ASSESSING THE QUALITY OF APPROXIMATE QUANTUM DYNAMICS IN CONDENSED PHASE

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Time correlation functions provide a convenient language for analyzing the rich variety of dynamical processes in condensed phase, including the rate of electron or proton transfer processes, vibrational relaxation, molecular diffusion, etc. However, the calculation of the corresponding time correlation function of systems where quantum behavior is significant is particularly challenging due to the intractability of the underlying quantum dynamics of a multidimensional system. As a result, approximate methods become in this context unavoidable.

In this talk, we discuss a general protocol for analyzing the quality of approximate quantum time correlation functions of non-trivial systems in many dimensions. This approach is motivated by the generalized deconvolution of the Kubo transformed correlation function onto a time correlation function at a given value of τ in imaginary time ($0 < \tau < \beta\hbar$), which leads to a series of sum rules that allow us to link derivatives of different order in the corresponding correlation functions. We focus on the case when $\tau = \beta\hbar/2$ for which all deconvolution kernels become real valued functions and their asymptotic behavior at long times exhibit a polynomial divergence. It is then shown that thermally symmetrized static averages, and the averages of the corresponding time derivatives, are ideally suited to investigate the quality of approximate correlation functions at successively larger, and up to arbitrarily long, times. This overall strategy is illustrated analytically for a harmonic system, and numerically for a multidimensional double-well potential and a Lennard-Jones fluid representing liquid neon at 30 K.