Excited State Wavefunction Methods

CC2, CIS(D_∞), ADC(2)

Theory

Solution of CC2 equations [$\hat{H} = \exp(-T_1)H\exp(T_1)$]:

$$\Omega_{\mu_1} = \langle\mu_1|\hat{H} + [\hat{H}, T_2]|\mathrm{HF}\rangle = 0 \qquad T_1 = \sum_{\mu_1} \tau_{\mu_1} t_{\mu_1}$$

$$\Omega_{\mu_2} = \langle\mu_2|\hat{H} + [F, T_2]|\mathrm{HF}\rangle = 0 \qquad T_2 = \sum_{\mu_2} \tau_{\mu_2} t_{\mu_2}$$

yields singles $\{t_{\mu_1}\}$ and doubles amplitudes $\{t_{\mu_2}\}$ with $\{\mu_1\}$ and $\{\mu_2\}$ being the single- and double-excitation manifolds. Derivative of vectorfunction w. r. t. perturbation in the cluster amplitudes spans Jacobian matrix $A_{\mu_i,\mu_j} = \partial\Omega_{\mu_i}/\partial t_{\nu_j}$:

$$A^{\mathrm{CC2}} = \begin{pmatrix} \langle\mu_1|[(\hat{H} + [\hat{H}, T_2]), \tau_{\nu_2}]|0\rangle & \langle\mu_1|[\hat{H}, \tau_{\nu_2}]|0\rangle \\ \langle\mu_2|[\hat{H}, \tau_{\nu_1}]|0\rangle & \delta_{\mu_2\nu_2}\epsilon_{\mu_2} \end{pmatrix}.$$

Restrict $\{t_{\mu_1}\}$ to zero and thus $\{t_{\mu_2}\}$ to MP2 amplitudes:

$$A^{\mathrm{CIS}(\mathrm{D}_\infty)} = \begin{pmatrix} \langle\mu_1|[(H + [H, T_2]), \tau_{\nu_2}]|0\rangle & \langle\mu_1|[H, \tau_{\nu_2}]|0\rangle \\ \langle\mu_2|[H, \tau_{\nu_1}]|0\rangle & \delta_{\mu_2\nu_2}\epsilon_{\mu_2} \end{pmatrix}.$$

Symmetrization:

$$A^{\mathrm{ADC}(2)} = \frac{1}{2}\left(A^{\mathrm{CIS}(\mathrm{D}_\infty)} + A^{\mathrm{CIS}(\mathrm{D}_\infty)\dagger}\right).$$

Recast into effective Jacobian $A^{\mathrm{eff}} = A^{\mathrm{eff}}(\omega)$ in $\{\mu_1\}$:

$$A^{\mathrm{eff}}_{\mu_1\nu_1}(\omega) = A_{\mu_1\nu_1} + \sum_{\gamma_2} \frac{A_{\mu_1\gamma_2}A_{\gamma_2\nu_1}}{\omega - \epsilon_{\gamma_2}},$$

with $\epsilon_{ij}^{ab} = (\epsilon_a - \epsilon_i - \epsilon_b - \epsilon_j)$. Singularities found as eigenvalues of effective Jacobian matrices as non-linear eigenvalue problem (due to dependence on ω):

$$A^{\mathrm{eff}}(\omega_n)R_n = \omega_n R_n, \quad L_n A^{\mathrm{eff}}(\omega_n) = L_n\omega_n.$$

Solution techniques necessitate transformations with guessvectors b yielding sigmavectors $\sigma = \sigma(\omega, b)$:

$$\sigma_{\mu_1}(\omega, b) = \sum_{\nu_1} A^{\mathrm{eff}}_{\mu_1\nu_1}(\omega)b_{\nu_1}.$$

Since the CC2 and CIS(D_∞) Jacobian matrices are non-symmetric, their left and right eigenvectors, though associated with the same eigenvalue, are generally not identical. First, the focus will be on right transformations with guessvectors.

Prerequisites

Coefficient matrix C and Fock matrix $F_{pq} = \delta_{pq}\epsilon_p$ of canonical reference orbitals, number of occupied orbitals n_{occ}. Also helper matrices:

$$t = \begin{pmatrix} 0 & 0 \\ \{t_{ai}\} & 0 \end{pmatrix} \qquad b = \begin{pmatrix} 0 & 0 \\ \{b_{ai}\} & 0 \end{pmatrix}$$

$$\Lambda^\rho_{\mu p} = [C(1 - t^\dagger)]_{\mu p} \qquad \bar{\Lambda}^\rho_{\mu p} = -[Cb^\dagger]_{\mu p}$$

$$\Lambda^\eta_{\nu q} = [C(1 + t)]_{\nu q} \qquad \bar{\Lambda}^\eta_{\mu q} = [Cb]_{\nu q}$$

RI Approximation

$$J^Q_{\mu\nu} = \sum_P (\mu\nu|P)[V^{-1/2}]_{PQ}$$

$$J^Q_{pq} = \sum_{\mu\nu} C_{\mu p}J^Q_{\mu\nu}C_{\nu q} \qquad (pq|rs) = \sum_Q J^Q_{pq}J^Q_{rs}$$

$$\hat{J}^Q_{pq} = \sum_{\mu\nu} \Lambda^\rho_{\mu p}J^Q_{\mu\nu}\Lambda^\eta_{\nu q} \qquad (pq\hat{|}rs) = \sum_Q \hat{J}^Q_{pq}\hat{J}^Q_{rs}$$

$$(pq\bar{|}rs) = \sum_Q (\bar{J}^Q_{pq}\hat{J}^Q_{rs} + \hat{J}^Q_{pq}\bar{J}^Q_{rs})$$

$$J^Q_{ij} = J^Q_{ji} \qquad J^Q_{ab} = J^Q_{ba} \qquad J^Q_{ia} = \hat{J}^Q_{ia}$$

$$\hat{J}^Q_{ij} \neq \hat{J}^Q_{ji} \qquad \hat{J}^Q_{ab} \neq \hat{J}^Q_{ba} \qquad J^Q_{ai} \neq \hat{J}^Q_{ai}$$

In case of CIS(D_∞) and ADC(2):

$$\hat{J}^Q_{ai} = J^Q_{ai} \qquad \hat{J}^Q_{ij} = J^Q_{ij} \qquad \hat{J}^Q_{ab} = J^Q_{ab}$$

Amplitudes

$$t^{ab}_{ij} = \begin{cases} \dfrac{(ai\hat{|}bj)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b} & \text{(CC2)} \\[2ex] \dfrac{(ai|bj)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b} & \text{(otherwise)} \end{cases} \qquad \tilde{t}^{ab}_{ij} = 2t^{ab}_{ij} - t^{ba}_{ij}$$

$$R^{ab}_{ij} = \frac{(ai\bar{|}bj)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b + \omega} \qquad \tilde{R}^{ab}_{ij} = 2R^{ab}_{ij} - R^{ba}_{ij}$$

Intermediates

$$\bar{J}^Q_{ai} = \begin{cases} \sum_b \hat{J}^Q_{ab}b^b_i - \sum_j b^a_j\hat{J}^Q_{ji} & \text{(CC2)} \\[1ex] \sum_b J^Q_{ab}b^b_i - \sum_j b^a_j J^Q_{ji} & \text{(otherwise)} \end{cases}$$

$$Y^Q_{ai} = \sum_{kc} \tilde{t}^{ac}_{ik}J^Q_{kc} \qquad Z^Q_{ai} = \sum_{kc} \tilde{R}^{ac}_{ik}J^Q_{kc}$$

Correlation Energy

$$\Delta E_{\mathrm{MP2/CC2}} = \sum_{ijab} [2(ia|jb) - (ib|ja)]\,[t^{ab}_{ij} + t^a_i t^b_j]$$

$$= \sum_{iaQ} Y^Q_{ai}J^Q_{ia} + \sum_{ia} \hat{F}_{ia}t^a_i$$

Inactive Fock Matrices

The inactive Fock matrices correspond to the regular Fock matrix if $\{t^a_i\}$ is zero.

$$\hat{F}_{ia} = \sum_{kc}\left[2(ia\hat{|}kc) - (ic\hat{|}ka)\right]t^c_k$$

$$= \sum_{kcQ}\left[2J^Q_{ia}J^Q_{kc}t^c_k - J^Q_{ic}t^c_k J^Q_{ka}\right]$$

$$\hat{F}_{ai} = \sum_{kc}\left[2(ai\hat{|}kc) - (ac\hat{|}ki)\right]t^c_k$$

$$= \sum_{kcQ}\left[2\hat{J}^Q_{ai}J^Q_{kc}t^c_k - \hat{J}^Q_{ac}t^c_k\hat{J}^Q_{ki}\right]$$

$$\hat{F}_{ab} = F_{ab} + \sum_{kc}\left[2(ab\hat{|}kc) - (ac\hat{|}kb)\right]t^c_k$$

$$= \delta_{ab}\epsilon_a + \sum_{kcQ}\left[2\hat{J}^Q_{ab}J^Q_{kc}t^c_k - \hat{J}^Q_{ac}t^c_k J^Q_{kb}\right]$$

$$\hat{F}_{ji} = F_{ji} + \sum_{kc}\left[2(ji\hat{|}kc) - (jc\hat{|}ki)\right]t^c_k$$

$$= \delta_{ij}\epsilon_i + \sum_{kcQ}\left[2\hat{J}^Q_{ji}J^Q_{kc}t^c_k - J^Q_{jc}t^c_k\hat{J}^Q_{ki}\right]$$

CC2 Residualfunction

$$\Omega_{ai} = \Omega^0_{ai} + \Omega^I_{ai} + \Omega^J_{ai} + \Omega^G_{ai} + \Omega^H_{ai}$$

$$\Omega^0_{ai} = (\epsilon_a - \epsilon_i)t^a_i$$

$$\Omega^I_{ai} = \sum_{kc} \tilde{t}^{ac}_{ik}\hat{F}_{kc} \qquad \Omega^J_{ai} = \hat{F}_{ai}$$

$$\Omega^G_{ai} = \sum_{bkc} \tilde{t}^{bc}_{ik}(kc\hat{|}ab) = \sum_{bQ} \hat{J}^Q_{ab}Y^Q_{bi} \qquad \Omega^H_{ai} = -\sum_{jkc} \tilde{t}^{ac}_{jk}(kc\hat{|}ji) = -\sum_{jQ} Y^Q_{aj}\hat{J}^Q_{ji}$$

Implementation

- Storage of all $\mathcal{O}^Q_{pq}$-like matrices with rows over pq and columns over Q (column-major fashion).
- If $pq = ia$ or ai, i is always the leading index, such that a map of a column in $\mathcal{O}$ will yield a matrix with n_{virt} rows and n_{occ} columns.
- Symmetry: J^Q_{ij}, J^Q_{ab} only storage of $n(n + 1)/2$ entries required (corresponding to the lower-triangular part).
- Map to matrix of columns in $\hat{J}^Q_{ij}, \hat{J}^Q_{ab}$ with ρ as row index and η as column index (see definition of $\hat{J}^Q_{pq}$ terms).
- All loop structures are parallelized either (i) over ij pairs where any amplitudes are contracted (simultaneous contraction with corresponding n^2_{virt} amplitudes in each iteration or (ii) otherwise Q to reduce memory overhead.

Sigmavector Expressions

General Information

- E-intermediates are indepedent of the guessvectors and are precomputed.
- Noting that $J_{pq} \neq \hat{J}_{pq}$ in case of CC2, the X-, Y- and Z-intermediates and the σ^{GH}-contributions are equivalent for all methods so the routines for computing them are shared among the sigma vectors.
- The Y-intermediates are known from the residual function iterations (CC2) or can be precomputed from the MP2 amplitudes [ADC(2) and CIS(D_∞)] and discarded after the E-intermediates are obtained.
- In case of ADC(2) and CIS(D_∞), the σ^J-contributions are equivalent to configuration interaction singles.
- $E^{\mathrm{ADC(2)}} = \frac{1}{2}(E^{\mathrm{CIS(D_\infty)}} + E^{\mathrm{CIS(D_\infty)}^\dagger})$
- Left transformation with CIS(D_∞) and CC2 Jacobians obtained as

$$\begin{aligned}\sigma_{\mu_1}(\omega, b) &= \sum\nolimits_{\nu_1} b_{\nu_1} A^{\mathrm{eff}}_{\nu_1\mu_1}(\omega)\\ &= \sum\nolimits_{\nu_1} (A^{\mathrm{eff}\dagger})_{\mu_1\nu_1}(\omega) b_{\nu_1}\end{aligned}$$

- The corresponding terms can easily be obtained by comparison to the expression of the ADC(2) sigma vector, since it also contains the "transposed components"

CC2

$$\sigma_{ai}(b,\omega) = \sigma^0_{ai} + \sigma^I_{ai} + \sigma^J_{ai} + \sigma^G_{ai} + \sigma^H_{ai}$$

$$\sigma^0_{ai} = \sum\nolimits_b E_{ab} b^b_i - \sum\nolimits_j b^a_j E_{ji}$$

$$\begin{aligned}E_{ab} &= \hat{F}_{ab} - \sum\nolimits_{jkc} \tilde{t}^{ac}_{jk} (kc\hat{|}jb)\\ &= \hat{F}_{ab} - \sum\nolimits_{jQ} Y^Q_{aj} J^Q_{jb}\end{aligned}$$

$$\begin{aligned}E_{ji} &= \hat{F}_{ji} + \sum\nolimits_{bkc} \tilde{t}^{bc}_{ik} (kc\hat{|}jb)\\ &= \hat{F}_{ji} + \sum\nolimits_{bQ} J^Q_{jb} Y^Q_{bi}\end{aligned}$$

$$\begin{aligned}\sigma^J_{ai} &= \sum\nolimits_{kc} \left[2(ai\hat{|}kc) - (ac\hat{|}ki)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2\hat{J}^Q_{ai} J^Q_{kc} b^c_k - \hat{J}^Q_{ac} b^c_k \hat{J}^Q_{ki}\right]\end{aligned}$$

$$\sigma^I_{ai} = \sum\nolimits_{jb} \left[\tilde{R}^{ab}_{ij} \hat{F}_{jb} + \tilde{t}^{ab}_{ij} \hat{F}'_{jb}\right]$$

$$\begin{aligned}\hat{F}'_{jb} &= \sum\nolimits_{kc} \left[2(jb\hat{|}kc) - (jc\hat{|}kb)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2J^Q_{jb} J^Q_{kc} b^c_k - J^Q_{jc} b^c_k J^Q_{kb}\right]\end{aligned}$$

$$\begin{aligned}\sigma^G_{ai} &= \sum\nolimits_{bkc} \tilde{R}^{bc}_{ik} (kc\hat{|}ab)\\ &= \sum\nolimits_{bQ} \hat{J}^Q_{ab} Z^Q_{bi}\end{aligned}$$

$$\begin{aligned}\sigma^H_{ai} &= -\sum\nolimits_{jkc} \tilde{R}^{ac}_{jk} (kc\hat{|}ji)\\ &= -\sum\nolimits_{jQ} Z^Q_{aj} \hat{J}^Q_{ji}\end{aligned}$$

CIS(D_∞)

$$\sigma_{ai}(b,\omega) = \sigma^0_{ai} + \sigma^I_{ai} + \sigma^J_{ai} + \sigma^G_{ai} + \sigma^H_{ai}$$

$$\sigma^0_{ai} = \sum\nolimits_b E_{ab} b^b_i - \sum\nolimits_j b^a_j E_{ji}$$

$$\begin{aligned}E_{ab} &= F_{ab} - \sum\nolimits_{jkc} \tilde{t}^{ac}_{jk} (kc|jb)\\ &= \delta_{ab}\epsilon_a - \sum\nolimits_{jQ} Y^Q_{aj} J^Q_{jb}\end{aligned}$$

$$\begin{aligned}E_{ji} &= F_{ij} + \sum\nolimits_{bkc} \tilde{t}^{bc}_{ik} (kc|jb)\\ &= \delta_{ji}\epsilon_i + \sum\nolimits_{bQ} J^Q_{jb} Y^Q_{bi}\end{aligned}$$

$$\begin{aligned}\sigma^J_{ai} &= \sum\nolimits_{kc} \left[2(ai|kc) - (ac|ki)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2J^Q_{ia} J^Q_{kc} b^c_k - J^Q_{ac} b^c_k J^Q_{ki}\right]\end{aligned}$$

$$\sigma^I_{ai} = \sum\nolimits_{jb} \tilde{t}^{ab}_{ij} F'_{jb}$$

$$\begin{aligned}F'_{jb} &= \sum\nolimits_{kc} \left[2(jb|kc) - (jc|kb)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2J^Q_{jb} J^Q_{kc} b^c_k - J^Q_{jc} b^c_k J^Q_{kb}\right]\end{aligned}$$

$$\begin{aligned}\sigma^G_{ai} &= \sum\nolimits_{bkc} \tilde{R}^{bc}_{ik} (kc|ab)\\ &= \sum\nolimits_{bQ} J^Q_{ab} Z^Q_{bi}\end{aligned}$$

$$\begin{aligned}\sigma^H_{ai} &= -\sum\nolimits_{jkc} \tilde{R}^{ac}_{jk} (kc|ji)\\ &= -\sum\nolimits_{jQ} Z^Q_{aj} J^Q_{ji}\end{aligned}$$

ADC(2)

$$\sigma_{ai}(b,\omega) = \sigma^0_{ai} + \sigma^I_{ai} + \sigma^J_{ai} + \sigma^G_{ai} + \sigma^H_{ai}$$

$$\sigma^0_{ai} = \sum\nolimits_b E_{ab} b^b_i - \sum\nolimits_j b^a_j E_{ji}$$

$$\begin{aligned}E_{ab} &= F_{ab} - 0.5\sum\nolimits_{jkc} \left[\tilde{t}^{ac}_{jk} (kc|jb) + \tilde{t}^{bc}_{jk} (kc|ja)\right]\\ &= \delta_{ab}\epsilon_a - 0.5\sum\nolimits_{jQ} \left[Y^Q_{aj} J^Q_{jb} + Y^Q_{bj} J^Q_{ja}\right]\end{aligned}$$

$$\begin{aligned}E_{ji} &= F_{ji} + 0.5\sum\nolimits_{bkc} \left[\tilde{t}^{bc}_{ik} (kc|jb) + \tilde{t}^{bc}_{jk} (kc|ib)\right]\\ &= \delta_{ji}\epsilon_i + 0.5\sum\nolimits_{bQ} \left[J^Q_{jb} Y^Q_{bi} + J^Q_{ib} Y^Q_{bj}\right]\end{aligned}$$

$$\begin{aligned}\sigma^J_{ai} &= \sum\nolimits_{kc} \left[2(ai|kc) - (ac|ki)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2J^Q_{ia} J^Q_{kc} b^c_k - J^Q_{ac} b^c_k J^Q_{ki}\right]\end{aligned}$$

$$\sigma^I_{ai} = 0.5\sum\nolimits_{jb} \left[\tilde{t}^{ab}_{ij} F'_{jb} + \left[2(ia|jb) - (ib|ja)\right] T'_{jb}\right]$$

$$T'_{jb} = \sum\nolimits_{kc} \tilde{t}^{bc}_{jk} b^c_k$$

$$\begin{aligned}F'_{jb} &= \sum\nolimits_{kc} \left[2(jb|kc) - (jc|kb)\right] b^c_k\\ &= \sum\nolimits_{kcQ} \left[2J^Q_{jb} J^Q_{kc} b^c_k - J^Q_{jc} b^c_k J^Q_{kb}\right]\end{aligned}$$

$$\begin{aligned}\sigma^G_{ai} &= \sum\nolimits_{bkc} \tilde{R}^{bc}_{ik} (kc|ab)\\ &= \sum\nolimits_{bQ} J^Q_{ab} Z^Q_{bi}\end{aligned}$$

$$\begin{aligned}\sigma^H_{ai} &= -\sum\nolimits_{jkc} \tilde{R}^{ac}_{jk} (kc|ji)\\ &= -\sum\nolimits_{jQ} Z^Q_{aj} J^Q_{ji}\end{aligned}$$

Transition Moments from CC2

Computational Protocol

1. Calculate RI-CIS amplitudes using a conventional Davidson procedure.
2. Calculate singles ground-state amplitudes t_i^a from residual equations.
3. Calculate right singles excitation amplitudes R_i^a using the RI-CIS eigenpairs as an initial guess for a robust quasi-linear Davidson procedure followed by a DIIS eigenvalue solver.
4. Calculate left singles excitation amplitudes L_i^a using right CC2 eigenpairs as an initial guess in combination with root following.
5. Assert that left and right eigenvalues match.
6. To provide a unique normalization of left and right eigenvectors (which are supposed to be biorthonormal), two normalization conditions are enforced:
$$\sum_{ia} L_i^a R_i^a + \frac{1}{2} \sum_{iajb} L_{ij}^{ab} R_{ij}^{ab} = 1,$$
$$\sum_{ia} R_i^a R_i^a + \frac{1}{2} \sum_{iajb} R_{ij}^{ab} R_{ij}^{ab} = 1.$$
However, any normalization satisfying the former of the two conditions is mathematically well defined and must lead to identical results.
7. Determine right-hand sides for ground-state singles Lagrangian multipliers $\{\varphi_{\mu_1}\}$.
8. Determine ground-state singles Lagrangian multipliers $\bar{t}_i^a$ by iteratively solving the linear system
$$\sum_{\nu_1} \bar{t}_{\nu_1} A(0)_{\nu_1,\mu_1} = -\varphi_{\mu_1},$$
using a simple subspace expansion and the zeroth order Jacobian $\bar{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i)$ as a preconditioning matrix.
9. Determine right-hand sides for transition-moment singles Lagrangian multipliers $\{\phi_{\mu_1}\}$.
10. Determine transition-moment singles Lagrangian multipliers $\bar{M}_i^a$ by iteratively solving the linear system
$$\sum_{\nu_1} \bar{M}_{\nu_1} [A(-\omega) + \omega 1]_{\nu_1,\mu_1} = -\phi_{\mu_1},$$
using a subspace expansion for all considered excited states and the eigenvalue-shifted zeroth order Jacobian $\bar{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i + \omega)$ as a root-specific preconditioning matrix.
11. Calculate $D^\eta(R)$, $D^\xi(\bar{M})$ and $D^\xi(L)$ density matrices of each considered excited state.
12. Obtain right T_{0n}^j and left T_{n0}^j transition moments according to
$$T_{0n}^{V^j} = \sqrt{2} \sum_{pq} \left[D_{pq}^\eta(R) + D_{pq}^\xi(\bar{M}) \right] \hat{V}_{pq}^j, \qquad T_{n0}^{V^j} = \sqrt{2} \sum_{pq} \left[D_{pq}^\xi(L) \right] \hat{V}_{pq}^j,$$
where V^j is a Cartesian component of dipole operator $V \in \{\mu, p, m\}$ and
$$\hat{V}_{pq}^j = \sum_{\mu\nu} \Lambda_{\mu p}^\rho V_{\mu\nu} \Lambda_{\nu q}^\eta$$
the corresponding similarity-transformed property integral.
13. Evaluate transition strengths $S_{0n}^{V_1^j V_2^j}$ (from which oscillator and rotatory strengths can readily be determined) according to
$$S_{0n}^{V_1^j V_2^j} = \frac{1}{2} \left[T_{0n}^{V_1^j} T_{n0}^{V_2^j} + \left(T_{0n}^{V_2^j} T_{n0}^{V_1^j} \right)^* \right].$$

Right transformed Fock Matrices

$$\bar{F}_{ia} = \sum\nolimits_{kc} \left[2(ia|kc) - (ic|ka)\right] R_k^c$$
$$= \sum\nolimits_{kcQ} \left[2 J_{ia}^Q J_{kc}^Q R_k^c - J_{ic}^Q R_k^c J_{ka}^Q \right]$$

$$\bar{F}_{ai} = \sum\nolimits_{kc} \left[2(ai\hat{|}kc) - (ac\hat{|}ki) \right] R_k^c + \sum\nolimits_b R_j^b \hat{F}_{ab} - \sum_j R_j^a \hat{F}_{ji}$$
$$= \sum_{kcQ} \left[2\hat{J}_{ai}^Q J_{kc}^Q R_k^c - \hat{J}_{ac}^Q R_k^c \hat{J}_{ki}^Q \right] + \sum\nolimits_b R_j^b \hat{F}_{ab} - \sum\nolimits_j R_j^a \hat{F}_{ji}$$

$$\bar{F}_{ab} = \sum\nolimits_{kc} \left[2(ab\hat{|}kc) - (ac\hat{|}kb) \right] R_k^c - \sum\nolimits_j R_j^a \hat{F}_{jb}$$
$$= \sum\nolimits_{kcQ} \left[2\hat{J}_{ab}^Q J_{kc}^Q R_k^c - \hat{J}_{ac}^Q R_k^c J_{kb}^Q \right] - \sum_j R_j^a \hat{F}_{jb}$$

$$\bar{F}_{ij} = \sum\nolimits_{kc} \left[2(ij\hat{|}kc) - (kj\hat{|}ic) \right] R_k^c + \sum\nolimits_b R_j^b \hat{F}_{ib}$$
$$= \sum\nolimits_{kcQ} \left[2\hat{J}_{ij}^Q J_{kc}^Q R_k^c - J_{jc}^Q R_k^c \hat{J}_{ki}^Q \right] + \sum_b R_j^b \hat{F}_{ib}$$

More Amplitudes

$$\eta_{ij}^{ab} = \frac{2(ia|jb) - (ib|ja)}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b} \qquad P_{pq}^{rs} f_{pq}^{rs} = f_{pq}^{rs} + f_{qp}^{sr}$$

$$\bar{t}_{ij}^{ab} = \eta_{ij}^{ab} + \frac{2(ia\breve{|}jb) - (ib\breve{|}ja) + P_{ij}^{ab}[2\bar{t}_i^a \hat{F}_{jb} - \bar{t}_j^a \hat{F}_{ib}]}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b}$$

$$\bar{L}_{ij}^{ab} = \frac{2(ia\breve{|}jb) - (ib\breve{|}ja) + P_{ij}^{ab}[2L_i^a \hat{F}_{jb} - L_j^a \hat{F}_{ib}]}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b}$$

$$F_{ij}^{ab} = \frac{2(ia\tilde{|}jb) - (ib\tilde{|}ja) + P_{ij}^{ab}[2\bar{t}_i^a \bar{F}_{jb} - \bar{t}_j^a \bar{F}_{ib}]}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b - \omega}$$

$$\bar{M}_{ij}^{ab} = F_{ij}^{ab} + \frac{2(ia\breve{|}jb) - (ia\breve{|}jb) + P_{ij}^{ab}[2\bar{M}_i^a \hat{F}_{jb} - \bar{M}_j^a \hat{F}_{ib}]}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b - \omega}$$

More Intermediates and Integral Transformations

Left transformed integrals:

$$\breve{J}_{ia}^Q = \sum_b \hat{J}_{ba}^Q b_i^b + \sum_j b_a^j \hat{J}_{ij}^Q$$

$$(ia\breve{|}jb) = \sum_Q (J_{ia}^Q \breve{J}_{jb}^Q + \breve{J}_{ia}^Q J_{jb}^Q)$$

Index-transformed integrals:

$$\tilde{J}_{ia}^Q = -\sum_{kc} \left(\bar{t}_i^c R_k^c J_{ka}^Q + J_{ic}^Q R_k^c t_k^a \right)$$

$$(ia\tilde{|}jb) = \sum_Q (J_{ia}^Q \tilde{J}_{jb}^Q + \tilde{J}_{ia}^Q J_{jb}^Q)$$

Right-hand side for ground-state Lagrangian singles:

$$\varphi_{ia} = \hat{F}_{ia} + \sum_{kcd} \eta_{ki}^{cd} (ck\hat{|}da) - \sum_{kcl} \eta_{kl}^{ca} (ck\hat{|}il)$$
$$= \hat{F}_{ia} + \sum_{dQ} \hat{J}_{da}^Q Y_{di}^Q - \sum_{lQ} Y_{al}^Q \hat{J}_{il}^Q$$

Transition Moments from CC2

References

For residual function and right-hand Jacobian transformation:
C. Hättig, F. Weigend, *J.Chem. Phys.* **113**, 5154 (2000)

For left-hand Jacobian transformation and transition moments:
C. Hättig, A. Köhn, *J.Chem. Phys.* **117**, 6939 (2002)

CC2 Left-Hand Transformation

$$\sigma_{ai}(b,\omega) = \sigma^0_{ai} + \sigma^I_{ai} + \sigma^J_{ai} + \sigma^G_{ai} + \sigma^H_{ai}$$

$$\sigma^0_{ai} = \sum\nolimits_b (E^\dagger)_{ab} b^b_i - \sum\nolimits_j b^a_j (E^\dagger)_{ji}$$

(The E intermediates are identical to before.)

$$\begin{aligned} E_{ab} &= \hat{F}_{ab} - \sum\nolimits_{jkc} \tilde{t}^{ac}_{jk} (kc\hat{|}jb) \\ &= \hat{F}_{ab} - \sum\nolimits_{jQ} Y^Q_{aj} J^Q_{jb} \end{aligned}$$

$$\begin{aligned} E_{ij} &= \hat{F}_{ij} + \sum\nolimits_{bkc} \tilde{t}^{bc}_{jk} (kc|ib) \\ &= \hat{F}_{ij} + \sum\nolimits_{bQ} Y^Q_{bj} J^Q_{ib} \end{aligned}$$

$$\begin{aligned} \sigma^J_{ai} &= \sum\nolimits_{kc} \left[2(ck\hat{|}ia) - (ca\hat{|}ik) \right] b^c_k \\ &= \sum\nolimits_{kcQ} \left[2\hat{J}^Q_{ck} J^Q_{ia} b^c_k - \hat{J}^Q_{ca} b^c_k \hat{J}^Q_{ik} \right] \end{aligned}$$

$$\begin{aligned} \sigma^I_{ai} &= \sum\nolimits_{jb} \left[2(jb|ia) - (ja|ib) \right] T'_{jb} \\ &= \sum\nolimits_{kcQ} \left[2J^Q_{jb} J^Q_{ia} b^b_j - J^Q_{ja} b^b_j J^Q_{ib} \right] \end{aligned}$$

$$T'_{jb} = \sum_{kc} \tilde{t}^{bc}_{jk} b^c_k$$

$$\begin{aligned} \sigma^G_{ai} &= \sum\nolimits_{bkc} L^{bc}_{ik} (ck\hat{|}ba) \\ &= \sum\nolimits_{bQ} \hat{J}^Q_{ba} Z^Q_{bi} \end{aligned}$$

$$\begin{aligned} \sigma^H_{ai} &= -\sum\nolimits_{jkc} L^{ac}_{jk} (ck\hat{|}ij) \\ &= -\sum\nolimits_{jQ} Z^Q_{aj} \hat{J}^Q_{ij} \end{aligned}$$

Right-hand Sides Tr. Moment Lagrangian Singles

$$\phi_{ai}(\omega) = \phi^0_{ai} + \phi^I_{ai} + \phi^J_{ai} + \phi^G_{ai} + \phi^H_{ai}$$

$$\phi^0_{ai} = \sum\nolimits_b (\bar{E}^\dagger)_{ab} \bar{t}^b_i - \sum\nolimits_j \bar{t}^a_j (\bar{E}^\dagger)_{ji}$$

$$\begin{aligned} \bar{E}_{ab} &= \bar{F}_{ab} - \sum\nolimits_{jkc} \tilde{R}^{ac}_{jk} (kc|jb) \\ &= \bar{F}_{ab} - \sum\nolimits_{jQ} Z^Q_{aj} J^Q_{jb} \end{aligned}$$

$$\begin{aligned} \bar{E}_{ij} &= \bar{F}_{ij} + \sum\nolimits_{kcb} \tilde{R}^{bc}_{jk} (kc|ib) \\ &= \bar{F}_{ij} + \sum\nolimits_{bQ} J^Q_{ib} Z^Q_{bj} \end{aligned}$$

$$\begin{aligned} \phi^J_{ai} &= \sum\nolimits_{kc} \left[2(ck\bar{|}ia) - (ca\bar{|}ik) \right] \bar{t}^c_k \\ &= \sum\nolimits_{kcQ} \left[2J^Q_{ia} \bar{J}^Q_{kc} \bar{t}^c_k - (\bar{J}^Q_{ac} \hat{J}^Q_{ki} + \hat{J}^Q_{ac} \bar{J}^Q_{ki}) \bar{t}^c_k \right] \end{aligned}$$

$$\begin{aligned} \phi^I_{ai} &= \bar{F}_{ia} + \sum\nolimits_{jb} \left[2(jb|ia) - (ja|ib) \right] \bar{T}'_{jb} \\ &= \bar{F}_{ia} + \sum\nolimits_{kcQ} \left[2J^Q_{ia} J^Q_{jb} \bar{T}'_{jb} - J^Q_{ja} \bar{T}'_{jb} J^Q_{ib} \right] \end{aligned}$$

$$\bar{T}'_{jb} = \sum\nolimits_{kc} \tilde{R}^{bc}_{jk} \bar{t}^c_k$$

$$\begin{aligned} \phi^G_{ai} &= \sum\nolimits_{bkc} \left[F^{bc}_{ik} (ck\hat{|}da) + \bar{t}^{bc}_{ik} (ck\bar{|}da) \right] \\ &= \sum\nolimits_{bkcQ} \left[F^{bc}_{ik} \hat{J}^Q_{ck} \hat{J}^Q_{da} + \bar{t}^{bc}_{ik} \left(\bar{J}^Q_{ck} \hat{J}^Q_{da} + \hat{J}^Q_{ck} \bar{J}^Q_{da} \right) \right] \\ &= \sum\nolimits_{bkcQ} \left[(F^{bc}_{ik} \hat{J}^Q_{ck} + \bar{t}^{bc}_{ik} \bar{J}^Q_{ck}) \hat{J}^Q_{da} + \bar{t}^{bc}_{ik} \hat{J}^Q_{ck} \bar{J}^Q_{da} \right] \end{aligned}$$

$$\begin{aligned} \phi^H_{ai} &= -\sum\nolimits_{jkc} \left[F^{ac}_{jk} (ck\hat{|}il) + \bar{t}^{ac}_{jk} (ck\bar{|}il) \right] \\ &= -\sum\nolimits_{jkcQ} \left[F^{ac}_{jk} \hat{J}^Q_{ck} \hat{J}^Q_{il} + \bar{t}^{ac}_{jk} \left(\bar{J}^Q_{ck} \hat{J}^Q_{il} + \hat{J}^Q_{ck} \bar{J}^Q_{il} \right) \right] \\ &= -\sum\nolimits_{jkcQ} \left[(F^{ac}_{jk} \hat{J}^Q_{ck} + \bar{t}^{ac}_{jk} \bar{J}^Q_{ck}) \hat{J}^Q_{il} + \bar{t}^{ac}_{jk} \hat{J}^Q_{ck} \bar{J}^Q_{il} \right] \end{aligned}$$

One-Particle Density Matrices

$$D^{\mathrm{CC2}}_{ij} = \sum_{kcb} \bar{t}^{cb}_{ik} t^{cb}_{jk} \qquad D^{\mathrm{CC2}}_{ab} = \sum_{kcj} t^{ac}_{kj} \bar{t}^{bc}_{kj}$$

$$\begin{aligned} D^\eta_{ij}(R) &= -\sum_b R^b_i \bar{t}^b_j - \sum_{abk} R^{ab}_{ik} \bar{t}^{ab}_{jk} \\ D^\eta_{ia}(R) &= R^a_i + \sum_{kc} \tilde{R}^{ac}_{ik} \bar{t}^c_k \\ &\quad - \sum_b D^{\mathrm{CC2}}_{ab} R^b_i - \sum_b R^a_j D^{\mathrm{CC2}}_{ji} \\ D^\eta_{ai}(R) &= 0 \\ D^\eta_{ab}(R) &= \sum_j \bar{t}^a_j R^b_j + \sum_{ijc} \bar{t}^{ac}_{ij} R^{bc}_{ij} \end{aligned}$$

$$\begin{aligned} D^\xi_{ij}(M) &= -\sum_{abk} t^{ab}_{ik} M^{ab}_{jk} \\ D^\xi_{ia}(M) &= \sum_{kc} \tilde{t}^{ac}_{ik} M^c_k \\ D^\xi_{ai}(M) &= M^a_i \\ D^\xi_{ab}(M) &= \sum_{ijc} M^{ac}_{ij} t^{bc}_{ij} \end{aligned}$$

$$\begin{aligned} D^\xi_{ij}(L) &= -\sum_{abk} t^{ab}_{ik} L^{ab}_{jk} \\ D^\xi_{ia}(L) &= \sum_{kc} \tilde{t}^{ac}_{ik} L^c_k \\ D^\xi_{ai}(L) &= L^a_i \\ D^\xi_{ab}(L) &= \sum_{ijc} L^{ac}_{ij} t^{bc}_{ij} \end{aligned}$$

Integral-Direct Routines and Miscellaneous

Integral-direct *J2G*

In order to avoid storage of J_{ab}^Q terms, integral-direct routines are implemented for each of their occurances.
The most important integral-direct function is the one for *J*.2- and *G*-type contributions.

$$\begin{aligned}
\sigma_{ai}^{J2G} &= \sum_{bj} (ab\hat{|}ji) t_j^b + \sum_{bkc} \tilde{t}_{ik}^{bc} (kc\hat{|}ab) \\
&= \sum_{bQ} \hat{J}_{ab}^Q \left[\sum_j b_{bj} \hat{J}_{ji}^Q + Y_{bi}^Q \right] \\
&= \sum_{bQ} \hat{J}_{ab}^Q \tilde{Y}_{bi}^Q \\
&= \sum_{\mu\nu PbQ} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \Lambda_{\nu b}^\eta \tilde{Y}_{bi}^Q \\
&= \sum_{\mu\nu PQ} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \Gamma_{\nu i}^Q \\
&= \sum_{\mu\nu P} \Lambda_{\mu a}^\rho (\mu\nu|P) \tilde{\Gamma}_{\nu i}^P.
\end{aligned}$$

Here, the indices ν and P are contracted in a parallel loop over each $(\mu\nu|P)$. Then finally

$$\sigma_{ai}^{J2G} = \sum_{aT} \Lambda_{\mu a}^\rho \eta_{\mu i}^T,$$

where T is a thread-identifier.

By insertion of arbitrary $\hat{J}_{ji}^Q$, Y_{ai}^Q, b_j^b and left and right coefficient matrices, a whole lot of contributions are covered, for instance apart from CIS, ADC(2) and CC2 sigmavectors, also the right-hand sides for the Lagrange multipliers and more contributions are obtained this way.

Integral-direct $\bar{J}$

For the calculation of $\bar{J}$ or $\breve{J}$, also J_{ab}^Q-like terms are needed:

$$\bar{J}_{ai}^Q = \sum_{bQ} \hat{J}_{ab}^Q R_i^b - \sum_{jQ} R_j^a \hat{J}_{ji}^Q.$$

Interesting is thus only the first contribution:

$$\begin{aligned}
\bar{J}_{ai}^{Q,1} &= \sum_{bQ} \hat{J}_{ab}^Q R_{bi} \\
&= \sum_{\mu\nu PbQ} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \Lambda_{\nu b}^\eta R_i^b \\
&= \sum_{\mu\nu PQ} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \eta_{\nu i}.
\end{aligned}$$

Here, the contraction of ν is performed in a loop over each $(\mu\nu|P)$. The final contractions of P and ν is performed by means of simple matrix–matrix multiplications

$$\bar{J}_{ai}^{Q,1} = \sum_{\mu PQ} \Lambda_{\mu a}^\rho \Gamma_{\mu i}^P [V^{-1/2}]_{PQ}.$$

Integral-direct $\hat{F}_{ab}$

A dedicated function in integral-direct fashion is for the computation of the F_{ab} block of similarity transformed Fock matrices (either transformed with t_i^a, b_i^a or R_i^a depending on the context) and is as follows:

$$\hat{F}_{ab} = \sum_{ck} [2(ab\hat{|}kc) - (ac\hat{|}kb)] t_k^c,$$

so that it follows for the first part

$$\begin{aligned}
\hat{F}_{ab}^1 &= 2 \sum_{ckQ} \hat{J}_{ab}^Q J_{kc}^Q t_k^c \\
&= 2 \sum_{\mu\nu QP} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \Lambda_{\nu b}^\eta X_Q \\
&= 2 \sum_{\mu\nu P} \Lambda_{\mu a}^\rho (\mu\nu|P) \tilde{X}_P \Lambda_{\nu b}^\eta \\
&= 2 \sum_{\mu\nu} \Lambda_{\mu a}^\rho \tilde{F}_{\mu\nu} \Lambda_{\nu b}^\eta.
\end{aligned}$$

The contraction of P is performed in a loop over each $(\mu\nu|P)$. The second part reads

$$\begin{aligned}
\hat{F}_{ab}^2 &= -\sum_{ckQ} \hat{J}_{ac}^Q t_k^c J_{kb}^Q \\
&= -\sum_{\mu\nu ckQP} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \left[\Lambda_{\nu c}^\eta t_k^c\right] J_{kb}^Q \\
&= -\sum_{\mu\nu kQP} \Lambda_{\mu a}^\rho (\mu\nu|P) [V^{-1/2}]_{PQ} \eta_{\nu k} J_{kb}^Q \\
&= -\sum_{\mu kQP} \Lambda_{\mu a}^\rho [V^{-1/2}]_{PQ} \Gamma_{\mu k}^P J_{kb}^Q \\
&= -\sum_{\mu kQ} \Lambda_{\mu a}^\rho \tilde{\Gamma}_{\mu k}^Q J_{kb}^Q.
\end{aligned}$$

The contraction of ν is performed in a loop over each $(\mu\nu|P)$.

Doubles Diagnostic for Right Eigenpairs

In a regular CC2 calculation, left and right eigenvectors are normalized according to the conditions above. A doubles diagnostic, that is the doubles contributions to a particular excitation, is then directly obtained by

$$\%T(\mu_2) = 1 - \sum_{\mu_1} L_{\mu_1} R_{\mu_1}.$$

If only excitation energies are to be obtained, left eigenvectors are not available. To obtain a doubles diagnostic nevertheless, the normalization condition

$$\sum_{ia} R_i^a R_i^a + \frac{1}{2} \sum_{iajb} \tilde{R}_{ij}^{ab} R_{ij}^{ab} = 1$$

is imposed on the right CIS(D_∞) or CC2 eigenvector. The doubles contributions obtained like this generally differ to the actual ones by only a few 0.01 %. This normalization is done for ADC(2) either way so that this is not an approximate strategy.

ADC(2) and CIS(D_∞) Density Matrices

I stick to the following expressions for the transition density matrices of ADC(2):

$$\begin{aligned}
D_{ij}^\xi(R) &= -\sum_{abk} t_{ik}^{ab} \tilde{R}_{jk}^{ab} \\
D_{ia}^\xi(R) &= \sum_{kc} \tilde{t}_{ik}^{ac} R_k^c \\
D_{ai}^\xi(R) &= R_i^a \\
D_{ab}^\xi(R) &= \sum_{ijc} \tilde{R}_{ij}^{ac} t_{ij}^{bc}
\end{aligned}$$

The corresponding expressions for the transition moments are

$$T_{0n}^{V^j} = \sqrt{2} \sum_{pq} D_{pq}^\xi(R) V_{pq}^j,$$

where left and right transition moments are identical and the regular SCF coefficient matrix is used for V_{pq}^j.

For the CIS(D_∞) method, I literally just leave the $\{t_i^a\}$ amplitudes at zero and let the CC2 routines do their thing. As can be expected, the results obtained like this are pretty similar to CC2 and ADC(2), are, however, probably not really justified by any theoretical model.

CIS(D) Method

The non-iterative variant of the CIS(D_∞) method, dubbed CIS(D), is also implemented:

$$\begin{aligned}
\omega^{\mathrm{CIS(D)}} &= \omega^{\mathrm{CIS}} + \omega^{\mathrm{(D)}} \\
&= \sum_{\mu_1\nu_1} R_{\mu_1}^{\mathrm{CIS}} \left[A_{\mu_1\nu_1}^{\mathrm{eff,CIS(D_\infty)}}\right] R_{\nu_1}^{\mathrm{CIS}},
\end{aligned}$$

where again

$$A_{\mu_1\nu_1}^{\mathrm{eff,CIS(D_\infty)}} = A_{\mu_1\nu_1}^{\mathrm{CIS(D_\infty)}} - \sum_{\gamma_2} \frac{A_{\mu_1\gamma_2}^{\mathrm{CIS(D_\infty)}} A_{\gamma_2\nu_1}^{\mathrm{CIS(D_\infty)}}}{\omega^{\mathrm{CIS}} - \epsilon_{\gamma_2}}.$$

Here, a subspace problem is not solved, such that the CIS eigenvectors are not allowed to mix if it was solved for more than one eigenstate in the preceeding CIS calculation.

CIS(D) can be understood as a perturbative doubles correction to CIS/CCS. The eigenvalue problem for CIS and CCS is identical, so the excitation energies of these two methods are in turn identical. Transition moments, however, are generally not due to different expression for the one-particle density matrices, which contain additional first-order terms for CCS.