The existence of thermodynamic limit and size-consistent design

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Why is energy extensive and is an application of statistical thermodynamics to chemistry valid? It has taken 40 years for mathematicians to complete the proof of the extensivity of energy or, equivalently, the existence of thermodynamic (infinite-volume) limit of energy density. I will offer an alternative, more accessible proof of the extensivity of energy for electrically neutral, metallic and nonmetallic crystals by establishing the same for its individual energy components, namely, the kinetic, Coulomb, exchange, and correlation energies. On this basis, I will address size-consistent design of electronic and vibrational many-body methods. Our findings are summarized as follows: The significance of the distinct use of the intermediate and standard normalization for extensive and intensive operator amplitudes, respectively; The extensive and intensive diagram theorems, which serve as the foolproof criteria for determining size consistency of a method for extensive and intensive quantities; The extensive-intensive operator consistency theorem, which stipulates the precise balance between the determinant spaces reached by extensive and intensive operators in a size-consistent excited-state method.

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