Supermatrix Operation Algorithms for Unified Analysis of Spectroscopy and Relaxation Data

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The main theoretical difficulties in Electron Spin Resonance (ESR) spectroscopy are caused by the fact that the electron spin system is beyond the validity range of perturbation treatments. This happens when the electron spin motions are driven by two large, non-commuting Hamiltonians; for example the Zeeman Hamiltonian, which arises from the interaction of an electron spin with a laboratory magnetic field, and the zero-field splitting interaction, which results from spin-orbit couplings for the electron spin quantum numbers $S \geq 1$. I shall present a general treatment of ESR spectra, valid for arbitrary motional conditions and interaction strengths, beyond the applicability of perturbation approaches. This treatment is known in the literature as the ‘slow motion theory’ or the ‘general theory’ [1,2]. The approach is based on expressing all relevant interactions and dynamic processes [3,4] (represented first in terms of Liouville operators) as a (super)matrix in a complete orthonormal basis set [1,2,5], including all relevant interactions and degrees of freedom of the system. The computationally heavy step is finding a small number of elements of the inverse of this complex matrix. ESR spectra are fully determined by only one element of the inverted supermatrix. The method has been extended to include other interactions, like higher terms of the zero field splitting and the anisotropy of the g-tensor. More complex dynamics is possible to handle, but at the expense of larger matrices representing degrees of freedom available for the system of interest. The presented method can also be used for the purpose of NMR (Nuclear Magnetic Resonance) relaxometry and spectroscopy of paramagnetic systems [6].