Modeling of the symmetry factor of electrochemical proton discharge via the Volmer reaction

A scheme for evaluating symmetry factors of elementary electrode reactions using a density functional theory (DFT) based model of the electrochemical double layer is presented. As an illustration, the symmetry factor is determined for hydrogen adsorption via the electrochemical Volmer reaction. The DFT results are compared with predictions of an analytical single electron transfer model with quadratic reactant and product free energy surfaces. The analytical model, fed with input parameters calculated by DFT, is shown to give symmetry factors in reasonable agreement with those of the full-scale DFT model. This suggests that qualitative estimates of symmetry factors can be obtained at a moderate cost by combining comparatively cheap DFT calculations with reasonably sophisticated analytical models.