A New Approach of Time-Ordered Exponential in NMR: the Path-Sum.

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The time-ordered exponential function U = OE[-iH](t',t) is the unique solution of the following system of differential equations: U'(t',t) = - i H(t) U(t',t) (eq. 1) where H(t) stands for the (usually) time-dependent hamiltonian of the spin system and such that OE[-iH](t,t) is the identity. Compact expressions for U(t',t) are easily obtained if H(t) is independent of time or if it commutes with itself at all times [H(t'),H(t)] = H(t')H(t)-H(t)H(t') = 0. Generally, solid state NMR experiments involving the combination of macroscopic reorientation of the sample and the application of RF fields lead to non zero values of the time commutator [H(t'),H(t)]. In such cases, various methods have been developed in the 50's and 60's: Dyson series, Magnus/Fer expansions, Floquet and Floquet-Magnus hamiltonians. All these important methods have their own strengths and weaknesses.

In this contribution, we propose an entirely new approach for the resolution of systems of differential equations by using **path-sums** [1]. The fundamental idea is to associate a graph to the matrix of the time dependent hamiltonian of the system and to evaluate the various matrix elements of the ordered exponential by rigorously resumming infinite families of walks on this graph.

The path-sum approach leads systematically to a *compact* and *exact* form of the ordered exponential corresponding to a branched continued fraction of finite depth and breadth, the convergence and existence of which is shown to be inconditional, in contrast to Magnus series.

The fundamental ingredients of the path sum formulation are [2]: **(i)** the description of OE as resolvent of operators ; **(ii)** mapping the resolvent to sums of walks on graphs ; **(iii)** theoretical results related to the algebraic structure of sets of walks. Finally, the path-sum formulation remains valid at all length-scales: it is capable of rigorously combining the OEs of any chosen ensemble of sub-systems to produce the OE of the full system. This unique capability also means that the path-sum approach is immediately employable in conjunction with existing methods. Most importantly, we demonstrate that path-sums reduce the difficulty of calculating OEs to solving selected Volterra equations with separable kernels.

Various examples will be fully analyzed during the presentation: Bloch-Siegert effect in two level systems [3] ; intense field excitation of three level atomic systems by laser pulses [4] ; extension to homogeneous interactions under MAS ; extension to large matrices related to N coupled spins through the dipolar interaction.

From a more theoretical point of view, Path-sum arises from exact resummations of infinite families of system histories, which are discrete analogs to Feynman-diagrams. Beyond applications to NMR, general solutions for quantum dynamical systems driven by time-varying Hamiltonians can be obtained.

References

[1] P.-L. Giscard, K. Lui, S.J. Thwaite, D. Jaksch, *J. Math. Phys*., 56, 053503 (2015).
[2] P.-L. Giscard, S.J. Thwaite, D. Jaksch, arXiv:1202.5523v5.
[3] a) F. Bloch, A. Siegert, *Phys. Rev*., 57, 522 (1940). b) J.H. Shirley, *Phys. Rev*., 138, 979 (1965).
[4] M.A. Lauder, P.L. Knight, P.T. Greenland, *Optica Acta: Int. J. Optics*, 33, 1231-1252 (1986).