Orbital optimized pair coupled-cluster

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- Main goal: explore solutions of coupled cluster methods for excited states
- Start simpler: pair coupled cluster doubles (pCCD)
- Interesting properties of pCCD:
  - virtually the same ground state energies as DOCI
  - reduced computational cost (N^3 vs e^N of DOCI)
  - captures static correlation
- How does pCCD compare with DOCI for excited states?
- pCCD energies depend on the set of orbitals, in contrast to CCD
- Implement an orbital optimized pCCD code

pCCD

Usual exponential ansatz:

$$|\Psi\rangle = e^T|0\rangle$$

where the excitation operator

$$T = \sum_{ia} t_i^a P_a^\dagger P_i$$

and singlet paired operators

$$P_q^\dagger = c_{q\alpha}^\dagger c_{q\beta}^\dagger$$

Substitution into the Schroedinger equation leads to

$$E = \langle 0|e^{-T}He^T|0\rangle$$
$$0 = \langle 0|P_i^\dagger P_a e^{-T}He^T|0\rangle$$

pCCD t-amplitudes

Equations for energy and t-amplitudes:

$$E = \langle 0|H|0\rangle + \sum_{ia} t_i^a v_{aa}^{ii}$$

$$0 = v_{ii}^{aa} + 2\left(f_a^a - f_i^i - \sum_j v_{aa}^{jj} t_j^a - \sum_b v_{bb}^{ii} t_j^a\right) t_i^a$$

$$- 2\left(2v_{ia}^{ia} - v_{ai}^{ai} - v_{aa}^{ii} t_i^a\right) t_i^a$$

$$+ \sum_b v_{bb}^{aa} t_i^b + \sum_j v_{ii}^{jj} t_j^a + \sum_{jb} v_{bb}^{jj} t_j^a t_i^b$$

where f_q^p is an element of the Fock operator and $v_{rs}^{pq} = \langle \phi_p \phi_q | V_{ee} | \phi_r \phi_s \rangle$ is a two-electron integral.

pCCD z-amplitudes

When we need properties, we have to introduce the de-excitation operator:

$$Z = \sum_{ia} z_a^i P_i^\dagger P_a$$

Then, the energy expectation value is given as

$$\varepsilon = \langle 0|(1+Z)e^{-T}He^T|0\rangle$$

$\partial\varepsilon/\partial z_a^i = 0 \rightarrow$ t-amplitudes; $\partial\varepsilon/\partial t_i^a = 0 \rightarrow$ z-amplitudes

$$
\begin{aligned}
0 =& v_{aa}^{ii} + 2\left(f_a^a - f_i^i - \sum_j v_{aa}^{jj}t_j^a - \sum_b v_{bb}^{ii}t_i^b\right)z_a^i \\
&- 2\left(2v_{ia}^{ia} - v_{ai}^{ai} - v_{aa}^{ii}t_i^a\right)z_a^i \\
&- 2v_{aa}^{ii}\left(\sum_j z_a^j t_j^a + \sum_b z_b^i t_i^b\right) \\
&+ \sum_b v_{aa}^{bb}z_b^i + \sum_j v_{jj}^{ii}z_a^j + \sum_{jb} t_j^b(v_{bb}^{ii}z_a^j + v_{aa}^{jj}z_b^i)
\end{aligned}
$$

Orbital optimization in pCCD

Orbital rotation can be performed with the operator

$$e^{\kappa}$$

where κ is the antihermitian operator

$$\kappa = \sum_{p>q} \sum_{\sigma} \kappa_{pq} \left(c^{\dagger}_{p\sigma} c_{q\sigma} - c^{\dagger}_{q\sigma} c_{p\sigma} \right)$$

For rotated orbitals, the energy is now given by

$$\varepsilon(\kappa) = \langle 0|(1+Z)e^{-T}e^{-\kappa}He^{\kappa}e^{T}|0\rangle$$

We are looking for the set of orbitals that minimize the energy:

$$0 = \frac{\partial \varepsilon(\kappa)}{\partial \kappa_{pq}}\Big|_{k=0}$$

We define the one and two electron reduced density matrices as

$$\gamma^{p}_{q} = \sum_{\sigma} \langle 0|(1+Z)e^{-T} c^{\dagger}_{q\sigma} c_{p\sigma} e^{T}|0\rangle$$

$$\Gamma^{pq}_{rs} = \sum_{\sigma\sigma'} \langle 0|(1+Z)e^{-T} c^{\dagger}_{r\sigma} c^{\dagger}_{s\sigma'} c_{q\sigma'} c_{p\sigma} e^{T}|0\rangle$$

Orbital optimization in pCCD

The gradient of the orbital rotations becomes

$$\frac{\partial \varepsilon(\kappa)}{\partial \kappa_{pq}}\bigg|_{k=0} = \mathcal{P}_{pq}\left[\sum_r \left(h_p^r \gamma_r^q - h_r^q \gamma_p^r\right) + \sum_{rst}\left(v_{pt}^{rs}\Gamma_{rs}^{qt} - v_{rs}^{qt}\Gamma_{pt}^{rs}\right)\right]$$

We might also need the Hessian of the orbital rotations:

$$\begin{aligned}
\frac{\partial^2 \varepsilon(\kappa)}{\partial \kappa_{pq}\partial \kappa_{rs}}\bigg|_{k=0} =& \mathcal{P}_{pq}\mathcal{P}_{rs}\Big\{\frac{1}{2}\sum_u \left[\delta_{qr}(h_p^u\gamma_u^s + h_u^s\gamma_p^u) + \delta_{ps}(h_r^u\gamma_u^q + h_u^q\gamma_r^u)\right]\\
&-(h_p^s\gamma_r^q + h_r^q\gamma_p^s) + \sum_{uv}(v_{pr}^{uv}\Gamma_{uv}^{qs} + v_{uv}^{qs}\Gamma_{pr}^{uv})\\
&-\sum_{tu}(v_{pu}^{st}\Gamma_{rt}^{qu} + v_{pu}^{ts}\Gamma_{tr}^{qu} + v_{rt}^{qu}\Gamma_{pu}^{st} + v_{tr}^{qu}\Gamma_{pu}^{ts})\\
&+\frac{1}{2}\sum_{tuv}\left[\delta_{qr}(v_{pt}^{uv}\Gamma_{uv}^{st} + v_{uv}^{st}\Gamma_{pt}^{uv}) + \delta_{ps}(v_{uv}^{qt}\Gamma_{rt}^{uv} + v_{rt}^{uv}\Gamma_{uv}^{qt})\right]\Big\}
\end{aligned}$$

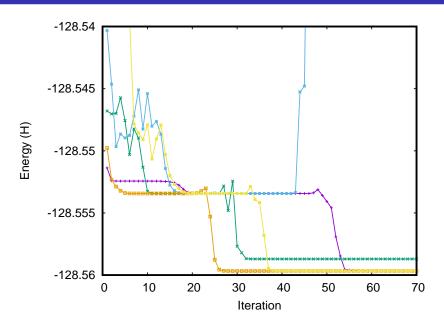$\mathcal{P}_{pq} = 1 - (p \leftrightarrow q)$ is a permutation operator.

The (preliminary) algorithm

1. Build the reference from the canonical Hartree-Fock orbitals
2. Solve for the pCCD t-amplitudes
3. Solve for the pCCD z-amplitudes
4. Compute one and two electron density matrices
5. Form the orbital gradient g (and hessian H)
6. Compare norm of gradient with a threshold value. If $|g| > \epsilon$, update orbitals via Newton-Raphson ($\kappa^{(N+1)} = \kappa^{(N)} - \mathbf{H}^{-1}\mathbf{g}$), and go back to step 2
7. Check for the eigenvalues h_n of the Hessian matrix. If $h_1 < 0$, move in the direction of the smallest eigenvector, and go back to step 2
8. Here, $|g| < \epsilon$ and $h_1 > 0$: stable stationary point

- Develop a robust algorithm for the orbital optimization
- Optimize orbitals for excited states
- Solve amplitude equations for excited states
- Implement DOCI
- How do pCCD and DOCI compare?