Finite-temperature Density Functional Developments and Some Computational Consequences

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To study matter from ambient to extreme conditions of pressure and temperature, the best available simulation approach is ab initio molecular dynamics (AIMD). AIMD uses ion-electron forces from Born-Oppenheimer electronic structure calculations. For computational feasibility, free-energy density functional theory is used to calculate the electronic free energy. Doing that introduces two challenges: (1) the accuracy of the required approximate exchange-correlation (XC) density functionals; (2) the KS computational cost-scaling bottleneck (cube of the number of thermally occupied orbitals). I will summarize progress on both.

First, more than thirty years after the ground-state local spin-density approximation (LSDA) XC functional was extracted from purely first-principles Monte Carlo data, we have produced the corresponding finite-temperature LSDA [1]. Comparison with use of a ground-state functional and finite-T density $n(\mathbf{r}, T)$ show the importance of the functional's intrinsic T-dependence. Early results from putting this functional into the FEFF9 code will be sketched, along with recent progress on a related finite-T GGA XC functional. Second, I will show AIMD calculations using orbital free DFT (OF-DFT) and our recently developed, fully non-empirical non-interacting free-energy generalized-gradient approximation functional [2] . OF-DFT in principle provides the same quantum statistical mechanics as KS but with computational cost scaling linear with system volume and T-independent. The OF-DFT AIMD calculations use our recently published Profess@QuantumEspresso code system. We are able to recover near KS-DFT equations of state for simple systems.

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