Methods for Coupled Electronic-Ionic Monte Carlo

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Quantum Monte Carlo (QMC) methods such as Variational Monte Carlo, Diffusion Monte Carlo or Path Integral Monte Carlo are the most accurate and general methods for computing total electronic energies. We will review methods we have developed to perform a coupled QMC for the electrons and another MC simulation for the ions.

Using QMC methods, one estimates the Born-Oppenheimer energy $E(Z)$ where Z represents the ionic degrees of freedom. That estimate of the energy is used in a Metropolis simulation of the ionic degrees of freedom where one compares $\exp(-[E(Z') - E(Z)]/k_B T)$ to a random number and accepts or rejects the move. We have shown [1] that one can modify the usual Metropolis acceptance probability to eliminate the bias caused by noise in this energy difference, thus allowing more noisy estimates of the energy difference and thereby drastically reduce the sampling time of the electronic degrees of freedom.

We have implemented several different QMC methods for estimating the energy change including Diffusion Monte Carlo and Variational Monte Carlo. We have also developed a correlated sampling technique [2,3] symmetrical in Z and Z', so that the variance of $[E(Z') - E(Z)]$ is smaller than of each energy individually.

Using these methods, we have performed simulations of liquid H_2 on a parallel computer. We have developed novel methods to move the H_2 molecules (separate translations, rotations and vibrations) and ways to pre-reject the moves using an empirical potential in an effort to speed up the simulation. We discuss some possible advantages of the CEIMC method concerning how the quantum effects of the ionic degrees of freedom can be included and how the boundary conditions can be integrated over.

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[1] D. M. Ceperley and M. Dewing, "The penalty method for Random Walks with Uncertain Energies", J. Chem. Phys., **110** 9812, (1999).

[2] M. Dewing, PhD thesis (2000), Available as arXiv:physics/0012030.

[3] M. Dewing and D. M. Ceperley, "Methods for Coupled Electronic-Ionic Monte Carlo"in *Recent Advances in Quantum Monte Carlo Methods II*, ed. S. Rothstein, World Scientific, in press 2001.