An efficient method was introduced for making the transition from exact dynamical equations of motion to irreversible transport equations. The method was based on use of projection operators to separate "relevant" from "irrelevant" variables. [The *SCI®* indicates that this paper has been cited in more than 575 publications.]

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A Shortcut to Irreversibility

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In the 1950s, the primary tools of non-equilibrium statistical mechanics were the Boltzmann equation (low density gases), the Pauli master equation (weakly coupled quantum systems), and the Langevin equation for Brownian motion (particles in fluids). It was recognized that these equations were correct only in limited circumstances, and a lot of effort went into attempts to extend their validity. Further, they are all dynamically irreversible equations, and their violation of time reversal symmetry led to a general unease about their consistency with exact dynamical equations of motion.

Two attacks on this question were due to I. Prigogine[1] and L. van Hove.[2] Their approach was a fashionable one at the time—use of infinite order perturbation expansions, as in quantum field theory. The resulting infinite series were rearranged, artfully chosen classes of terms were dropped, and what was left was re-summed to arrive at the desired result. Prigogine visited the National Bureau of Standards in 1959 to give a series of lectures on his diagrammatic version of the perturbation expansion method. Many experts in statistical mechanics attended his lectures; some were skeptical about his method, perhaps because of its complexity.

I decided to try to understand an apparently simpler approach, van Hove's derivation of the Pauli master equation. On studying his work, it occurred to me that both van Hove's and Prigogine's methods could be summarized as the partitioning of a dynamical problem into relevant and irrelevant parts, followed by elimination of the irrelevant parts. I immediately saw that this could be done in a quite general way by introducing projection operators to account for the partitioning. I was then able to arrive at the main results of Prigogine and van Hove in a remarkably simple and direct way, without doing infinite order expansions and re-summations. Further, my approach could clearly be generalized in many directions, for example, to include non-Markovian or "memory" effects. Finally, I could see that there was no inconsistency between the requirements of time reversal symmetry and the actual behavior of many body systems.

When I was invited to submit a paper to a special issue of the *Journal of Chemical Physics* (*JCP*), honoring the memory of my mentor, the late John G. Kirkwood, I decided to write a short summary of my ideas about projection operators. An extended version of the paper was published[3] as my 1960 "Boulder lectures." That paper has received even more citations than the *JCP* paper.

It took many years for this work to gain substantial recognition. An early application by H. Mori[4] led to what is now commonly referred to as the Zwanzig-Mori formalism. Physical chemists in particular became interested in my work because it provided a conceptual framework for dealing with the kinds of complex situations that come up so often in their world. A monograph, in 1982,[5] and a volume of *Advances in Chemical Physics*, in 1985,[6] were devoted entirely to applications of the projection operator method. And, a recent application in solid-state physics was discussed by Lax et al.[7]

1. **Prigogine I.** *Nonequilibrium statistical mechanics.* New York: Interscience, 1962. (Cited 700 times.)
2. **van Hove L.** Quantum mechanical perturbations giving rise to a statistical transport equation. *Physica* 21:517-40, 1955. (Cited 510 times.)
3. **Zwanzig R.** Statistical mechanics of irreversibility. *Lectures in theoretical physics* (Boulder). New York: Interscience, 1961. (Cited 665 times.)
4. **Mori H.** Transport, collective motion and Brownian motion. *Prog. Theor. Phys. Suppl.* 33:423-55, 1965. (Cited 1,755 times.)
5. **Grabert H.** Projection operator techniques in nonequilibrium systems. *Springer tracts in modern physics, volume 95.* Berlin, Germany: Springer, 1982.
6. **Evans M W, Grigolini P & Pastori-Parravicini G,** eds. Memory function approaches to stochastic problems in condensed matter. (Whole volume.) *Advan. Chem. Physics* 62, 1985.
7. **Lax M, Cai W, Hu P, Zheng T F & Marchetti M C.** Coupling between 2-D electrons in quantum wells and 3-D phonons. *Ann. NY Acad. Sci.* 581:195-206, 1990.