

Coupled Ion-Electron 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. Taking many-body hydrogen at high pressure as an example, each QMC method has a limited range of applicability. For example PIMC is limited to temperatures greater than 5000K, and DMC to zero temperature.

We have introduced a method[1] to perform a coupled QMC for the electrons and another MC simulation for the ions (CIEMC). Using quantum Monte Carlo, one estimates the Born-Oppenheimer energy change which is then used in a Metropolis simulation of the ionic degrees of freedom. We have shown 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 reducing the sampling time of the electronic degrees of freedom. We have implemented[2] 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 so that the variance of the difference is smaller than of each energy individually.

One of the time-consuming steps was optimization of the trial wavefunction, typically taken to be of the Slater-Jastrow form. We are using a completely analytic form[3], generalized from the backflow function useful for strongly correlated systems, to the electron-proton system, thereby avoiding optimization, without sacrificing accuracy.

Using these methods, we have performed simulations of liquid H₂ and liquid metallic H down to temperatures as low as 300K. We discuss some possible advantages of the CEIMC method relative to Car-Parrinello simulations concerning how the quantum effects of the ionic degrees of freedom can be included and how the boundary conditions on the phase of the wavefunction can be integrated over[4].

References

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