The importance of quantum mechanical models to explain hydrogen evolution

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Advancing water electrolysis is key to the hydrogen energy transition, with the hydrogen evolution reaction (HER) at its core. Despite its simplicity, HER has been studied for over a century, focusing on how a proton transfers from a donor (water, hydronium, or acid) to the electrode or catalyst. Understanding has evolved from early phenomenological models to modern quantum approaches that include proton tunneling and electron–nucleus coupling.

In the present day, we understand that HER is a complex quantum-mechanical process. Key milestones along this path include: • Classical kinetics (Volmer-Tafel-Heyrovsky): defined the process's stage-by-stage nature; • Marcus theory: introduced the concept of solvent reorganization as the main source of activation energy; • Dogonadze-Kuznetsov-Levich (DKL) theory: first applied quantum mechanics to the proton, explaining tunneling and isotope effects; • Concerted Proton-Electron Transfer (CPET) theory (Hammes-Schiffer): combined electron and proton transfer in a single, coordinated event, essential for describing modern catalysts.

While Marcus's theory treated the electron as a quantum particle, and the nuclei and solvent according to classical definition, this was insufficient for the proton, which is heavier than the electron but lighter than ordinary ions. In the 1960s, V.G. Levich, R.R. Dogonadze, and A.M. Kuznetsov developed a consistent quantum theory of proton transfer [1], which became the basis for understanding cathodic hydrogen evolution. While acidic electrolysis (PEM) depends on scarce platinum-group metals, alkaline electrolysis (AEL) can use cheaper nickel and iron but suffers from HER kinetics that are 2–3 orders of magnitude slower. This slowdown is explained by the quantum-mechanical framework of Dogonadze–Kuznetsov–Levich [2], which accounts for proton–electron transfer at the electrode. The theory clarifies the unusually large hydrogen/deuterium isotope effects that classical models cannot explain [3]. It also introduced both stepwise and concerted proton–electron transfer mechanisms, anticipating modern CPET concepts.

In electrochemical kinetics, theoretical developments have often outpaced experimental confirmation. Here, we will examine examples of the application of the quantum-mechanical DKL theory of proton transfer to current problems in electrochemical hydrogen production.

In the work of Nazmutdinov et al. [4], it was shown that modern calculations using density functional theory (DFT) and molecular dynamics confirm the main conclusions of the LDC for the discharge of the hydronium ion on a mercury electrode. This unified quantum rate theory (Quantum Rate Theory) was developed. This complex reaction has attracted attention for many years, and microscopic modeling finally confirmed the previously made theoretical conclusion about the proton transfer from excited energy levels as the key effect leading to the famous Tafel plot over a wide overpotential region.

Modern strategies for creating catalysts for "Green" hydrogen directly or indirectly rely on the DKL theory provide a framework to understand how the reaction rate of HER is influenced by factors like overpotential, pH, and the nature of the electrode material. The theory has been used to predict and explain the dependence of the activation energy on the total reorganization energy of the system, which is a key parameter in understanding electrocatalytic activity. It helps to explain why certain materials are more active catalysts for HER than others, and allows calculation of the reorganization energy, required to re-arrange the solvent molecules and the internal structure of the reactants and products during the charge transfer [5]. For HER, this can be broken down into two components: the solvent reorganization energy and the reorganization energy of the discharging species (e.g., a water cluster). Researchers have applied the theory to calculate these values for HER on various metal alloys, such as molybdenum with iron subgroup metals (Fe, Co, Ni), to understand how the catalyst and solvent affect the reaction rate [6].

The current stage of theoretical development is characterized by a striving for unification. As shown in the recent work of Bueno [7], there is a deep connection between the classical Marcus theory, the quantum theory of the LDC, and modern concepts of quantum coherence.

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