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Targeted method for diagram generation,

These are roughly in order of interest/implementation, we should discuss a plan of attack

0. Existing methods for verification

0.a CCD energy
0.b CCD lambda
0.c CCSD energy
0.d CCSD lambda
0.e CCSD ground state one-body and two-body density matrices

1. New implementations for ground-state higher-order approaches

1.a. CCSDT: energies and lambda equations

For the energies, I think I have the diagrams (in a naive form?) for CCSDT-1, CCSDT-1a and CCSDT-1b in place (branch gomesasp/caar-higher), and I am in the process of implementing the remaining CCSDT diagrams, and would like to be able to have CCSDT-2 and CCSDT-3 as well. **This all still requires debugging and validation**.

My idea is to complement at least some of these with the ability to obtain ground-state expectation values, and thus have part of the ingredients for defining EOM-CCSDT (below)

I like the way e.g. Shavitt, Bartlett etc treat this, by building the higher excitation ranks as supplementing the the T1/T2 etc equations for lower-excitation rank, and would definitely like to try to keep that, as I think that would be the simplest for us to maintain.

I haven't yet refactored the ground state code this way, but cnce the CCSDT energie validated, I'd like to try it.

I haven't yet looked at the different perturbative corrections, though that could be interesting.

1.b. CCSDTQ : energies, lambda equations

When setting up for CCSDT I have made space for CCSDTQ, but haven't gone much further than that.

I think it wold be interesting to have CCSDTQ (and some other approximate iterative approaches, but not necessarily the whole zoology) energies and expectation values.

We'd not really be able to use it beyond fairly small systems, but it may give us an edge over other implementations, especially with the automatic generation of diagrams.

1.c. CC3: energy and lambda equations

This would be a logic complement to CC2, and would make sense for response theory (see below).

Here my question is more on how such approximate iterative approaches would be defined with the automatic generation code.

2. New implementations for excited state higher-order approaches

2.a. EOM-IP/EE/EA/DEA/DIP-CCSDT (and with approximated treatment of triples)

It is important for us to start providing methods beyond CCSD for excited states, so this is my main immediate interest, and the ground-state work serves as a base for it. Since energy only are not very useful, we should target both the right and left-hand sides.

I think the main issues here are how to (a) define intermediates, involving the ground-state amplitudes; (b) generate expressions for the left and right-hand sigma vectors.

2.b. Completely renormalized (CR) EOM methods

I think that apart the standard EOM approaches, the completely renormailzed methods developed by Piecuch and coworkers (CR-CC(n,m)) seem quite interesting as targets, in particular for treating more multi-reference like problems.

I'm not sure if one should target them first, or the methods in 2.a.

3. Second-order properties, response theory, EOM-CCSD two-body density matrices

Loïc has been working on the working equations for a few things apart CC2: second-order properties, one- and two-body density matrices for EOM-EE/IP/EA.

For a more general setting for defining properties, we wanted to stick to the quasienergy formulation by Christiansen, Jorgensen and Hattig, since the response properties are derived in a rather algebraic manner. However, to get the working equations he's using diagrammatics.

He's got most of the diagrams (re)derived for that. We would therefore be interested in using the automatic generation as a cross-check to begin with.

A first check we have in mind is for the expressions that appear in the linear CC response equations:

F t^X, where $t^X(\omega^X)$ are perturbed amplitudes (X for instance being a dipole operator) and

$F_{\mu \nu} = \langle \Lambda | [[H_0, \hat{\tau}_{\mu}], \hat{\tau}_{\nu}] | CC \rangle$,

μ, ν being singly or doubly (or triply, for CCSDT for example) excited determinants, $\hat{\tau}_{\nu}$ a corresponding excitation operator, and H_0 the unperturbed Hamiltonian.

I recall that an important quantity, the CC jacobian ($A_{\mu \nu} = \langle \bar{\mu} | [H_0, \hat{\tau}_{\nu}] | CC \rangle$, with $\bar{\mu} = \langle HF | \bar{\tau}^\dagger_\mu e^{-T^{0}}$), is equivalent to the matrix representation of the similarity-transformed Hamiltonian, that we diagonalize in EOM-EE for example.

Apart from that, if one goes to quadratic response, as will be the case for the thesis of Xiang, we will have terms with higher number of commutators when assembling the response functions, for instance, in the quadratic response function we will have

F^X t^Y (ω^Y), where

    t^Y are perturbed amplitudes;
    and
    $F^X_{\mu \nu} = \langle \Lambda | [[\hat{X}, \hat{\tau}_{\mu}], \hat{\tau}_{\nu}] | CC \rangle$

And Gt^X t^Y, where

    t^X, t^Y are perturbed amplitudes;
    and
    $G_{\mu \nu \sigma} = \langle \Lambda | [[[\hat{X}, \hat{\tau}_{\mu}], \sigma], \hat{\tau}_{\nu}] | CC \rangle$

We shold note, much like in EOM we will not necessarily form the tensor F by itself but but rather the contractions, and that particularly for the quadratic response function.