419f Quantum Mechanical Single Molecule Partition Function from Path Integral Monte Carlo Simulations

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Single molecule partition function is a very useful quantity in thermodynamic and chemical kinetic calculations. We have developed a method for calculating the quantum mechanical partition function of any given molecule. Currently rigid-rotor harmonic-oscillator approximation (RRHO) is used for calculating single molecule partition functions. The minimum energy structure of a molecule is obtained with standard quantum chemistry software and then the RRHO approximations are applied. The single molecule partition function obtained is then used for evaluating free energies, equilibrium constants and rate constants. However the RRHO approximation fails in many cases, especially for larger molecules. In case of a transition metal with many ligands, most of the ligands are free to rotate and these rotations can not be treated using harmonic approximation. In addition to rotations there are many other "floppy degrees of freedom", which correspond to very low frequency anharmonic oscillations. The new method which we present uses path integral Monte Carlo (PIMC) to calculate the single molecule partition function without any approximations.

A molecular mechanical (MM) force field with fitted parameters is used to describe the potential energy of the molecules. The parameters are fitted to match the Born-Oppenheimer surface as closely as possible. Since partition functions can not be estimated directly by a Monte Carlo procedure we estimate the difference between the true partition function and a reference partition function. The reference in our case is another MM force field, where the spring constants of the force field are made very large. For this set of parameters with larger spring constants, the harmonic approximation gives the partition function very accurately. The PIMC technique combined with thermodynamic perturbation is used to calculate the difference between true and reference partition functions. In general a PIMC simulation generates an ensemble of configurations which satisfy the quantum mechanical density matrix at the given temperature.

The details of the PIMC techniques which we have used is published elsewhere (Predescu C. , 2005 Phys. Rev. E). This method is based on a Trotter product that utilizes a short-time approximation that has quartic convergence with respect to the total number of path variables. The resulting Trotter-Suzuki product is utilized in the so-called Levy-Ciesielski form to take advantage of a new sampling technique called the fast sampling algorithm. The overall scaling as number of calls to the potential function vs. the number of path variables is n*log_2(n), which makes the algorithm one of the most efficient. Nevertheless, to further reduce the time necessary to attain ergodicity, we also perform exchanges between parallel replicas that are characterized by slightly different spring constants. The exchanges are accepted or rejected according to the parallel tempering logic.

We have tested the method against the test cases of model linear alkanes (ethane to octane) and of hydrogen peroxide molecule for which partition function values are available in the literature. The partition functions are calculated with an accuracy of 0.001. Currently this method is being used for studying larger molecules such as Pd(HSO4)2 which is important for our studies in catalysis. The oral presentation at the conference will involve a simple description of the method and illustrative examples.