In this talk, I will discuss the formulation and applications of the multi-space constrained-search DFT (MS-DFT) formalism we have been developing at KAIST for the past decade plus [1-4]. Seeking an alternative to the standard Landauer picture for quantum transport, we first propose a viewpoint that maps quantum transport processes to space-resolved (drain-to-source) optical excitation counterparts. The multi-space excitation picture for quantum transport then allows the formulation of microcanonical approaches for quantum transport, and the resulting MS-DFT provides unique opportunities in understanding and designing nanoscale devices in operando conditions. For example, unlike in the grand-canonical DFT-NEGF, the non-equilibrium total energy, as well as quasi-Fermi level or voltage drop profile information, can be obtained within the microcanonical MS-DFT [3,4]. As an appropriate thermodynamic potential for biased electrode/channel interfaces, I then establish the concept of electric enthalpy of formation. Key initial results obtained for electrified water/electrode interfaces will be outlined.