Quantum breaking of ergodicity in adiabatic electron transfer

The problem of ergodic *vs.* non-ergodic behavior alludes, generally speaking, to the following question: Can we deduce from a collective behavior of a large ensemble of *noninteracting identical* entities statistical properties of single individual objects entering this ensemble? For example, there are single identical objects, say ion channels, which can be in one of two states: A, e.g. nonconducting closed state, and B, e.g. open conducting state. Assume that each ion channel undergoes a closed-open stochastic dynamics and their ensemble shows an exponential relaxation dynamics. Given a stationary value of the mean number of open channels and the ensemble relaxation rate, can we deduce opening and closing rates of individual ion channels? The vast majority will answer in affirmative.

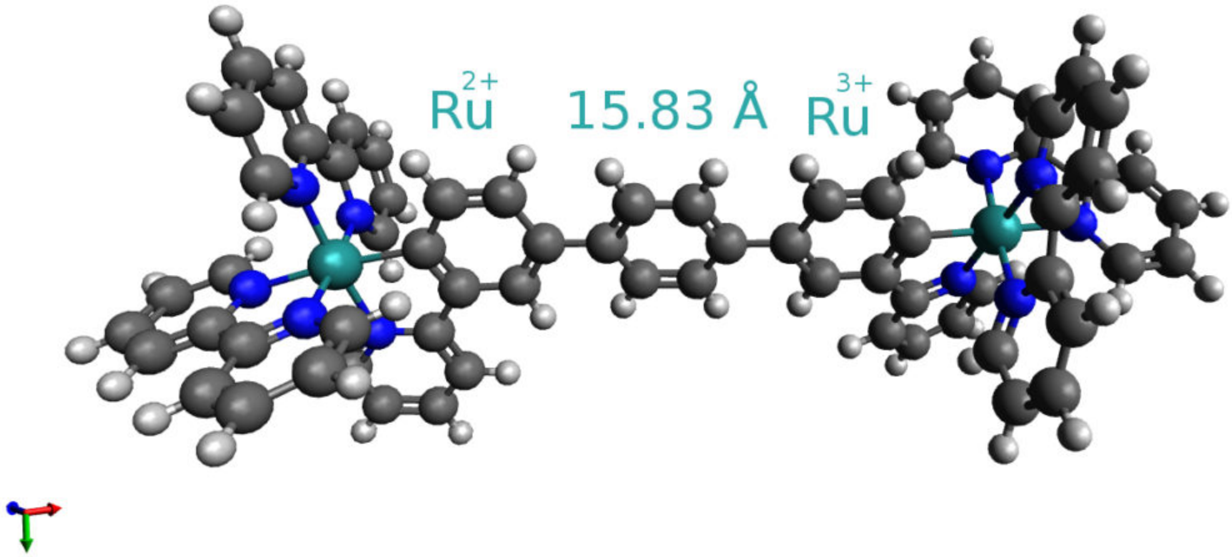

Fig. 1. Some binuclear ruthenium complex. The spacer is a benzene group. It can be different, which can strongly affect the tunnel coupling between metallic ions. A huge variety of such complexes exist. The displayed structure is created using Avogadro molecule editor and visualizer.

However, this common belief is heavily based on the assumed ergodicity, which is taken for granted. Indeed, recent discoveries of ergodicity breaking in the nanoscale dynamics of single quantum dots, single molecules, as well as in nano- and mesoscopic classical transport suggest that one should be more careful. Non-ergodic behavior is more common in nature than earlier thought. The work published in Phys. Chem. Chem Phys. 2017, 19, 3056, focuses on a very popular semi-classical model of quantum transport involving dissipative Landau-Zener tunneling (curve-crossing problem) between two centers of electron localization. For example, in mixed-valence metallic binuclear complexes, like a cyclometalated ruthenium complex displayed in Figure

1, electron can be temporally localized on one of metallic centers. It is jumping between them in a stochastic manner due to electronic tunnel coupling mediated by the molecular bridge between two metallic ions. This physical picture of incoherent electron tunneling jumps stands well when the tunneling matrix element (which depends on the bridge nature and length) is much smaller than the medium's reorganization energy (that includes both a molecular vibrational part and one of the surrounding medium in which the electron-transferring complex is immersed), and it is also smaller than the thermal energy kT. In the so-called solvent-controlled adiabatic regime, electron transfer rates can be controlled by an effective medium's relaxation time in a Debye medium approximation. This basic model leads, in particular, to such famous results of widespread use as Marcus rates in the electron transfer (ET) theory. Can statistics of ET events within a single-electron trajectory description be predicted based on a single-exponential ensemble kinetics? This fundamental question of ergodic vs. non-ergodic behavior is scrutinized in the featured paper. It is shown that in the limit of non-adiabatic electron transfer (weak tunneling) well-described by the Marcus-Levich-Dogonadze (MLD) rate the answer is yes. However, in the limit of solvent-controlled adiabatic ET a profound breaking of ergodicity occurs. Namely, the equilibrium ensemble theory predicts an exponential distribution of ET events for sufficiently high activation barriers with the inverse rate given by the sum of the adiabatic curve crossing (Kramers) time and the inverse MLD rate. However, in the adiabatic regime, the real distribution of ET events judging from single-trajectory jump realizations turns out to be a non-exponential Mittag-Leffler distribution tempered with an exponential tail which agrees well with the ensemble description. Paradoxically, the mean transfer time in this classical on the ensemble level regime is well described by the inverse of quantum MLD rate on a single particle level. This theoretical work, which is based on both exact analytical results and precise numerics, which remarkably agree, elucidates the quantum origin of this paradoxical result. Namely, adiabatic ET remains fundamentally quantum-mechanical on the level of a single particle description being at the same time almost classical on the ensemble level, in agreement with adiabatic Marcus-Hush theory. Quantum ergodicity breaking is at heart of this paradox.

Igor Goychuk
University of Potsdam, Germany

Publication

Quantum ergodicity breaking in semi-classical electron transfer dynamics.
Goychuk I
Phys Chem Chem Phys. 2017 Jan 25