Quantum transport of ions through atomically thin materials

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Atomically thin two-dimensional materials are increasingly being explored as a possible platform for developing novel separation technologies such as water desalination and proton-exchange membranes in fuel cells. Particular attention is given to the utilization of layered 2D materials for selective sieving of molecules, atoms, and ions. The key role in the transport phenomena is played by the membrane penetration mechanism which can be substantially affected by nuclear quantum effects. For instance, the experimentally deduced barrier for thermal proton transport through pristine graphene sheet (PGS) of 0.78 eV is at least 0.65 eV lower than those predicted by electronic structure calculations [1, 2]. Moreover, the observed difference in PGS areal conductivity for protons and deuterons is an unresolvable challenge for such calculations because the nuclear mass does not appear in the electronic Hamiltonian. Accounts for structural optimization, the role of the solvent, surface curvature and proton transport through hydrogenated samples does not resolve the observed discrepancies between theory and experiment if the nuclei are considered as classical particles [3].

We propose a hierarchical quantum-mechanical approach [4] which provides an efficient way to study quantum ion transport in low-dimensional materials. We start from an effective one-dimensional transport model, which already reveals the main features of the transmission process. Then, we extend our study to three dimensions by performing a free energy thermodynamic integration employing Born-Oppenheimer potential energy surface computed with density functional theory. Finally, we account for membrane relaxation and atomic motion in membrane by performing *ab inito* imaginary-time Feynman-Kac path integral molecular dynamics simulations [5].

We have found that the proton quantum nature and its strong repulsion with graphene repulsion causes substantial proton delocalization in the vicinity of the graphene layer. As a result, *deep quantum tunneling* becomes a leading proton transport mechanism. In contrast, the thermal transport of heavier isotopes, such as deuterons and tritons, through PGS at ambient conditions demonstrates a quasi-classical nature. Different transport mechanisms opens an avenue for efficient isotopes separation. Another key factor which can substantially modify the ion transport process is the impact of chemisorption sites and covering material [6]. In the case of quantum tunneling the transmission coefficient is defined by both the height and the shape of the barrier. Covering the membrane with some material changes the shape of the barrier playing a vital role in the proton transport process – an effect which is attributed to specific experimental conditions.

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