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*Perspective*

# Perspective on "The transition state method"

## Wigner E (1938) Trans Faraday Soc 34: 29–41

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**Abstract.** A perspective is provided on Wigner's classic paper on transition-state theory (TST). After providing a brief review of the historical context of this work, we review its key contributions including Wigner's dynamical perspective on TST, the fundamental assumption of TST, and the upper-bound property of classical TST. A discussion is also presented of subsequent progress in the field, which was stimulated by this work. This progress includes the following:

1. Demonstrations of the validity of the fundamental assumption for classical systems.
2. Further investigations into the classical foundations of TST that helped elucidate relationships between classical trajectories and TST.
3. The development of a variational form of the theory.
4. The development of variational TST into a quantitative tool for predicting rate constants.
5. The search for an "exact" quantum mechanical version of TST.
6. The development of TST-like expressions for the exact quantum mechanical rate constant.
7. The extension of TST to reactions in condensed phases.

**Key words:** Transition-state theory (TST) – Variational TST (VTST) – Fundamental assumption of TST – Quantum mechanical TST

## 1 Historical context and perspective

The early to mid 1930s was a time of intensive activity in the formulation of transition-state theory (TST). Laidler and King [1] have provided an excellent review of the early history of TST, tracing the development of rate theories using treatments based upon thermodynamics, kinetic theory, and statistical mechanics, and focusing on Eyring's 1935 contribution to the formulation of TST [2]. A snapshot of the state of the development of TST and some of the controversy surrounding it in 1937 is captured in volume 34 of the *Transactions of the Faraday Society*, which was published in 1938. This volume is a compilation of papers and discussion comments from the 1937 General Discussion of the Faraday Society on "Reaction kinetics" and it includes contributions from many of the founders of TST (e.g., E. Wigner, H. Eyring, M. Polanyi, and M.C. Evans). Wigner's contribution [3] presented one of two prevailing perspectives on TST at that time – a dynamical perspective that is firmly based on a statistical mechanical approach to formulating the theory. The subsequent paper in this volume was a presentation of Eyring's alternative perspective on "The theory of absolute reaction rates" [4], which is based upon quasiequilibrium thermodynamics. A historical discussion of the 1937 General Discussion of the Faraday Society has recently been presented by Miller [5], including a detailed analysis of Wigner's seminal contribution. The current paper parallels Miller's review and presents a complementary view that should help provide an even broader perspective on Wigner's important contribution.

In the early days of TST, it was apparent that there was great hope that the method would allow quantitative predictions of reaction rate constants. This hope was reflected in the title of Eyring's contribution to the 1937 General Discussion of the Faraday Society which refers to the ability of the theory to provide the absolute magnitude of the pre-exponential factor and thereby the absolute value of the rate constant. In addition, there was much activity comparing TST with recent experimental studies. As stated by Wigner in the discussion comments to this volume "there seems to be, however, a discrepancy between theory and experiment in practically all cases in which a numerical comparison is possible" [6]. In the same discussion comment, Wigner made the prescient observation that energy surfaces may be more complicated than assumed. Largely because of the inability to accurately predict reaction energetics (particularly barrier heights), the realization of the hope of using TST to quantitatively predict rate constants waited nearly 40 years.

The popularity of TST during the intervening years (1940s–1960s) was largely due to Eyring's thermodynamic formulation that provided the basis for correlating and interpreting kinetic data (including isotope effects). A testament to the popularity of the thermodynamic formulation of TST was the development of the field of thermochemical kinetics [7]. In the 1970s, as it became possible to accurately predict potential-energy surfaces using ab initio electronic structure methods and to perform accurate quantum dynamical calculations, interest was revived in developing methods to calculate absolute rate constants from first principles. During this time the approximations in TST were examined more carefully to understand when TST could be expected to give quantitative predictions of rate constants. Wigner's 1938 work played a crucial role in the revival of the hope to develop TST into an accurate, predictive tool and in advancements in this area over the last 25 years.

## 2 Key contributions

The major contribution of the title work was an exceptionally clear exposition of the approximations inherent in TST. Wigner first stated that elementary chemical reactions were considered in which the (equilibrium) Maxwell–Boltzmann velocity and energy distribution was maintained, and for which the potential-energy surface was known. He then went on to state "that the transition state method is based, in addition to well-established principles of statistical mechanics, on only three assumptions, two of which are generally accepted." The first two assumptions were those that Wigner categorized as "generally accepted": the electronic adiabaticity of the reaction and the adequacy of classical mechanics to treat the motion of the nuclei. The third assumption has become known as the fundamental assumption, the fundamental dynamical assumption, or the no-recrossing assumption of TST.

### *2.1 The fundamental assumption of TST*

Wigner first defined a dividing surface, through the saddle point of the potential-energy surface and perpendicular to the direction of steepest descent, through which all reactive trajectories must pass. Wigner then identified the fundamental dynamical assumption as follows: a reactive trajectory originating in reactants must cross the dividing surface only once and proceed to products. The TST expression for the rate constant could then be expressed using equilibrium statistical mechanics without the need to calculate classical trajectories.

### *2.2 The upper-bound principle*

In analyzing the validity of the fundamental dynamical assumption, Wigner pointed out the effect of trajectories that recross the dividing surface: the TST rate constant "will lead, in general, to too high values of the reaction rate and should be corrected by a factor $\gamma$, smaller than 1, ...". He also provided a compelling argument for why $\gamma$ will go to 1 with decreasing temperature for activated reactions. Thus, he showed that classical TST is accurate (for reactions with barriers) at sufficiently low temperatures and its overestimation of the exact classical rate constant generally increases with increasing temperature.

### *2.3 Variational TST*

In the final section of the paper, Wigner discussed the application of TST to three-atom recombination reactions, $A + B + C \rightarrow AB + C$. For these barrierless reactions, Wigner suggested using dividing surfaces that are more complicated functions of both coordinates and momentum (e.g., dividing surfaces depending on an energy), instead of just spatial coordinates. This idea was developed in more detail in a slightly earlier paper by Wigner [8] (the "received" dates on the two publications differ by only 11 days). In the 1937 paper, Wigner presented the obvious corollary to the upper-bound principle, that the best estimate of the rate constant can be obtained by optimizing the dividing surface to minimize the rate constant. In the 1937 paper, Wigner went further to state that the accurate (classical) rate constant is the minimum value of the TST rate constant for a properly chosen dividing surface.

## 3 Subsequent progress in the field

Advancements in TST have been well documented in the literature over the past 23 years [9–16]. Much of the work on TST has focused on understanding the dynamical foundations of the theory and the extension of the theory to allow for quantitatively accurate estimates of rate constants. Advancements in these areas can be attributed to the fact that the TST expression for the classical equilibrium rate constant can be formulated by making a single approximation, Wigner's fundamental assumption.

### *3.1 Accuracy of the fundamental assumption of TST*

As computational capabilities increased in the 1960s and 1970s, it became possible to test the accuracy of Wigner's fundamental assumption by comparing classical TST with the results of accurate classical trajectory studies. The first such comparisons can be attributed to Bunker's work on unimolecular reactions [17, 18]. Karplus and coworkers [19–21] performed the first comparisons for bimolecular reactions. Many tests of conventional TST were performed on atom–diatom ($A + BC$) reactions [22–30], and these tests confirmed Wigner's argument that classical TST is accurate at low temperatures (or equivalently at energies close to and above the barrier). An interesting observation was that the validity of TST extended over a broader energy range for the three-dimensional $H + H_2$ reaction compared to the collinear reaction [23]. The implication is that classical trajectories in the higher-dimensional phase space are less likely to make it back to the dividing surface to recross.

Wigner's dynamical perspective on TST also led naturally to the development of efficient methods to calculate the transmission coefficient (or Wigner's recrossing factor $\gamma$). This approach is outlined by Keck [31, 32] for recombination reactions and by Anderson and coworkers [33, 34] for bimolecular reactions. This work helped elucidate the connection between classical TST and classical trajectory calculations.

The fact that classical TST can be derived from a single dynamical assumption was the impetus for researchers in the 1970s to begin examining in detail the classical foundations of TST. This area of research was initiated by the paper by Pechukas and McLafferty [22]. In this work, they described conditions (e.g., features of the potential and energy range above threshold) such that classical trajectories will not recross the dividing surface and classical TST will reproduce the exact classical rate constant. Subsequent research by Pechukas and Pollak [10, 35–37] further elucidated the relationship between classical trajectories and TST. This work showed that for collinear A + BC reactions, the best possible TST dividing surfaces for a microcanonical ensemble are so-called periodic-orbit dividing surfaces, which are generated by classical trajectories that vibrate back and forth between two equipotentials in the interaction region. Furthermore, Pechukas and Pollak [37] demonstrated that for collinear A + BC reactions TST is exact for energies at which the potential surface admits only one periodic-orbit dividing surface.

### *3.2 Variational TST*

Although a variational formulation of TST was not presented in Wigner's 1938 paper, it is clear that the development of a variational approach to TST follows naturally from the upper-bound principle of TST. This was also recognized in the 1930s by Horiuti [38], who adopted the dynamical perspective and developed a variational approach to TST. These ideas were extensively developed by Keck [39, 40] to formulate a more formal variational procedure for finding the best dividing surface. As already mentioned for collinear A + BC reactions periodic-orbit dividing surfaces are the optimum configuration-space dividing surfaces for a microcanonical ensemble. For reactions with larger numbers of degrees of freedom, practical techniques have been developed based upon dividing surfaces that are required to be orthogonal to the minimum energy path [27] (see Ref. [15] for further discussion and review). This approach has also proved useful for including approximate quantum mechanical effects (see later). In numerical tests, the variational TST (VTST) procedures were seen to give practical improvement over conventional TST, in which the dividing surface is constrained to pass through the saddle point (see Ref. [15] for a review of tests of classical VTST).

### *3.3 Practical methods for predicting absolute rate constants*

As computational capabilities continued to improve in the 1970s and 1980s, it became possible to calculate potential-energy surfaces sufficiently accurately to allow accurate predictions of rate constants. This advancement, as well as progress in the development of TST itself, rekindled hope of developing TST into a tool that would provide quantitative accuracy for computed rate constants. For many reactions of practical interest, particularly those involving hydrogen-atom transfer, quantitative accuracy in computed rate constants requires that quantum mechanical effects be included in the theory; however, as Wigner already realized in 1938, the rigorous implementation of the fundamental dynamical assumption in a quantum mechanical theory is difficult because "one cannot speak about the mean velocity at the activation point. (Heisenberg's indetermination principle)" [3]. The earliest attempt to develop an approximate treatment of quantum effects in chemical reaction rate constants is that due to Wigner [41]. By considering the lowest-order terms in an expansion in $\hbar$ of the phase-space probability distribution function around the saddle point, Wigner developed a separable approximation, in which partition functions for bound modes are quantized and a correction is included for quantum motion along the reaction coordinate. Eyring [2] systematized the procedure of quantizing the partition functions for the bound modes of the reactants and the transition state, and this became the standard approach to including quantum mechanical effects. In the 1960s and 1970s, tests of TST against accurate quantum mechanical results indicated the deficiency of this separable approach. The failure of the standard approach was attributed largely to nonseparable effects, particular on quantum mechanical tunneling [42, 43].

Encouraged by the validity of the fundamental assumption of TST for classical TST and VTST, efforts were made to develop improved methods for including quantum mechanical effects into TST. One approximate approach is to quantize the partition functions for bound modes and focus on developing improved methods for tunneling that include some aspects of the multidimensional nature of the tunneling process. The development of tunneling methods that are consistent with VTST was greatly facilitated by the realization that the adiabatic theory of reactions is equivalent to one form of variational TST (microcanonical VTST) when the reaction coordinate is treated classically [27, 44]. In addition, an important advancement was the development of methods that consistently treat threshold contributions in the quantized partition functions and tunneling correction factors [45]. The first successful nonseparable tunneling correction was that developed by Marcus and Coltrin [46] for the collinear H + $H_2$ reaction. Marcus and Coltrin sought the tunneling path with the smallest tunneling action integral and thereby least exponential damping. They found the optimum tunneling path for the H + $H_2$ reaction was the path of turning points of the quantized adiabatic vibrations, where the turning points are chosen so that the path "cuts the corner" and reduces the length of the tunneling path. This method was subsequently extended to other systems with small-to-moderate reaction-path curvature [44, 47, 48]. The idea of finding the optimum tunneling path was further extended to systems with large reaction-path curvature in the least-action tunneling method [49]. A more detailed review of tunneling methods implemented within this framework is presented elsewhere [48, 50]. With the implementation of these new tunneling methods and demonstration of their accuracy [51, 52], quantum mechanical VTST has turned into a standard tool for studies of the kinetics of gas-phase reactions.

The success of the fundamental assumption of TST also provided impetus to develop a rigorous quantum mechanical TST, i.e., a quantum mechanical theory that employs the fundamental assumption as its only approximation and treats the problem as nonseparable [10, 53–55]. Although semiclassical approximations to the quantum mechanical TST expression of Miller were developed and successfully applied to the H + $H_2$ reaction [56, 57], by 1993 it was concluded that no rigorous quantum mechanical version of TST exists which does not require a solution of the full multidimensional reaction dynamics [58]. The effort to develop a rigorous quantum mechanical TST was productive as it provided the foundation for the development of accurate quantum mechanical methods to directly calculate thermal rate constants. (See Miller [58, 59] and references therein.) These methods are not a form of TST (since they do not invoke the fundamental assumption), but exploit the use of short-time quantum dynamics in the interaction region to calculate the reactive flux through the transition-state dividing surface. In this sense, this approach is the quantum analog of the classical approach of Keck and Anderson [31–34]. Further advances in reaction rate theory, which have benefited from research and advances in TST, are documented in Miller's recent paper [5].

### 3.4 *Reactions in liquids*

TST has also been widely used to treat reactions in condensed phases. Wigner's dynamical perspective has particularly had an impact on the extension of TST to reactions in liquids. Most applications to liquid-phase reactions have used the thermodynamic formulation of TST [60], which includes the effects of the condensed phase on reaction free energies in an approximate manner. Chandler [61] provided a more rigorous formulation of classical TST for liquids. The new element introduced by the liquid phase is collisions of solvent molecules with the reacting species that can lead to recrossings of the dividing surface and a breakdown of the fundamental assumption. A recent review [16] documents many more advances in the extension of TST to the kinetics of condensed-phase processes.

## Summary

In 1981 Pechukas wrote [12] "Transition state theory (TST) is 50 years old, and it is a tribute to the power and subtlety of the theory that work on the foundations of it is still a respectable and popular activity". To a large extent, this is still true today. The development and advancement of TST can be credited to many workers over the years. H. Eyring, M. Polanyi, and E. Wigner were all involved with early development of the theory and Eyring's work in particular played a major role in popularizing TST in the early years. Many of the advancements in TST over the last 20-plus years were aimed at understanding the foundations of the theory and developing TST into a more rigorous framework for accurately predicting rate constants. These advancements have drawn from many contributions in the field, some of which are described in this special issue; however, the foundation for these advancements can be traced back to Wigner's classic work that clearly described the dynamical nature of the theory and the one, fundamental approximation needed to derive the classical TST rate constant.

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