

Exact Computations of Acidities based on the Integrated Hellmann-Feynman Theorem

Tore Brinck

*Department of Chemistry, CBH School
KTH Royal Institute of Technology, Stockholm, Sweden
tore@kth.se*

Although the Hohenberg-Kohn theorem proves that the energy of a ground-state system of electrons and nuclei is a functional of the electronic density, it has not been possible to determine the exact form of that relationship. In contrast Peter Politzer derived exact expressions for relating the energies of atoms or molecules to the electrostatic potential at the nuclei.^{1,2} These expressions were obtained by integrating the derivative of the energy with respect to nuclear charge using the Hellmann-Feynman theorem. Inspired by Politzer's work, I have investigated the use of the integrated Hellmann-Feynman theorem to obtain acidities by integrating the electrostatic potential at the acidic hydrogen nucleus as the nuclear charge decreases from 1 to 0. This procedure, which in principle should provide the exact deprotonation energy, has the advantage over directly calculating the energy difference between acid and conjugate base that the deprotonation processes in systems of varying size are directly comparable. As an example, the integration curve for a particular proton in a protein can be compared to the integration curve of the acidic hydrogen in methanol. Furthermore, this method makes it possible to determine how the different stages of the deprotonation process influence the acidity, e.g. the effect on the acidity of toluene by the resonance stabilization of the deprotonated toluene can be quantified. I have devised a computational procedure for numerically integrating the electrostatic potential at a particular nucleus under full nuclear relaxation to obtain deprotonation energies. This procedure has been applied to a range of different acids, and some representative examples will be presented. The validity of the approach has been analyzed for different electronic structure methods ranging from Hartree-Fock and Kohn-Sham DFT to coupled cluster with iterative single and double excitations, i.e. CCSD. The basis set dependence on the accuracy of the results will also be analyzed and discussed.

- (1) Politzer, P.; Parr, R. G. *J. Chem. Phys.* **1974**, *61*, 4258-62.
- (2) Politzer, P.; Murray, J. S. *Theo. Chem. Acc.* **2002**, *108*, 134-42.