Finite-Temperature Many‐Body Perturbation Theory for Electrons

So Hirata and Punit K. Jha

Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
Email: sohirata@illinois.edu

(1) Low‐order perturbation corrections to the electronic grand potential, internal energy, chemical potential, and entropy in the *grand canonical ensemble* are determined numerically as the λ‐derivatives of the respective quantity calculated exactly (by thermal full configuration interaction) with a perturbation‐scaled Hamiltonian, $H_0+\lambda V$. The first‐ and second‐order corrections from textbook finite‐temperature many‐body perturbation theory disagree with these benchmark data, proving that the theory is incorrect and does not converge at the exact limit. This is because it neglects the variation of chemical potential with λ, allowing the average number of electrons to fluctuate, violating the net charge neutrality of the system as a basic tenet of thermodynamics.

(2) The correct *analytical first‐order correction formulas* for the grand potential, internal energy, and chemical potential are derived in the sum‐over‐state and reduced analytical expressions algebraically. The time‐independent, non‐diagrammatic derivation is based on straightforward analytical differentiation of thermal full configuration interaction using the sum rules of the Hirschfelder–Certain degenerate perturbation energy corrections and several identities of Boltzmann sums introduced by us. They shed new light on the so‐called Kohn–Luttinger inconsistency.

(3) Benchmark data are presented for the zeroth‐ through third‐order many‐body perturbation corrections to the electronic Helmholtz energy, internal energy, and entropy in the *canonical ensemble* in a wide range of temperature. Sum‐over‐states analytical formulas for up to the third‐order corrections to these properties are also derived as analytical λ‐derivatives.

References

(1) P. K. Jha and S. Hirata,
Annu. Rep. Comput. Chem., **15**, 3 (2019), arXiv:1809.10316,
"Numerical evidence invalidating finite‐temperature many‐body perturbation theory."

(2) S. Hirata and P. K. Jha,
Annu. Rep. Comput. Chem., **15**, 17 (2019), arXiv:1812:07088,
"Converging finite‐temperature many‐body perturbation theory in the grand canonical ensemble that conserves the average number of electrons."

(3) P. K. Jha and S. Hirata
Phys. Rev. E, under revision (2019), arXiv: 1910.07628,
"Finite‐temperature many‐body perturbation theory in the canonical ensemble."