Fundamentals of Spin Exchange
Kev M. Salikhov  
Zavoisky Physical-Technical Institute  
of Russian Academy of Sciences  
Kazan, Russia
The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.”

William Lawrence Bragg: Physicist 1957

Preface

This book is about the paradigm shift in spin exchange and its manifestations in Electron Paramagnetic Resonance (EPR). Since I entered the area of spin exchange research in the 1970s and until now the understanding of spin exchange has changed to the point that we now have to admit there is a definite shift in the paradigm of how we understand spin exchange, how we measure the rate of spin exchange using EPR methods, and how we can use the spin exchange.

The paradigm shift came about as a result of the following achievements. Initially, when considering the elementary act of spin exchange in the course of bimolecular collisions, only a large exchange interaction was usually considered, while much smaller spin dependent interactions of individual paramagnetic particles were neglected. But these minor interactions can give major consequences for the spin exchange if the duration of collision of two particles is long enough. So in the new paradigm, we differentiate equivalent and nonequivalent spin exchange cases.

A novel description of the spin dynamics for dilute solutions of paramagnetic particles was formulated based on the independent collective modes. For example, based on this, the physical nature of the exchange narrowing effect of the EPR spectra in the case of fast spin exchange can be elucidated at a much deeper level than previously possible. It was shown that resonance lines of these collective modes in the case of slow spin exchange manifest an asymmetric shape, as they are sums of the Lorentzian symmetric absorption and asymmetric dispersion terms. This asymmetric shape of collective resonances forced the reconsideration of the algorithm of finding the rate of spin exchange from EPR data. In strong microwave fields, the new collective modes are formed which can be considered as spin polaritons.

To study bimolecular collisions of paramagnetic particles in solution using spin exchange, the effects of dipole-dipole interactions must be taken into account. I have theoretically predicted (see [3], Chap. 4) that dipole-dipole interaction also produces a dispersion term but with a sign opposite to that for Heisenberg exchange interaction. This fact had escaped the attention of workers in the field for a long time. It had also been overlooked in previous theories (see, e.g., [4], Chap. 8).
As we all know, the scientific community has a reasonable level of inertia when it comes to adopting new ideas. And this is a great thing, because it forces us to scrupulously scrutinize every fact and every observation to ensure that every little bit of knowledge is well researched and proven.

I hope that this book will help the reader to learn about the modern understanding of spin exchange and give enough of a foundation to continue research in this field. Because of the volume of confirmed concepts and solutions we now have, it allows me to confidently conclude that we are experiencing a paradigm shift in the field of spin exchange. This paradigm shift happened as a result of theoretical predictions and fundamental experiments.

In the late 1970s along with Yu.N. Molin and K.I. Zamaraev, we wrote the book *Spin Exchange: Principles and Applications in Chemistry and Biology* which was published by the Publishing House of the USSR Academy of Sciences [1] and was later released in English with minor revisions [2]. Over the last 40 years, the aforementioned book continues to be the most popular book on this subject.

My contribution to this book (Chap. 2) was a comprehensive overview of the state of theoretical achievements in this area. There were even a number of predictions which first appeared in this book which had previously never been published before.

As a scientist and theoretician, I feel fulfilled and fortunate because practically every theoretical prediction I made in this book and in some other publications [5–11] have now been proven experimentally [12–18].

The purpose of this book is to present the current state of the theory of spin exchange, the theory of paramagnetic relaxation in a liquid due to dipole-dipole interaction, and a theoretical analysis of the manifestations of spin exchange in EPR spectroscopy. In addition to the theoretical results presented in [1, 2, 3], new theoretical results [5–11] are presented here. They are confirmed by experimental data (see, e.g., [12–18]). All this led to a qualitatively new understanding of the role of spin exchange in the dynamics of electron spins in liquids and its manifestations in EPR spectroscopy. In fact, there was a change in the spin exchange paradigm in dilute solutions of paramagnetic particles, and especially its manifestations in EPR spectroscopy, in algorithms for measuring the rate of spin exchange using EPR spectroscopy.

Experimental data on spin exchange are an important part of this book: they provide confirmation of the theory of spin exchange and its manifestations in EPR spectroscopy. For experimenters, sections of the book in which the modern protocol for determining the spin exchange rate constant from the analysis of the shape of the EPR spectra which is described in detail will be of particular interest. The modern protocol is very different from the protocol that was used in previous years [1, 2].

At present, studies dedicated to spin exchange are expanding, which is largely facilitated by the development of methods for preparing spin-labeled samples (see, e.g., [19]). It is especially important to note that chemists have developed methods for targeted incorporation into biopolymer molecules of spin labels. As such, many other new promising areas of spin exchange have been developed. For example, it turns out that spin exchange plays an important role in the formation of dynamic polarization of nuclei. This makes it possible to significantly increase the intensity of
the observed nuclear magnetic resonance signals without lowering the temperature or using very high inductions of a constant magnetic field (see, e.g., [20, 21]).

I consider myself very lucky to have been involved in studying the very interesting problem of spin exchange and over the years have greatly enjoyed my collaborative work with many colleagues around the world – all to whom I am very thankful. It was always especially stimulating to work alongside experimenters, as, for the paradigm shift to happen, it was crucial that theoretical predictions were confirmed by experiments.

I’d like to express my gratitude for the opportunities to work with colleagues in the Institute of Chemical Kinetics and Combustion of the Russian Academy of Sciences in Novosibirsk, the Zavoisky Physical-Technical Institute of the Russian Academy of Sciences in Kazan, Physics Department of the Free University of Berlin, as well as the Department of Physics and Astronomy, Center for Biological Physics, California State University at Northridge.

A special thank you to my daughter, Assia, who helped me to achieve greater clarity of communication about the nature of this paradigm shift and to Igor Axenov who has been helping me with beautiful presentation of images and illustrations for over 30 years.

Scientific research demands total concentration, and I consider my achievements to have been made possible due to the tremendous support of my wife, Zoya, who passed away when I was starting to write this book.

Kazan, Russia

Kev M. Salikhov

References

# Contents

1 Introduction: Development of the Study of Spin Exchange from a Bird’s Eye View ................................... 1
References .................................................................................. 5

2 Theory of Spin Exchange in Dilute Solutions .................. 7
2.1 Bimolecular Spin Exchange Process ....................... 8
2.2 The Exchange Interaction Between Two Paramagnetic Particles . 13
  2.2.1 The Nature of Exchange Interaction ................ 14
  2.2.2 Spin Hamiltonian of the Exchange Interaction ... 15
  2.2.3 Exchange Integral ...................................... 16
  2.2.4 Exchange Interaction of Multi Electron Systems,
      Electron Delocalization and Spin Polarization ..... 20
  2.2.5 Semiempirical Estimates of the Exchange Integral . 22
2.3 Dynamics of Spins Caused by the Exchange Interaction ..... 23
  2.3.1 Spin Density Matrix. Quantum Spin Coherence ...... 23
  2.3.2 Elementary Act of Spin Exchange. Spin Dynamics 
      of a Pair of Paramagnetic Particles ................ 26
2.4 Modified Bloch Equations Taking into Account Spin Exchange
      for Paramagnetic Particles with Spin S = 1/2 ............ 30
2.5 On the Potential of Steady State EPR Spectroscopy in the Study
      of Spin Exchange .............................................. 32
2.6 Kinetic Equations for Magnetization of Solutions of Free
      Radicals with the Arbitrary Hyperfine Structure of EPR Spectra
      Taking into Account Equivalent Spin Exchange .......... 35
2.7 Theoretical Calculations of the Spin Exchange Rate Constant . 36
  2.7.1 Phenomenological Description of Spin Exchange ..... 36
  2.7.2 Early Theories of Spin Exchange ..................... 37
  2.7.3 Kinetic Equations for the Spin Density Matrix 
      in a Model of Sudden Collisions .......................... 39
2.8 Calculations of the Spin Exchange Rate Constant in the Approximation of the Sudden Collisions ........................................... 43

2.8.1 Spin Exchange Between Particles with Spin \( S = 1/2 \) .... 43

2.8.2 On the Interpretation of the Change in the Sign of the Spin Frequency Shift (\( S = 1/2 \)) Due to the Spin Dynamics Caused by the Influence of Both the Exchange Interaction and the Difference in the Frequencies of Isolated Spins ........................................... 54

2.8.3 The Role of Re-Encounters on Spin Exchange (\( S = 1/2 \)) at Sudden Switching on of the Exchange Interaction at the Collision Radius ........................................... 56

2.8.4 Spin Exchange Between Triplet Excitons ...................... 63

2.8.5 Equivalent Spin Exchange Between Paramagnetic Particles with Spin 1/2 and Particles with Arbitrary Spin \( S \) ........................................... 67

2.8.6 The Influence of the Paramagnetic Relaxation of Spins on the Spin Exchange Efficiency ............................. 77

2.8.7 Quenching of Positronium with Paramagnetic Particles ...... 79

2.8.8 Effect of Rotational and Translational Diffusion of Particles on Spin Exchange in the Case of Anisotropic Spin Density Distribution in Paramagnetic Particles .... 80

2.9 Kinetic Equations for Single-Particle Spin Density Matrices in Dilute Solutions of Paramagnetic Particles in the General Case . 84

2.10 Calculations of the Effective Spin Exchange Radius Taking into Account the Extended Exchange Interaction ................................ 93

2.10.1 Paramagnetic Particles with Spin \( S = 1/2 \) .................. 93

2.10.2 Comparison of Results for Models of Sudden Collisions and Diffusion Passage of the Exchange Interaction Region. Possible Modification of the Model of Sudden Collisions ................................ 98

2.10.3 Paramagnetic Particles with Arbitrary Spins .................. 100

2.11 Spin Exchange in Electrolytes Between Charged Particles with Spin \( S = 1/2 \) ........................................... 104

2.12 Approximate Estimates of the Effective Spin Exchange Radius for Charged Particles ........................................... 113

References ........................................... 115

3 Paramagnetic Relaxation Caused by the Spin-Spin Dipole-Dipole Interaction of Paramagnetic Particles in a Liquid .................................. 119

3.1 Spin Hamiltonian of the Dipole-Dipole Interaction of Paramagnetic Particles ........................................... 120

3.2 Kinetic Equations for the Description of Electron Paramagnetic Relaxation in Liquids Caused by the Dipole-Dipole Interaction Between Paramagnetic Particles with Arbitrary Spins .................. 122
3.3 Kinetic Equations to Describe Electron Paramagnetic Relaxation in Liquids Caused by the Dipole-Dipole Interaction between Free Radicals .................................................. 124
3.4 Kinetic Equations for Typical Conditions of EPR Experiments .................................................. 130
References .......................................................................................................................... 131

4 Modified Bloch Equations for Dilute Solutions of Free Radicals Taking into Account Exchange and Dipole-Dipole Interactions ............................................... 133
References .......................................................................................................................... 137

5 Manifestation of Exchange and Dipole-Dipole Interaction in Solutions in Linear Response Case .......................................................... 139
5.1 Features of the EPR Spectrum of the Solution of Radicals, Which Have a Single Magnetic Nucleus I = 1/2, in the Presence of Equivalent Spin Exchange ................................................. 140
5.2 General Solution for the Shape of the EPR Spectrum ................................................................. 143
5.3 Early Paradigm of Spin Exchange in Solutions of Paramagnetic Particles .......................................................... 148
5.4 A New View on the Manifestation of Spin Exchange in EPR Spectra. Collective Modes of Evolution of Quantum Coherence of Spins .......................................................... 152
5.5 Collective Modes of Motion of the Spin Coherence for Model Systems .................................................. 154
5.6 What Happens When Dipole-Dipole Interaction Is Giving a Dominant Contribution to the Spin Coherence Transfer? .................................................. 167
5.7 The Quintessence of the New Paradigm of Spin Exchange and Its Manifestations in EPR Spectroscopy .......................................................... 170
References .......................................................................................................................... 173

6 Experimental Determination of the Spin Exchange Rate from the Analysis of the EPR Spectrum Shape .......................................................... 175
6.1 The Ratio Between the Parameters of the Observed EPR Spectrum and the Physical Parameters of the Spin System. Simple Example .......................................................... 178
6.2 Potential of the Linear Response EPR Spectra for Determining the Spin Decoherence and the Spin Coherence Transfer Rates .......................................................... 186
6.2.1 General Speculations .......................................................... 186
6.2.2 EPR Spectrum in the Case of Intermediate Spin Coherence Transfer Rates .......................................................... 192
6.3 Algorithms for Finding the Spin Decoherence and the Spin Coherence Transfer Rates from EPR Spectra of Nitroxide Radicals in Linear Response Case .......................................................... 200
6.3.1 Fitting Spectra .......................................................... 200
References .......................................................................................................................... 206
7 Other Methods of Measuring the Spin Exchange Rates

7.1 Continuous-Wave Saturation Method

7.1.1 Review of the Paramagnetic Resonance Saturation Theory

7.1.2 Peculiar Features of the Spectrum Under Saturation Conditions When Equivalent Spin Exchange Operates. System with Two Frequencies

7.1.3 Shape of the EPR Spectrum in Strong Microwave Fields for Paramagnetic Particles with Spin 1/2. Equivalent Spin Exchange Case

7.2 Electron-Electron Double Resonance (ELDOR)

7.3 Saturation Recovery Methods

7.4 Electron Spin Echo

7.5 Dynamic Nuclear Polarization

References

8 In Conclusion: Brief Summary of New vs Existing Paradigm of Spin Exchange

8.1 The Dynamics of the Spins of the Unpaired Electrons of Paramagnetic Particles in Solutions

8.1.1 An Elementary Act of Spin Exchange in Bimolecular Collisions. Minor Interactions with Major Consequences

8.1.2 Collective Modes of Motion of the Spins Due to Spin Exchange in the Bimolecular Collisions of Particles

8.1.3 Contribution of Dipole-Dipole Interaction of Paramagnetic Particles to Spin Dynamics in Solutions

8.2 Manifestation of Spin Exchange in the Shape of EPR Spectra

8.2.1 The Shape of Individual Lines in the EPR Spectrum

8.2.2 The Exchange Narrowing

8.2.3 Saturation Effect

8.3 The Determination of the Rate of the Bimolecular Spin Exchange Processes with the Help of EPR Spectroscopy

References

Afterword
About the Author

**Kev M. Salikhov** is professor, full member of the Russian Academy of Sciences, Lenin Prize winner (USSR), gold medalist of the International EPR (ESR) Society, fellow of Wissenschaftskolleg zu Berlin, winner of Humboldt research award and eminent scientist of RIKEN (Japan).

He is the founder of *Applied Magnetic Resonance* journal and initiator of the international prize named after Zavoisky, which is annually awarded to scientists for their outstanding contribution to the development of magnetic resonance and its application.

Kazan-Akademgorodok (Novosibirsk)