

Theoretical Chemistry

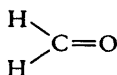


Fig. 3. Formaldehyde. The double line between oxygen and carbon indicates a double bond.

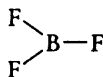


Fig. 4. Boron trifluoride. Each bond is polar, but the net of the three yields zero dipole for the molecule.



Fig. 5. Ethyne. The triple line between the carbons indicates a triple bond.

cause of its linear symmetric structure, ethyne has no net dipole moment. The exact nature of the vibrations and rotations will depend upon the connectivity of the atoms within the molecule. As with all molecules, there is a characteristic energy associated with each vibrational and rotational motion; thus, the vibrations and rotations may be studied by a variety of spectroscopic techniques.

BIBLIOGRAPHY

- ATKINS, P. W. *Physical Chemistry*, 5th ed.; New York: Freeman, 1994.
- McMURRY, J.; FAY, R. C. *Chemistry*; Englewood Cliffs, NJ: Prentice Hall, 1995.

KELLY S. GRIFFITH

Theoretical Chemistry

Theoretical chemistry is concerned with the use of quantum mechanics (see QUANTUM THEORY), classical mechanics, and statistical mechanics to understand the structures and dynamics of chemical systems and to correlate, understand, and predict their thermodynamic and kinetic properties (see BIOENERGETICS; KINETICS; THERMOCHEMISTRY). Modern theoretical chemistry may be divided roughly as follows:

1. Chemical structure
 - a. Electronic structure, potential energy surfaces, and force fields

- b. Vibrational-rotational motion
 - c. Equilibrium properties of condensed-phase systems and macromolecules
2. Chemical dynamics
 - a. Bimolecular kinetics and the collision theory of reactions and energy transfer
 - b. Unimolecular rate theory and metastable states
 - c. Condensed-phase and macromolecular aspects of dynamics

A critical issue that crosses all boundaries is the interaction of matter and radiation, since spectroscopic experiments are used as both structural and dynamic probes, and they must be understood theoretically. There are also many subfields of theoretical chemistry—e.g., biomedical structure-activity relationships, the molecular theory of NUCLEAR MAGNETIC RESONANCE spectra, and electron-molecule scattering—that fit into two or more of the areas listed.

Another source of overlap among the categories is that some of the techniques of theoretical chemistry are used in more than one area. Thus, statistical mechanics comprises the theory and the set of techniques used to relate macroscopic phenomena to those at the atomic level, and it is used in all six subfields listed. Furthermore, the techniques of quantum mechanics are used in all six subfields, and classical mechanical approximations to quantum mechanics are used profitably in all six subfields as well. Condensed-phase phenomena are often treated with gas-phase theories when solvent or lattice effects are not expected to dominate. Often progress in one subfield is made by importing techniques developed originally for use in another, but there are many specialized theories, models, and approximations as well. Thus, the outline provides a useful starting point for understanding the main areas of current work in theoretical chemistry.

Because quantum and statistical mechanics are also parts of physics, theoretical chemistry is sometimes considered a part of chemical physics. There is no clear border between theoretical physical chemistry and theoretical chemical physics.

Sometimes modern science is said to proceed by three modes—experiment, theory, and computation. This same division may be applied to chemistry. From this point of view, theoretical chemistry is based on analytical theory, whereas computational chemistry is concerned with predicting the properties of a complex system in terms of the laws of quantum mechanics (or classical approximations to quantum mechanics, in the domain of validity of such classical approximations) governing its constituent atoms or its constituent nuclei and electrons without using in-

intermediate levels of analytical chemical theory. Most researchers, however, consider that computational chemistry is a subfield of theoretical chemistry, and indeed computational advances and theoretical understanding are becoming more and more closely linked as the field progresses. Computational chemistry is sometimes called MOLECULAR MODELING or molecular simulation.

Perhaps the single most important concept in theoretical chemistry is the separation of electronic and nuclear motions, often called the Born-Oppenheimer approximation, after the seminal work of Max Born and Robert Oppenheimer (in 1927), although the basic idea is also due to Walter Heitler, Fritz London, and John Slater. The critical facts that form a basis for this approximation are that the electrons are coupled to the nuclei by coulomb forces, but they are much lighter—by a factor of 1,800 to 500,000—and thus, under most circumstances, they may be considered to adjust instantaneously to nuclear motion. Technically we would describe this situation by saying that a chemical system is usually electronically adiabatic. In such cases, the treatment of a chemical system is greatly simplified. For example, the H₂ molecule is reduced from a four-body problem to a pair of two-body problems: one, called the electronic structure problem, for the motion of two electrons moving in the field of fixed nuclei; and another, called the vibration-rotation problem or the dynamics problem, for the two nuclei moving under the influence of a force field set up by the electronic structure. In general, since the energy of the electronic subsystem depends on the nuclear coordinates, the electronic structure problem provides an effective potential energy function for nuclear motion. This is also called the potential energy hypersurface. The atomic force field—i.e., the set of all the forces between the atoms—is the gradient of this potential energy function.

Thus, when the separation of electronic and nuclear motion is valid, topic 1a in the chart becomes a problem in electronic structure, and the results of this step become the input function for work on topics 1b, 1c, and 2. Some important problems where the Born-Oppenheimer separation breaks down are photochemical reactions involving visible and ultraviolet radiation and electrical conductivity. Even for such cases, though, it provides a starting point for more complete treatments of electron-nuclear coupling.

In the subfield of theoretical dynamics, the most important unifying concept is TRANSITION STATE THEORY. A transition state is a fleeting (lifetime on the order of 10 femtoseconds, fs) intermediate that represents the hardest-to-achieve configuration of a molecular system in the process of transforming itself

from reactants to products. A transition state is sometimes called an ACTIVATED COMPLEX or a dynamical bottleneck. In the language of quantum mechanics, it is a resonance or metastable state, and in the language of classical mechanics, it is a hypersurface in phase space. Transition states are often studied by semiclassical methods as well; these represent a hybrid of quantum mechanical and classical equations.

In the early days of theoretical chemistry, the field served mainly as a tool for understanding and correlating data. Now, however, owing to advances in computational science, theory and computation can often provide reliable predictions of unmeasured properties and rates. In other cases where measurements do exist, theoretical results are more accurate than measured ones. Examples are the properties of simple molecules and reactions like $D + H_2 \rightarrow HD + H$. Computational chemistry often provides other advantages over experimentation too. For example, it provides a more detailed view, such as of the structure of transition states or a faster way to screen possibilities. An example of the latter is provided in the field of drug design, where thousands of candidate molecules may be screened for their likely efficiency by approximate calculations, for example, of the electronic structure or free energy of desolvation, and only the most promising candidates synthesized and tested in laboratory studies.

BIBLIOGRAPHY

- ALMLÖF, J.; TRUHLAR, D. D.; LYBRAND, T. P. *Interdisciplinary Science Reviews* 1990, 15, 252–263.
EYRING, H.; WALTER, J.; KIMBALL, G. E. *Quantum Chemistry*; New York: John Wiley, 1944.
LIPKOWITZ, K. B.; BOYD, D. B., eds. *Reviews in Computational Chemistry V*; New York: VCH Publishers, 1994.

DONALD G. TRUHLAR

Thermochemistry

Literally, *thermochemistry* is the study of the temperature changes caused by chemical reactions. Reactions that produce hot products are said to be *exothermic*, as when methane (a fuel, CH₄) burns, producing hot gases, mostly CO₂ and H₂O. Reactions that produce cold products are said to be *endothermic*, as when ammonium nitrate NH₄NO₃ dissolves in water to produce a cold solution in the cold packs applied to sprains.

By predicting a reaction's heat effects, the chemist or engineer can provide for heating or cooling sufficient to control the process. Otherwise, exothermic