When two is better than one: new wavefunctions from the seniority scheme

Stijn De Baerdemacker

Center for molecular modelling – Ghent University

Email: stijn.debaerdemacker@ugent.be

"Strong quantum correlation" is one of the unsolved problems of electronic structure theory. It was recently observed [1] that the seniority scheme offers a much better partitioning of the Hilbert space than the conventional particle-hole scheme to capture strong static correlations. This scheme organizes the electron configurations into electron pairs, rather than in single-particle excitations on top of a reference state. Full Configuration Interaction (fCI) calculations limited to the fully paired space only (or Doubly-Occupied Configuration Interaction) are able to describe bond-breaking processes with very high accuracy. Unfortunately, as a fCI method, the computational scaling of DOCI remains exponential, and hence impractical for large systems.

The mean-field picture associated with electron pairing is known as the theory of Antisymmetric Product of Interacting Geminals (APIG)[2]. This ties in with the intuitive Lewis picture of chemical bonding, however the exponentially scaling computational cost of an APIG wavefunction is hardly better than DOCI. A recent breakthrough in APIG theory came with the connection with Richardson-Gaudin (RG) integrable systems [3,4], in which we have identified a new family of APIG states with mean-field like computational cost and the same accuracy as DOCI.

In this presentation, I will discuss recent research from the Ghent-McMaster collaboration on the seniority scheme, APIG theory and its connection to Richardson-Gaudin integrability [5,6,7].

[1] Bytautas L, Henderson T M, Jimenez-Hoyos C A, Ellis J K and Scuseria G E 2011 J. Chem. Phys. 135 044119

[2] Geminus: [Latin] double, paired (substantive) one who is a twin.

[3] Johnson P A, Ayers P W, Limacher P A, De Baerdemacker S, Van Neck D and Bultinck P 2013 Comp. Theor. Chem. 1003 101

[4] Limacher P A, Ayers P W, Johnson P A, De Baerdemacker S, Van Neck D and Bultinck P 2013 J. Chem. Theor. Comp. 9 1394

[5] Van Raemdonck M, Alcoba D R, Poelmans W, De Baerdemacker S, Torre A, Lain L, Massaccesi G E, Van Neck D, and Bultinck P, 2015 J. Chem. Phys. 143 104106

[6] Claeys P, Van Neck D and De Baerdemacker S, 2017 arXiv:1706.05511

[7] Claeys P, Caux J-S, Van Neck D and De Baerdemacker S (in preparation)