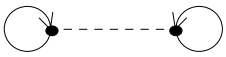
The lost and found relation between connectivity and size-extensivity

Dmitry I. Lyakh and Rodney J. Bartlett
Quantum Theory Project, University of Florida, Gainesville, 32611, USA

Diagrammatic techniques together with the linked diagram theorem (LDT) are well-established tools for the derivation and analysis of quantum many-body methods describing inter-particle correlations. In nuclear physics, where the LDT appeared first, a particular interpretation implies individual size-extensivity of connected closed diagrams. This interpretation was later imported to the electronic structure theory, where it provides the basis for developing size-extensive correlated methods. Indeed the 1-1 correspondence between connectivity of tensorial equations and proper size-extensivity/size-intensivity of computed expectation values is very convenient in practice. However, strictly speaking, it turns out that this relation can be violated when the interaction tensor is generated by the Coulomb law (weak potential). In particular, it can be easily shown that in the localized-orbital representation the following connected closed diagram



produces a super-extensive scalar (in the limit of an infinite number of particles) when no truncations are made (arbitrary precision). Hence, in principle (on an arbitrary precision computer), size-extensivity of the computed energy is achieved by the appropriate cancellation of non-size-extensive terms spawned by infinite summations of the Coulomb “tails” (long-range part of the Coulomb potential). In practice, small tensor elements are always ignored, making the above diagram size-extensive. In order to restore the convenient relation between connectivity of tensorial equations and size-extensivity/size-intensivity of computed expectation values, we introduced a simple assumption which states that a complete neglect of the long-range part of the Coulomb potential (on a sufficiently large distance) does not cause qualitative changes in the chemical system described by some quantum many-body method, such that all computed expectation values preserve their principal scaling with respect to the number of interacting particles. We believe that this assumption is valid for all stable chemical systems (chemical systems with a size-extensive exact total energy). This formal simplification rigorously restores the 1-1 correspondence between connectivity and size-extensivity, thus making the application of the LDT to extended (generally inhomogeneous but stable) chemical systems theoretically consistent.

Subsequently, based on the tensor formulation of the second-quantized electronic structure theory, we define the notion of tensor connectivity and investigate how it is affected in different tensor operations. We show that tensor connectivity is a complex phenomenon (different types of connectivity are possible). The mathematical framework developed is tested by analyzing different electronic structure theories (CI/MBPT/CC/EOMCC/MRCC). To make the connectivity analysis unambiguous, we recast all formalisms into the exponential form. In particular, we demonstrate that the EOMCC equations (as well as the truncated-CI equations for excited states) can be reformulated in a purely connected (exponential) form with the same number of variables. We also show that the active orbitals naturally appear when insisting on the exponential representation of the excited-state wavefunction.

1. D.I. Lyakh. Submitted to *Mol. Phys.* (2011).
2. D.I. Lyakh, R.J. Bartlett. Submitted to *Mol. Phys.* (2011).