
FEMTOCHEMISTRY

Ultrafast Dynamics of the Chemical Bond

Volume I

Ahmed H. Zewail

World Scientific Series in 20th Century Chemistry

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Volume I

WORLD SCIENTIFIC SERIES IN 20TH CENTURY CHEMISTRY

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by Kenneth S. Pitzer

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by Glenn T. Seaborg

Vol. 3: Femtochemistry: Ultrafast Dynamics of the Chemical Bond
by Ahmed H. Zewail

To all who have made it possible:

My family, my mentors, and my students.

-- A. H. Z.



General Introduction

The study of chemical events that occur in the femtosecond time scale is the ultimate achievement in half a century of development and, although many future events will be run over the same course, chemists are near the end of the race against time.

Lord George Porter

In *Principia Mathematica*, Isaac Newton captured the essence of one of the most fundamental problems relating to the nature of the chemical bond with the following words: *I wish we could derive the rest of the phenomena of Nature by the same kind of reasoning from mechanical principles, for I am induced by many reasons to suspect that they may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled toward one another, and cohere in regular figures, or are repelled and recede from one another.*¹ After centuries, this problem of how atoms behave due to the forces between them remains at the heart of chemistry and biology.

This collective work on the dynamics of the chemical bond – femtochemistry – reflects contributions we have made to the field over the past fifteen years. I do not use “we” here rhetorically; it is truly meant to acknowledge the efforts of many Caltech graduate (and undergraduate) students, postdoctoral fellows, and visiting associates (page xxiii). While putting together these volumes, I recalled many wonderful memories of colleagues, members of the group, and of exciting snapshots of events which led to the significant advances in our research and to some discoveries of the unknown!

From the systematics and chronology of the volumes, it may appear that this work was part of a grand plan and that femtochemistry emerged from continuous strides of successes. This was not really the case. I only had the intuition to ask “simple” questions and to design experiments directly addressing phenomena of interest. Following this intuition, we went after what appeared exciting to us. The coherence evident in the volumes reflects our continued interest in real-time molecular dynamics, and happily defines the field of femtochemistry with its basic constituents: Intramolecular vibrational-energy redistribution (IVR), reaction rates, and transition-state dynamics. They all occur on the ultrashort time scale, 10^{-12} second (picosecond, ps) to 10^{-15} second (femtosecond, fs).

In constructing the two volumes, I followed the theme of the Sir Cyril Hinshelwood lecture series I gave at Oxford in November and December of 1991. The concepts involved in describing or probing the ultrafast dynamics of the chemical bond are covered first in a general way and then in more detail. We also discuss the fundamentals and present the different techniques developed for direct-time resolution of the underlying dynamics. Elementary and more complex systems are examined to illustrate the scope of applications in the studies of structures and dynamics in different phases and substances on the appropriate time scale.

This century has witnessed great strides in *space* and *time* resolutions, down to the atomic-scale limit, providing chemists, biologists, and physicists with unprecedented opportunities for seeing microscopic structures and dynamics.²⁻⁴ From the early days of molecular structure determination, led by Max von Laue, the Braggs (father, William H., and son, W. Lawrence), Linus Pauling, and others, X-ray crystallography has continued to be an important tool for mapping the *static* nature of chemical bonds in substances. More recently, major breakthroughs have been made in determining the structure of life molecules: DNA, proteins, nucleic acid-protein complexes, viruses and the photosynthetic reaction center (see the articles by Pauling, Max Perutz, Francis Crick, Alexander Rich in Ref. 5). Gas-phase electron diffraction has also played a major role in elucidating molecular structures.⁶ In addition to these diffraction techniques, spectroscopic methods (microwave, optical and NMR) have become basic tools for structural determination, and are discussed in essentially all textbooks on spectroscopy. The powerful 2-D NMR techniques have added a new dimension⁷ — the ability to obtain structures of proteins *in situ*.

For dynamics to be observed at the atomic-scale resolution of motion, not only must the structures be determined, but also their change with time.⁸ Near the turn of this century, Svante Arrhenius's famous work provided a *macroscopic* description of the change in rates of chemical reactions with temperature; the rate constant, $k = A \exp(-E_a/kT)$, describes the time scale at a given temperature T ; A is a pre-exponential factor and E_a is the energy of activation. Only after the Second World War did time resolution, on the scale of 10^{-3} to 10^{-6} s, allow for studies of "fast reactions" (see the article by Lord George Porter in Ref. 5) or what Manfred Eigen⁹ called "Immeasurably fast reactions", on the scale of 10^{-9} s.

Femtochemistry is concerned with the time resolution of the most elementary motion of atoms during chemical change, bond breaking and bond making on the femtosecond time scale. Just as X-rays probe the distance scale for molecular structure, ultrashort laser pulses probe the time scale for the dynamics of the chemical act itself — the ephemeral (less than ps) transition-state structures, central to chemical reactivity. With such atomic-scale time resolution, one reaches the "limit of time" in chemistry and biology. In Ref. 10, Porter describes the state of the art in the quotation given on the first page. The history of time resolution in chemistry and biology is fascinating and Figs. 1 and 2 present only some of the relevant strides made over this century — the arrow of time tracks world events! The progress of our studies at Caltech is described in Table III of the first article in Volume I. Some of the diverse applications and advances in studies of dynamics in chemistry and biology are represented in two recent books and a special issue of the *Journal of Physical Chemistry* (Refs. 10–12).

For some time, theory was ahead of experiment in the studies of microscopic molecular reaction dynamics. The effort started shortly after the famous publication of the Heitler-London quantum-mechanical treatment (in 1927) of the hydrogen molecule.¹³ One year later (1928), at Arnold Sommerfeld's Festschrift (60th birthday), Fritz London presented an approximate expression for the potential energy of triatomic systems, e.g., H_3 , in terms of the coulombic and exchange energies of the "diatomic" pairs.¹⁴ In 1931 Henry Eyring and Michael Polanyi,¹⁵ using the London equation, provided a semiempirical calculation of a potential energy surface (PES) of the $H + H_2$ reaction describing the journey of nuclei from the reactant state of the system to the product state, passing through the crucial transition state. The birth of "reaction dynamics" resulted from this pioneering effort and, for the first time, one could think of the PES and the dynamics on it — the path of the reaction (Fig. 3) from reactants to products, through valleys

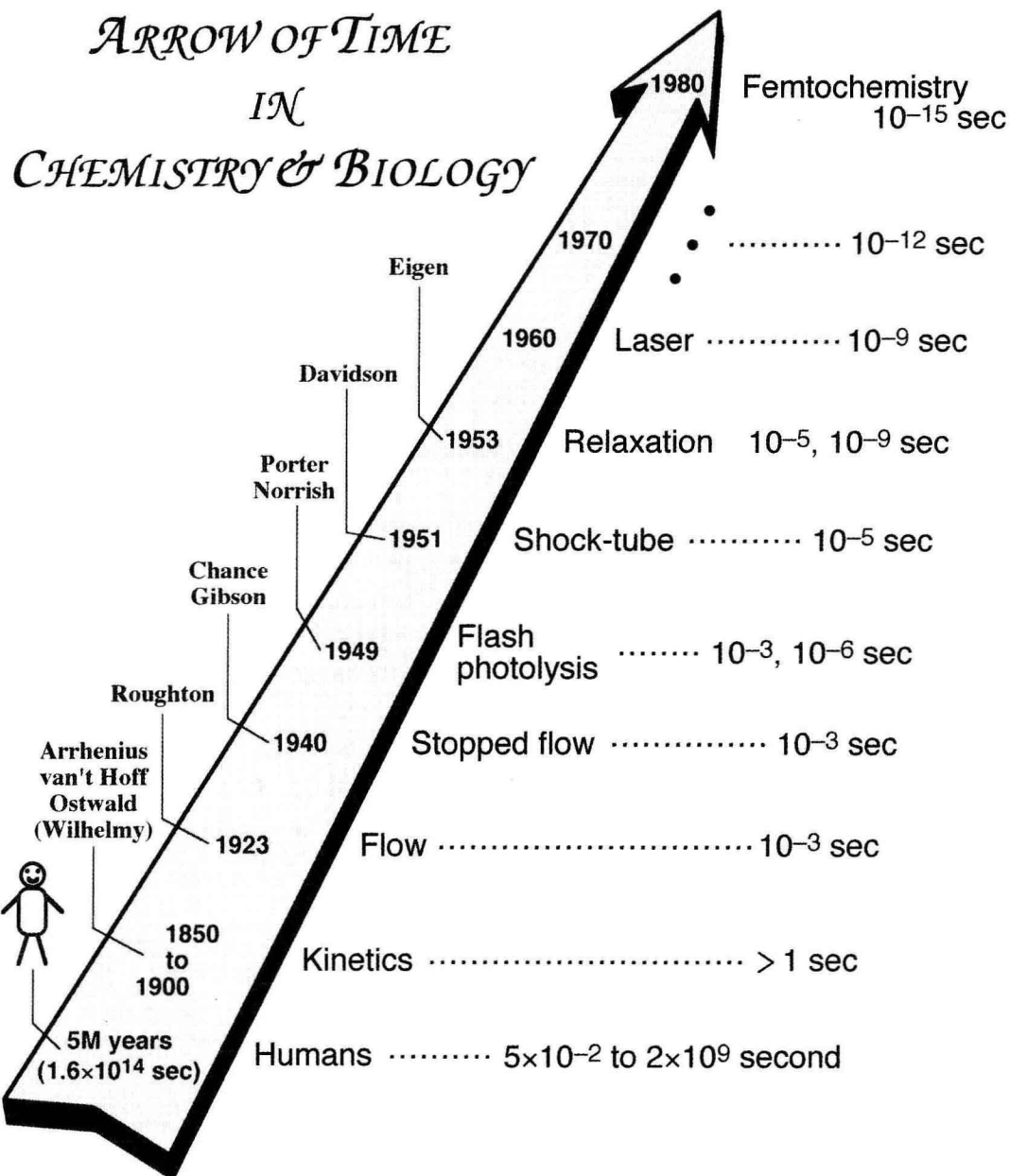


Fig. 1. Historical evolution of time resolution over a century, representing the "arrow of time" in the studies of *fast* and *ultrafast* reactions in chemistry and biology (see text).

and mountains, with the transition state at the saddle point. Figure 4 reproduces some results of the theoretical studies of the dynamics and the time scale for elementary reactions — *in those days, often, expressed in atomic units of time!* With this picture in mind, some new concepts in reaction dynamics¹⁶ evolved over the years and John Polanyi, the son of Michael, played a central role in their evolution.¹⁷

Nobody could have dreamed in the 1930s of observing the transient molecular structures of a chemical reaction, since the time scale for those far-from-equilibrium activated complexes in the transition state was estimated to be less than picosecond. Such a time scale was rooted in the theory developed for the description of reaction rates. In 1935, Eyring¹⁸ and, independently, M. G. Evans and M. Polanyi¹⁹ formulated *transition-state theory*, which gave an explicit expression for Arrhenius' pre-exponential factor; with the energy of activation known from the thermodynamic treatment of J. H. van't Hoff and Arrhenius and with the pre-exponential factor explicitly derived by invoking statistical mechanics, the theory of reaction rates was completed. The theory made four assumptions,^{18,19} including equilibration of the activated complexes, and gave an analytical formula for the rate constant with a "frequency" for the passage through the transition state. This frequency factor typically corresponds to $\sim 10^{-13}$ second, the time scale of vibrations. From a classical mechanical point of view, this estimate is consistent with knowledge of the velocities of nuclei and distance changes involved in a chemical reaction: For a velocity of one kilometer per second and a distance of one angstrom, the time scale is about 100 fs. Molecular dynamics simulations have shown a range for the time scales, ps to fs, depending on the reaction; an example from the work of Martin Karplus and colleagues (1965) is presented in Fig. 4.

Experimentally, great progress has been made over the past three decades (see the articles by Polanyi and Dudley Herschbach, in Refs. 5, 17, 20 and the article by Yuan Lee²¹). Two technological advances that have helped revolutionize experimental studies of molecular reaction dynamics are molecular beams and lasers. A large body of results has accumulated involving the characterization of such "*before*" (reactant) and "*after*" (product) observables and has led to a deeper understanding of reactive processes. The time scale was deduced from knowledge of the angular distribution of products. In addition to the large number of crossed molecular beams and chemiluminescence studies, an expanding literature of crossed molecular beam-laser results has probed dynamics via careful analyses of product internal energy (vibrational and rotational) distributions and steady-state

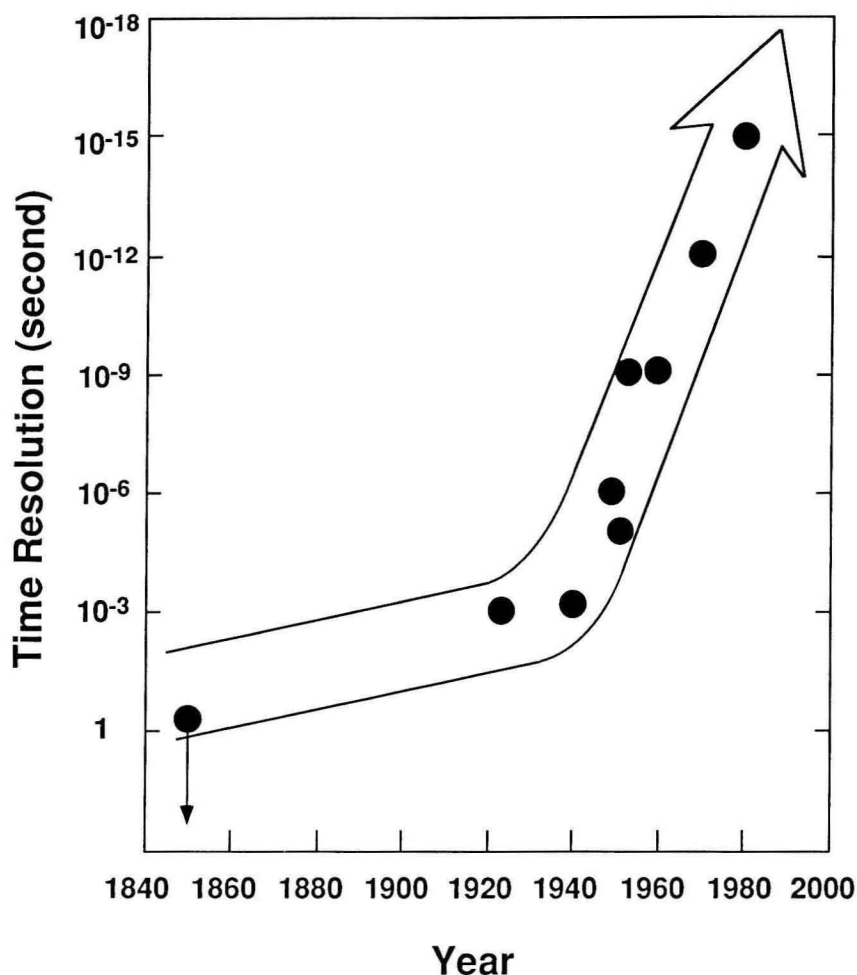


Fig. 2. The data of Fig. 1 presented in a plot of the time resolution (logarithmic scale) vs. year. The dramatic change, ironically after World War II, is due to advances in electronics and optics.

alignment and orientation of products (see the article by Richard Zare and Richard Bernstein in Ref. 22).

To probe the transition-state region more directly, various techniques have been advanced, thus initiating transition-state spectroscopy (see the article by Polanyi in Ref. 5). Emission, absorption, scattering and electron photodetachment are some of the novel concepts presented for such "time-integrated" spectroscopies. The key idea was to obtain, as James Kinsey²³ puts it, *short-time dynamics from long-time experiments*.

The resolution in time of the elementary dynamics (femtochemistry) offers an opportunity to observe a molecular system in the continuous process of its evolution from reactants to transition states and then to products. Important to such transformations, as mentioned before, are three fundamentals of the dynamics, namely: (1) intramolecular vibrational-energy redistribution (IVR), (2) reactant-state to product-state rates and (3) the nature of transition states. Generally, the time scale for IVR is on the order of picoseconds, the rates are tens of picoseconds and longer, and the “lifetime” of transition-state species is picoseconds to femtoseconds. Because the phenomena are ultrafast in nature, the sensitivity in femtochemistry is enhanced by orders of magnitude.

IVR is a description of how energy *initially localized* in a specific mode of vibrational motion is shared among other types of accessible nuclear motion. When a large number of states and couplings are involved, the average effect of redistribution can be described in terms of simple kinetics and rate constants. However, this process of IVR is fundamentally a manifestation of the loss of quantum coherence imposed on the initial state via the preparation process. The relevance of IVR to reaction dynamics lies in a possible reduction of the dimensionality of the general problem — mode or bond specific dynamics. If IVR is fast and complete, then the reaction is characterized only by conserved quantities, the energy and total angular momentum. Under these conditions, the reaction is said to be *statistical* and statistical theories of reaction rates may be applied. If the rate of reaction is intrinsically faster than the rate of energy redistribution, then one would expect the outcome of the reaction to be deterministic — the initial state influences both the rate and the product distributions. A single rate constant cannot be defined, and all possible combinations of initial and final quantum states would have to be considered for a complete description of the reaction.

IVR has a long history and has played a major role in the early theories of reaction rates since the 1920s through the work of F. A. Lindemann, Hinshelwood, O. K. Rice, H. C. Ramsperger, L. S. Kassel, R. A. Marcus and others.²⁴ Although IVR was not directly observed, it was invoked as an essential part of the understanding of energy transport and relaxation in gases, liquids and solids. For laser chemists the interest stems from the hope that if enough energy can be localized in a bond for a period of time longer than the reaction time, one may achieve selective bond fission.²⁵ Hence, a key question is the following: What is the time scale for energy redistribution and what determines its selectivity or lack thereof?

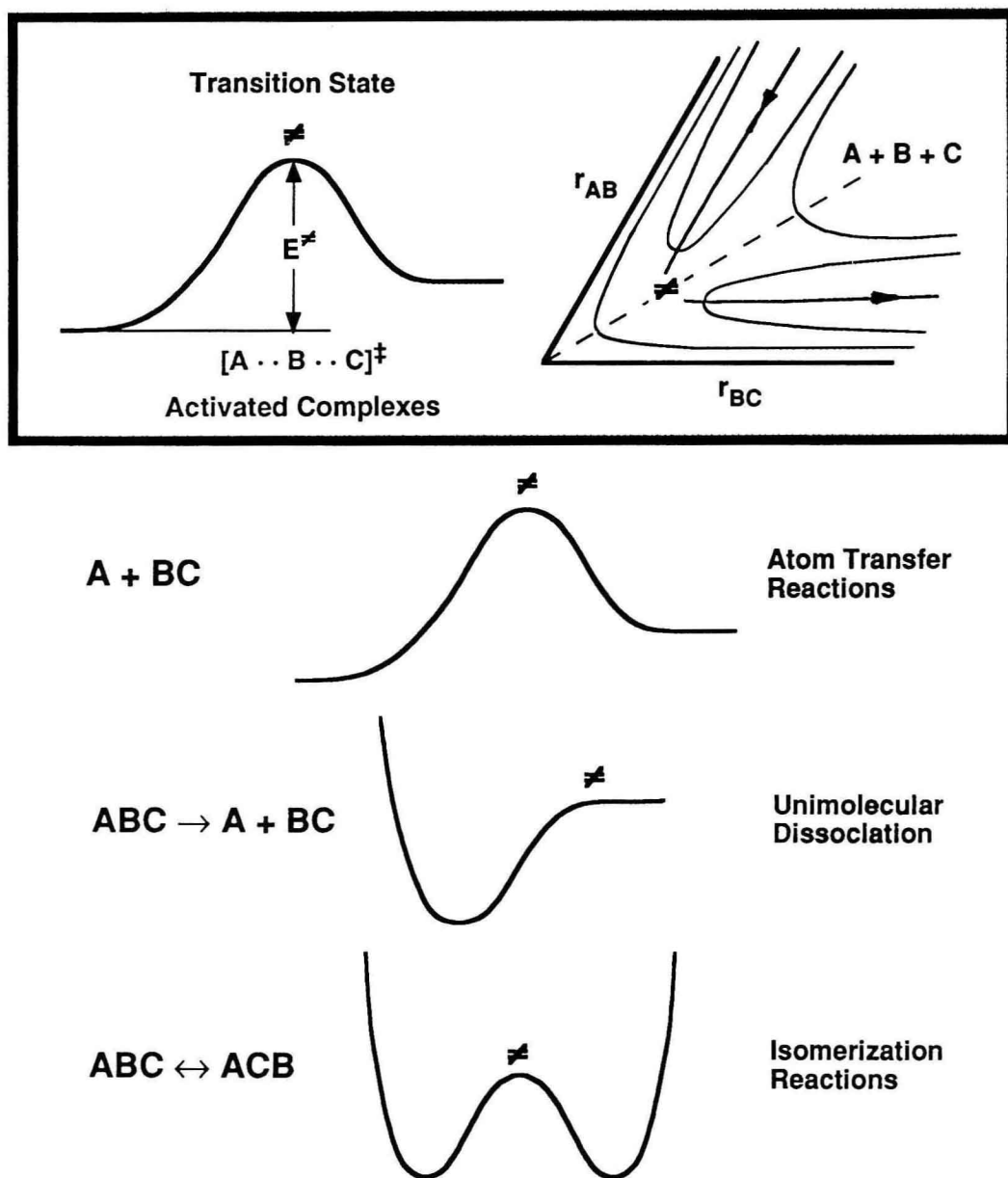


Fig. 3. The concept of the potential energy surface for a chemical reaction. The transition state is denoted by \ddagger and the activated complex by $[A \cdots B \cdots C]^\ddagger$. This symbol (\ddagger), which is conventionally used, was introduced in an interesting episode. Eyring, in his handwritten manuscript, used an asterisk, his secretary typed it as \pm sign, the printer set it as the Lorraine cross \ddagger . As told by K. Laidler, Eyring was later amused to learn that \ddagger is close in resemblance to the Japanese word for "crazy". Some generic potentials for different types of reactions are shown with the transition state indicated by \ddagger .

The ultrashort time scale is one common feature of the dynamics involved in IVR, reaction rates and the dynamics of transition states. Another underlying feature is the concept of *coherence*. This concept has been fundamental not only to dynamics but also to the structure of the chemical bond. Pauling's valence bond description of the H_2^+ bond in his book of 1939 involves the tracking of phase coherence between orbitals.²⁶ This phase coherence is responsible for the bonding or antibonding character of the bond. Coherence is also a key concept to diffraction experiments, such as X-ray or electron diffraction.

Coherent motion of nuclei allows one to think about reactivity in terms of time evolution, and to make the fundamental distinction between *dynamics* and *kinetics*. The dynamics relates to the actual forces bringing about motion, while kinetics is concerned with the rates; kinematics considers properties of the motion independent of forces. Normally, we speak of atom or molecule A getting close to atom or molecule B to form a new molecule C. The picture is temporal. Measurements that do not probe the motion are ultimately transformed to a time-dependent picture. As Kinsey pointed out²³ *"Because of them [developments in ultrafast dynamics], the community has begun to think about simple chemical processes in ways that were not common previously, despite the fact that the explicit ability to observe actual temporal behavior meshes quite naturally with the vocabulary in which the ordinary chemist or physicist thinks about molecular processes."*

How can one create such coherences, and how are they probed? In femtochemistry, the uncertainty in the position of the nuclei in the course of a change is reduced to the sub-angstrom scale. This is to be contrasted with the extended wave function one obtains from the solution of the time-independent Schrödinger equation, characteristic of "long-time" experiments. In fact, physicists in the 1920s were concerned with the connection between such extended states and states of the motion described by Isaac Newton. Erwin Schrödinger wrote a letter to Hendrik Lorentz in 1926 to emphasize the urgent need for a theoretical construction of wave groups [or wave packets] which mediate the transition to macroscopic mechanics of Newton.²

In more recent times, it has been shown that the wave packet approach represents a clear space of the motion where one can directly describe the time evolution. Eric Heller made a significant step forward in formulating such a description.²⁷ With fast computers it became possible to actually solve the Schrödinger equation, as shown by Ronnie Kosloff, and to compare theory