

Finite-temperature coupled-cluster calculations of Peierls systems

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One-dimensional (1D) polymers such as polyynes and polyacetylenes exhibit a variety of electronic structure motifs including charge- and spin-density waves (CDW and SDW), and are subject to the Peierls theorem which states that at zero temperature, a 1D system predicted by band theory to be a metal will spontaneously dimerize and open a finite band gap, while at higher temperatures, this band gap closes (a “Peierls transition”). These Peierls systems cannot be modeled using density functional theory calculations due to severe self-interaction errors. We have implemented finite-temperature coupled-cluster doubles (CCD) and unrestricted Hartree-Fock (UHF) methods in order to perform *ab initio* calculations on polyynes and polyacetylenes, expanding upon previous calculations using finite-temperature restricted Hartree-Fock (RHF) and renormalized MP2 methods. At low temperatures, RHF describes the potential energy surface along the dimerization coordinate as a double well with a maximum at the equidistant geometry in agreement with Peierls' theorem, and CCD agrees qualitatively. CCD predicts shallower double wells with lower maxima, implying that RHF overestimates the Peierls transition temperature. However, UHF gives a qualitatively different picture, with a single-well potential and an SDW state at the equilibrium geometry. As the temperature is raised, the UHF potential has a minimum first at the equidistant geometry (with an SDW electronic structure) and then at dimerized geometries (with insulating electronic structure) and then at the equidistant geometry again (now with a gapless, metallic electronic structure).