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Transition State Theory: Variational Formulation, Dynamical Corrections, and Error Estimates ERIC VANDEN-EIJNDEN, Courant Institute — Transition state theory (TST) is discussed from an original viewpoint: it is shown how to compute exactly the mean frequency of transition between two predefined sets which either partition phase space (as in TST) or are taken to be well separate metastable sets corresponding to long-lived conformation states (as necessary to obtain the actual transition rate constants between these states). Exact and approximate criterions for the optimal TST dividing surface with minimum recrossing rate are derived. Some issues about the definition and meaning of the free energy in the context of TST are also discussed. Finally precise error estimates for the numerical procedure to evaluate the transmission coefficient κ_S of the TST dividing surface are given, and it shown that the relative error on κ_S scales as $1/\sqrt{\kappa_S}$ when κ_S is small. This implies that dynamical corrections to the TST rate constant can be computed efficiently if and only if the TST dividing surface has a transmission coefficient κ_S which is not too small. In particular the TST dividing surface must be optimized upon (for otherwise κ_S is generally very small), but this may not be sufficient to make the procedure numerically efficient (because the optimal dividing surface has maximum κ_S, but this coefficient may still be very small).

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