III) chloride with the triethanolamine ligand and sodium azide in methanol and acetonitrile [82]. The structure of 9 revealed the alternation of \( \text{Fe}^{\text{III}} \) and \( \text{Dy}^{\text{III}} \) centers (Fig. 6b) along the ring. Each of the Dy centers is chelated by two doubly-deprotonated teaH\(^2\) ligand, and four oxygens also bridge the \( \text{Dy}^{\text{III}} \) ion with the two neighboring \( \text{Fe}^{\text{III}} \) ions. The couple of monocoordination of azide groups completes the coordination environment of each of the iron centers up to \( \text{N}_2\text{O}_4 \) octahedron. The \( \text{Dy}^{\text{III}} \) center has a distorted square antiprismatic \( \text{N}_2\text{O}_6 \) coordination environment, except for one that additionally coordinates the aqua ligand giving a capped square antiprismatic \( \text{N}_2\text{O}_7 \) coordination environment. The Fe…Dy distances vary between 3.4572(6) and 3.512(1) Å. Comprehensive magnetic studies revealed dominant ferromagnetic interactions in 9 (\( \text{Dy}^{\text{III}} \) and \( \text{Fe}^{\text{III}} \) of \( S = 5/2 \)). AC measurements showed that the octanuclear wheel is frequency dependent in-phase and out-of-phase. The energy barrier was calculated by the Arrhenius law and resulted in 30.5 K with a relaxation time of \( 2.0 \times 10^{-9} \text{ s} \). The authors reported a hysteresis loop for 9 at 1.4 K; at 6.8 K, the hysteresis disappears.

![Fig. 6. Structure of (a) \([\text{Fe}_4\text{Ln}_2(\mu_3-\text{O})_2(\text{NO}_3)_2(\text{piv})_b(\text{edteH})_2]\) (8) and (b) \([\text{Fe}_4\text{Dy}_2(\text{teaH})_8(\text{N}_3)_8(\text{H}_2\text{O})]\) (9).](image-url)

A hexanuclear \( [\text{Fe}_4\text{Dy}_2(\text{thdH})_2(\text{thdH})_2\text{thd}_2(\text{CH}_3\text{OH})_2(\text{piv})_2(\text{NO}_3)_2] \) [\( \text{Dy}(\text{NO}_3)_4(\text{thdH})_3(\text{CH}_3\text{OH})\cdot(\text{NO}_3)\cdot\text{H}_2\text{O} \) (10)] SMM cluster (\( \text{thdH} = \) trihydroxy Schiff-base ligand, see Scheme 1) was obtained from the interaction of thdH\(^3\) ligand, which was prepared by the reaction of apdhH (2-amino-1,3-propanediol) with sadH\(^2\) ligand (salicylaldehyde) in a methanol/acetonitrile solution, with \( \text{Ln}(\text{NO}_3)_3\cdot\text{H}_2\text{O} \) and \([\text{Fe}_3(\mu_3-\text{O})(\text{H}_2\text{O})_3(\text{piv})_2](\text{piv}) \) resulted in 10. The compound is composed of a \([\text{Fe}_4\text{Dy}_2]^2^+ \) cation and a mononuclear \([\text{Dy}^-]^+ \) anion (Figs. 7a, 7b). The metallic atoms in the core are organized in an “S” shape and coordinated by the \( \mu \)-pivalato ligands and \( \mu \)-phenoxide and \( \mu \)-alkoxide groups of the Schiff-based ligand. \( \text{Dy}^{\text{III}} \) ions are located at the terminal positions and \( \text{Fe}^{\text{III}} \) ions occupy the central position of the
core. Each of the Dy ions is nine-coordinated with one chelating nitrate, one methanol molecule, one μ-pivalate, and two Schiff-based ligands. The Fe...Dy distances are 3.3918(9) Å; the Fe...Fe distances are 3.074(1) and 3.192(1) Å. The mononuclear anion consists of a Dy center coordinated with four chelating nitrates, one thdH₃ ligand, and a monodentate methanol molecule. Reported magnetic studies revealed the presence of both strong antiferromagnetic and weak ferromagnetic interactions between the FeIII ions in 10. Cluster 10 showed a frequency-dependent out-of-phase signal, which suggests that 10 really acts as an SMM at low temperatures.

Sanudo et al. [84] synthesized the first largest at that time Fe₁₂Sm₄ cluster with composition [Fe₁₂Sm₄(μ₄-O)₆(μ₁-O)₉(μ₃OH)₄(benz)]₂⁺ (11) and an SMM behavior, prepared by the solvothermal reaction of [Fe₃O(benz)_6(H₂O)₃](benz) with Sm(NO₃)₃·9H₂O in acetonitrile under autogenous pressure. The structure of 11 consists of two [Fe₄O₂(OH)₂] cuban sub-units, where four FeIII ions bridged by two μ₃-OH and two μ-O²⁻ ligands. These two cuban sub-units sandwich four FeIII centers via four μ₁-O²⁻ bridges. Four SmIII ions are linked with two [Fe₄O₂(OH)₂] cuban sub-units through six μ₄-O²⁻ bridges to form the {Fe₁₂Sm₄} core (Fig. 7c). The SmIII...FeIII distances vary between 3.980(2) and 4.092(2) Å. The Fe...Fe distances in each of the [Fe₈O₂(OH)₂] cuban sub-units are in a range of 3.393(2)–3.432(2) Å. Twenty μ₂-PhCO²⁻ and four μ₃-PhCO²⁻ carboxylate groups of benz ligands on the periphery of the cluster complete the environment around the {Fe₁₂Sm₄} core. Direct current (DC) susceptibility data indicated an antiferromagnetic coupling between the SmIII and FeIII ions in 11. AC susceptibility of 11 showed a strong frequency dependent χ'' signal at 1.5 K. A hysteresis loop was observed at 0.5 K. High-nuclearity complex 11 has an energy barrier of U eff = 16 K with a relaxation time of τ₀ = 2 × 10⁻⁸ s.

![Fig. 7. Structure of (a) [Fe₄Dy₂(thdH₂)₃(thdH₂)₃(thd₃)H₂O(µiv)₉(NO₃)₈]²⁺ cation (10), (b) [Dy(NO₃)₃(thdH)₃(Ph₃CH)]⁻ anion (10), and (c) Fe₁₂Sm₄(µ₄-O)₆(µ₁-O)₉(µ₃OH)₄(benz)]₂⁺ (11).](image)

In 2013, was published another example of the tetranuclear SMM complex [FeDy₃(Bpz₃H)₆(dto)₃] ·4(MeCN)·2(CH₂Cl₂) (12) (Bpz₃H=hydrotris(pyrazolyl)borate, dto=dithiooxalato dianion ligand) (Fig. 8a) [85]. The tetranuclear FeDy₃ cluster has a propeller-like geometry and consists of three [Dy(HBpz₃)] units that coordinate to the central iron ion via three dto ligands. Each of the Dy centers has a square antiprismatic N₆O₂ coordination environment, while the Fe center comprises an S₆ coordination sphere. The bond lengths are in a range of 2.260–2.277 Å for Fe–S, 2.356(5)–2.395(1) Å for Dy–O, and 2.413(4)–2.520(6) Å for Dy–N. Magnetic susceptibility measurements revealed very weak intramolecular magnetic interaction because the Fe...Dy distances are 6.156 and 6.188 Å. The
authors reported a frequency-dependent out-of-phase signal of complex 12 that exhibits maxima above 1.8 K. The energy barrier is 15 K and the relaxation time is \(1.5 \times 10^{-6}\) s.

![Fig. 8. Structure of (a) [FeDy3(HBpz3)6(dto)3] (12) and (b) [Fe3Dy2(μ3-OH)2(n-bdea)4(benz)6] (14). Color definition: Fe, bright green; Dy, yellow; N, blue; O, red; Cl, green-yellow; S, lavender; B, lime; and C, grey spheres.](image)

Two more SMM compounds were reported, namely, hexanuclear \([\text{Fe}_4\text{Dy}_2(\text{OH})_2(\text{bdea})_4(\text{benz})_6]\)·(MeCN) (13) [86] and nonanuclear \([\text{Fe}_6\text{Dy}_2(\text{C}_2\text{H}_2\text{O}_4)(\text{tea})_2(\text{teaH})_3(\text{N}_3)_2(\text{N}_6)(\text{NO}_3)_3]2(\text{EtOH})\) (14) [87]. The reaction of \([\text{Fe}_3\text{O}(\text{benz})_6(\text{H}_2\text{O})_2]\)·(benz) with Dy(NO3)3·6H2O and butyldiethanolamine (bdeaH2) resulted in \([\text{Fe}_6\text{Dy}_2(\text{OH})_2(\text{bdea})_4(\text{benz})_6]\)·MeCN (14) (Fig. 8b). In 14, two peripheral dimeric \([\text{Fe}_2(\text{n-bdea})_2]^{2+}\) units are bridged by the \([\text{Dy}_2(\mu_3-\text{OH})_2]^{4+}\) dimer to form a hexanuclear core. Four FeIII ions have an octahedral NO3 environment; two DyIII centers are eight-coordinated to form an almost ideal square antiprism O8 coordination environment. The Dy–O distances vary in a range of 2.272(2)–2.617(4) Å; the Fe–O bonds are 1.929(4) and 2.068(4) Å; the Fe–N bond lengths are 2.199(5) and 2.206(5) Å. DC magnetic susceptibility studies of 14 revealed dominant antiferromagnetic interactions between spin carriers. According to the Arrhenius law, the anisotropy barrier in 14 is \(U_{eff} = 21.4\) K with a relaxation time of \(2.7 \times 10^{-8}\) s.

The nonanuclear \([\text{Fe}_6\text{Dy}_3(\text{C}_2\text{H}_2\text{O}_4)(\text{tea})_2(\text{teaH})_3(\text{N}_3)_2(\text{N}_6)(\text{NO}_3)_3]2(\text{EtOH})\) (C2H2O4)\(=\)tetaanion of 1,1,2,2-tetrahydroxyethane) (15) cluster was obtained by the reaction of \([\text{Fe}_2\text{O}(\text{acet})_6(\text{H}_2\text{O})_2]\)NO3 (acetH=acetic acid) and Dy(NO3)3·6H2O with triethanolamine and sodium azide in the presence of Fe(NO3)3·9H2O [88]. The compound consists of six FeIII and three DyIII centers to form a cone-like metallic core (Fig. 9a). The metal centers of iron and dysprosium are linked through tetraanion of 1,1,2,2-tetrahydroxyethane, bi- and tridentate triethanolamine ligands, and two bidentate azides. The structure is completed by six monodentate azides which cupped the iron ions and nitrate anion coordinated to the Dy center on the top of the cone. The Dy centers are eight-coordinated to adopt a square antiprismatic and dodecahedral geometry. The Fe centers are six-coordinated to adopt a distorted octahedral geometry. Magnetic susceptibility studies showed a dominant ferromagnetic behavior in 15. The AC susceptibility data were analyzed according to the Arrhenius law and gave an estimate for the energy barrier at 65.1 K with a relaxation time of \(1.64 \times 10^{-12}\) s. Cluster 15 displayed the highest energy barrier known to date among Fe–Ln SMM complexes.

In 2014, a tetranuclear \([\text{Fe}_2\text{Tb}_2(\text{hhpmH}_2)_4(\eta_2-\text{NO}_3)_3]\)·2(ClO4)·2(CH3OH)·2(H2O) (16) SMM complex (hhpmH4=(E)-2,2’-(2-hydroxy -3-((2-hydroxyphenylimino)methyl)-5-
methylbenzyl-azanediyl)-diethanol) was obtained by the reaction of iron(III) perchlorate with triethylamine in the presence of an hhpmH$_3$ ligand, Tb(NO$_3$)$_3$·xH$_2$O, and trimethylamine (Figure 9b) [89]. This cluster contains two Fe$^{III}$ ions at the periphery and two Dy$^{III}$ ions in the center. The entire structure is held by four doubly deprotonated [hhpmH$_3$]$^2$ ligands possessing an overall Z-type topology. The two iron centers are hexa-coordinated adopting a N$_3$O$_4$ distorted octahedral geometry, while the dysprosium centers are octa-coordinated with a NO$_3$ trigonal dodecahedral geometry. The Fe...Tb distances are 3.552(2) Å; the distance between two Dy ions is 3.749(1) Å. Magnetic data revealed the presence of predominant ferromagnetic coupling at low temperatures; Tb(III) has an effective spin of $S = 3$. AC susceptibility analysis showed a frequency dependent out-of-phase signal; no maxima were observed.

![Fig. 9. (a) Structure of the cone-type Fe$_6$Dy$_3$(C$_2$H$_5$O$_3$)(tea)$_2$(teaH)$_3$(N$_3$)$_6$(NO$_3$)](15) cluster and (b) Z-type topology of the cationic [Fe$_2$Tb$_2$(hhpmH$_3$)$_4$(η$_2$-NO$_3$)$_3$]$^{2+}$(16) cluster.

Powell et al. [90] synthesized a tetranuclear [Fe$_2$Dy$_2$(μ$_3$-OH)$_2$(teg)$_2$(N$_3$)$_2$(benz)$_4$] cluster (17), where tegH$_2$=triethylene glycol, and studied the magnetic properties of the compound. The central core of the compound represents a Fe$_2$Dy$_2$ butterfly topology, where Fe$^{III}$ and Dy$^{III}$ ions are held together by two μ$_3$-OH groups (Fig. 10a). Two teg$^-$ anionic ligands coordinate to Dy centers in a tetradenate coordinate mode and bridge to two Fe centers with two deprotonated alkoxide arms. Azides and benzoate groups complete the coordination sphere of the Dy and Fe centers. The Fe centers are six-coordinated and have a slightly distorted NO$_5$ octahedral coordination geometry, whereas Dy centers are eight-coordinated with an O$_3$ trigonal dodecahedral coordination geometry. The Dy...Fe distances are 3.3557(6) and 3.3952(6) Å; the Dy...Dy distance is 3.9347(5) Å. The Dy–O distances are in a range of 2.280(2)–2.417(2) Å. Magnetic studies revealed dominant antiferromagnetic interactions between the metal ions in 17. AC magnetic susceptibility measurements of [FeDy$_2$Fe(μ$_3$-OH)$_2$(teg)$_2$(N$_3$)$_2$(benz)$_4$] (17) showed frequency-dependent $\chi''$ signals; however, there was no maxima above 1.8 K.

2015 was a year marked by achievements in the preparation of five heterometallic SMM clusters with terbium and dysprosium. Two hexanuclear SMM clusters [Fe$_6$Ln$_2$(μ$_3$-O)$_2$(btpH$_4$)$_2$(Piv)$_{12}$_0.5(DMF)-(EtOH)-2.5(H$_2$O) (Ln=Dy (18) and Tb (19), btpH$_4$=bis-tri propane) were formed using the solvothermal reaction of trinuclear [Fe$_3$O(piv)$_3$(H$_2$O)$_3$](piv), Ln(NO$_3$)$_3$·xH$_2$O (Ln=Dy(18), Tb(19)), bis-tris propane, and Li(OH)·H$_2$O in a mixed solvent of EtOH and DMF [91]. Clusters 18 and 19 are isostructural; their structures include six Fe$^{III}$ and two Dy$^{III}$ ions linked via 2 μ$_3$−OH groups, 2 btpH$_4^2$-ligands, and 12 pivalates (Fig. 9b). Four iron sites are hexa-coordinated to adopt an O$_6$ octahedral geometry; two in the center have an N$_2$O$_4$ environment. The Fe–N bond distances
vary in a range of 2.152(5)–2.187(5) Å, while the Fe–O bond distances are from 1.852(3) to 2.177(4) Å. The Dy–O distances lie in a range of 2.259(4)–2.615(3) Å. Magnetic measurements indicate that the complexes exhibit a slow magnetic relaxation. AC measurements suggest that these compounds exhibit a slow magnetic relaxation.

![Figure 10](image)

**Fig. 10.** Structure of (a) [FeDy$_2$Fe$_3$(μ$_3$-OH)$_2$(teg)$_2$(N$_3$)$_2$(benz)$_4$] (17) and (b) [Fe$_3$Ln$_2$(μ$_3$-O)$_2$(btp)$_4$(Piv)$_{12}$] (Ln=Dy (18) and Tb (19)).

A heteronuclear complex [Fe$_2$Dy$_3$(μ$_5$-O)(edteH)$_2$(NO$_3$)$_5$(H$_2$O)(MeOH)]·0.5(MeOH) (20) (edteH$_4$=N,N,N,N-tetakis(2-hydroxyethyl) ethylenediamine) is the first example of pentanuclear Fe-Ln SMM. Cluster 20 was prepared by the reaction of Fe(NO$_3$)$_3$·9H$_2$O, Dy(NO$_3$)$_3$·6H$_2$O and edteH$_4$ in the presence of triethylamine in a solvent mixture of MeOH and MeCN [92]. The cluster core consists of three Dy$^{III}$ and two Fe$^{III}$ ions, which reside in the vertexes of a square pyramid. All metal ions are held by the central μ$_5$-O bridge (Fig. 11a). Two Fe$^{III}$ and two Dy$^{III}$ ions form the base of the pyramid, while one Dy$^{III}$ ion occupies the vertex. It is of interest that each of the Fe$^{III}$ ions is seven-coordinated and adopts an N$_2$O$_5$ capped octahedral polyhedron, whereas Dy$^{III}$ ions are nine-coordinated and surrounded by O$_9$ donor atoms. The Fe–O, Fe–N, and Dy–O bond lengths are in a range of 1.965(5)–2.266(4) Å, 2.258(5)–2.240(6), and 2.283(4)–2.626(4) Å, respectively. The static magnetic susceptibilities of 20 revealed that the cluster undergoes strong antiferromagnetic interactions. The out-of-phase AC magnetic susceptibilities of 20 exhibit frequency dependence below 6 K, which indicates a slow relaxation of magnetization, with an energy barrier of $U_{eff} = 6.78$ K and a relaxation time of $\tau_0 = 2.01 \times 10^{-5}$ s.

Reaction of Dy(NO$_3$)$_3$·6H$_2$O and 1-(2-hydroxyethyl)-2-pyrrolidone in the presence of K$_3$[Fe(CN)$_6$] in an aqueous solution produces the dinuclear SMM complex [FeDy(CN)$_6$·(hep)$_2$(H$_2$O)$_4$] (21) (hep=1-(2-hydroxyethyl)-2-pyrrolidone) [93]. The structure consists of the [Fe(CN)$_6$]$^{3-}$ entity which acts as a bridging ligand toward a Dy$^{III}$ ion to form a heterodinuclear structure (Fig. 11b). The Dy ion has a distorted pentagonal-bipyramidal geometry with a NO$_6$ donor set, whereas Fe$^{III}$ ion resides in a C$_6$ octahedral environment. The DC magnetic measurements showed an antiferromagnetic coupling between the intradimer Dy$^{III}$ and Fe$^{III}$ ions. Under an external field, the compound shows an AC magnetic relaxation dynamics, which gives rise to antiferromagnetic interaction in 21. Fitting the data to the Arrhenius law, the characteristic SMM energy gap, $U_{eff}$ was estimated at 63 K and the relaxation time was $7.1 \times 10^{-11}$ s.

Another hexanuclear SMM cluster [Fe$_2$Dy$_4$(μ$_4$-O)$_2$(μ$_3$-OH)$_2$$_3$(μ$_3$-OMe)$_2$$_3$(cyan)$_{10}$(MeOH)$_5$(H$_2$O)]·3(MeOH)·0.36(H$_2$O) (cyanH= cyanoacetic acid) (22) was reported by Powell et al. [94]; it was derived from the
reaction of trinuclear \([\text{Fe}_3\text{O(cyan)}_6\text{(H}_2\text{O})_3\text{]}(\text{NO}_3)\text{)}_5\text{H}_2\text{O}\) and \(\text{Dy(NO}_3)_3\text{)}_2\cdot\text{H}_2\text{O}\) in the presence of (±)-3-diisopropylamino-1,2-propanediol in methanol. Compound (±)-3-diisopropylamino-1,2-propanediol does not coordinate to complex 22; however, the presence of it in the reaction is mandatory for growing orange crystals of 22. The structure consists of four Dy\(^{III}\) and two Fe\(^{III}\) ions linked via two \(\mu_4\text{-O}^{2-}\) and \(\mu_3\text{-OH}\) ligands in the vertexes of square pyramid, while iron ions occupy the axial positions (Fig. 11b). The metal atoms in the core is additionally linked by ten cyanoacetate groups; eight of them coordinate in a \(\text{syn},\text{syn}\cdot\eta^1:\mu_2\)-bridging mode, while the remaining two coordinate in a \(\eta^1:\mu_2\)-bridging mode. The peripheral environment of the Dy ions is provided by one aqua and five MeOH ligands. Each of the Dy\(^{III}\) ions has an eight-coordinated oxygen atoms environment with a nearly square antiprismatic geometry, whereas each of the Fe\(^{III}\) ions coordinates six oxygen atoms to adopt a slightly distorted octahedral geometry. Magnetic studies displayed that antiferromagnetic coupling in the squashed octahedral topology core are dominant. In 22, the anisotropy barrier was estimated at 34 K (\(\tau_0 = 2.0 \times 10^{-11}\) s).

Fig. 11. Structure of (a) \([\text{Fe}_3\text{Dy}_3\text{O(edteH)}_3\text{(NO}_3)_3\text{(H}_2\text{O})_5\text{(MeOH)}]\) (20), (b) \([\text{FeDy(CN)}_6\text{(hep)}_2\text{(H}_2\text{O)}_4\]) (21), and (c) \([\text{Fe}_2\text{Dy}_4\text{O}_2\text{(OH)}_2\text{MeCN}_1\text{Me}_1\text{O}_2\text{CCH}_2\text{CN})_1\text{MeOH}_2\text{(H}_2\text{O)}]\) (22).

In the beginning of 2016, Powell et al. [95] increased the number of Fe–Ln SMM complexes by publishing hexanuclear cluster \([\text{Fe}_4\text{Dy}_2\text{(µ}_3\text{-OH)}_2\text{mdea})_4\text{(µ-nbenz)}_8\text{]}\cdot3\text{(MeCN)}\) (23) (nbenzH\(_2\text{=m-NO}_2\text{C}_6\text{H}_4\text{COOH}\) and nonanuclear cluster \([\text{Fe}_4\text{Dy}_3\text{(µ}_3\text{-O})_4\text{(µ}_3\text{-O})(\text{mdea})_6\text{(nbenz)}_8\text{]}\cdot3\text{(MeCN)}\) (24). Cluster 23 was derived from the interaction of \([\text{Fe}_3\text{O(nbenz)}_6\text{(H}_2\text{O})_3\text{]}\cdot\text{(nbenz)}, \text{Ln(NO}_3)_3\cdot\text{xH}_2\text{O}\) with a methyldiethanolamine ligand; it contains a \{Fe\(_2\text{Dy}_2\}\) core with a butterfly-shaped central \{Fe\(_2\text{Dy}_2\}\) unit, where each of the two \{Fe\(_2\text{Dy}_2\}\) triangles is bridged by a \(\text{µ}_3\text{-OH}\) ligand, a \(\text{syn},\text{syn}\) \(\text{µ}\)-benzoate ligand, and a doubly-deprotonated mdea\(^{2-}\) ligand (Fig. 12a). The remaining two Fe\(^{III}\) ions coordinate to the butterfly-like core through the oxygens that arrive from the double deprotonated mdea\(^{2-}\) ligand and bridging benzoate. The Fe–Fe distance is 5.1884 Å; Dy–Dy is 3.8750 Å, while Fe–Dy distances are 3.3583 and 3.5546 Å. Compound 23 was used as a precursor to prepare a higher nuclearity cluster \([\text{Fe}_6\text{Dy}_5\text{(µ}_4\text{-O})_3\text{(µ}_3\text{-O})(\text{mdea})_5\text{(nbenz)}_9\text{]}\cdot3\text{(MeCN)}\) (24). The molecular structure of 24 consists of six Fe\(^{III}\) ions and three Dy\(^{III}\) ions that are linked via three \(\mu_4\text{-O}^{2-}\) and one \(\mu_3\text{-O}^{2-}\) to form the metallic core of 24 (Fig. 12b). Five mdea and nine benzoate ligands complete the peripheral ligation of the metal core. The Dy–Dy distances are 3.7412(6), 3.7635(7), and 3.8347(7) Å. Temperature dependent magnetic measurements indicated dominant antiferromagnetic interactions between Fe\(^{III}\) ions and weakly ferromagnetic interactions between Dy\(^{III}\) ions in 23. In 24, the Fe\(^{III}\)–Fe\(^{III}\) interactions are antiferromagnetic and Dy\(^{III}\)–Dy\(^{III}\) interactions are weakly antiferromagnetic. Magnetic AC measurements of the \{Fe\(_2\text{Dy}_2\}\} (23) cluster revealed the slow relaxation of magnetization.
Fitting the frequency-dependent AC susceptibility data of 23 with the Arrhenius law gives a characteristic SMM effective energy barrier of $U_{\text{eff}} = 7.1 \text{ K}$ with a relaxation time of $\tau_0 = 6.4 \times 10^{-6} \text{ s}$. The AC susceptibility measurements for 24 in a zero DC field showed an extremely weak $\chi''$ signal. However, a DC field of 1000 Oe provides a clear out-of-phase signal. Calculations for the data with the Arrhenius law yield an effective energy barrier of 17.1 K and a relaxation time of $7.4 \times 10^{-8} \text{ s}$.

**Fig. 12.** Structure of (a) $[\text{Fe}_4\text{Dy}_2(\mu_1-\text{OH})_3(\text{mdea})_4(\text{nbenz})_8]$ (23) and (b) $[\text{Fe}_6\text{Dy}_3(\mu_4-\text{O})(\mu_3-\text{O})(\text{mdea})_5(\text{nbenz})]$ (24).

Recently, Baca et al. [96] have contributed to this area by reporting two hexanuclear carboxylate wheels $\{\text{Fe}_4\text{TB}_2\}$ (25) and $\{\text{Fe}_4\text{Ho}_2\}$ (26) and the two largest Fe-4f SMM wheels to date $\{\text{Fe}_{18}\text{Dy}_6\}$ (27) and $\{\text{Fe}_{18}\text{TB}_6\}$ (28) to display slow magnetic relaxation. Clusters $[\text{Fe}_4\text{Ln}_2(\text{piv})_6(\text{N}_3)_4(\text{teaH})_4] \text{ (Ln= Tb} \text{ (25) and Ho (26)-2(ETOH)} \text{ (pivH=pivalic ac} \text{ id; teaH}_3=\text{triethanolamine})$ were synthesized by the interaction of $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{piv})_{12}]$ with terbium(III) nitrate or holmium(III) nitrate in the presence of sodium azide and triethanolamine in an ethanol solution. Clusters 25 and 26 composed of four Fe$^{\text{III}}$ and two Ln$^{\text{III}}$ ions linked by an array of bridging carboxylate, azide, and aminopolyalcoholato-based ligands into a cyclic structure with a cavity and ethanol solvents for 26 (Fig. 13a). Each of the Fe$^{\text{III}}$ atoms has a distorted octahedral N$_2$O$_4$ coordination environment, whereas each of the Ln$^{\text{III}}$ atoms is eight-coordinated with an N$_2$O$_6$ donor set. The reported temperature-dependent magnetic susceptibility data are consistent with dominant ferromagnetic exchange interactions within the complexes. AC susceptibility data of 25 and 26 showed an energy barrier of $U_{\text{eff}} = 31.68 \text{ K}$ and $\tau_0 = 1.2 \times 10^{-9} \text{ s}$. 
Large wheels \([\text{Fe}_{18}\text{Ln}_6\text{(is)}_{12}\text{(teaH)}_{18}\text{(tea)}_{6}\text{(N}_3\text{)}_{6}]\cdot\text{n(solvent)} (\text{Ln}=\text{Dy} (27) \text{ and } \text{Tb}(28); \text{isH}=\text{isobutyric acid}) \text{ were derived from the reaction of } [\text{Fe}_3\text{O}\text{(is)}_6\text{(H}_2\text{O)}_3]\text{NO}_3\cdot\text{2(MeCN)}\cdot\text{2(H}_2\text{O)} \text{ with disprosium(III) nitrate or terbium(III) nitrate in the presence of sodium azide and triethanolamine in a MeOH/MeCN solution. The molecular core structures in } 27 \text{ and } 28 \text{ involve } 18 \text{ Fe}^{\text{III}} \text{ and six } \text{Ln}^{\text{III}} \text{ ions interconnected by 6 isobutyrate and 24 amino alcohol ligands into a ring with alternating three } \text{Fe}^{\text{III}} \text{ ions and one } \text{Ln}^{\text{III}} \text{ ion (Fig. 13b). All Fe centers are six-coordinated in a distorted octahedral environment: 12 of them have a NO}_3 \text{ donor set, and the remaining 6 Fe atoms have a N}_2\text{O}_4 \text{ donor set. All Ln atoms are eight-coordinated having a distorted square antiprismatic NO}_7 \text{ environment. Temperature magnetic measurements of } 27 \text{ and } 28 \text{ indicated predominant antiferromagnetic exchange interactions within each of the } \text{Fe}_3 \text{ units (} S = 5/2 \text{) and ferromagnetic interactions within the ring structure. The magnetic AC measurements revealed out-of-phase signals of the compounds and, thus, slow relaxation above 2.0 K and below 1500 Hz.}

The Table 1 lists the heterometallic Fe–Ln SMMs published in a period of 2005–2016, along with relevant parameters used to characterize their SMM properties. Specifically, the table shows the range in which the hysteresis loops of the compounds were observed, the effective energy barrier \((U_{\text{eff}})\), and the relaxation time \((\tau_0)\) of the obtained Fe–Ln SMM compounds.
<table>
<thead>
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<th>#</th>
<th>Fe–Ln SMM’s</th>
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<th>$\tau$ (s) (rel. time)</th>
<th>Hysteresis (K)</th>
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4. Conclusions

The review shows the advances that have been achieved in the preparation of SMM compounds based on a Fe–Ln core. Over the last decade, the field of iron–lanthanide SMMs has been rapidly developed by synthesizing more and more interesting SMM compounds. Chemists and researchers have synthesized and studied a number of SMMs to understand the properties of these materials. A rational design involving N-/O-containing donor ligands gives glorious architectures exhibiting properties required to be SMMs. This review describes SMM species possessing different architecture topologies: linear, s-shaped, propeller-, ring-, Z-, butterfly-, wheel-type cores, and other structures. Over the last decade, 28 Fe–Ln heteronuclear coordination clusters have revealed an SMM behavior. The effective preparation of SMM compounds depends on the types of structures and on basic and complementary ligands binding metal ions. A huge number of various types of ligands could be employed in different combinations for assembling other Fe–Ln complexes exhibiting better magnetic behavior.

There are two main criteria that determine 3d–4f compounds as an SMM; one of them is a hysteresis loop, which can be observed at extremely low temperatures; the other criterion is frequency-dependent signals of out-of-phase susceptibility of AC measurements, which enable calculations of energy barriers with relaxation times.

References


O. Botezat


ASPECTS OF DIRECTED SYNTHESIS OF PROTEASES IN MYCELIAL FUNGI USING METAL NANO-OXIDES

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Abstract

Data on the effect of some metal nano-oxides on the biosynthesis of individual components of proteolytic enzymes complex of micromycetes Trichoderma koningii CNMN FD 15 and Fusarium gibbosum CNMN FD 12 have been described. For each strain, optimum conditions of cultivation in the presence of the studied nanoparticles, which provide an increased level of proteolytic activity, have been determined. It has been emphasized that the stimulating effect depends on the composition, size, and concentration of the nanomaterials and on the initial pH value of the medium.

1. Introduction

In the last few years, the use of extracellular enzymes produced by microorganisms has expanded with the intensive development of biotechnology. Thus, optimization of enzyme biosynthesis remains relevant. A particular interest is given to finding ways to stimulate biosynthesis with the use of different factors (physical, chemical, etc.).

In this context, the use of nanometer materials involved in the vital processes of organisms at the cellular and subcellular level is promising. The range of physicochemical properties of nanoparticles differs from that of larger particles (increased reactivity and catalytic activity, adsorption capacity, formation of a large number of chelated compounds, possibility of crossing biological membranes, etc.). Nanoparticles are used in various branches of industry owing to their unique properties. In recent years, it has been shown that they also exhibit biological activity and can be used in various fields of medicine, biology, and biotechnology to control the physiological and biochemical functions in cells [1–8].

The importance of studying the effect of nanoparticles on living organisms has significantly increased. Reports on the toxic [9–11] and stimulating effect of different types of nanoparticles on growth, development, and productivity (synthesis of biologically active substances) in microorganisms [12–14] have been published.

The aim of the paper was to study the effect of some metal nano-oxides on the biosynthesis of microorganisms Trichoderma koningii Oudemans CNMN FD 15 and Fusarium gibbosum CNMN FD 12, which are active producers of exocellular protease enzymes [15, 16].
2. Materials and Methods

The objects of study were two strains of micromycetes with a high level of hydrolase biosynthesis—Trichoderma koningii Oudemans CNMN FD 15 and Fusarium gibbosum CNMN FD 12—producers of proteases.

Cultivation of micromycetes was carried out in 1.0-L Erlenmeyer flasks with 200 mL of a nutritive medium at a temperature of 28–30°C under agitation at a rate of 180–200 rpm using a culture medium with the following composition (g/L): wheat bran, 20.0; soybean flour, 10.0; (NH₄)₂SO₄, 1.0; and CaCO₃, 2.0; a pH of 6.25.

The seed material was a spore suspension with a density of 2 × 10⁶–3 × 10⁶ spores/mL, which was prepared by washing a 15-day culture grown on malt-agar oblique columns with sterile distilled water. The amount of the seed material in each flask was 10% v/v.

Metal oxides ZnO and Fe₂O₃ selected in previous studies as a stimulator of proteolytic enzymes were used in the research. Nanoparticles with different sizes (10, 30, 65–70 nm; 1 µm) were added to the sterile culture medium in a concentration of 1, 5, 10, and 15 mg/L concomitantly with the inoculum.

Solutions with a required concentration of nanoparticles were prepared from the solid or liquid initial preparations using deionized water at a pH of 6.25. Immediately before introduction into the nutrient medium, the prepared solutions were ultrasonically treated in an AOYU-9050 WilTec ultrasonic bath (Wildanger Technik GmbH, Germany, 30–50W, frequency of 40 kHz) for 5 min to provide the dispersion of the nanoparticles.

The basic culture medium without nanomaterials was used as a reference medium.

Proteolytic activity was assayed in the dynamics of cultivation on the 4th–6th day for the Fusarium gibbosum CNMN FD 12 and on the 8th–10th day for Trichoderma koningii Oudemans CNMN FD 15; this is the period of maximum accumulation of enzymes in the growth of this strain under conventional conditions.

The activity of exocellular protease was determined by the Willstatter method via measuring the amount of released free carboxyl groups in an ethanol solution of amino acids and polypeptides obtained by hydrolysis of a 5% gelatine substrate with a pH of 7.4 for neutral proteases and a pH of 3.6 for acid proteases after 3-h incubation at 40°C [17].

All the experiments were performed thrice; the results were averaged over three measurements. The level of significance was P < 0.05 [18].

3. Results and Discussion

Proteases represent a complex of enzymes that provide partial or complete hydrolysis of proteins to oligomers and monomers (amino acids) owing to their ability to hydrolyze the peptide bonds. Depending on the nature of the functional groups in the active center, proteases are classified into six large groups: serine proteases, cysteine proteases, threonine proteases, aspartic proteases, glutamic proteases, and metalloproteases [19], which determine their use for solving both theoretical problems (study of the metabolism of living organisms) and practical problems by applying them in various fields of industry, agriculture, medicine, etc.

As a result of the screening of nanomaterials reported in [20], it was found that the most effective way to stimulate protease biosynthesis in micromycetes Trichoderma koningii and Fusarium gibbosum is to use nanoparticles from composite ZnO/MgO (1 : 4), ZnO, and Fe₂O₃. The obtained results suggest that the effect of nanomaterials on the biosynthesis of exocellular hydrolases in micromycetes depends on the type and structure of the nanocompounds, the
physiological and biochemical properties of the strain, and the properties of the synthesized enzyme complex.

In this study, ZnO nanoparticles were selected for *Trichoderma koningii* strain and Fe$_3$O$_4$ nanoparticles were used for *Fusarium gibbosum*. An essential parameter of nanoparticles, which determines their physicochemical and biological properties, is their size. Another equally important parameter is their concentration in the culture medium that can affect the living organism. Thus, for a number of metals, a narrow concentration range is required to provide the vital activity of living organisms or express their toxicity [21]. The effect of different sizes and concentrations of ZnO and Fe$_3$O$_4$ nanoparticles on the proteolytic activity of *T. koningii* CNMN FD 15 and *F. gibbosum* CNMN FD 12, respectively, was estimated to determine the biologic properties of the tested nanoparticles.

To reveal the effect of ZnO nanoparticles on the activity of acid, neutral, and alkaline protease of *T. koningii* producer, ZnO nano-oxides with a size of 10 and 30 nm and 1 µm in a concentration of 5, 10, and 15 mg/L were studied (Fig. 1).

![Fig. 1. Effect of ZnO nanoparticles with different sizes and concentrations on the proteolytic activity of fungal strain *Trichoderma koningii* CNMN FD 15.](image)

The highest level of proteolytic activity in the reference samples was observed on the 9\textsuperscript{th} day of cultivation of the strain, being 2.10 U/mL for neutral proteases, 2.23 U/mL for acid proteases, and 1.85 U/mL for alkaline proteases. In the optimized versions, the ZnO nanoparticles showed different effects on the activity of these three types of proteases synthesized by micromycete, depending on the particular size and concentration. Thus, for acid proteases, the 10-nm ZnO nanoparticles retained the biosynthesis for 24 h; the highest values were observed on the 10\textsuperscript{th} day of the cultivation. The level of activity of acid proteases in the presence of ZnO nano-oxide on the 10\textsuperscript{th} day was similar to the activity of the reference sample on the 9\textsuperscript{th} day of cultivation. The 30-nm nanoparticles showed a moderate stimulating effect (16.6% compared with the reference sample at a concentration of 10 mg/L) on the 9\textsuperscript{th} day of cultivation. The size of 1 µm showed a neutral effect.

In the case of neutral proteases, ZnO nanoparticles of all tested sizes showed a significant positive action depending on the applied concentration of 5–15 mg/L. The stimulating effect varied as follows: from 36.2 to 22.8% for a size of 10 nm; from 151.9 to 117.1% for 30 nm; and from 88.1 to 33.8% for 1 µm. The highest proteolytic activity was obtained in the case of 30 nm;
the activity increased by 2.5 times on the 9th day of the cultivation.

For alkaline protease, the use of ZnO nanoparticles of all sizes, except for the concentration of 5 mg/L, provided an increase in protease activity; however, the effect was less significant than that for neutral proteases: by 13.5% for 10 nm, by 11.3% for 30 nm, and by 17.8% for 1 µm compared with the reference sample on the 9th day of cultivation. For all types of proteases, an inhibitory effect of ZnO nanoparticles was observed with an increase in the concentration to 15 mg/L. Regardless of size, the proteolytic activity of T. koningii micromycete decreased.

On the 10th day of cultivation, the enzyme activity of neutral and alkaline proteases in the presence of ZnO nanoparticles was reduced; the samples with 10-nm ZnO in all tested concentrations for neutral proteases and all experimental samples of alkaline proteases showed values at the level of the reference sample. The moderate stimulating effect of some samples grown with 30-nm ZnO in the case of acid proteases and 30-nm and 1-µm ZnO in the case of neutral proteases did not exceed the level of the reference sample on the 9th day of cultivation.

The results showed that ZnO nanoparticles with a size of 30 nm taken in a concentration of 5–10 mg/L are the most promising for stimulating the protease biosynthesis of fungal strain T. koningii CNMN FD 15. These parameters of ZnO nanoparticles provide an increase in the activity of neutral proteases—the basic enzymes of the strain—by 2.5 times compared with the maximal value obtained for the reference sample, with an increase in the activity of acid and alkaline proteases by 16.6 and 11.3%, respectively, without any modification of the period of maximal synthesis of proteases (on the 9th day of cultivation).

A similar study was conducted for the F. gibbosum CNMN FD 12 micromycete—the producer of acid (pH of 3.6) and neutral proteases (pH of 7.4)—using Fe₃O₄ nanoparticles of different sizes (10, 30, 65–70 nm) taken in three concentrations (5, 10, 15 mg/L) (Fig. 2). The most significant level of proteolytic activity in the reference samples was observed on the 5th day of cultivation: 2.04 U/mL for acid proteases and 2.52 U/mL for neutral proteases.

![Fig. 2. Effect of Fe₃O₄ nanoparticles with different sizes and concentrations on the proteolytic activity of fungal strain Fusarium gibbosum CNMN FD 12.](image)

In the optimized samples, the addition of Fe₃O₄ nanoparticles in the nutrient medium of the strain, regardless of size, had hardly any effect on the activity of acid proteases; their value remained at the control level of 98.5% (for 10 nm), 105.9% (for 30 nm), and 106.8%
Iron oxide was more effective for the production of neutral proteases than for acid proteases. The optimum concentration was 10 mg/L, regardless of size. This concentration stimulated the activity of neutral proteases as early as the 4th day of cultivation of the micromycete; it was 22.7% (for 10 nm), 28.5% (for 30 nm), and 30.9% (for 65–70 nm) higher than that of the reference sample in the same day (1.23 U/mL). On the 5th day of cultivation, the stimulating effect increased to 26.6% (for 10 nm), 39.7% (for 30 nm), and 50.8% (for 65–70 nm) compared with the maximum of the reference sample (2.52 U/mL) observed in the same day.

On the 6th day of cultivation, the activity of both neutral and acid proteases decreased in both the reference and optimized samples.

The optimum parameters of the Fe$_3$O$_4$ nanoparticles that provide the stimulating effect on the biosynthesis of proteases in micromycete *Fusarium gibbosum* are the nanoparticle size of 65–70 nm and the concentration of 10 mg/L. These conditions provide a 6.8 and 50.8% increase in the biosynthesis of acid proteases and neutral proteases, respectively, while maintaining the period of maximum synthesis of proteases (on the 5th day).

The next stage of the research was the submerged cultivation of *T. koningii* and *F. gibbosum* strains on a nutrient media supplemented with selected ZnO and Fe$_3$O$_4$ nano-oxides and different values of initial pH of the media, namely, acidic (pH of 4.0), neutral (pH of 6.25), and alkaline (pH of 8.5). The aim of the study was the estimation of the effect of the initial pH of the medium on the capacity of the strains to produce enzymes and on the biological properties of the nanoparticles.

For micromycete *T. koningii*, the experiment was conducted in the presence of ZnO nanoparticles with an optimum selected size of 30 nm in a wider concentration range—1, 5, 10, and 15 mg/L—and at the three above mentioned initial pH values of the nutrient medium (Fig. 3).

The results showed that, in the reference samples containing no ZnO nanoparticles, the maximum activity of all the three types of proteases was observed on the 9th day of the cultivation of the strain, regardless of the modification of the pH of the medium. The use of the media with an initial pH of 6.25 was the most favorable for biosynthesis. The activity of acid proteases was 2.12 U/mL; neutral proteases, 2.48 U/mL; and alkaline proteases, 1.75 U/mL.
The most optimum concentrations of ZnO nanoparticles (30 nm) were concentrations of 5–10 mg/L; they provided an increase in all the three types of proteases. The maximum activity (similar to that of the reference sample) was observed on the 9th day of the cultivation of the strain; however, the proteolytic activity was modified as a function of the initial pH of the medium. The most significant enzyme activity was observed at an initial pH of the medium of 6.25 in the case of an optimum concentration of nanoparticles of 5 and 10 mg/L. Thus, the activity of acid proteases was 2.58 and 2.67 U/mL, respectively; it was higher than the activity in the reference sample by 21.7 and 25.9%, respectively. In the case of neutral proteases, the activity was 6.32 and 6.28 U/mL, respectively, compared with 2.48 U/mL in the reference sample. The stimulating effect was higher by 154.8 and 153.2%, respectively. The activity of alkaline proteases was 2.09 and 1.88 U/mL, respectively, compared with 2.48 U/mL in the reference sample.

For *F. gibbosum* micromycete, the experiment was conducted in the presence of Fe$_3$O$_4$ nanoparticles with an optimum selected size of 65–70 nm taken in a concentration of 5, 10, and 15 mg/L at three values of the initial pH of the nutrient medium (Fig. 4).

![Graph](image)

**Fig. 4.** Effect of Fe$_3$O$_4$ nanoparticles with a size of 65–70 nm on the proteolytic activity of *Fusarium gibbosum* CNMN FD 12 as a function of the initial pH values of the nutrient medium.

The results showed that the reference samples had the maximal activity of both acid and neutral proteases on the 5th day of cultivation, regardless of the initial pH of the medium. The use of acidic pH of the medium was the most effective for the biosynthesis of acid proteases; in this case, the enzyme activity was 2.77 U/mL. An increase in the pH value to 6.25 and 8.5 led to a decrease in the activity of acid proteases to 1.54 and 1.25 U/mL, respectively. The use of the initial pH of the medium that was close to the neutral pH (pH of 6.25 and (less significant) pH of 8.5) was the most promising for the biosynthesis of neutral proteases. The determined proteolytic activity was 2.78 and 2.58 U/mL, respectively.

The most optimum concentration of the Fe$_3$O$_4$ nanocompound (65–70 nm) was 10 mg/L. The maximum activity of both acid and neutral proteases was observed on the 5th day of the cultivation of the producer (similar to the reference sample). Thus, the use of nano-oxide did not change the period of maximum synthesis of proteases; however, it led to an increase in the
enzyme activity. In addition, as the enzymatic activity of the reference was lower, the stimulatory effect in the optimized samples was higher; it varied as a function of the initial pH of the medium.

The highest activity of acid proteases was observed at a pH of 4.0; it was 2.77 U/mL in the reference samples and 2.87 U/mL in the optimized samples. The stimulatory effect was insignificant: at a level of 3.6%. The highest activity of neutral proteases was observed at a pH of 6.25; it was 2.78 U/mL in the reference samples and 4.49 U/mL in the optimized samples. The stimulatory effect was 67.5%.

Comparative analysis of the results obtained for both *T. koningii* and *F. gibbosum* strains showed that the initial pH value significantly affects the genesis of proteases and the biological properties of ZnO and Fe$_3$O$_4$ nano-oxides. For *T. koningii* micromycete, the most optimum value of pH is 6.25; it provided the biosynthesis of all the three types of proteases and determined the highest stimulating effect.

For *F. gibbosum*, the highest activity of the acid proteases was obtained at a pH of 4.0; however, the stimulating effect was hardly observed. The alkaline proteases of the strain were less significantly affected by changes in the pH of the medium. The highest activity of alkaline proteases and the most significant stimulating effect were observed at a pH of the medium of 6.25.

A decrease in the stimulating effect with a variation in the initial pH of the medium from an optimum value (pH of 6.25) can indicate changes in the biological properties of the ZnO and Fe$_3$O$_4$ nanoparticles, which can be attributed to a change in another important parameter, which is referred to as zeta potential; it is no less important as the particle size and, according to some authors, depends on the pH of the medium [11, 22].

4. Conclusions

It has been found that the biological effect of the nanoparticles varies as a function of the taxonomy of micromycetes and their physiological and biochemical properties and as a function of parameters of nanoparticles (size, concentration, and zeta potential).

ZnO and Fe$_3$O$_4$ nanoparticles can be used as potential stimulators of the biosynthesis of all the three types of proteases of micromycete *Trichoderma koningii* Oudemans CNMN FD 15. The highest stimulating effect has been achieved in the case of using ZnO nanoparticles with a size of 30 nm taken in a concentration of 5–10 mg/L for the cultivation of the strain on a nutrient medium with an initial pH value of 6.25. These conditions provide an increase in the activity of neutral proteases—the basic component of the proteolytic complex in this strain—by 2.5 times, with an increase in the activity of acid and alkaline proteases by 16.6 and 11.3%, respectively.

For strain *Fusarium gibbosum* CNMN FD 12, the most significant stimulating effect has been achieved in the case of using Fe$_3$O$_4$ nanoparticles with a size of 65–70 nm taken in a concentration 10 mg/L for the cultivation of the micromycete on a nutrient medium with an initial pH value of 6.25. These conditions provide an increase in the activity of neutral proteases by 61.5% compared with the reference sample and a less significant increase in the activity of acid proteases—by 14.3%.

The tested nanoparticles did not affect the duration of the life cycle of the micromycetes. In both cases, the period of maximum synthesis of exocellular proteases coincided with the optimum period of cultivation under conventional conditions: on the 5th and 9th day of the cultivation of *Fusarium gibbosum* CNMN FD 12 and *Trichoderma koningii* Oudemans CNMN FD 15, respectively.
References

By thermal annealing of InSe, GaSe, and GaTe crystals in Zn vapors at 800, 870, and 1050K, respectively, a material consisting of ZnSe crystallites in both GaSe and InSe and ZnTe in GaTe has been prepared. Structural defects induced by intercalated atoms shield excitonic bonds in primary compounds and form both radiative recombination levels and electron trapping levels localized deep in the band gap of A\textsuperscript{III}B\textsuperscript{VI} crystals. The energies of trapping levels have been determined from thermally stimulated luminescence curves.

1. Introduction

The A\textsuperscript{III}B\textsuperscript{VI} layered compounds (GaS, GaSe, GaTe, and InSe) are semiconductors of high natural anisotropy determined by the layered structure formed of planar packings of B–A–A–B type [1, 2]. These materials have the band gap in a wide energy range of 1.2 eV (InSe) to 2.5 eV (GaS) and reduced adsorption at the packing surface of atoms from the atmosphere. These are few properties that stimulate their intense research due to their perspective use in different optoelectronic and photoelectronic devices and ionizing radiations [3–8].

Anisotropy of the physical properties of these layered semiconductors in the single crystalline state is determined by the presence of two types of atoms bonding [9]. Strong ionic-covalent forces act between atomic planes within packings, while polarization forces act between elementary packings [10, 11]. Elementary packings have an arrangement that lead to the formation of cracks between them, which have a width sufficient for intercalation of both atoms and molecules; as a result, micro and nanocrystallites are formed [11–13]. At the same time, a surplus of dopant atoms introduced into these semiconductors to expand the range of their physical properties accumulates between the packings [14–18]. Under certain temperature conditions, the dopant and intercalant atoms form chemical bonds with chalcogen atoms from outside the planes of the elementary packings [13, 19]. At high temperatures, simultaneously with the formation of chemical bonds between the packings, materials composed of micro- and nanocrystallites of both the base compound and the chalcogenenides of intercalant are formed [20–24].

In this paper, the crystalline structure and photo- and thermoluminescence of composites obtained by the thermal annealing of GaSe, GaTe, and InSe single crystals in Zn vapors are studied.
2. Experimental

GaSe, InSe, and GaTe single crystals used as a primary material for obtaining composites with ZnSe and ZnTe were grown by the vertical Bridgman–Stockbarger method [25]. At the initial stage, GaSe, InSe, and GaTe compounds were synthesized from elementary components Ga (5N), In (5N), Te (5N), and Se (5N) taken in stoichiometric quantities. The synthesis of ~20-g ingots was performed in quartz tubes with an internal diameter of ~12 mm, evacuated to a remnant pressure of $<5 \times 10^{-6}$ Torr. The synthesis temperature was ~50 K higher than the melting temperature of the synthesized compound (1230 K for GaSe, 1100 K for GaTe, and 933 K for InSe). After 24-h synthesis, the melt was passed through a temperature gradient of 5 K/cm at a rate of 0.3 mm/h.

Both $p$-GaSe and $p$-GaTe single crystals were obtained with a hole concentration of $2 \times 10^{14}$ to $3 \times 10^{14}$ cm$^{-3}$ and $6 \times 10^{15}$ to $8 \times 10^{15}$ cm$^{-3}$, respectively, at the chamber temperature. The obtained InSe single crystals were of $n$ type with an electron concentration of $2 \times 10^{15}$ cm$^{-3}$ and a mobility of $\sim 6 \times 10^{2}$ cm$^2$/V s at the chamber temperature. Due to weak bonds between the elementary packings, the GaSe and InSe single crystals cleave in a direction perpendicular to the $C_6$ axis. The splitting direction of the GaTe single crystals coincides with the $C_2$ axis of a monoclinic lattice.

For photoluminescence (PL) and thermally stimulated luminescence (TSL) measurements, plates with an area of about 0.5–1.0 cm$^2$ and a thickness of 50 µm to 3–4 mm were cleaved from single-crystalline ingots. To prepare composite materials, GaSe, InSe, and GaTe single-crystalline plates were introduced together with Zn metal (2 mg/cm$^2$) in different tubes with an internal diameter of 15–16 mm. After gas evacuation to a pressure of $\sim 5 \times 10^{-6}$ Torr, the tubes were sealed. Thermal annealing was performed at temperatures of 800, 870, and 1050 K for the InSe, GaSe, and GaTe samples, respectively. At these temperatures, the Zn vapor pressure was $10^{-3}$–$10^3$ Torr [26]. The treatment duration was 4–24 h. Before treatment, the samples surface, which was smooth at nanometric scale, was covered with a granular layer without any well-defined structure.

The structure and composition of the resulting material was studied by XRD method with a Rigaku Ultima IV diffractometer (Cu$K_a$ radiation, $\lambda = 1.54060$ Å, 40 kV at 40 mA; a Rigaku D/teX Ultra silicon strip detector (Japan)) in the Bragg–Brentano (0–20) geometry.

PL in a temperature range of 78–293 K was excited with an Nd–YAG laser ($\lambda = 532$ nm, $P = 100$ mW) for GaSe and the GaSe composite and with a He–Ne laser ($\lambda = 632.8$ nm, $P = 20$ mW) for GaTe and InSe and their composites. PL spectra were recorded using a system with a MDR-2 monochromator with a 600-mm$^{-1}$ diffraction grating at a resolution of $\sim$1 meV.

TSL curves of the primary single crystals and the resulting composites were recorded in a continuous radiation flow mode. A photomultiplier with a multialkali photocathode was used as a photoreceptor.

3. Experimental Results and Discussion

The XRD pattern of the GaSe single crystals thermally annealed in Zn vapors at a temperature of 870 K for 3 h is shown in Fig. 1a. It exhibits diffraction lines from the atomic planes oriented perpendicular to the $C_6$ crystallographic axis. The GaSe single crystals have a hexagonal lattice with parameters $a = 3.7569$ Å and $c = 15.944$ Å characteristic of the ε-polytype of GaSe (PDF 37-0931). Annealing leads to an increase in the number of free bonds in the surface layer of elementary packings and, accordingly, to an increase in structural defects, which can become
formation centers for the ZnSe compound. At a high temperature, the accumulation of dislocations occurs [27]; this process contributes to the amplification of XRD lines from the planes oriented oblique to the C_6 crystallographic axis. As can be seen from the XRD pattern, the composite obtained by thermal annealing of GaSe in Zn vapors exhibits reflections from GaSe crystallites with Miller indexes (1 0 0), (1 0 5), (1 0 7), and (2 0 2) and from the atomic planes with Miller indexes (1 1 1), (2 2 0), (3 1 1), and (4 2 0) of ZnSe crystallites with a cubic lattice with parameter \( a = 5.663 \, \text{Å} \) [28]. The formation of chemical bonds by the Zn atoms intercalated in the space between the elementary packings leads to the appearance of free Ga atoms that form Ga crystallites. This assumption is confirmed by the XRD lines present at 2\( \theta \) angles of 23.20°, 30.26°, 30.56°, 45.41°, and 46.38°, which, according to PDF 01-074-6392, are reflections from atomic planes of Ga crystallites. Thus, thermal annealing of gallium selenide at temperatures lower than the melting point of this material in Zn vapors leads to the formation of a composite consisting of GaSe base crystallites, ZnSe crystallites, and Ga.

Fig. 1. XRD patterns of single crystals thermally annealed in Zn vapors: (a) GaSe, 1050 K, 3 h.  
● - GaSe, PDF 37-0931; ◊ - ZnSe, PDF 70-0777; ○ - Ga, PDF 74-6392; (b) GaTe, 1070 K, 3 h.  
● - GaTe, PDF 74-8974; ◊ - ZnTe, PDF 72-4848; ○ - Ga, PDF 74-6392.

Figure 1 shows the XRD pattern of the material obtained by thermal treatment of GaTe crystals in Zn vapors at 1050 K. It is evident that, in addition to XRD lines of the GaTe compound, lines from the atomic planes with Miller indexes (0 0 2), (1 0 0), (1 0 1), (1 1 0), (4 0 0), (4 2 0), and (4 2 2) characteristic of ZnTe crystallites are present. Moreover, the composite contains Ga crystallites, as determined from the presence of the lines observed in the case of the GaSe–ZnSe–Ga composite.

Figure 2 shows the PL spectra of the GaSe–ZnSe composite at 80 K. At this temperature, the PL spectrum of the pure GaSe single crystals exhibits emission lines of localized direct excitons (\( A_1 \)), first LO phonon repetition (\( A_2 \)), a weak emission band of indirect excitons (D), and band C determined by the radiative recombination through lattice defects [29]. Intercalation process of Zn atoms at a temperature of 870 K in the space between the elementary packings contributes to an increase in the intrinsic defect concentration in the GaSe crystallites, which efficiently shield
the excitonic bonds. The PL spectrum contour at 80 K covers a wide energy range of 1.8–2.62 eV and is well deconvoluted in four elementary curves with maxima at energies of 1.920, 2.040, 2.193, and 2.550 eV. The dominant band with maximum at an energy of 2.040 eV and a Gauss contour is analyzed in detail in [30]. The band with maximum at an energy of 1.920 eV is shifted by ~180 meV toward lower energies beside the emission band of free direct excitons and can be considered as an impurity PL. This interpretation is confirmed by the fact that a similar PL band is contained in the PL spectrum of GaSe doped with Cu [31]. The C and D bands are localized at energies higher than the band gap width of gallium monoselenide of 2.124 eV at 80 K [32]. The symmetric contour and the FWHM larger than that of excitonic emission bands indicate PL through ionized centers.

The PL spectrum of pure ZnSe crystals at 110 K contains one band with maximum at an energy of 2.77 eV and a contour slightly asymmetric toward low energies and is considered to be the emission of the acceptor bound excitons [33]. The impurity atoms and ions manifest themselves in the ZnSe crystals by the generation of impurity PL bands; e.g., Cr$^+$ ions form a PL band with maximum at an energy of 2.20 eV [33]. An impurity that leads to the formation of PL bands C and D can be free Ga atoms and structural defects in ZnSe crystallites present in the composite.

Fig. 2. PL spectra of (a) the GaSe–ZnSe, (b) InSe–ZnSe, and (c) GaTe–ZnTe composites at 80 K.
The PL spectrum of the InSe–ZnSe composite at 80 K is shown in Fig. 2b. Since the PL emission bands of InSe–ZnSe are shifted deep into the fundamental band of InSe, they can be caused by the presence of recombination levels in ZnSe crystallites present in the composite. At the chamber temperature, the PL spectrum of the composite is well described by a Gauss curve with maximum at an energy of 1.923 eV and a FWHM of ~240 meV. At 80 K, along with the dominant PL band with maximum at an energy of 1.938 eV, there is a band of lower intensity with a Gauss contour and maximum at an energy of 2.257 eV. The energetic position and the contour shape indicate the donor–acceptor nature of these two bands. The recombination levels involved in these bands are probably determined by the In surplus present in the composite.

The shape of the PL spectrum of the ZnTe–GaTe composite at a temperature of 80 K (Fig. 2c) is well described by three Gauss curves with maxima at energies of 1.764, 1.739, and 1.714 eV. The band gap width of the GaTe single crystals at 77.3 K is 1.787 eV [34]. As can be observed from Fig. 2c, the PL bands of GaTe–ZnTe are found in the region of the absorption edge of the GaTe crystallites. The maximum of the absorption band of excitons in the \( n = 1 \) state is found at an energy of 1.771 eV [34] and is shifted by ~7 meV toward energies higher than the maximum of the edge PL band. Thus, we can consider that the PL band with maximum at an energy of 1.764 eV represents the radiative annihilation of acceptor bound excitons with a bonding energy of 7 meV. The PL band with maximum at an energy of 1.739 eV has an analog in the PL spectrum of the pure GaTe crystals; it is determined by the lattice defects of GaTe crystals from the composite. The PL band with maximum at 1.714 eV has a Gauss contour and can be associated with the recombination mechanism through the center formed by the Zn\(^+\) ions in the GaTe crystallites. As a result of GaTe lattice degradation determined by the presence of both ZnTe crystallites and intercalated atoms (Zn), in the band gap of the composite components (ZnTe and GaTe), both supplementary recombination levels for nonequilibrium charge carriers and electron trapping levels are formed.

The trapping levels diagram in the component crystallites of the resulting composites was studied by the TSL method. The TSL curves of the GaSe–ZnSe, InSe–ZnSe, and GaTe–ZnTe composites (Fig. 3) were analyzed by their deconvolution in Randall–Wilkins elementary curves, in which a semiconductor with one trapping level with energy \( E_t \) is considered and repeated trapping is neglected. In this approximation, the TSL curve contour is described by the formula [35]

\[
I(T) = I_M \exp \left[ 1 + \frac{E}{kT} - \frac{T}{T_M} \right] - \frac{T^2}{T_M^2} \left( 1 - \frac{T}{T_M} \right) \exp \left( \frac{E}{kT} \right) - \frac{2kT}{E} \right]}
\]

where \( I_M \) is the maximum intensity of emitted radiation, \( T_M \) is the temperature corresponding to the TSL peak, and \( E_t \) is the trapping level energy. The temperatures corresponding to elementary TSL curves (1) and energies of trapping levels calculated using the Urbach empirical formula \( E_t = 25 kT_M \) [36] are included in the table.
Fig. 3. TSL curves of (a) the GaSe–ZnSe, (b) InSe–ZnSe, and (c) GaTe–ZnTe composites.

 Energies of trapping levels for the GaSe–ZnSe, InSe–ZnSe, and GaTe–ZnTe composites determined from TSL curves

<table>
<thead>
<tr>
<th>GaSe–ZnSe</th>
<th>InSe–ZnSe</th>
<th>GaTe–ZnTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_M, K$</td>
<td>$E, \text{meV}$</td>
<td>$T_M, K$</td>
</tr>
<tr>
<td>115</td>
<td>248</td>
<td>104</td>
</tr>
<tr>
<td>120</td>
<td>259</td>
<td>112</td>
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<td>137</td>
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<td>228</td>
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4. Conclusions

GaSe, InSe, and GaTe crystals are composed of layered packings bound by polarization forces. The Zn atoms from the vapor state intercalates in the space between the elementary
packings at 800 K for InSe, 870 K for GaSe and 1050 K for GaTe form composites consisting of InSe and ZnSe crystallites, GaSe and ZnSe crystallites, and GaTe and ZnTe crystallites, respectively. As a result of the formation of the composites, impurity levels are formed in the band gap of the primary compounds (GaSe, InSe, and GaTe) and the resulting compounds. These levels function as radiative recombination levels and electron trapping levels. The PL emission bands of the composites are formed by characteristic bands of composite components.

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References

OPTICAL AND ELECTRICAL CHARACTERISTICS OF ACID-DOPED THIN POLYANILINE FILMS

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Abstract

Conjugated conducting polymers, such as polypyrrole (PPY), polyaniline (PANI), and polythiophene (PT), are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. In this work, three samples of thin PANI films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using ammonium peroxydisulfate as an oxidizing agent. Two samples of the synthesized thin PANI films were doped with tetraoxosulphate(VI) acid (H$_2$SO$_4$) and citric acid, while the third sample was left undoped to serve as a control. We used a VeecoDektak 150 profiler to measure the film thickness; a UV-Visible spectrometer Shimadzu UV-1601 was used to determine the optical absorption spectra of the films. The measurement of DC conductivities was accomplished through the four-point probe technique with a Signatone V3.7 QuadPro resistance mapping system using a Keithley 2400 source meter. The thin films were found to be of the same thickness (0.2 µm); their absorption spectra revealed two absorption peaks at around 300 and 650 nm for the pure and citric acid-doped samples, while the H$_2$SO$_4$-doped PANI exhibited peaks at 300 and 880 nm. Doping reduced the direct band gap of the PANI from 2.75 to 2.4 eV. In addition, the results obtained from electrical characterization revealed that the H$_2$SO$_4$-doped PANI has the best conductivity among the doped samples, while the pure sample showed no value for electrical conductivity.

1. Introduction

Conjugated polymers, most notably polypyrrole (PPY), polythiophene (PT), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly($p$-phenylene vinylene) (PPV), have been synthesized in the form of free-standing films and bulky powders using electrochemical or chemical polymerization methods [1, 2]. PPY and PANI can be formed chemically or electrochemically through oxidative polymerization of pyrrole and aniline monomers; the final form of PPY and PANI is that of a long conjugated backbone, as shown in Fig. 1 [1, 3]. These polymers have resonance structures that resemble the aromatic or quinoid forms [1]. Some polymers can become conductive after certain modifications [4–6]. Conducting polymers are a new class of sensing materials, which can be prepared by simple oxidative polymerization method. These polymers provide a suitable structure for the immobilization of ligands, enzymes, and antibodies; therefore, their use in the development of novel chemical and biological sensors has received considerable attention [3].
Among all conducting polymers, PANI and derivatives thereof have attracted much interest worldwide because of their chemical stability, simple polymerization, and high conductivity [2, 7, 8]. PANI is a good material for various applications, such as chemical and biological sensors, actuators, photocells, circuit boards, corrosion protection, electromagnetic protection, optoelectronic devices, gas sensors, and microelectronics [2, 9–13]. Several methods of preparation of PANI film, such as spin coating, drop coating, electrochemical deposition, thermal evaporation, emulsion polymerization, and Langmuir–Blodgett (L–B) technique [2, 14–19] have been reported by various authors. Conducting polymers have other advantages, such as smaller weight, greater workability, resistance to corrosion, and lower cost [20]; therefore, they can be regarded as suitable candidates for the replacement of metals [21]. PANI is unique among conductive polymers because the electrical properties of this material can be reversibly controlled both by charge transfer doping and by protonation.

PANI is a phenylene-based polymer having an –NH– group on either side of the phenylene ring. The oxidation and reduction of this polymer takes place on this –NH– group resulting in various forms due to the number of imine and amine segments on the PANI chain. Among conducting polymers, PANI has the highest number of revealed and characterized forms with different properties. Due to interaction with acids, each of three protonated forms has a corresponding deprotonated form with low conductivity. Thus, the polymer can exist in at least six forms differing in both the degree of oxidation and the protonation state. These are both salt and base versions of leucoemeraldine, pernigraniline, and emeraldine. The polymer can occur in different redox states with an emeraldine base being considered as the most useful form of PANI due to high stability at room temperature [22]. It is insulating and the only form of PANI which can be doped with acids [23]. Acid doping converts the insulating emeraldine base to the conductive form, the emeraldine salt [24]. This is the most conducting form of PANI with conductivity on a semiconductor level on the order of 100 S cm$^{-1}$, which is many orders of magnitude higher than that of conventional polymers ($<10^{-9}$ S cm$^{-1}$), yet lower than that of metals ($>10^4$ S cm$^{-1}$) [1, 20].

In this work, three samples of PANI thin films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using ammonium peroxydisulfate.
(APS) as an oxidizing agent. Aniline hydrochloride and APS solutions were prepared by mixing 0.25 M of aniline and 1.5 M of APS, respectively, in 1 M of HCl. Two samples of the synthesized thin PANI films were doped with tetroxo sulphate(VI) acid (H$_2$SO$_4$) and citric acid, while the third sample was left undoped to serve as a control. The film thickness was measured using a profilometer, while the optical and electrical properties of the films were investigated.

2. Materials and Methods

2.1 Reagents and apparatus

The chemicals used in the preparation of PANI were aniline (Merck), APS [(NH$_4$)$_2$S$_2$O$_8$] (Qualickems), hydrochloric acid (HCl) (Merck), tetroxo sulphate(VI) acid (H$_2$SO$_4$) (BDH), and citric acid (biology grade, BDL). Precleaned microscope slides (micropoint), a Veeco Dektak 150 Surface Profiler, a Shimadzu UV-1601 UV-Visible spectrophotometer, and Four-point probe with a Signatone V3.7 QuadPro resistance mapping system were used.

2.2 Synthesis of PANI

Thin PANI films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using APS as an oxidizing agent. Aniline hydrochloride and APS solutions were prepared by mixing 0.25 M of aniline and 1.5 M of APS, respectively, in 1 M of HCl. The process involved the dropwise addition of aniline hydrochloride and APS solutions on a glass substrate in the ratio of 3 : 1 at room temperature. The solution was thoroughly mixed by stirring and left for about 80 s, within which the solution started to take on a blue-black color. The conducting emeraldine salt form of PANI (green color) was obtained by the addition of about 3 more drops of aniline hydrochloride solution under continuous stirring for about 1 min. This procedure was repeated on two additional substrates to obtain three thin films which were redoped by dipping each into ammonium hydroxide (NH$_2$OH) to form PANI (emeraldine base) films.

2.3 Doping of PANI

Two of the thin films were redoped by dipping each into solutions of H$_2$SO$_4$ and Citric acids, respectively, for about 2 min and then they were rinsed with distilled water and allowed to dry.

2.4 Measurement of thickness

The thickness of the synthesized samples (both doped and pure) was measured with a Veeco Dektak 150 profiler. This machine was computerized; therefore, measurements were taken with the help of experts. The major precaution taken was to measure the thickness of each sample many times and calculate the average value.

2.5 Optical measurements

The absorption spectra of the as synthesized PANI thin films were recorded over a wavelength range of 300–1000 nm in the ultraviolet (UV) region, the visible light (VIS) region and, the near infrared (NIR) region. A UV–Visible spectrophotometer (Shimadzu UV-1601) was
used for the optical measurements; with the help of professional machine experts, we constructed graphs of optical absorbance versus wavelength. To have a quantitative estimate of the optical band gap of the film, the Tauc relation was employed [25–28]:

\[ a h v = A (h v - E_g) \]  

(1)

where \( a \) is the absorption coefficient, \( h v \) is the photon energy, \( E_g \) is the optical band-gap, \( A \) is a constant that depends on the properties of the material, and \( \gamma \) is a constant that can take different values depending on the type of electronic transition: for a permitted direct transition, \( \gamma = \frac{1}{2} \); a prohibited direct transition, \( \gamma = \frac{3}{2} \); a permitted indirect transition, \( \gamma = 2 \); and for a prohibited indirect transition, \( \gamma = 3 \) [29, 30]. In this work, the direct transition band gap of the films was determined by plotting a graph of \((ahv)^2\) versus \(h v\), where the band gap values were obtained by extrapolating the linear part of the graph to the axis of abscissa.

### 2.6 Electrical characterization

The measurement of DC conductivities was accomplished through the four-point probe technique with a Signatone V3.7 QuadPro resistance mapping system using a Keithley 2400 source meter. The four-point probe apparatus has four probes in a straight line with an equal inter-probing spacing of 1.27 mm; the radius of the probe needle is 125 µm. In order to take the measurements, the user lowers the four-point probe head onto the sample and then selects the test button in the software.

### 4. Results and Discussion

#### 4.1 Absorbance spectra for pure and doped samples

The UV–VIS absorbance spectra in the region of 300–1080 nm for pure and doped PANI are shown in Fig. 2. The figure shows two absorption peaks at around 300 and 650 nm for the pure PANI corresponding to \( \pi \rightarrow \pi^* \) electronic transitions related to the benzenoid form of PANI and electronic transitions in the quinoid rings of PANI, respectively [31]. The absorption spectra for PANI doped with \( H_2SO_4 \) and citric acid also exhibit two peaks around 300 and 880 nm assigned to \( \pi \rightarrow \pi^* \) electronic transitions and polaron–\( \pi^* \) transitions, respectively [32]. Generally, the \( H_2SO_4 \) doped PANI exhibited the best optical absorbance in the UV, visible, and NIR regions among the three PANI samples.
4.2 Optical band gap

Considering the Tauc’s relation in Eq. (1) above, the band gap of the thin films were obtained by plotting graphs of $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the straight portion of the graph on $h\nu$ axis at $\alpha h\nu = 0$ [33, 34].

The optical band gap values obtained for pure PANI, citric acid-doped PANI, and $\text{H}_2\text{SO}_4$-doped PANI were 2.75, 2.70, and 2.40 eV, respectively (see Fig. 3). The optical band gap value was found to decrease from 2.75 to 2.4 eV after doping with different acids implying an increase in conductivity [34]. The decrease in the optical band gap can be due to a reduction in the disorder of the system [8] and modifications of the polymer [34].
4.3 Electrical properties

The obtained electrical conductivity values were 6.36 and 0.01 S/cm for H$_2$SO$_4$-doped PANI and citric acid-doped PANI, respectively. These values can be compared with conductivities on a semiconductor level on the order of 100 S/cm, which is higher than that of conventional polymers ($<10^{-9}$ S/cm), yet lower than that of typical metals (>10$^4$ S/m). These results clearly show that the synthesized samples are conductive polymer films. Moreover, the pure PANI showed no values of electrical conductivity; this phenomenon was verified using a multi-meter. The electrical properties of the films are summarized in the table.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sheet resistance (Ω/sq)</th>
<th>Electrical conductivity (S/cm)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI + H$_2$SO$_4$</td>
<td>$7.85 \times 10^2$</td>
<td>6.36</td>
<td>0.2</td>
</tr>
<tr>
<td>PANI + Citric Acid</td>
<td>$3.83 \times 10^6$</td>
<td>0.01</td>
<td>0.2</td>
</tr>
</tbody>
</table>

5. Conclusions

Three samples of thin PANI films were synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid using APS as an oxidizing agent. Two samples of the synthesized thin PANI films were doped with tetraoxosulphate(VI) acid (H$_2$SO$_4$) and citric acid, while the third sample was left undoped to serve as a control. Their absorption spectra revealed two peaks at 300 and 650 nm for pure PANI and PANI doped with citric acid with the second peak occurring at about 880 nm for PANI doped with H$_2$SO$_4$. It was found that H$_2$SO$_4$-doped PANI has the best optical absorbance of the three samples in the ultraviolet, visible, and infrared regions. The H$_2$SO$_4$-doped PANI had the least optical band gap energy of 2.4 eV, while we obtained 2.70 and 2.75 eV for the citric acid-doped PANI and pure PANI, respectively. In addition, the results obtained from four-point probe revealed that the H$_2$SO$_4$-doped sample has the best electrical conductivity followed by that of the citric acid-doped PANI. Meanwhile, the pure PANI sample was found to be nonconductive.

References

FEATURES OF CONTACT AND SURFACE PROCESSES IN GLASSY
As$_2$Te$_{13}$Ge$_8$S$_3$-BASED STRUCTURES WITH Pt ELECTRODES UPON INTERACTION
WITH NITROGEN DIOXIDE

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Abstract

The capacitance spectra of the interdigital Pt–glassy As$_2$Te$_{13}$Ge$_8$S$_3$–Pt structures have been investigated in a range of 5–10$^6$ Hz with respect to temperature effects in both dry air and its mixture with a controlled concentration of nitrogen dioxide. It has been found that a decrease in the frequency of applied voltage to 10$^3$ Hz results in a rapid increase in the capacitance by several orders of magnitude. Environmental conditions dramatically influence the capacitance at low frequencies and, together with temperature regime, control the capacitance spectra and current–voltage characteristics of the films. The results are explained in terms of formation of a Schottky–Mott barrier that controls the properties of the contact junction. The contact-free part of the chalcogenide film surface, being more conducting than the bulk, acts as a capacitor, which can be controlled by interaction with gaseous species from the environment.

1. Introduction

Tellurium-based thin films are of great interest due to their high electrical sensitivity to surface processes induced by interaction with environmental gaseous species [1, 2]. This interaction affects both the electric resistivity [3, 4] and impedance [5, 6] of the films, being controlled by alloys composition [7], fabrication technology [8], the nature and concentration of gaseous species [9], annealing [10], temperature regime of operation [11], and so on. Recently, we have shown the high sensitivity of both impedance and work function of quaternary Te-based thin films to nitrogen dioxide, as well as the cross sensitivity to water vapour and other gases, at room temperature [12, 13]. It is strange, but so far, there have been no communications concerning the effect of gas adsorption on capacitance of these films, although the experimental specimens usually consist of a layer of a chalcogenide-based film enclosed between metallic electrodes in a “sandwich,” “planar,” or interdigital design. Apparently, this fact is attributed to a high value of dielectric relaxation time of disordered chalcogenides materials, including the Te-based ones, which leads to the independence of metal–chalcogenide glassy semiconductor (ChGS) junctions of frequency, the phenomenon observed already at early stages of investigation of these materials [14]. On the other hand, in some cases, a strong increase of capacitance of the metal–ChGS–metal structures at low frequencies occurs. This effect was observed in structures based on both As$_2$S$_3$ and Sb$_2$S$_3$ with nonsymmetric electrodes made of Al and Au [15] as well as in either aged or annealed Au–Ge$_{16}$As$_{32}$Te$_{28}$S$_{21}$–Au structures [16]. In both cases, this behaviour was analysed by assuming that, with a decrease in frequency, the period of applied voltage variation becomes comparable to a dielectric relaxation time. It was concluded that, in both cases,
at high frequencies, the capacitance corresponds to a geometric capacitor with a ChGS as a passive insulator; however, at low frequencies, the capacitance is controlled by a high-resistance layer adjacent to the contacts. The high resistive layer at the Al–As$_2$S$_3$(Sb$_2$S$_3$) contact was found to be a Schottky barrier; however, at the Au–Ge$_{16}$As$_{35}$Te$_{28}$S$_{21}$ contact, it is an alloying layer produced by aging or annealing. Later, it was demonstrated that the capacitance of Al–ChGs (As$_2$Se$_3$) is very sensitive to the prehistory and ambient environment in which the experiment is conducted [17].

The present work is focused on the investigation of the effect of frequency of applied voltage and toxic (e.g., NO$_2$) gases on the capacitance of thin film layers of quaternary glassy chalcogenides with Pt interdigital electrodes. For an unambiguous interpretation of the results, the effect of temperature on the capacitance spectra is also considered.

2. Experimental

Glassy alloy As$_2$Te$_{13}$Ge$_8$S$_3$, obtained by the procedure described in [12, 13], was used as the primary material for growing the relevant thin-film structures. The films were grown by thermal “flash” evaporation of the original material in a vacuum from tantalum boats onto sintered alumina ceramic substrates containing previously deposited platinum interdigital electrodes produced by SIEMENS AG with an electrode width of 15 µm and interelectrode distances of 45 µm. The growth velocity of the film was on the order of 30 nm/s; the area of deposition was about 5 mm$^2$. Structural investigations were carried out by X-ray diffraction analysis using a DRON YM1 diffractometer using FeK$_\alpha$ radiation; the surface morphology of the films was made visible with a VEGA TESCAN TS 5130 MM scanning electron microscope (operating voltage 30 kV). The films were encapsulated in standard TO-8 sockets, and their contacts were thermally bonded to socket pins by means of copper wires. The sockets with thin-film devices were placed into a test cell (volume of 10 mL), which was combined with an electrical refrigerator allowing cooling the sample to 10°C. These two pieces were together contained in an electric furnace for heating and regulating the operating temperature of the film. A platinum resistance temperature detector PT-100 close to the film was used for assisting the temperature control.

A gaseous NO$_2$ mixture with a concentration of 1.5 ppm was obtained with a calibrated permeation tube (Vici Metronics, United States), which was incorporated into the experimental setup described elsewhere. Dry air was used as the carrier and reference gas. The capacitance of the films was measured either in air or in a gaseous nitrogen dioxide environment in a frequency range of 5 Hz to 13 MHz, using an HP 4192A impedance analyzer. The same samples were used for both the frequency and temperature effect studies.

The gases were injected parallel to the film surface using a flow rate of 100 mL/min. The experiments were accomplished as follows:

(a) Measurement of $C$–$\omega$ characteristics at a lower (11°C) temperature in pure air and in gaseous media with different concentration of NO$_2$.

(b) Heating to room temperature and performing the measurements of capacitance spectra in pure air and in gaseous media with NO$_2$ again.

(c) This cycle of measurements was repeated at temperatures 38 and 53°C.

Additionally, the current–voltage ($I$–$U$) characteristics were measured in normal ambient at different temperatures. The measurements were performed in a quasi-stationary regime: the applied voltage varied between −6.0 V and +6.0 V in steps, increasing by 20 mV at each step, while the respective values of the current were measured. The delay time between two
measurements was 2 s. The measurements were performed at temperatures between 25 and 100°C.

3. Results and Discussion

3.1. Film morphology and structure

Figure 1a shows the surface morphology of an As$_2$Te$_{13}$Ge$_8$S$_3$ film with interdigital Pt electrodes physically grown by evaporation in a vacuum onto sintered Al$_2$O$_3$ substrates. It is evident that the film shows a great surface roughness; however, no crystalline tracks are observed. The last fact is confirmed by Fig. 1b, where a portion of the ChGS film from interdigital space is shown at a $10^3$ higher magnification. The sample surface consists of typical interconnected agglomerates of islands at micrometric scale [12]. No crystalline tracks were observed from XRD spectra analysis either; these findings are consistent with the results published in my previous work [18].

![Figure 1](image_url)

**Fig. 1.** (a) SEM of an As$_2$Te$_{13}$Ge$_8$S$_3$ film with interdigital Pt electrodes and (b) the morphology of the ChGS surface magnified by $10^3$ times.

3.2. Capacitance in normal ambient

The dependence of capacitance of the Pt–As$_2$Te$_{13}$Ge$_8$S$_3$–Pt structure on the frequency of applied voltage at 22°C in normal ambient is shown in Fig. 2. It is seen that the capacitance, being independent of frequency at $\omega > 10^4$ Hz, sharply increases by several orders of magnitude at lower frequencies. Obviously, the constant value of capacitance at frequencies higher than $10^4$ Hz corresponds to geometric capacitor $C_h = \varepsilon \varepsilon_0 S / d$, where $d$ and $\varepsilon$ are the interdigital distance and permittivity of ChGS, respectively, and $S$ is the contacting area. The rapid and huge increase in the capacitance with a frequency decrease lower than $10^4$ Hz indicates the existence of narrow high resistive regions near contacts and the equalization of dielectric relaxation time $\tau_r = \varepsilon \varepsilon_0 \rho$ ( $\rho$ is the resistivity of the film ) with the period of applied voltage variation. As mentioned above, the high resistive regions at the contacts can be attributed either to the depletion of majority carriers near the surface or to the formation of narrow insulating layers at the interface. This statement was partially confirmed by measurements of current–voltage characteristics. The insert in Fig. 2 shows the $I–U$ characteristics measured at several temperatures. It is evident that the curves really show a weak rectification that appears to be
symmetric relative to the polarity of the applied voltage regardless of temperature. This result gives evidence that the symmetric contact barriers are formed by the two sides of the ChGS film. These barriers control the total structure capacitance at a low frequency of the applied voltage, that is \( C_j = \frac{\varepsilon \varepsilon_0 S}{L_1 + L_2} \), where the \( L_1 \) and \( L_2 \) are the width of high resistive regions.

![Capacitance spectra of Pt–As₁₀Te₁₃Ge₈S₃–Pt structures in normal ambient. The insert shows the current–voltage characteristics at different temperatures.

The huge increase in the capacitance—by more than 4 orders of magnitude—at low frequencies (<10⁴ Hz) indicates the low width of high resistive regions by the contacts, which, in principle, is also confirmed by the weak rectification.

On the other hand, the transition from geometric capacitance (\( C_h \)) to contact (\( C_j \)) ones can be implemented only under conditions of equalization (or overcoming) of the period of applied voltage variation with dielectric relaxation time \( \tau_r \). As the \( \tau_r \) value decreases with increasing temperature (see insert in Fig. 2), it is reasonable to expect the frequency-dependent enhancement of capacitance owing to sample heating, especially at low frequencies. Figure 3 shows the capacitance–frequency dependence of structures in question at several temperatures. The inset in this figure illustrates the effect of temperature on the structure capacitance for several frequencies of applied voltage. It is evident that, at low frequencies, the structure capacitance increases with increasing temperature.

Thus, the structure capacitance increases either owing to raising the temperature at a fixed frequency or owing to lowering the frequency at a fixed temperature. In both cases, the effect is due to a reduction in the dielectric relaxation time caused by an increase in the ChGS
conductivity.

**Fig. 3.** Capacitance versus frequency of applied voltage at different temperatures. The insert shows the temperature dependence of capacitance in dry air.

In principle, it means the temperature-induced shift of the rising edge of capacitance spectra toward higher frequencies. We observed that this shift—much enhanced—can be also induced by a change in the ambient environment.

### 3.3. Effect of gas adsorption

Capacitance measurements for a Pt–As$_2$Te$_{13}$Ge$_{8}$S$_3$–Pt structure showed that a change in the ambient environment from dry air to a mixture containing even a very small concentration of nitrogen dioxide has a significant effect on the $C$–$\omega$ characteristics. Figure 4 shows the frequency dependence of a sample in question at room temperature in both dry air and its mixture with 1.5 ppm of NO$_2$. It is seen that, although the target gas does not modify the shape of the $C$–$\omega$ spectra, it leads to an increase in the sample capacitance in a definite frequency range by approximately 100 times. This effect looks like a strong gas-induced shift of the rising edge of capacitance spectra toward higher frequencies. In addition, note that the adsorption of the gas (e.g., NO$_2$) affects the capacitance of the structure precisely at low frequencies, that is, in a frequency range where the sample capacitance is assumed to be controlled by high resistive barriers at the contacts. This behavior is analyzed by assuming the equivalent circuit inserted in Fig. 4.

The equivalent circuit of the Pt–As$_2$Te$_{13}$Ge$_{8}$S$_3$–Pt structure can be represented by a parallel combination of the bulk resistance ($R_b$) and capacitance ($C_b$) connected in parallel with a further parallel combination of the surface resistance ($R_s$) and capacitance ($C_s$). As the device
structure has a planar design (Fig. 1a), there is also a parallel combination of the resistance \( R_c \) and capacitance \( C_c \) corresponding to thin insulating layers usually formed at the contacts put in series with the above mention circuit.

Let us consider all the components of this equivalent circuit separately. According to many experimental works, including our previous one [13], it is generally accepted that amorphous semiconductors exhibit a tendency of forming a space-charge layer near the surface, which is more conducting as the bulk; that is, by the surface the bands bend up, as shown in Fig. 5a. This effect is due to the interaction of lone-pair electrons of chalcogenide atoms with dangling bonds on the surface. The screening length can be calculated by the standard expression:

\[
\lambda = \left( \frac{\varepsilon \varepsilon_0}{q^2 N_F} \right)^{1/2},
\]

where \( N_F \) is the density of localized states at the Fermi level and \( q \) is the electronic charge. Assuming that \( N_F \approx 1.3 \times 10^{21} eV^{-1} cm^{-3} \) [19], we found that the value of the screening length \( \lambda \) is as low as a few dozens of Angstroms. Under these conditions, the dielectric relaxation time of the layer adjacent to the surface is shorter than that of the bulk; consequently, surface capacitance \( C_s \) cannot control the device capacitance at high frequencies.

The same can be argued for capacitance \( C_c \) corresponding to thin insulating layers at the contacts (Fig. 5b). The formation of a thin (10–100 Å) insulating layer at the metal–ChGS interface, as well as the major role of surface states at this interface, has been proved by very weak dependence of contact barrier height on work function of the metal [17, 20].
The theoretical model for this Schottky–Mott barrier is known as the Bardeen model, which, in addition to many remarkable features, assumes that the contact insulating layer can be transparent for carriers due to the tunnelling effect [21]. According to the small thickness of the contact insulating layer, it can be assumed that $C_c \gg C_b$ and, at high frequencies, the total capacitance can be approximated as $C_h = C_c C_b / C_c + C_b \approx C_h$. The asymptotic values for low-frequency capacitance derived using the approach of Wey [16] are as follows:

$$C_i = C_c R_c^2 / (R_c + R_s + R_b)^2$$

Assuming that $R_c \ll R_s \ll R_b$:

$$C_i \approx \frac{C_c R_c^2}{R_c}$$

This expression shows that the low-frequency capacitance should quite strongly increase with increasing surface conductance; this finding meets the above presented experimental results. The fact of increase in the conductivity of $\text{As}_2\text{Te}_{13}\text{Ge}_8\text{S}_3$ owing to the adsorption of the gas (e.g., NO$_2$) was clearly demonstrated in our recent works [22, 23]; therefore, the noticeable increase in capacitance induced by interaction with NO$_2$ molecules (Fig. 4) is due namely to this reason.

4. Conclusions

The capacitance spectra and current–voltage characteristics of the Pt–$\text{As}_2\text{Te}_{13}\text{Ge}_8\text{S}_3$–Pt structure indicate the formation of Schottky–Mott contact barriers with narrow insulating layers
at the interfaces. The huge increase in the capacitance with a decrease in frequency below $10^4$ Hz is attributed to these narrow high resistive regions near contacts and the equalization of the dielectric relaxation time of $\text{As}_2\text{Te}_{13}\text{Ge}_8\text{S}_3$ with the period of applied voltage variation. The capacitance spectra in the low-frequency range are significantly affected by ambient environment. In particular, the application even of a very low concentration (a few units of ppm) of nitrogen dioxide results in a frequency-dependent increase in the capacitance by a few hundreds of times. This finding gives evidence that the surface phenomena control the electric properties of ChGS in question and, in this particular case, the contact-free part of the film surface, which is more conducting than the bulk, acts as a capacitor, which is controlled by interaction with gaseous species from the environment.

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References

A STUDY OF CHANGES IN THE PRECIPITATION REGIME IN THE REGION OF LONG-TERM HAIL SUPPRESSION ACTIVITIES IN THE CENTRAL REGION OF THE REPUBLIC OF MOLDOVA

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Abstract

The paper presents the results of a comparative analysis of the statistical characteristics of summer precipitation totals for the period of 50–60 years of their observations on hail-protected and adjacent territories. It is shown that, against the background of the general tendency of decrease in the amount of summer precipitation, an increase in the totals in a range of 4–9% is recorded at weather stations located in the center of the protected territory compared with the amount recorded at the weather station outside the hail-protected territory.

Results of theoretical and experimental studies show the possibility of changing the summer precipitation totals by active impacts (AIs) on hail processes both on protected (PTs) and adjacent territories (ATs) [1, 2]. A decrease in the amount of precipitation under the action of AIs on PTs is attributed to a reduction in the duration and intensity of their fallout from reagent-seeded convective cells owing to the premature destruction of the cells. On the territory leeward to the PTs, the amount of precipitation can increase up to 15% of the seasonal norm. In some experiments, a long-term aftereffect of cloud seeding (increase in precipitation) after AI seasons with the use of silver iodide reagents was recorded on the ATs [4]. On the basis of experimental data, it can be assumed that some elements of the cloud seeding aftereffect can lead to a change in the precipitation regime on PTs directly during the periods of hail-suppression activities [6]. It was found that a significant role in this effect is played by changes in the climatic factors in the region [5].

Taking into account the urgency of the problem, in the 1980s, special experiments were conducted on the PTs in Moldova; they showed that the effect of decrease in the amount of precipitation takes place owing to the suppression of "intense showers" by AIs. This decrease is partially compensated by an increase in the amount of "moderate and significant" rainfalls with a total balance for the season of minus 4% [3]. This value is an expectation-driven index.

In this aspect, of undoubted scientific and practical interest are estimates of the actual change in the precipitation regime in regions of long-term and systematic activities on AIs. This region is the Republic of Moldova, where hail-suppression activities based on the rocket technology have been carried out since 1964.

In this paper, estimates of changes in the precipitation regime in the central part of Moldova are presented on the basis of the historical data of the precipitation network of the Hydrometeo Service of the Republic of Moldova. The research results are based on the statistical processing of summer precipitation totals (May–August) by means of MS Excel at the following weather stations (WSs):
(1) WS Cornesti; years of observation 1946–2014. It is located in the center of the region of hail-suppression activities in the Republic of Moldova from the very beginning of their onset (1964).

(2) WS Ungheni; years of observation 1954–2014. It is located 23 km to the west of WS Cornesti directly near the region of AIs (control territory (CT)).


(4) WS Orhei; years of observation 1949–2014 (CT). It is located 62 km to the east of Cornesti directly outside the region of AIs. Relative to Cornesti, this is the direction of the main motions of reagent-seeded hail-hazardous clouds on the PT.

The authors understand the complexity of solving the problem owing to the low density of the analyzed precipitation network with respect to the characteristics of the spatiotemporal variability of precipitation from convective clouds.

1. Brief Information on Hail-Suppression Activities in the Republic of Moldova in 2014
   - Beginning of hail-suppression activities dates back to 1964 with the center in the village of Cornesti.
   - In the period of 1964–1982, PbI₂-based formulations were used as a reagent for cloud seeding; since 1983, AgI-based formulations have been used everywhere.
   - Most probably, AIs, regardless of the motion of reagent-seeded clouds, will affect the precipitation regime recorded at WS Cornesti because the predominant intrusion of hail processes into the territory of the Republic of Moldova has a western component.
   - In the season of 2000, no hail-suppression activities were carried out in the Republic of Moldova. In 2001, they resumed in July.

2. Time Variation in Summer Precipitation Totals: Coefficients α are a Trend from Regression Equations

Changes in the precipitation regime were estimated using arrays of data on totals recorded at WSs located in the different regions of the central part of Moldova for the years indicated above. This approach is a widespread and important form of studying the meteorological phenomena; it gives an idea of the change in their qualitative and quantitative characteristics over time.

Figure 1 and Tables 1–3 show the results of analysis of summer precipitation for WSs Cornesti, Ungheni, and Orhei for the entire period of observations.

Fig. 1. Summer precipitation totals of and their trends (linear) for WSs Cornesti, Ungheni, and Orhei for the entire period of observations.
Table 1. Values of coefficients $\alpha$ (mm/season) of regression equations for summer precipitation totals at the WSs in different measurement periods

<table>
<thead>
<tr>
<th>WS</th>
<th>$\alpha$ (mm/season)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Over the entire period of observations of precipitation</td>
</tr>
<tr>
<td>Falesti</td>
<td>0.2758</td>
</tr>
<tr>
<td>Ungheni</td>
<td>-1.4238</td>
</tr>
<tr>
<td>Orhei</td>
<td>-0.2205</td>
</tr>
<tr>
<td>Cornesti</td>
<td>-0.5646</td>
</tr>
</tbody>
</table>

Table 2. Relationship between the amount of precipitation at WS Cornesti and the data of other WSs in different observation periods

<table>
<thead>
<tr>
<th>WS</th>
<th>Regression equations before AIs and in the period of AIs</th>
<th>$R^2$ before AIs and in the period of AIs</th>
</tr>
</thead>
</table>
| Cornesti–Falesti | $y = 0.8699x – 0.1916$  
$y = 0.6582 + 90.165$ | 0.4527  
0.4745 |
| Cornesti–Ungeni | $y = 0.8009x + 77.572$  
$y = 0.7858x + 90.979$ | 0.6307  
0.6848 |
| Cornesti–Orhei | $y = 0.3124x + 200.39$  
$y = 0.49x + 167.2$ | 0.0846  
0.2323 |

$R^2$ is the square of the mixed correlation; it is a number of 0 to 1, which represents the proximity of the trend line values to the actual data. The trend line most realistically represents the facts if $R^2$ is close to unity.

Table 3. Statistical characteristics of summer precipitation totals for periods of their measurements

<table>
<thead>
<tr>
<th>Statistical characteristics</th>
<th>WS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Falesti</td>
</tr>
<tr>
<td>$Q_{av}$, mm</td>
<td>273</td>
</tr>
<tr>
<td>$Q_{max}$, mm</td>
<td>491</td>
</tr>
<tr>
<td>$Q_{min}$, mm</td>
<td>107</td>
</tr>
<tr>
<td>$\sigma$, mm</td>
<td>84.5</td>
</tr>
<tr>
<td>Coefficient of variation ($v$)</td>
<td>0.31 (homogeneous series)</td>
</tr>
</tbody>
</table>
Analysis of the time variation in the summer precipitation totals and coefficient $\alpha$ showed the following:

- In the studied WSs, regardless of their location relative to the region of hail-suppression activities, except for WS Falesti, there has been a steady tendency to decrease in the summer precipitation totals over the 60-year period. The largest of them — $\alpha = -1.42$ mm/season—was recorded at WS Ungheni, the smallest — $\alpha = -0.22$ mm/season—at WS Orhei.

- In the series of precipitation totals, a large temporal variation is recorded: up to 2.0–2.5 times in the cycle of two to four years; it complicates the identification of the effect of AIs on their change.

- In the period of AIs (1964–2014), at all the WSs, trends $\alpha < 0$. The greatest trend — $\alpha = -1.36$ — was recorded at WS Cornesti. For the period of 1983–2014 (use of AgI in AIs) for WS Cornesti, $\alpha = -1.91$; that is, an increase in the trend of decrease in the summer precipitation totals is recorded, while at WS Ungheni (CT) the trend value hardly changed at all.

- During the period of 1983–1984 (period of use of a reagent based on AgI), the trend to decrease in the amount of precipitation increased according to the data of WS Orhei.

- Based on the data presented in the section, including statistical characteristics, it is impossible to make unambiguous conclusions about any effect of AIs on changes in summer precipitation totals recorded at WSs located in the region of hail-suppression activities.

3. Results of Analysis of Autocorrelation Functions of the Series of Summer Precipitation Totals

Studies of the relationship between summer precipitation totals revealed elements of quasi-periodicity in their time variation. The presence of these structures is confirmed by analysis of second-order autocorrelation functions, which are the basic tool for analyzing time series (Figs. 2, 3). (Autocorrelation is a statistical relationship between random variables from one series taken with a shift, for example, over time).
The above figures suggest the following:

- Historically, the change in summer precipitation totals has a pronounced quasi-periodic nature with a period of about 30 years. Their greatest synchronization is found in the transfer of air masses Ungheni–Cornesti–Orhei.

- The uniformity of the structures of autocorrelation functions for different WSs can indicate a unified natural mechanism of their formation in the studied territory.

4. Verification of the Hypothesis about the Possible Effect of AIs on Summer Precipitation Totals for WSs Located on the PTs: Double Ratios

For a statistical verification of the hypothesis of a possible change in the amount of summer precipitation in the region of AIs on hail processes, estimates of series of precipitation totals recorded at the studied WSs were made using the t-test (Student's criterion) and the F-criterion (Fisher criterion). Hypotheses about changes in the statistical characteristics of precipitation series during the period of hail-suppression activities can be adopted in the presence of these changes with a probability of \( P \geq 95\% \) (level of statistical significance of 0.05).

To estimate quantitative changes in precipitation totals over the period of hail-suppression activities at WSs located on the PTs in comparison with changes recorded at WSs located in ATs, the so-called double ratio method was used (formula 1); it is commonly used in similar studies [4]:

\[
\left( \frac{\bar{Q}_{CO}}{\bar{Q}_{EO}} \right)_{AA} / \left( \frac{\bar{Q}_{CO}}{\bar{Q}_{EO}} \right)_{AA}
\]

(1)
Table 4. Estimates of changes in the amount of precipitation by the $t$-test (for independent samples, comparison of samples before AIs with the period of AIs)

<table>
<thead>
<tr>
<th>WS</th>
<th>Sample length (number of years)</th>
<th>Calculated $t$-test value</th>
<th>Tabulated $t$-test value for $P = 95%$</th>
<th>Implementation of hypothesis $H_0$ (no changes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Falesti</td>
<td>20/37</td>
<td>0.688</td>
<td>1.959</td>
<td>$H_0$ is accepted</td>
</tr>
<tr>
<td>Ungheni</td>
<td>14/47</td>
<td>0.623</td>
<td>1.959</td>
<td>$H_0$ is accepted</td>
</tr>
<tr>
<td>Orhei</td>
<td>47/19</td>
<td>0.154</td>
<td>1.959</td>
<td>$H_0$ is accepted</td>
</tr>
<tr>
<td>Cornesti</td>
<td>22/47</td>
<td>0.979</td>
<td>1.959</td>
<td>$H_0$ is accepted</td>
</tr>
</tbody>
</table>

For $P = 95\%$, $t$ values calculated from the actual data are lower than the tabulated $t$ values for all the WSs. This means that, for the compared periods, this test has not revealed any significant changes in the series of summer precipitation totals.

Table 5. F-criterion values and significance levels in estimating the effect of AIs (comparison of samples before AIs with the period of AIs)

<table>
<thead>
<tr>
<th>WS</th>
<th>Beginning of precipitation measurements</th>
<th>F-criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated $F$ value</td>
<td>$F_\alpha$ (tabulated)</td>
</tr>
<tr>
<td></td>
<td>$P = 95%$</td>
<td>$P = 50%$</td>
</tr>
<tr>
<td>Falesti</td>
<td>1958</td>
<td>1.046</td>
</tr>
<tr>
<td>Ungheni</td>
<td>1954</td>
<td>1.173</td>
</tr>
<tr>
<td>Orhei</td>
<td>1949</td>
<td>1.324</td>
</tr>
<tr>
<td>Cornesti</td>
<td>1946</td>
<td>2.105</td>
</tr>
</tbody>
</table>

The $F$ value calculated for $P = 95\%$ is higher than the tabulated value only for WS Cornesti; this fact indicates statistically significant changes in the series of precipitation amounts for this WS in comparing the data before and during the hail-suppression activities.

The calculations revealed the following:

- In the series of precipitation amounts for all the WSs, no statistically significant changes determined by the $t$-test were revealed (for independent samples, comparison of the samples before AIs with the AI period).
- Analysis of the series of precipitation totals for WSs using the $F$-criterion (comparison of sample variances before AIs with the AI period) showed that the null hypothesis with a probability of more than $95\%$ can be rejected only for WS Cornesti; that is, statistically significant changes were revealed.
- The presence of an "additional" source that affects the formation of the spectrum of precipitation totals at WS Cornesti during the hail-suppression activities is indirectly confirmed by the specific features of the probability of distribution of these totals at WS
Ungheni: the presence of a second mode in the region of large precipitation totals for WS Cornesti.

Comparative analysis of summer precipitation totals at WSs Cornesti and Falesti (PTs) with the data of WSs located outside the PTs using the “double ratio” method showed that the gain in precipitation recorded at WSs Cornesti and Falesti relative to WS Ungheni is 4.6% and 9.0%, respectively; in comparison with WS Orhei (territory leeward to the PT), minus 6.3% and minus 4.0%

5. Conclusions

Comparative analysis of statistical data on precipitation in summer periods at WSs located on PTs and ATs (CTs) has shown the following:
1. At all the WSs, regardless of their location relative to the region of hail-suppression activities, except for WS Falesti, over the 60-year period, there has been a steady trend of decrease in the summer precipitation totals.
2. Historically, the change in the summer precipitation totals has a pronounced quasi-periodic pattern with a period of about 30 years.
3. During the period of activities on AIs at WSs located on the PTs, an increase in the negative values of trends in summer precipitation totals was observed, especially in 1983–2014, i.e., in the period of use of silver iodide. In the CTs, the changes in the trend values in this period are insignificant.
4. A high correlation between the summer precipitation totals recorded at WSs located on the PTs with the data of WS Ungheni (territory windward to the PT), regardless of the period of precipitation measurement, has been revealed. This fact can indicate the priority of unified natural sources (mechanisms) of their formation.
5. The values of trends in precipitation totals (mm/season) for the period of 1964–2014 are as follows: for WS Ungheni, minus 2.08; Orhei, minus 0.24; Falesti, minus 0.03; and Cornesti, minus 1.36.
6. Differences in the trends of summer precipitation totals at WSs located on the PT and CT before the beginning of hail-suppression activities and during the period of activities were evident as an increase in the summer precipitation totals for the period of AIs at WSs Cornesti and Falesti relative to WS Ungheni by 4.6% and 9.0%, respectively; in comparison with WS Orhei, minus 6.3% and minus 4.0%, respectively.
7. Statistical verification of the hypothesis of changes in the characteristics of summer precipitation totals at WS Cornesti (PT) by the Fisher’s criterion has confirmed this assumption at the level of statistical significance of 0.05 (95%). For other WSs, this hypothesis has been found to be inapplicable.

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