

Quantum Chemistry

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Quantum chemistry applies quantum mechanics to the theoretical study of chemical systems. It aims, in principle, to solve the Schrödinger equation for the system under scrutiny; however, its complexity for all but the simplest of atoms or molecules requires simplifying assumptions and approximations, creating a trade-off between accuracy and computational cost.

Quantum chemistry, also called **molecular quantum mechanics**, is a branch of chemistry focused on the application of quantum mechanics to chemical systems. Understanding electronic structure and molecular dynamics using the Schrödinger equations are central topics in quantum chemistry.

Chemists rely heavily on spectroscopy through which information regarding the quantization of energy on a molecular scale can be obtained. Common methods are infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and scanning probe microscopy. Quantum chemistry studies the ground state of individual atoms and molecules, and the excited states, and transition states that occur during chemical reactions.

On the calculations, quantum chemical studies use also semi-empirical and other methods based on quantum mechanical principles, and deal with time dependent problems. Many quantum chemical studies assume the nuclei are at rest (Born-

Oppenheimer approximation). Many calculations involve iterative methods that include self-consistent field methods. Major goals of quantum chemistry include increasing the accuracy of the results for small molecular systems, and increasing the size of large molecules that can be processed, which is limited by scaling considerations – the computation time increases as a power of the number of atoms.

Electronic structure

The first step in solving a quantum chemical problem is usually solving the Schrödinger equation (or Dirac equation in relativistic quantum chemistry) with the electronic molecular Hamiltonian. This is called determining the electronic structure of the molecule. It can be said that the electronic structure of a molecule or crystal implies essentially its chemical properties. An exact solution for the Schrödinger equation can only be obtained for the hydrogen atom (though exact solutions for the bound state energies of the hydrogen molecular ion have been identified in terms of the generalized Lambert W function). Since all other atomic, or molecular systems, involve the motions of three or more "particles", their Schrödinger equations cannot be solved exactly and so approximate solutions must be sought.

Valence bond

Although the mathematical basis of quantum chemistry had been laid by Schrödinger in 1926, it is generally accepted that the first true calculation in quantum chemistry was that of the German physicists Walter Heitler and Fritz London on the hydrogen (H_2) molecule in 1927. Heitler and London's method was extended by the American theoretical physicist John C. Slater and the American theoretical chemist Linus Pauling to become the valence-bond (VB) [or Heitler-London-Slater-Pauling (HLSP)] method. In this method, attention is primarily devoted to the pairwise interactions between atoms, and this method therefore correlates closely with classical chemists' drawings of bonds. It focuses on how the atomic orbitals of an atom combine

to give individual chemical bonds when a molecule is formed, incorporating the two key concepts of orbital hybridization and resonance.

Molecular orbital

An alternative approach was developed in 1929 by Friedrich Hund and Robert S. Mulliken, in which electrons are described by mathematical functions delocalized over an entire molecule. The Hund–Mulliken approach or molecular orbital (MO) method is less intuitive to chemists, but has turned out capable of predicting spectroscopic properties better than the VB method. This approach is the conceptual basis of the Hartree–Fock method and further post Hartree–Fock methods.

Density functional theory

The Thomas–Fermi model was developed independently by Thomas and Fermi in 1927. This was the first attempt to describe many-electron systems on the basis of electronic density instead of wave functions, although it was not very successful in the treatment of entire molecules. The method did provide the basis for what is now known as density functional theory (DFT). Modern day DFT uses the Kohn–Sham method, where the density functional is split into four terms; the Kohn–Sham kinetic energy, an external potential, exchange and correlation energies. A large part of the focus on developing DFT is on improving the exchange and correlation terms. Though this method is less developed than post Hartree–Fock methods, its significantly lower computational requirements (scaling typically no worse than n^3 with respect to n basis functions, for the pure functionals) allow it to tackle larger polyatomic molecules and even macromolecules. This computational affordability and often comparable accuracy to MP2 and CCSD(T) (post-Hartree–Fock methods) has made it one of the most popular methods in computational chemistry.

Chemical dynamics

A further step can consist of solving the Schrödinger equation with the total molecular Hamiltonian in order to study the motion of molecules. Direct solution of the Schrödinger equation is called *quantum molecular dynamics*, within the semiclassical approximation *semiclassical molecular dynamics*, and within the classical mechanics framework *molecular dynamics (MD)*. Statistical approaches, using for example Monte Carlo methods, and mixed quantum-classical dynamics are also possible.

Adiabatic chemical dynamics

In adiabatic dynamics, interatomic interactions are represented by single scalar potentials called potential energy surfaces. This is the Born–Oppenheimer approximation introduced by Born and Oppenheimer in 1927. Pioneering applications of this in chemistry were performed by Rice and Ramsperger in 1927 and Kassel in 1928, and generalized into the RRKM theory in 1952 by Marcus who took the transition state theory developed by Eyring in 1935 into account. These methods enable simple estimates of unimolecular reaction rates from a few characteristics of the potential surface.

Non-adiabatic chemical dynamics

Non-adiabatic dynamics consists of taking the interaction between several coupled potential energy surface (corresponding to different electronic quantum states of the molecule). The coupling terms are called vibronic couplings. The pioneering work in this field was done by Stueckelberg, Landau, and Zener in the 1930s, in their work on what is now known as the Landau–Zener transition. Their formula allows the transition probability between two diabatic potential curves in the neighborhood of an avoided crossing to be calculated. Spin-forbidden reactions are one type of non-adiabatic reactions where at least one change in spin state occurs when progressing from reactant to product.

Basis Of Quantum Theory

Basic considerations

At a fundamental level, both radiation and matter have characteristics of particles and waves. The gradual recognition by scientists that radiation has particle-like properties and that matter has wavelike properties provided the impetus for the development of quantum mechanics. Influenced by Newton, most physicists of the 18th century believed that light consisted of particles, which they called corpuscles. From about 1800, evidence began to accumulate for a wave theory of light. At about this time Thomas Young showed that, if monochromatic light passes through a pair of slits, the two emerging beams interfere, so that a fringe pattern of alternately bright and dark bands appears on a screen. The bands are readily explained by a wave theory of light. According to the theory, a bright band is produced when the crests (and troughs) of the waves from the two slits arrive together at the screen; a dark band is produced when the crest of one wave arrives at the same time as the trough of the other, and the effects of the two light beams cancel. Beginning in 1815, a series of experiments by Augustin-Jean Fresnel of France and others showed that, when a parallel beam of light passes through a single slit, the emerging beam is no longer parallel but starts to diverge; this phenomenon is known as diffraction. Given the wavelength of the light and the geometry of the apparatus (i.e., the separation and widths of the slits and the distance from the slits to the screen), one can use the wave theory to calculate the expected pattern in each case; the theory agrees precisely with the experimental data.

Early developments

Planck's radiation law

By the end of the 19th century, physicists almost universally accepted the wave theory of light. However, though the ideas of classical physics explain interference and

diffraction phenomena relating to the propagation of light, they do not account for the absorption and emission of light. All bodies radiate electromagnetic energy as heat; in fact, a body emits radiation at all wavelengths. The energy radiated at different wavelengths is a maximum at a wavelength that depends on the temperature of the body; the hotter the body, the shorter the wavelength for maximum radiation. Attempts to calculate the energy distribution for the radiation from a blackbody using classical ideas were unsuccessful. (A blackbody is a hypothetical ideal body or surface that absorbs and reemits all radiant energy falling on it.) One formula, proposed by Wilhelm Wien of Germany, did not agree with observations at long wavelengths, and another, proposed by Lord Rayleigh (John William Strutt) of England, disagreed with those at short wavelengths.

In 1900 the German theoretical physicist Max Planck made a bold suggestion. He assumed that the radiation energy is emitted, not continuously, but rather in discrete packets called quanta. The energy E of the quantum is related to the frequency ν by $E = h\nu$. The quantity h , now known as Planck's constant, is a universal constant with the approximate value of 6.62607×10^{-34} joule-second. Planck showed that the calculated energy spectrum then agreed with observation over the entire wavelength range.

Quantum Mechanics

HOW DO YOU STUDY SOMETHING THAT SEEMINGLY MAKES NO SENSE?

We talk about electrons being in orbits and it sounds like we can tell where that electron is at any moment. We can draw pictures of electrons in orbit, but the reality is that we just don't know exactly where they are. We are going to take a quick look at an area of science that even leaves scientists puzzled. When asked about quantum mechanics, Niels Bohr (who proposed the Bohr model of the atom) said: "Anyone who is not shocked by quantum theory has not understood it." Richard Feynman (one of the

founders of modern quantum theory) stated: "I think I can safely say that nobody understands quantum theory." So, let's take a short trip into a land that challenges our every-day world.

The study of motion of large objects such as baseballs is called mechanics, or more specifically classical mechanics. Because the quantum nature of the electron and other tiny particles moving at high speeds, classical mechanics is inadequate to accurately describe their motion.

Quantum mechanics is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. In classical mechanics, the size and mass of the objects involved effectively obscures any quantum effects so that such objects appear to gain or lose energies in any amounts. Particles whose motion is described by quantum mechanics gain or lose energy in the small pieces called **quanta**.

One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particle and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic at the atomic scale.

At the heart of quantum mechanics is the idea that we cannot specify accurately the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time.