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Many-Body Perturbation Theory à la Coupled Cluster

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https://lcpq.github.io/pterosor

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- The random-phase approximation (RPA) is a quasibosonic approximation
  Bohm & Pines, Phys. Rev. 82 (1951) 625; 85 (1952) 338; 92 (1953) 609
- In the ph channel, fermionic excitations and deexcitations are treated as bosons
- RPA corresponds to a resummation of the (time-independent) ring diagrams
- Hence, it is adequate for weak correlation and captures long-range correlation (e.g. dispersion)
- It does not exhibit divergences for small-gap or metallic systems
  Gell-Mann & Brueckner, Phys. Rev. 106 (1957) 364

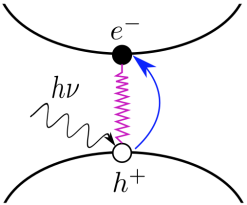
Chen et al. Ann. Rev. Phys. Chem. 68 (2017) 421

- Bethe-Salpeter equation (BSE) is a cheap and efficient way to go beyond RPA physics
  Blase et al. JPCL 11 (2020) 7371
- BSE is performed on top of *GW* to get quasiparticle energies and dynamical screening *W*
  Reining, WIREs Comput. Mol. Sci. 18 (2017) e1344
- *W* obtained via RPA polarizability (resummation of the time-dependent ring diagrams)
- *GW* provides accurate fundamental gaps
- Remaining excitonic effect caught by BSE kernel, hence providing accurate optical gaps

Martin, Reining & Ceperley, *Interacting Electrons: Theory and Computational Approaches*

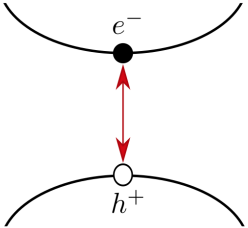
Optical gap

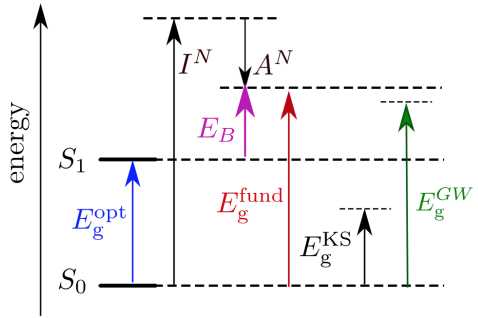
$E_{\mathrm{g}}^{\mathrm{opt}} = E_1^N - E_0^N$



Fundamental gap

$E_{\mathrm{g}}^{\mathrm{fund}} = I^N - A^N$





$$\underbrace{E_{\mathrm{g}}^{KS}}_{\text{KS gap}} = \epsilon_{\mathrm{LUMO}}^{KS} - \epsilon_{\mathrm{HOMO}}^{KS} \ll \underbrace{E_{\mathrm{g}}^{GW}}_{\text{GW gap}} = \epsilon_{\mathrm{LUMO}}^{GW} - \epsilon_{\mathrm{HOMO}}^{GW}$$

$$\underbrace{E_{\mathrm{g}}^{\mathrm{opt}}}_{\text{optical gap}} = E_1^N - E_0^N = \underbrace{E_{\mathrm{g}}^{\mathrm{fund}}}_{\text{fundamental gap}} + \underbrace{E_{\mathrm{B}}}_{\text{excitonic effect}}$$

Shortcomings of BSE@*GW*

👎 Computing the BSE@*GW* total energy is tricky and not well-defined
Loos et al. JPCL 11 (2020) 3536

🤜 Hence, although accurate, properties are challenging to compute (e.g. nuclear gradients)
Knysh et al. JCP 157 (2022) 194102

💩 It hampers the applicability of BSE@*GW* in computational photochemistry

👍 Coupled cluster (CC) is a mature theory with a well-defined route to get properties (Λ equations)
Shavitt & Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory*

👊 Can we link BSE@*GW* to CC to cure these problems?
Quintero-Monsebaiz, Monino, Marie & Loos, JCP (in press) arXiv:2210.07043

BSE linear eigenproblem in the static approximation [Strinati, Riv. Nuovo Cimento 11 (1988) 1]

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \cdot \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} X \\ Y \end{pmatrix} \cdot \boldsymbol{\Omega} \quad \text{with} \quad \begin{cases} A_{ia,jb} = \overbrace{(\epsilon_a^{GW} - \epsilon_i^{GW})}^{\text{“dressed” orbital energies}} \delta_{ij}\delta_{ab} + \widetilde{\langle ib||aj \rangle} \\ B_{ia,jb} = \widetilde{\langle ij||ab \rangle} = \underbrace{\langle ij||ab \rangle}_{\text{Hartree-exchange}} - \underbrace{W^c_{ib,ja}(\omega = 0)}_{\text{correlation via static screening}} \end{cases}$$

Ricatti version of BSE [Scuseria et al. JCP 129 (2008) 231101]

Assuming X^{-1} exists, $T = Y \cdot X^{-1}$ and

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \cdot \begin{pmatrix} \mathbf{1} \\ T \end{pmatrix} = \begin{pmatrix} \mathbf{1} \\ T \end{pmatrix} \cdot \underbrace{X \cdot \boldsymbol{\Omega} \cdot X^{-1}}_{R}$$

$$\begin{cases} A + B \cdot T = R \\ -B - A \cdot T = T \cdot R \end{cases} \Leftrightarrow \boxed{B + A \cdot T + T \cdot A + T \cdot B \cdot T = \mathbf{0}} \quad \text{Ricatti equation!!}$$

$$\boxed{B + A \cdot T + T \cdot A + T \cdot B \cdot T = 0}$$

$$\Downarrow$$

$$\widetilde{\langle ij||ab\rangle} + (\epsilon_a^{GW} + \epsilon_b^{GW} - \epsilon_i^{GW} - \epsilon_j^{GW}) t_{ij}^{ab} + \sum_{kc} \widetilde{\langle ic||ak\rangle} t_{kj}^{cb} + \sum_{kc} \widetilde{\langle kb||cj\rangle} t_{ik}^{ac} + \sum_{klcd} \widetilde{\langle kl||cd\rangle} t_{ik}^{ac} t_{lj}^{db} = 0$$

$$\Downarrow$$

"Dressed" ring CCD amplitude equations!!

$$\Downarrow$$

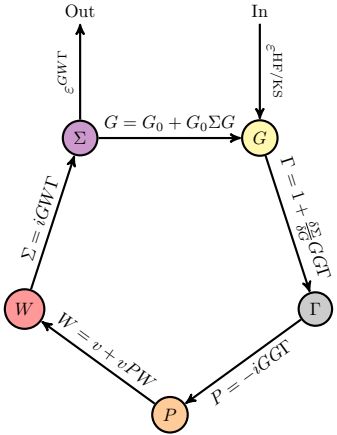
$$E_c^{\mathrm{BSE}} = \frac{1}{4} \sum_{ijab} \widetilde{\langle ij||ab\rangle} t_{ij}^{ab} = \frac{1}{4} \mathrm{Tr}(B \cdot T) = \frac{1}{4} \mathrm{Tr}(\Omega - A) \quad \Leftrightarrow \quad \text{Plasmon (or trace) formula!!}$$

$$\Downarrow$$

BSE@*GW* is equivalent to a dressed rCCD problem* (and it is also true for excitation energies!)

Berkelbach, JCP 149 (2018) 041103; Rishi et al. JCP 153 (2020) 234101

*similar to STEOM-CC



Hedin, Phys Rev 139 (1965) A796

The wonderful equations of Hedin

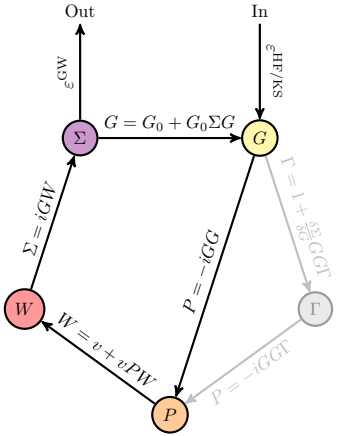
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i \int G(13)\Gamma(342)G(41)d(34)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i \int G(14)W(13)\Gamma(423)d(34)$$



Hedin, Phys Rev 139 (1965) A796

The *GW* approximation

$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i \int G(12)\Gamma(342)G(21)d(34) = -iG(12)G(21)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i \int G(12)W(12)\Gamma(423)d(34) = iG(12)W(12)$$

$$\left.\begin{aligned} \left[\boldsymbol{\epsilon} + \boldsymbol{\Sigma}^{GW}\left(\omega = \epsilon_p^{GW}\right)\right]\psi_p^{GW} &= \epsilon_p^{GW}\psi_p^{GW} \\ \boldsymbol{\Sigma}^{GW}(\omega) = \boldsymbol{V}^{2h1p} \cdot \left(\omega\mathbf{1} - \boldsymbol{C}^{2h1p}\right)^{-1} &\cdot (\boldsymbol{V}^{2h1p})^{\dagger} \\ + \boldsymbol{V}^{2p1h} \cdot \left(\omega\mathbf{1} - \boldsymbol{C}^{2p1h}\right)^{-1} &\cdot (\boldsymbol{V}^{2p1h})^{\dagger} \end{aligned}\right\} \underset{\text{upfolding}}{\overset{\text{downfolding}}{\rightleftharpoons}} \begin{cases} H\Psi_{p,s} = \epsilon_{p,s}^{GW}\Psi_{p,s} \\ H = \begin{pmatrix} \boldsymbol{\epsilon} & \boldsymbol{V}^{2h1p} & \boldsymbol{V}^{2p1h} \\ (\boldsymbol{V}^{2h1p})^{\intercal} & \boldsymbol{C}^{2h1p} & \mathbf{0} \\ (\boldsymbol{V}^{2p1h})^{\intercal} & \mathbf{0} & \boldsymbol{C}^{2p1h} \end{pmatrix} \end{cases}$$

1h & 1p conf.	$\boldsymbol{\epsilon}$	$\boldsymbol{V}^{2h1p}$	$\boldsymbol{V}^{2p1h}$	internal space $\boldsymbol{P}$
2h1p conf.	$\boldsymbol{V}^{2h1p}$	$\boldsymbol{C}^{2h1p}$	$\mathbf{0}$	external space $\boldsymbol{Q}$
2p1h conf.	$\boldsymbol{V}^{2p1h}$	$\mathbf{0}$	$\boldsymbol{C}^{2p1h}$	

Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos JCP 156 (2022) 231101.

$$\begin{pmatrix} \epsilon & V^{2h1p} & V^{2p1h} \\ (V^{2h1p})^\intercal & C^{2h1p} & 0 \\ (V^{2p1h})^\intercal & 0 & C^{2p1h} \end{pmatrix} \cdot \begin{pmatrix} X \\ Y^{2h1p} \\ Y^{2p1h} \end{pmatrix} = \begin{pmatrix} X \\ Y^{2h1p} \\ Y^{2p1h} \end{pmatrix} \cdot \epsilon^{GW} \quad \Leftrightarrow \quad \text{“EOM” version of } GW$$

$$\Downarrow$$

$$\begin{pmatrix} \epsilon & V^{2h1p} & V^{2p1h} \\ (V^{2h1p})^\intercal & C^{2h1p} & 0 \\ (V^{2p1h})^\intercal & 0 & C^{2p1h} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ T^{2h1p} \\ T^{2p1h} \end{pmatrix} = \begin{pmatrix} 1 \\ T^{2h1p} \\ T^{2p1h} \end{pmatrix} \cdot R \quad \text{with} \quad \underbrace{T^{2h1p/2p1h}}_{GW \text{ amplitudes}} = Y^{2h1p/2p1h} \cdot X^{-1}$$

$$\Downarrow$$

$$\begin{cases} \epsilon + V^{2h1p} \cdot T^{2h1p} + V^{2p1h} \cdot T^{2p1h} = R \\ (V^{2h1p})^\intercal + C^{2h1p} \cdot T^{2h1p} = T^{2h1p} \cdot R \\ (V^{2p1h})^\intercal + C^{2p1h} \cdot T^{2p1h} = T^{2p1h} \cdot R \end{cases} \quad \Rightarrow \quad \begin{cases} (V^{2h1p})^\intercal + C^{2h1p} \cdot T^{2h1p} - T^{2h1p} \cdot \epsilon - T^{2h1p} \cdot V^{2h1p} \cdot T^{2h1p} \\ \qquad - T^{2h1p} \cdot V^{2p1h} \cdot T^{2p1h} = 0 \\ (V^{2p1h})^\intercal + C^{2p1h} \cdot T^{2p1h} - T^{2p1h} \cdot \epsilon - T^{2p1h} \cdot V^{2h1p} \cdot T^{2h1p} \\ \qquad - T^{2p1h} \cdot V^{2p1h} \cdot T^{2p1h} = 0 \end{cases}$$

$$\Downarrow$$

Two coupled Ricatti equations!! 😱

2h1p amplitude equations

$$r^{2h1p}_{ija,p} = \langle pa|ij\rangle + \Delta^{2h1p}_{ija,p} t^{2h1p}_{ija,p} - \sum_{kc} \langle jc|ak\rangle \, t^{2h1p}_{ikc,p} - \sum_{klcq} \langle qc|kl\rangle \, t^{2h1p}_{ija,q} t^{2h1p}_{klc,p} - \sum_{kcdq} \langle qk|dc\rangle \, t^{2h1p}_{ija,q} t^{2p1h}_{kcd,p}$$

2p1h amplitude equations

$$r^{2p1h}_{iab,p} = \langle pi|ba\rangle + \Delta^{2p1h}_{iab,p} t^{2p1h}_{iab,p} + \sum_{kc} \langle ak|ic\rangle \, t^{2p1h}_{kcb,p} - \sum_{klcq} \langle qc|kl\rangle \, t^{2p1h}_{iab,q} t^{2h1p}_{klc,p} - \sum_{kcdq} \langle qk|dc\rangle \, t^{2p1h}_{iab,q} t^{2p1h}_{kcd,p}$$

Updating amplitudes

$$t^{2h1p}_{ija,p} \hookleftarrow t^{2h1p}_{ija,p} - \left(\Delta^{2h1p}_{ija,p}\right)^{-1} r^{2h1p}_{ija,p} \qquad t^{2p1h}_{iab,p} \hookleftarrow t^{2p1h}_{iab,p} - \left(\Delta^{2p1h}_{iab,p}\right)^{-1} r^{2p1h}_{iab,p}$$

$$\Delta^{2h1p}_{ija,p} = \epsilon^{GW}_i + \epsilon^{GW}_j - \epsilon^{GW}_a - \epsilon_p \qquad \Delta^{2p1h}_{iab,p} = \epsilon^{GW}_a + \epsilon^{GW}_b - \epsilon^{GW}_i - \epsilon_p$$

Diagonalize $\boldsymbol{\epsilon} + \boldsymbol{\Sigma}^{GW}$ with $\boxed{\boldsymbol{\Sigma}^{GW} = \boldsymbol{V}^{2h1p} \cdot \boldsymbol{T}^{2h1p} + \boldsymbol{V}^{2p1h} \cdot \boldsymbol{T}^{2p1h}}$ to get ϵ^{GW}_p and ψ^{GW}_p and iterate...

Perspectives

- It can potentially provide a well-defined route to compute ground- and excited-state properties
- Hence, broadening the applicability of BSE@*GW* in computational photochemistry
- However, one must derive Λ equations for approximated CCD
  Rishi et al. JCP 153 (2020) 234101
- It may provide new directions for the development of multireference *GW* methods to treat strong correlation
  Evangelista, JCP 149 (2018) 030901

- Open-source software: https://quantumpackage.github.io/qp2/

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- Anthony Scemama
- Michel Caffarel

https://pfloos.github.io/WEB_LOOS

https://lcpq.github.io/PTEROSOR

Wave operator

$$\underbrace{\Phi}_{\text{exact wave function}} = \underbrace{\hat{\Omega}}_{\text{wave operator}} \underbrace{\Phi_0}_{\text{reference wave function}}$$

Schrödinger equation

$$\hat{H}\,\Phi = E\,\Phi \quad \rightarrow \quad \hat{H}\,\hat{\Omega}\,\Phi_0 = E\,\hat{\Omega}\,\Phi_0 \quad \rightarrow \quad \bar{H}\,\Phi_0 = E\,\Phi_0$$

Similarity transformation of the Hamiltonian

$$\underbrace{\hat{\Omega}}_{\text{wave operator}} : \underbrace{\hat{H}}_{\text{bare Hamiltonian}} \rightarrow \underbrace{\bar{H}}_{\text{effective Hamiltonian}} = \hat{\Omega}^{-1}\,\hat{H}\,\hat{\Omega}$$

In coupled-cluster theory, we have

$$\hat{\Omega} = e^{\hat{T}} \quad \text{and} \quad \bar{H} = e^{-\hat{T}}\,\hat{H}\,e^{\hat{T}}$$

Amplitude equations

The amplitudes are obtained via the following equations

$$\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0 \qquad\qquad \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0$$

and the energy is

$$E_{\mathrm{CC}} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

$$\hat{H}^{(\mathrm{EE})} = \begin{array}{c} \\ \langle\Phi_0| \\ \langle\Phi_i^a| \\ \langle\Phi_{ij}^{ab}| \end{array} \begin{array}{c} \begin{array}{ccc} |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle \end{array} \\ \begin{bmatrix} E_{\mathrm{HF}} & \mathbf{0} & \mathbf{X} \\ \mathbf{0} & \mathbf{X} & \mathbf{X} \\ \mathbf{X} & \mathbf{X} & \mathbf{X} \end{bmatrix} \end{array} \qquad \bar{H}^{(\mathrm{EE})} = \begin{array}{c} \\ \langle\Phi_0| \\ \langle\Phi_i^a| \\ \langle\Phi_{ij}^{ab}| \end{array} \begin{array}{c} \begin{array}{ccc} |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle \end{array} \\ \begin{bmatrix} E_{\mathrm{CC}} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \\ \mathbf{0} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \\ \mathbf{0} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \end{bmatrix} \end{array}$$

Faucheaux et al. JCP 148 (2018) 054104

Second similarity transformation

We perform a second similarity transformation

$$\boxed{\bar{\bar{H}} = \{e^{\hat{S}}\}^{-1} \bar{H} \{e^{\hat{S}}\}}$$

that decouples the 1h determinants from the 2h1p ones in the IP sector and the 1p determinants from the 2p1h ones in the EA sector

$$\langle \Phi_{ij}^{a} | \bar{\bar{H}} | \Phi_k \rangle = 0 \qquad\qquad \langle \Phi_{i}^{ab} | \bar{\bar{H}} | \Phi^c \rangle = 0$$

where $\hat{S}$ contains up to 2h1p and 2p1h operators

Nooijen & Bartlett, JCP 106 (1997) 6441; 106 (1997) 6449; 107 (1997) 6812.

IP-EOM-CC

$$\bar{H}^{(\mathrm{IP})} = \begin{array}{c} \\ \langle\Phi_i| \\ \langle\Phi_{ij}^a| \end{array} \begin{array}{c} \begin{array}{cc} |\Phi_i\rangle & |\Phi_{ij}^a\rangle \end{array} \\ \begin{bmatrix} \bar{\bar{\mathbf{X}}} & \bar{\mathbf{X}} \\ \bar{\mathbf{X}} & \bar{\bar{\mathbf{X}}} \end{bmatrix} \end{array} \qquad \bar{\bar{H}}^{(\mathrm{IP})} = \begin{array}{c} \\ \langle\Phi_i| \\ \langle\Phi_{ij}^a| \end{array} \begin{array}{c} \begin{array}{cc} |\Phi_i\rangle & |\Phi_{ij}^a\rangle \end{array} \\ \begin{bmatrix} \bar{\bar{\bar{\mathbf{X}}}} & \bar{\bar{\mathbf{X}}} \\ \mathbf{0} & \bar{\bar{\bar{\mathbf{X}}}} \end{bmatrix} \end{array}$$

EA-EOM-CC

$$\bar{H}^{(\mathrm{EA})} = \begin{array}{c} \\ \langle\Phi^a| \\ \langle\Phi_i^{ab}| \end{array} \begin{array}{c} \begin{array}{cc} |\Phi^a\rangle & |\Phi_i^{ab}\rangle \end{array} \\ \begin{bmatrix} \bar{\bar{\mathbf{X}}} & \bar{\mathbf{X}} \\ \bar{\mathbf{X}} & \bar{\bar{\mathbf{X}}} \end{bmatrix} \end{array} \qquad \bar{\bar{H}}^{(\mathrm{EA})} = \begin{array}{c} \\ \langle\Phi^a| \\ \langle\Phi_i^{ab}| \end{array} \begin{array}{c} \begin{array}{cc} |\Phi^a\rangle & |\Phi_i^{ab}\rangle \end{array} \\ \begin{bmatrix} \bar{\bar{\bar{\mathbf{X}}}} & \bar{\bar{\mathbf{X}}} \\ \mathbf{0} & \bar{\bar{\bar{\mathbf{X}}}} \end{bmatrix} \end{array}$$

Purpose of the second similarity transformation

The $\bar{\bar{H}}$ operator largely, albeit not completely, decouples the one- and two-electron excited determinants also, i.e.,

$$\langle \Phi_{ij}^{ab} | \bar{\bar{H}} | \Phi_k^c \rangle \approx 0$$

$$\bar{H}^{(\mathrm{EE})} = \begin{array}{c} \\ \langle\Phi_0| \\ \langle\Phi_i^a| \\ \langle\Phi_{ij}^{ab}| \end{array} \begin{array}{c} \begin{array}{ccc} |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle \end{array} \\ \begin{bmatrix} E_{\mathrm{CC}} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \\ \mathbf{0} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \\ \mathbf{0} & \bar{\mathbf{X}} & \bar{\mathbf{X}} \end{bmatrix} \end{array} \qquad \bar{\bar{H}}^{(\mathrm{EE})} = \begin{array}{c} \\ \langle\Phi_0| \\ \langle\Phi_i^a| \\ \langle\Phi_{ij}^{ab}| \end{array} \begin{array}{c} \begin{array}{ccc} |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle \end{array} \\ \begin{bmatrix} E_{\mathrm{CC}} & \bar{\bar{\mathbf{X}}} & \bar{\bar{\mathbf{X}}} \\ \mathbf{0} & \bar{\bar{\mathbf{X}}} & \bar{\bar{\mathbf{X}}} \\ \mathbf{0} & \approx \mathbf{0} & \bar{\bar{\mathbf{X}}} \end{bmatrix} \end{array}$$

Owing to this matrix structure of $\bar{\bar{H}}$, the diagonalization of this matrix in its tiny singles-singles block yields size-intensive excitation energies of all predominantly one-electron character simultaneously that are roughly of the same accuracy and distinctly superior to EOM-CCSD

How to perform a STEOM-CC calculation?

1. Solve the CCSD equations to get $\hat{T}$
2. Calculate the matrix elements of $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$
3. Solve the IP-EOM-CCSD eigenvalue problem.
   From the IP-EOM-CCSD solutions obtain transformation coefficients
4. Solve the EA-EOM-CCSD eigenvalue problem.
   From the EA-EOM-CCSD solutions obtain transformation coefficients
5. Calculate the matrix elements of $\bar{\bar{H}} = \{e^{\hat{S}}\}^{-1} \bar{H} \{e^{\hat{S}}\}$
6. Diagonalize $\bar{\bar{H}}$ over the subspace of singly-excited determinants to obtain excitation energies

NB: STEOM-CCSD (and its extended version) is implemented in ORCA