

Pulsed Electron–Electron Double Resonance

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Pulsed Electron–Electron Double Resonance

Nanoscale Distance Measurement
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Preface

Following the discovery of electron paramagnetic resonance (EPR) by E. K. Zavoisky in the Russian city of Kazan more than 70 years ago, applications of EPR for studies of the structure and properties of paramagnetic particles and materials have flourished. This is due, in part, to the technical development and growth of the EPR method itself. Starting from the 1960s, pulse EPR has overtaken continuous-wave EPR methods. This occurred through the development of electron spin echo, multipulse and two-dimensional sequences; double electron–nuclear and electron–electron resonance techniques; triple resonance; EPR tomography; and high-frequency EPR methods extending into the millimeter wavelength range. All these directions of EPR development are based on its unique combination of high sensitivity, selectivity, and resolution in both the frequency and time domains. New horizons continue to arise for applications in physics, chemistry, and biology. Traditionally, pulse EPR methods and their numerous variants are most widely used in physicochemical applications, such as the structure and properties of atoms, ions, radicals, and molecules; chemical kinetics; and physical dynamics.

In this book, we have tried to summarize the development and application of a relatively novel variant of EPR spectroscopy, i.e., the method of pulsed electron–electron double resonance (PELDOR) or double electron–electron resonance (DEER); we will use the first abbreviation in this book. PELDOR was proposed and developed in 1981 in Novosibirsk in the Voevodsky Institute of Chemical Kinetics and Combustion by A. D. Milov, K. M. Salikhov, and M. D. Schirov.

PELDOR is the offspring of other pulse EPR methods, particularly electron spin echo (ESE), in which all of the authors worked. One prominent ESE application in chemistry is to the study of dipole–dipole magnetic interactions between paramagnetic centers. Such work provides information about the spatial distribution and distances between spins in disordered systems. However, this information is hard to extract because the analysis of ESE data about dipole–dipole interactions is complicated by other interactions within the spin system, i.e., electron–nuclear interactions and relaxation processes such as spectral diffusion. The potential of ESE is also restricted by the so-called dead time, which limits the measurement of short relaxation times.

PELDOR overcomes many of these difficulties. It became possible: to measure the distances and the distribution of distances between pairs of spins for biradicals and radical pairs; to determine the geometry spin-labeled molecules; to estimate the number of interacting spins in spin clusters; and to characterize the spatial distribution of paramagnetic centers. The limitations, caused by instrumental dead time which limited ESE to distances greater than 1.5 nm, are absent in PELDOR.

As a result, PELDOR is now a fairly popular method in EPR spectroscopy, particularly as applied to biologically important systems. PELDOR is becoming more readily accessible to researchers due to the appearance of PELDOR spectrometers in a wide range of frequency bands.

This book covers the basic theory of PELDOR, the basic techniques, and some applications. Already, several hundred published articles concern applications of PELDOR in chemistry and biology. The choice of examples in our book is, of course, subjective and we cannot claim to completely cover all application of PELDOR. We do hope that the interested reader will come to an appreciation of the opportunities PELDOR provides and will find the key to solve their own physicochemical and biochemical problems.

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