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Laboratoire de Chimie et Physique Quantiques

Scan of pCCD t-amplitudes

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https://lcpq.github.io/pterosor

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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

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

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

Equations for energy and t-amplitudes:

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

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.

- 2 electrons, 2 molecular orbitals (one occupied, one virtual)
- 1 amplitude in pCCD

$$\begin{aligned} E =& \langle 0|H|0\rangle + t v_{aa}^{ii} \\ 0 =& v_{ii}^{aa} + \left(2f_a^a - 2f_i^i - 4v_{ia}^{ia} + 2v_{ai}^{ia} + v_{aa}^{aa} + v_{ii}^{ii}\right) t - v_{aa}^{ii} t^2 = p(t) \end{aligned}$$

- One second order polynomial equation
- We look for the roots: $p(t) = 0$

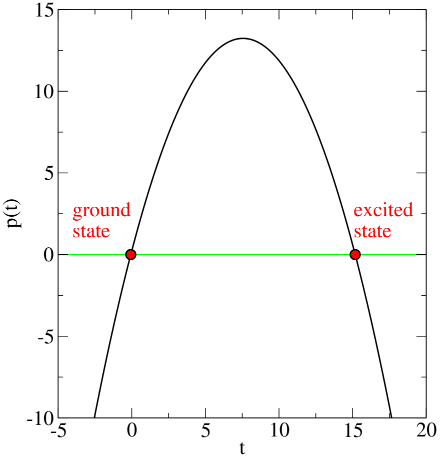

Figure: pCCD polynomial $p(t)$

- We look for the roots:

$$p(t) = 0 \tag{1}$$

- This is equivalent to finding the stationary points of its integral:

$$\frac{d}{dt}\int p(t)dt = 0 \tag{2}$$

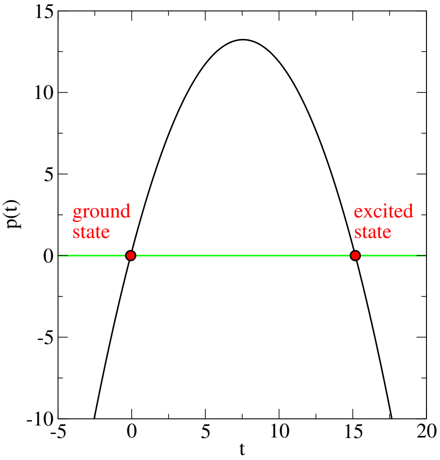

Figure: pCCD polynomial $p(t)$

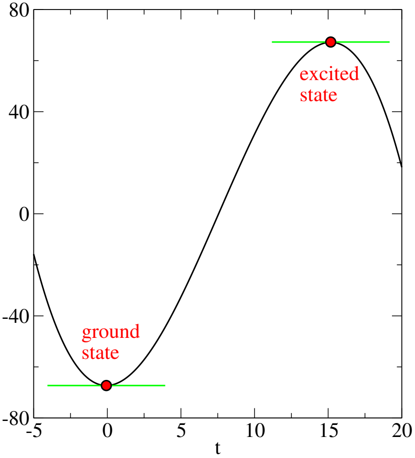

Figure: Integrated pCCD polynomial $\int p(t)dt$

- Initial guess for the t-amplitudes (MP2 amplitudes)
- Evaluate the polynomials $p(t)$
- Update the amplitudes according to

$$t \leftarrow t - \frac{p(t)}{2f_a^a - 2f_i^i} \tag{3}$$

- How does it work?

- Initial guess for the t-amplitudes (MP2 amplitudes)
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$$t \leftarrow t - \frac{p(t)}{2f_a^a - 2f_i^i} \tag{3}$$

- How does it work?
- We find the ground state, but not the excited state! The problem is the algorithm

- With the Newton-Raphson root finding method, we use information about the first derivative,

$$t \leftarrow t - \frac{p(t)}{p'(t)} \tag{4}$$

- The correct derivative is

$$p'(t) = 2f_a^a - 2f_i^i - 4v_{ia}^{ia} + 2v_{ai}^{ia} + v_{aa}^{aa} + v_{ii}^{ii} - 2v_{aa}^{ii}t \tag{5}$$

- but in the standar algorithm the red terms are missing
- How should it work?

- Multidimensional problem is more complicated:

$$
\begin{aligned}
p_1(t1, t2 \ldots t_k) &= 0 \\
p_2(t1, t2 \ldots t_k) &= 0 \\
&\vdots \\
p_k(t1, t2 \ldots t_k) &= 0
\end{aligned}
$$

- Topic for next week!