

Abstract Submitted  
for the MAR06 Meeting of  
The American Physical Society

**First-Principles pH Theory**<sup>1</sup> YONG-HYUN KIM, S. B. ZHANG, National Renewable Energy Laboratory — Despite being one of the most important macroscopic measures and a long history even before the quantum mechanics, the concept of pH has rarely been mentioned in microscopic theories, nor being incorporated computationally into first-principles theory of aqueous solutions. Here, we formulate a theory for the pH dependence of solution formation energy by introducing the proton chemical potential as the microscopic counterpart of pH in atomistic solution models. Within the theory, the general acid-base chemistry can be cast in a simple pictorial representation. We adopt density-functional molecular dynamics to demonstrate the usefulness of the method by studying a number of solution systems including water, small solute molecules such as  $\text{NH}_3$  and  $\text{HCOOH}$ , and more complex amino acids with several functional groups. For pure water, we calculated the auto-ionization constant to be 13.2 with a 95 % accuracy. For other solutes, the calculated dissociation constants, i.e., the so-called  $\text{pK}_a$ , are also in reasonable agreement with experiments. Our first-principles pH theory can be readily applied to broad solution chemistry problems such as redox reactions.

<sup>1</sup>Work supported by the U. S. DOE/BES and EERE under contract No. DE-AC36-99GO10337.

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Date submitted: 29 Nov 2005

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