[Interview was translated from Russian]

Kev Minullinovich, one of your recent scientific accomplishments is the formulation of a new spin exchange paradigm. Can you tell us more about it?

Thank you, I will gladly do so. You'll have to be a little patient; I want to answer this question in detail.

In the last few years, the main place in my scientific work has been occupied by the problem of spin exchange and its manifestations in EPR spectroscopy for dilute solutions of paramagnetic particles.

Spin exchange is the change in the spin state of unpaired electrons of two paramagnetic particles during their random collisions.

At the moment of the closest approach of two particles, a strong Heisenberg exchange interaction is activated at the van der Waals collision radius. If the exchange interaction is much larger than all other spin-dependent interactions, then as a result of the collision, the spin of each of the particles appear in a different state compared to its state immediately before the collision. But due to the large exchange interaction, the total spin and all projections of the total spin of the two particles are preserved during the collision. The spin exchange leads to very characteristic changes in the line shapes in the EPR spectrum. And therefore, EPR spectroscopy is the best method for determining the spin exchange rate.

Why is spin exchange so interesting?

The interest in this process is due to many circumstances, for example:

- Spin exchange serves as a model bimolecular process for determining the frequency of bimolecular collisions (encounters) of particles in complex systems, such as polymer solutions, biological systems.

- Spin exchange is one of the reactions in spin chemistry.

- The effective spin exchange radius can be relatively easily calculated for a given exchange interaction between paramagnetic particles.

- EPR spectroscopy offers many possibilities for determining the spin exchange rate.

When did you start to notice that a new paradigm was needed for description of spin exchange?

For half a century, from time to time I participated in the interpretation of experimental data obtained in the laboratories of Yu.N. Molin (ICKC SB RAS, Novosibirsk) and K.I. Zamaraev (ICP RAS, Moscow). For example, K.I. Zamaraev obtained an unexpected result: in a binary solution containing free radicals and complexes of paramagnetic ions (Mn^{2+}), the spin exchange rate constants found from the concentration broadening of the lines in EPR spectra for the radical and the complex differed by an order of magnitude. This **contradicted** the spin exchange paradigm that existed at that time, according to which the specified spin exchange rate constants were expected to coincide. I was able to show that this contradiction can be resolved without changing the main provisions of the accepted paradigm.

The spin exchange paradigm adopted by the mid-1970s and its study by EPR methods were summarized in [4, 5]. Already in this book, in the section describing the theory for the situation of slow spin exchange, I showed that the resonance lines should have a so-called mixed shape.

Recently, I got from the USA a copy of a collection of articles, in which D. Kivelson and K. Ogan independently obtained this mixed line shape and called it a generalized Lorentzian. For many years **no one noticed** this mixed shape of the lines in the experiment.

From time to time I was back to the problem of spin exchange and its manifestations in EPR spectroscopy and made new interesting observations. For example, one of the main goals in the study of spin exchange is ultimately to determine the frequency of bimolecular collisions.

How is the current paradigm used to describe the spin exchange?

In the accepted paradigm of spin exchange, the main source of the information about the spin exchange is the concentration line broadening in the EPR spectra. However, along with the exchange interaction between the spin probes, the dipole – dipole interaction leads to concentration broadening of lines in EPR spectra. The problem of separating the contributions of these interactions to line broadening arises. In the accepted paradigm, this problem is solved as follows. It is assumed that the exchange interaction (spin exchange) and the dipole-dipole interaction contribute fundamentally differently to paramagnetic relaxation. In spin exchange, as a result of the collision, each partner gives its quantum coherence and spin excitation energy, but also receives coherence and excitation energy from the collision partner. In accordance with the theory of paramagnetic relaxation in liquids, it was believed that as a result of the dipole-dipole interaction, each spin only loses coherence and does not receive any coherence from the interaction partner in return.

As a result, it turns out that the concentration shift of the resonance frequencies, the fusion of all components into one homogeneous line in the EPR spectra are due only to the spin exchange, and the dipole-dipole interaction does not in any way affect these characteristic changes in the spectra. Back in 1976, **I pointed out a fallacy** of the accepted description of transverse paramagnetic relaxation in liquids, caused by dipole-dipole interaction.

In fact, as a result of the dipole-dipole interaction, each spin receives coherence from the interaction partners as a recoil effect, similar to the situation with spin exchange. But there is also a fundamental difference. In the case of a dipole-dipole interaction, partners give their coherence with a phase shifted by π, that is, partners give their transverse magnetization with a change in sign. This leads to interesting consequences in the form of the EPR spectrum (see, for example, [7]). Note that in the case of nuclear spins, the change in the sign of the transfer of longitudinal magnetization between the spins is well known due to scalar and dipole-dipole interactions. This effect occurs for the transverse components of spin magnetization under EPR conditions. And again, theoretical predictions have been neglected for many years.

How did you end up formulating your own paradigm?

Today the situation has changed radically, this gave me the basis to formulate a new paradigm of spin exchange and its manifestations in EPR spectroscopy. I'll tell you how it happened. I hope my experience will encourage others to do the same work.

Before I begin to present my experience, let me briefly recall what is meant by a paradigm.

A paradigm is a model that has been adopted by the scientific community for solving problems of fundamental science and applied problems.

There are paradigms on a universal scale, like a Big Bang theory. There are paradigms in different sections, in certain areas of science and technology. As new achievements are accumulated, scientists revise the accepted paradigm, formulate a new paradigm.

The paradigm makes it possible to reveal truly qualitatively new knowledge. If the paradigm is not formulated, that is, the existing knowledge is not reduced to a clear model, and then it is very difficult to decide whether a new observation is fundamentally new knowledge. Or is it just replication of already known knowledge, increasing the database, which in itself is also a very necessary thing.

I will talk about the experience of changing the scientific paradigm in one specific discipline – THE SPIN EXCHANGE.

It turned out like this. Three years ago, at the request of Springer, I began to prepare a new edition of a book on the spin exchange. The first edition was published in Nauka in 1977 and in Springer in 1980. That book was written jointly with Yu.N. Molin and K.I. Zamaraev. I wrote the theoretical section of that book.

I started writing a new book. I raised all my theoretical works in this area and assessed the situation with a fresh look. Over the years, I received a number of theoretical results that did not fit into the accepted spin exchange paradigm. But they have not been confirmed by experiments. However, in recent years my theoretical predictions have been confirmed by careful experiments carried out in the USA by B. Bales and his colleagues, and also at the Kazan Physical Technical Institute of the RAS [8-13]. After reviewing everything that had been done in the spin exchange, and rethinking my theories, I realized that **the totality of the new findings exceeded the critical mass**. The generally accepted spin exchange paradigm is bursting at the seams and hinders the development of science.

As a result, it became obvious that there was a need to formulate a new spin exchange paradigm. Which I did. So in 2019 the book [1] was published.

What are the main provisions of the new paradigm?

From the new paradigm, the following moments can be singled out [1-3, 14]:

1. An elementary act of **spin exchange can be nonequivalent from the quantum coherence exchange point of view**, even if the exchange interaction at the instant of collision of spin probes exceeds the other spin-dependent interactions by several orders of magnitude. A “butterfly effect” may appear if the time of meeting of two spin probes is sufficiently long, taking into account their re-encounters (repeated approaches to the collision radius) [1, 2, 15].

2. Dipole-dipole interaction also contributes to the transfer of spin coherence. This contribution destructively interferes with the contribution of the exchange interaction: exchange and dipole-dipole interactions contribute to the rate of transfer of spin coherence of the opposite sign.

3. Due to the transfer of spin coherence, **collective modes** of spin motion are formed in dilute solutions of paramagnetic particles.

4. **Each resonance line of the collective mode in the observed spectrum has a mixed shape** and it is the sum of the absorption line and dispersion.

5. In the case of fast transfer of spin coherence, the microwave field excites only one symmetric collective mode. The resonance frequency of this mode is equal to the frequency of the center of gravity of the EPR spectrum. Other collective modes with different frequencies turn out to be “forbidden lines”.

6. The best method for determining the rate of transfer of spin coherence is to find the contribution of dispersion to the mixed line shape, rather than broadening the spectral lines.

7. In dilute solutions, due to the transfer of spin coherence, the electron spins of paramagnetic particles and the strong microwave field create combined states, which are called **the spin polariton**.

What is something new you discovered in the process of working on the paradigm?

Working on a new paradigm opened up new degrees of freedom for me, broadened my horizons and gave a great impetus to my scientific research. I realized that a paradigm is practically an important tool for scientific knowledge and its effective development. The paradigm serves as a basis for planning research, a tool for assessing the value of the result obtained in the course of research. The paradigm accelerates scientific research.

I would like to point out that the paradigm I have proposed can have a direct impact on other disciplines as well.

We are well aware of examples of how random collisions of particles lead to macroscopically observed "ordered motion". An example is Fick's law, the occurrence of particle flux, which is proportional to the particle concentration gradient. Due to the recoil of coherence in random bimolecular collisions in an ensemble of spin probes, it turns out that the motion of spin magnetization can be represented as a set of collective modes of motion of these magnetizations, independent of each other. These collective modes are similar to phonons in crystals. There are such combinations of spin magnetizations that, even in spite of random collisions of particles, persist, one combination does not transform into another.

To illustrate this, consider the simplest model system: a dilute solution consisting of an equal number of two types of spin probes that differ in their Zeeman frequency. For example, in the case of fast spin exchange, there are two types of collective modes of motion that conserve the sum and difference of the transverse components of the magnetization. In an EPR experiment, a coherent microwave field acts on all spins in the same phase. Consequently, in this situation, the microwave field will excite only one of the collective modes, which is created by the motion of the sum of the magnetizations of all spins. This is what we observe under the conditions of the exchange narrowing of the spectrum. It turns out that all characteristic changes in the shape of the EPR spectrum with an increase in the spin exchange rate are naturally explained using collective modes of motion [1-3].

The amazing thing here is that random collisions create organized modes of movement that don't mix with each other.

Thank you for such a detailed story about your new spin exchange paradigm! We hope that it will resonate with readers and will soon become generally accepted.

Thank you for your interest to my work.

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