Symbolic Derivation and Evaluation of Coupled-Cluster Models

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With the introduction of work into new wavefunction parameterizations[1] in the Ayers group, our group started deriving expressions heavily in the second quantization formalism. The notation greatly simplifies the task of proving and deriving certain theories in ab initio quantum chemistry. For example, the field of coupled cluster also uses the second quantized formalism, as does the field of configuration interaction, and many others (DFT being the notable exception).

The weakness of the formalism is the excessive number of commutators to evaluate algebraically. When developing wavefunction parameterization models, it is necessary to try several parameterizations before finding a successful model, each of which must be evaluated algebraically. In addition, implenting these models are not trivial. Coupled-cluster variants contain several thousand terms, all of which must be coded by hand normally.

Our solution to this problem has been to create a package in HORTON to derive second quantized expressions, normal order them, and evaluate them numerically. We can also obtain derivatives to arbitrary order for use with numerical solvers. The equations we obtain can be printed as LaTeX and we can also parse LaTeX equations with second quantized operators. As a proof of concept, we have derived the energy and amplitude equations for Coupled-Cluster up to quadruple excitations.

Referencias: [1] Peter A Limacher, Paul W Ayers, Paul A Johnson, Stijn De Baerdemacker, Dimitri Van Neck, Patrick Bultinck, “A New Mean-Field Method Suitable for Strongly Correlated Electrons: Computationally Facile Antisymmetric Products of Nonorthogonal Geminals” (2013) JCTC 9:3 1394-1401