Wave function theories for finite-temperature electronic structure

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Wave function methods have offered a robust, systematically improvable means to study the ground-state properties in quantum many-body systems. Theories like coupled cluster and their derivatives provide highly accurate approximations to the energy landscape at a reasonable computational cost. Analogs of such methods to study thermal properties, though highly desirable, have been lacking because evaluating thermal properties involve a trace over the entire Hilbert space. Approximating every state in the Hilbert space is an impossible task. Besides, excited-state theories are not as well studied as ground-state ones.

In this poster, I will introduce our recently developed framework to overcome these difficulties by employing the theory of thermofield dynamics, a theory that allows us to construct a single wave function that encodes the equilibrium thermal behavior of the system. Ensemble averages become expectation values over this so-called thermal state. Around this thermal state, we have developed a framework to extend ground-state wave function theories to non-zero temperatures.

I will present explicit formulations of mean-field, configuration interaction, and coupled cluster theories for thermal properties of fermions in the grand-canonical ensemble. To assess the quality of these approximations, I will show benchmark studies for both model electronic and spin systems, while comparing against exact results.

We will see that the thermal methods perform similarly to their ground-state counterparts, while merely adding a pre-factor to the computational cost. They also inherit all the properties, good or bad, from the ground-state methods, signifying the robustness of our formalism and the scope for future development.