The theoretical underpinning of molecular structure studies has largely been based on the fixed nuclei approximation, which adiabatically separates the electronic and nuclear dynamics under the assumption that the nuclei are nearly fixed with respect to electron motion and the electrons follow the nuclear motion instantaneously. The assumption led to the so-called Born–Oppenheimer approximation, and the notion of stationary states that instantaneously adjust themselves to any nuclear configurations in space. The success of the Born-Oppenheimer approximation is attributed to the large difference between nuclear and electronic masses. The approximation has been an important tool in molecular structure studies, and even to this day, nearly all quantum chemical computations of molecular wavefunctions make use of the approximation. In the cases in which the Born-Oppenheimer approximation breaks down, it is used as a point of departure in quantum chemical computations. However, the non-adiabatic interactions arising from the breakdown of the Born–Oppenheimer approximation are of crucial importance in chemical reactions because nearly every chemical or biological process involves non-adiabatic events.

The difficulty in describing the nuclei quantum mechanically arises from the fact that the nuclei are much more massive than the electrons, engendering the wavelengths of the quantum matter waves for nuclei much shorter than those of electrons. The nuclear component of the wave function is spatially much more localized than the electronic component. For many decades, the theoretical underpinning of non-adiabatic molecular structure and the difficulty in quantum mechanical treatment of nuclear dynamics remained one of the most difficult challenges in theoretical chemistry. Beginning in the 1980's, theorists in Japan [1–9] began to question the validity or the accuracy of the Born–Oppenheimer approximation for bound states and they reformulated the Hartree-Fock and CI theory with intrinsic non-adiabaticity.

In his pioneering work on non-Born-Oppenheimer electronic structure, Fukutome [1] put forth a non-adiabatic method in solving the Schrödinger equation of molecular systems with strong or intrinsic non-adiabaticity. The method is based on the fact that the electrons undergo orbital motion with nuclear coordinate dependence and the nuclei exchanging recoil momenta. In a series of seminal studies on nuclear quantum effects, Tachikawa et al. [3,5,8], Shigeta et al. [4,6], and Nakai et al. [7,9] formulated novel non-Born-Oppenheimer electronic structure methods, the so-called non-adiabatic molecular orbital (MO), to describe the nuclear motion. Both electronic and nuclear wavefunctions are simultaneously solved with the fully variational Hartree-Fock method, by which exponents and centers of Gaussian-type function (GTF) basis sets are optimized as well as the linear combination of GTF coefficients [3]. All the light nuclei and electrons are treated quantum mechanically to include nuclear quantum effects, such as zero point energy, isotope effects, and nuclear tunneling. The initial studies employed mean-field approaches that resulted in somewhat over-localized nuclear densities due to the lack of sufficient electron-nuclear dynamic correlation. Subsequent studies [4,6–9] focused on the development of correlated non-adiabatic MO approaches.

The present JCCJ special issue on Quantum Hydrogen edited by Professor M. Tachikawa addresses the hydrogen nuclear quantum effects in a series of articles [10–22] with a focus on...
the non-adiabatic electron-nuclear dynamics. All the authors are renowned experts in their fields and many topics covered in this special issue represent the forefront of today's research on electron-nuclear dynamics.

The present issue describes the essential details of the theoretical methods to account for nuclear quantum effects and place them into the context of modern applications [10–15,17], of broad interest to theoretical chemists. It also includes articles covering computational methods and applications to experimental aspects of interest for chemists in both academia and industry. See the reviews by Ueda and Mori [16], Kinoshita et al. [18], Matsui et al. [19], Takahashi and Morita [20], Ishimoto et al. [21].


All the light nuclei and electrons may be treated quantum mechanically to include nuclear quantum effects. The approach is particularly useful for the description of hydrogen bonding. Kawashima et al. [22] investigate the nuclear quantum effect on the intermolecular hydrogen bond of acetic acid – phosphorous acid anion cluster, a model system for periplasmic phosphate binding protein (PPBP). Proton delocalization in the center region of the hydrogen bond is found in the quantum simulation taking nuclear fluctuation effect into account. The intermolecular hydrogen bond in acetic acid–phosphorous acid anion cluster showed the same tendency as the PPBP with low-barrier hydrogen bond.

The largest kinetic isotope effects are associated with the substitution of 2H or 3H for 1H. However, with the use of muons, one can achieve the kinetic isotope effects corresponding to isotopic mass ratios much greater than 3. Takayanagi and Yoshida [10] present large quantum mass effects with two "isotopes" of the H atom, muonium and muonic helium, in chemical reactions.

Hydrogen nuclear quantum effect is manifest on surfaces as well as in solution and solids [11,12,16,17]. First-principles methods for the quantum states of small mass atom motion in solid materials and on their surfaces are given by Nakanishi [11]. The importance of nuclear quantum effect in molecular hydrogen is demonstrated by Miura [12] in the example of hydrogen molecular cluster (H2)3. Cooperative phenomena between protons and electrons, such as the proton-coupled electron transfer, play an important role in biological and chemical systems. In crystalline/solid materials, however, such phenomena have rarely been seen before. Ueda and Mori [16] uncovered a unique interplay between hydrogen-bond dynamics and π-electrons in an organic conductor crystal. Okuyama [17] reviews some experimental and theoretical studies that reveal the quantum delocalization of hydrogen atoms on the surfaces.