Challenges and open problems related to the algebraic diagrammatic construction scheme

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Contents

Contents

Why excited-state calculations?

- Interaction light and matter
  - Spectroscopy (UV/vis, UV, X-ray)
  - Photoreactivity
- Application in materials and chemistry:
  - Colour
  - Energy production, storage and transport
  - UV durability / Photosynthesis
  - Molecular motors / sensors

Comparison of methods for $n = 2^1$

	CISD	CC2	**ADC(2)**
Ground state	CISD	CC2	**MP2**
Ground state order	3	3	**2**
Size consistency	No	(Yes)	**Yes**
Hermiticity	Yes	No	**Yes**
Max. excitation	2	2	**2**
Order properties	2	2	**2**
Naive scaling	n^6	n^5	n^5

[1] M. Wormit, D. R. Rehn, P. H. Harbach, J. Wenzel, C. M. Krauter, E. Epifanovsky and A. Dreuw. Mol. Phys., **112**, 774 (2014)

Comparison of methods for $n = 3^1$

	CISDT	CC3	**ADC(3)**
Ground state	CISDT	CC3	**MP3**
Ground state order	4	4	**3**
Size consistency	No	(Yes)	**Yes**
Hermiticity	Yes	No	**Yes**
Max. excitation	3	3	**2**
Order properties	3	3	**3**
Naive scaling	n^8	n^7	n^6

[1] M. Wormit, D. R. Rehn, P. H. Harbach, J. Wenzel, C. M. Krauter, E. Epifanovsky and A. Dreuw. Mol. Phys., **112**, 774 (2014)

Current status of ADC methods

- ADC(2): Established, excitation errors around 0.5eV
- ADC(3): Error comparable to benchmark methods
- Specialised variants exist (ionisation, core, spin-flip)

- Method limits:
  - Strong multi-reference cases
  - MP ground state fails

- Mathematical and numerical aspects:
  - Barely investigated
  - E.g. solvers unreliable for poor guesses / challenging cases

Contents

Green's functions and the polarisation propagator

- One-particle Green's function or propagator:

$$G_{p,p'}\left(t_p - t_{p'}\right) = -\imath \left\langle \Psi_0^N \middle| \hat{\mathcal{T}} \hat{\mathrm{c}}_p(t_p) \hat{\mathrm{c}}_{p'}^\dagger(t_{p'}) \middle| \Psi_0^N \right\rangle$$

  Time-evolution of wave function

- Two-particle Green's function or two-particle propagator:

$$G_{pq,p'q'}(t_p, t_q, t_{p'}, t_{q'}) = -\imath \left\langle \Psi_0^N \middle| \hat{\mathcal{T}} \hat{\mathrm{c}}_p(t_p) \hat{\mathrm{c}}_q(t_q) \hat{\mathrm{c}}_{p'}^\dagger(t_{p'}) \hat{\mathrm{c}}_{q'}^\dagger(t_{q'}) \middle| \Psi_0^N \right\rangle$$

  Time-evolution of $G_{p,p'}$

- Polarisation propagator or particle-hole propagator:

$$\Pi_{jk,j'k'}(t - t') = -\imath \left\langle \Psi_0^N \middle| \hat{\mathcal{T}} \hat{\mathrm{c}}_j(t) \hat{\mathrm{c}}_{k'}(t') \hat{\mathrm{c}}_k^\dagger(t) \hat{\mathrm{c}}_{j'}^\dagger(t') \middle| \Psi_0^N \right\rangle$$

  Special case of $G_{pq,p'q'}(t_p, t_q, t_{p'}, t_{q'})$*, evolution after excitation*

Polarisation propagator (1)[1]

- Spectral or Lehmann representation:

$$\Pi_{jk,j'k'}(\omega) = \sum_{m\neq 0} \frac{\left\langle \Psi_0 \middle| \hat{c}_k^\dagger \hat{c}_j \middle| \Psi_m \right\rangle \left\langle \Psi_m \middle| \hat{c}_{j'}^\dagger \hat{c}_{k'} \middle| \Psi_0 \right\rangle}{\omega - (E_m - E_0) + \imath\eta} - \sum_{m\neq 0} \frac{\left\langle \Psi_0 \middle| \hat{c}_{j'}^\dagger \hat{c}_{k'} \middle| \Psi_m \right\rangle \left\langle \Psi_m \middle| \hat{c}_k^\dagger \hat{c}_j \middle| \Psi_0 \right\rangle}{\omega + (E_m - E_0) - \imath\eta},$$

  where $\eta \to 0$

- Both terms contain same physical information:
  - Poles: Excitation energies $E_m - E_0$
  - Transition amplitudes

$$x_{m,jk} \equiv x_{m,j\leftarrow k} = \left\langle \Psi_m \middle| \hat{c}_j^\dagger \hat{c}_k \middle| \Psi_0 \right\rangle$$

[1] J. Schirmer. Phys. Rev. A, **26**, 2395 (1982)

Polarisation propagator (2)[1]

- Only consider

$$\Pi^{+}_{jk,j'k'}(\omega) = \sum_{m\neq 0} \frac{\left\langle \Psi_0 \middle| \hat{\mathrm{c}}^{\dagger}_k \hat{\mathrm{c}}_j \middle| \Psi_m \right\rangle \left\langle \Psi_m \middle| \hat{\mathrm{c}}^{\dagger}_{j'} \hat{\mathrm{c}}_{k'} \middle| \Psi_0 \right\rangle}{\omega - (E_m - E_0)}$$
$$= \underline{\boldsymbol{x}}^{\dagger}_{jk} \left(\omega \mathbf{I} - \boldsymbol{\Omega}\right)^{-1} \underline{\boldsymbol{x}}_{j'k'}$$

where
$$\omega_i \equiv E_i - E_0$$
$$\boldsymbol{\Omega} \equiv \mathrm{diag}(\omega_1, \omega_2, \ldots, \omega_m)$$
$$x_{m,jk} = \left\langle \Psi_m \middle| \hat{\mathrm{c}}^{\dagger}_j \hat{\mathrm{c}}_k \middle| \Psi_0 \right\rangle$$

[1] J. Schirmer. Phys. Rev. A, **26**, 2395 (1982)

Algebraic-diagrammatic construction (ADC) (1)

- Last slide: Diagonal representation

$$\Pi^{+}_{jk,j'k'}(\omega) = \underline{\boldsymbol{x}}^{\dagger}_{jk} \left(\omega\mathbf{I} - \boldsymbol{\Omega}\right)^{-1} \underline{\boldsymbol{x}}_{j'k'}$$

- Insert unitary transformation $\mathbf{Y}$ to generalise:

$$\Pi^{+}_{jk,j'k'}(\omega) = \underline{\boldsymbol{x}}^{\dagger}_{jk} \mathbf{Y}^{\dagger}\mathbf{Y} \left(\omega\mathbf{I} - \boldsymbol{\Omega}\right)^{-1} \mathbf{Y}^{\dagger}\mathbf{Y} \underline{\boldsymbol{x}}_{j'k'}$$

$\Rightarrow$ ADC representation

$$\Pi^{+}_{jk,j'k'}(\omega) = \underline{\boldsymbol{f}}^{\dagger}_{jk} \left(\omega\mathbf{I} - \mathbf{M}\right)^{-1} \underline{\boldsymbol{f}}_{j'k'}$$

with

- Modified transition amplitudes $\underline{\boldsymbol{f}}_{jk} = \mathbf{Y}\underline{\boldsymbol{x}}_{jk}$
- ADC matrix $\mathbf{M} = \mathbf{Y}\boldsymbol{\Omega}\mathbf{Y}^{\dagger}$

Algebraic-diagrammatic construction (2)[1]

- Well-known expansion via Feynman-Dyson perturbation theory:

$$\Pi^{+} = \Pi^{(0)} + \Pi^{(1)} + \Pi^{(2)} + \cdots$$

- From these diagrams ADC scheme constructs

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \cdots$$
$$\underline{\boldsymbol{f}}_{jk} = \underline{\boldsymbol{f}}^{(0)}_{jk} + \underline{\boldsymbol{f}}^{(1)}_{jk} + \underline{\boldsymbol{f}}^{(2)}_{jk} + \cdots$$

  based on Møller-Plesset partitioning and HF reference

$\Rightarrow$ n-th order in $\mathbf{M}$ & $\underline{\boldsymbol{f}}_{jk}$ equivalent to n-th order in Π^{+}

[1] J. Schirmer. Phys. Rev. A, **26**, 2395 (1982)

Algebraic-diagrammatic construction (3)

- Some ambiguity in construction of terms[1] ($\mathbf{M}^{(n)}$ versus $\underline{\boldsymbol{f}}^{(n)}$)

$\Rightarrow$ ADC: Make $\mathbf{M}$ least diagonal

  - Avoids "dangerous denominators"[2]
  - Leads to "compactness advantage"[2] in $\mathbf{M}$

- Other choices[2]:
  - Rayleigh-Schrödinger perturbation theory (RSPT) ($\mathbf{Y} = \mathbf{I}$)
  - Configuration-interaction (CI)

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[1] J. Schirmer. Phys. Rev. A, **26**, 2395 (1982)

[2] J. Schirmer. Phys. Rev. A, **43**, 4647 (1991)

Algebraic-diagrammatic construction (4)

Diagonal representation

$$\Pi^{+}_{jk,j'k'}(\omega) = \underline{\boldsymbol{x}}^{\dagger}_{jk} \left(\omega\mathbf{I} - \boldsymbol{\Omega}\right)^{-1} \underline{\boldsymbol{x}}_{j'k'}$$

$\Rightarrow$ Directly yields ω_m and $x_{m,jk}$

ADC representation

$$\Pi^{+}_{jk,j'k'}(\omega) = \underline{\boldsymbol{f}}^{\dagger}_{jk} \left(\omega\mathbf{I} - \mathbf{M}\right)^{-1} \underline{\boldsymbol{f}}_{j'k'}$$

1. Obtain N_{states} lowest eigenpairs $(\omega_m, \underline{\boldsymbol{y}}_m)$

$$\mathbf{M}\underline{\boldsymbol{y}}_m = \omega_m \underline{\boldsymbol{y}}_m$$

where $\underline{\boldsymbol{y}}_m$ is m-th column of $\mathbf{Y}$, the m-th transition vector.

2. Transition amplitude is

$$x_{m,jk} = \left(\underline{\boldsymbol{y}}_m\right)^{\dagger} \underline{\boldsymbol{f}}_{jk}$$

Algebraic-diagrammatic construction (5)

- ADC generalises to higher excitations: doubles, triples, ...
  - Transition amplitudes $x_{m,j\leftarrow k,j'\leftarrow k'}$
  - Modif. transition amplitudes $f_{iajb,j\leftarrow k,j'\leftarrow k'}$
  - Transition vectors $Y_{iajb,m}$
- Collect block-wise: E.g. transition vector

$$\mathbf{Y} = \begin{pmatrix} \vdots & \vdots & \iddots \\ Y_{ia,1} & Y_{ia,2} & \cdots \\ \vdots & \vdots & \\ Y_{iajb,1} & Y_{iajb,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad \underline{\boldsymbol{y}} = \begin{pmatrix} \vdots \\ y_{ia} \\ \vdots \\ y_{iajb} \\ \vdots \end{pmatrix}$$

- Elements written as $Y_{I,m}$ and y_I where I runs over all index tuples (i,a) and (i,a,j,b)

Intermediate states representation (1)

- Basis of $\mathbf{\Omega}$: Exact Schrödinger states
- Alternative basis for this space:

$$\left\{\Psi_0,\ \hat{\mathrm{c}}_a^\dagger \hat{\mathrm{c}}_i \Psi_0,\ \hat{\mathrm{c}}_b^\dagger \hat{\mathrm{c}}_j \hat{\mathrm{c}}_a^\dagger \hat{\mathrm{c}}_i \Psi_0,\ \ldots\right\} \equiv \left\{\hat{\mathrm{C}}_I \Psi_0\right\}_I$$

  where Ψ_0 is the *exact* ground state
- $\mathbf{Y}$ unitary transforms $\mathbf{\Omega}$ to $\mathbf{M}$

$\Rightarrow$ Direct construction of intermediate state basis $\{\tilde{\Psi}_I\}_I$:

- Intermediate states representation[1]:

$$M_{IJ} = \left\langle \tilde{\Psi}_I \middle| \hat{\mathcal{H}} - E_0 \middle| \tilde{\Psi}_J \right\rangle$$

$$f_{I,jk} = \left\langle \tilde{\Psi}_I \middle| \hat{\mathrm{c}}_j^\dagger \hat{\mathrm{c}}_k \middle| \Psi_0 \right\rangle$$

[1] J. Schirmer. Phys. Rev. A, **43**, 4647 (1991)

Intermediate states (2)

- Based on MP partitioning of $\hat{\mathcal{H}}_{\text{elec}}$
- Use MP ground state and build $\left\{\hat{\mathrm{C}}_I \Psi_0\right\}_I$
- Block-wise QR orthogonalsation singles, doubles, triples, ...

$\Rightarrow$ Intermediate states

- Allows systematic construction:
  - $\mathbf{M}$ (shifted Hamiltonian)
  - $\mathbf{f}$ (state projection)
  - arbitrary operators

Other propagators for ADC

- Polarisation propagator: Evolution after excitation
- Complex polarisation propagator: Models relaxation as well
- Particle propagator: Evolution after particle attachment
- Hole propagator: Evolution after particle removal

$\Rightarrow$ Can apply ADC scheme to all of them!

$\Rightarrow$ Very similar structure of equations

Connection to RPA[1]

- ADC: Eigenproblem, p-h, 2p-2h, ...

$$\mathbf{M}\underline{\boldsymbol{y}} = \omega\underline{\boldsymbol{y}}$$

- RPA: Pseudo-Eigenproblem, p-h, h-p

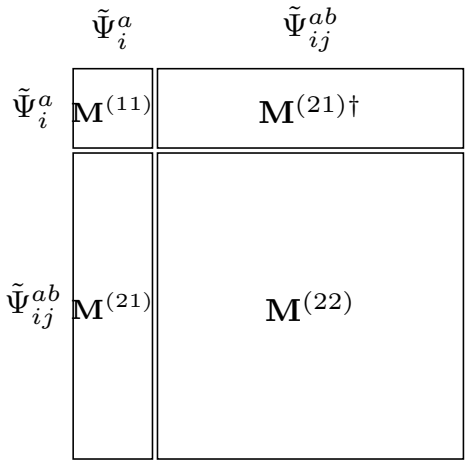
$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{A} \end{pmatrix} \begin{pmatrix} \underline{\boldsymbol{y}} \\ \underline{\boldsymbol{z}} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix} \begin{pmatrix} \underline{\boldsymbol{y}} \\ \underline{\boldsymbol{z}} \end{pmatrix}$$

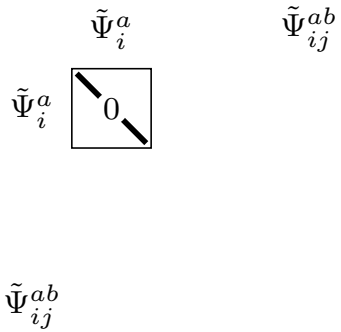
- RPA *and* TDA excitation energies: *Both* exact up to first order
  - Generally too large
  - Note: RPA no increase in perturbation order[1]
- ADC(1) exci. energies $\equiv$ CIS / TDA-RPA on HF reference

[1] J. Schirmer. Phys. Rev. A, **26**, 2395 (1982)

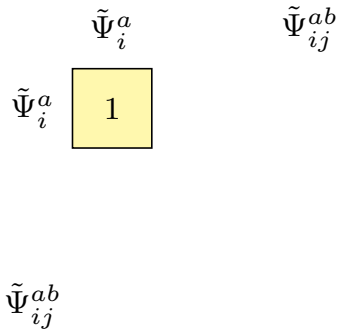
Contents

Structure of the ADC matrix (1)

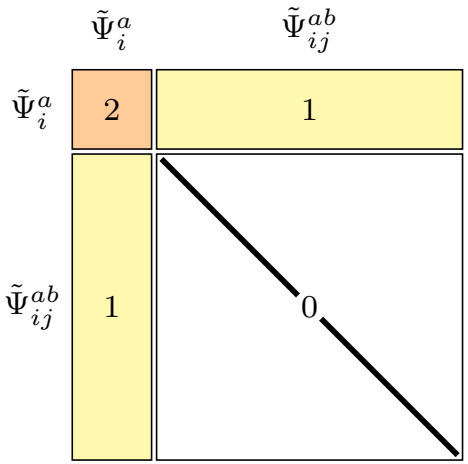




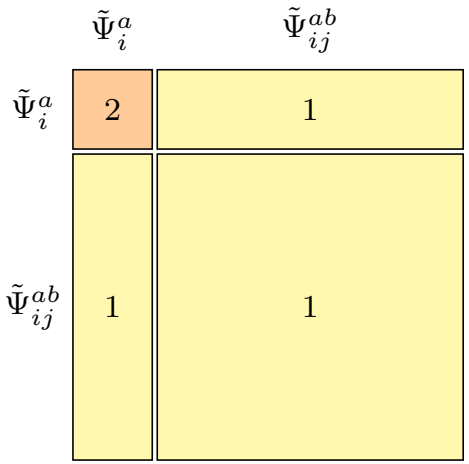
ADC(0)



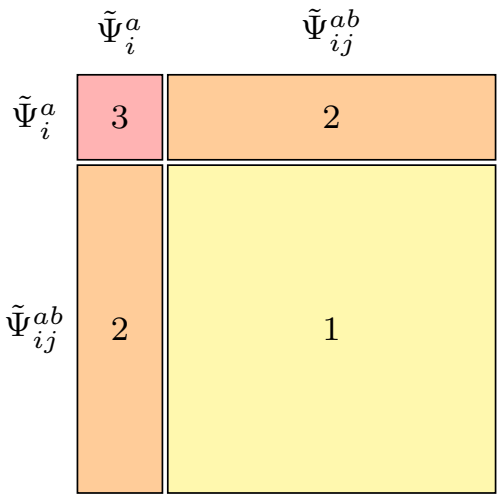
ADC(1)



ADC(2)



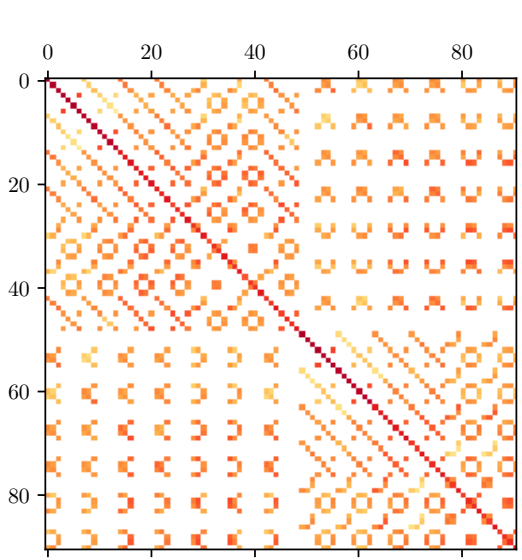
ADC(2)-x



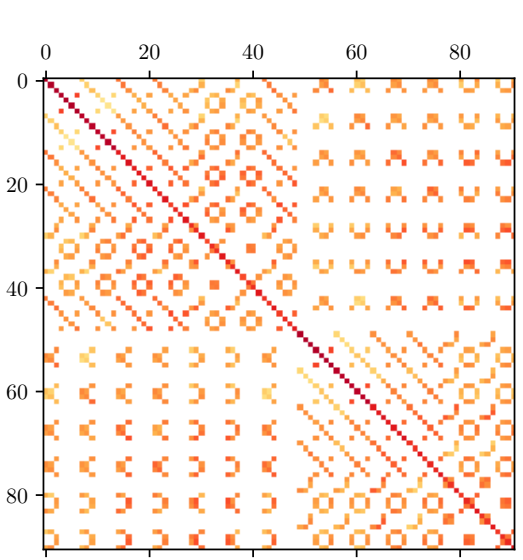
ADC(3)

Structure of the ADC matrix (2)

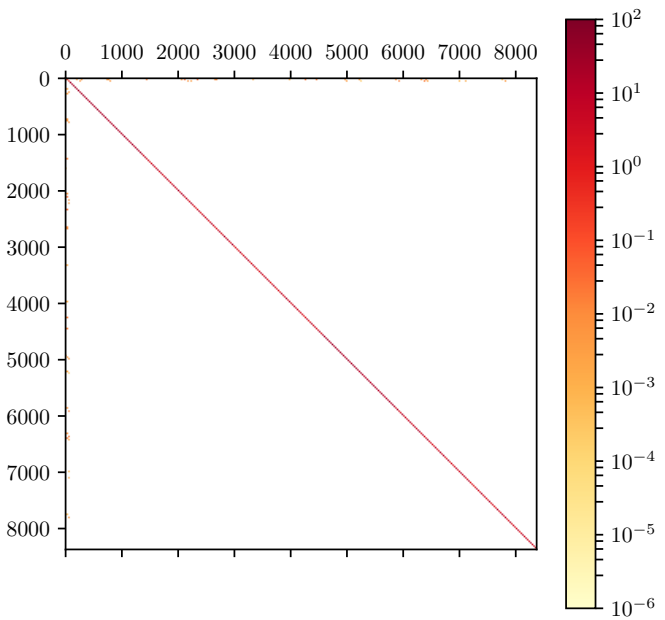
- Problem: $CN^{\bullet}$ (STO-3G)



ADC(1)



ADC(2)
(singles)



ADC(2)

Diagonalisation procedure $\mathbf{M}\underline{\boldsymbol{y}} = \omega\underline{\boldsymbol{y}}$

- $\mathbf{M}$ quickly becomes large
- Iterative diagonalisation procedures required
- Usually only smallest few eigenpairs $(\omega, \underline{\boldsymbol{y}})$ needed
- $\mathbf{M}$ is well diagonally dominant

$\Rightarrow$ Contraction-based Jacobi-Davidson algorithm

- Guess: Smallest diagonal elements
- Davidson-type "preconditioning": Diagonal of $\mathbf{M}$
- Expressions to perform block-wise matrix-vector product

- Typical cases: Convergence within 30 steps

Jacobi-Davidson algorithm

- Subspace algorithm:
  - Current Ritz pair $\left(\theta^{(j)}, \underline{\boldsymbol{y}}^{(j)}\right)$
  - Current residual $\underline{\boldsymbol{r}}^{(j)} = \mathbf{M}\underline{\boldsymbol{y}}^{(j)} - \omega\underline{\boldsymbol{y}}^{(j)}$
- Jacobi orthogonal component correction: Add $\underline{\boldsymbol{t}}^{(j)} \perp \underline{\boldsymbol{v}}^{(j)}$ to subspace, s.t.

$$\mathbf{M}\left(\underline{\boldsymbol{y}}^{(j)} + \underline{\boldsymbol{t}}^{(j)}\right) = \omega\left(\underline{\boldsymbol{y}}^{(j)} + \underline{\boldsymbol{t}}^{(j)}\right)$$

- ω unknown, so instead solve

$$\mathbf{M}_\theta \underline{\boldsymbol{t}}^{(j)} \equiv \left(\mathbf{I} - \underline{\boldsymbol{v}}^{(j)}\underline{\boldsymbol{v}}^{(j)\,*}\right)\left(\mathbf{M} - \theta^{(j)}\mathbf{I}\right)\left(\mathbf{I} - \underline{\boldsymbol{v}}^{(j)}\underline{\boldsymbol{v}}^{(j)\,*}\right)\underline{\boldsymbol{t}}^{(j)} = -\underline{\boldsymbol{r}}^{(j)}$$

- Davidson suggested to solve:

$$\left(\mathbf{I} - \underline{\boldsymbol{v}}^{(j)}\underline{\boldsymbol{v}}^{(j)\,*}\right)\left(\mathbf{D} - \theta^{(j)}\mathbf{I}\right)\underline{\boldsymbol{t}}^{(j)} = -\underline{\boldsymbol{r}}^{(j)},$$

  where $\mathbf{D}$ is an approximation to $\mathbf{M}$.

- Sleijpen-van-der-Vorst preconditioning:

$$\mathbf{K}_\theta^+ \mathbf{M}_\theta \underline{\boldsymbol{t}}^{(j)} = -\mathbf{K}_\theta^+ \underline{\boldsymbol{r}}^{(j)}$$

  where $\mathbf{K}_\theta^+$ is an approximate iterative inverse of $\mathbf{M}_\theta$.

Jacobi-Davidson algorithm

- Subspace algorithm:
  - Current Ritz pair $\left(\theta^{(j)}, \underline{\boldsymbol{y}}^{(j)}\right)$
  - Current residual $\underline{\boldsymbol{r}}^{(j)} = \mathbf{M}\underline{\boldsymbol{y}}^{(j)} - \omega\underline{\boldsymbol{y}}^{(j)}$
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  where $\mathbf{D}$ is an approximation to $\mathbf{M}$.
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  where $\mathbf{K}_\theta^+$ is an approximate iterative inverse of $\mathbf{M}_\theta$.

Linear-response-like ansatz (1)

- HF provides good guesses for $(\omega, \underline{\boldsymbol{y}})$: Almost there

$\Rightarrow$ Why not directly solve

$$\mathbf{M}\underline{\boldsymbol{y}} - \omega\underline{\boldsymbol{y}} = \underline{\mathbf{0}}$$

- Jacobi iterations:

$$\underline{\boldsymbol{r}}^{(j)} = \mathbf{M}\underline{\boldsymbol{y}}^{(j)} - \theta^{(j)}\underline{\boldsymbol{y}}^{(j)}$$
$$\underline{\boldsymbol{y}}^{(j+1)} = \underline{\boldsymbol{y}}^{(j)} - \left(\mathbf{D} - \theta^{(j)}\mathbf{I}\right)^{-1}\underline{\boldsymbol{r}}^{(j)}$$

  where $\theta^{(j)}$ is the current Rayleigh quotient

- Anderson / DIIS acceleration
- Need to solve one linear equation per eigenpair $(\omega, \underline{\boldsymbol{y}})$

Linear-response-like ansatz (2)

\+ ADC(2) becomes very fast (next slide)

– Multiple guess pairs $(\omega, \underline{\boldsymbol{y}})$ may collapse to one result

– Missing states, unnatural resulting multiplicities

$\Rightarrow$ Nowadays only done for ADC(2)

PP-ADC: Doubles folding (1)

$$\underline{\boldsymbol{r}} = \mathbf{M}\underline{\boldsymbol{y}} - \theta\underline{\boldsymbol{y}}$$

$$\begin{pmatrix} \underline{\boldsymbol{r}}^{(1)} \\ \underline{\boldsymbol{r}}^{(2)} \end{pmatrix} = \begin{pmatrix} \mathbf{M}^{(11)} - \theta\mathbf{I} & \mathbf{M}^{(21)\dagger} \\ \mathbf{M}^{(21)} & \mathbf{M}^{(22)} - \theta\mathbf{I} \end{pmatrix} \begin{pmatrix} \underline{\boldsymbol{y}}^{(1)} \\ \underline{\boldsymbol{y}}^{(2)} \end{pmatrix}$$

Enforce zero doubles residual:

$$\underline{\mathbf{0}} \overset{!}{=} \underline{\boldsymbol{r}}^{(2)} = \mathbf{M}^{(21)}\underline{\boldsymbol{y}}^{(1)} + \left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(2)}$$

$$\Rightarrow \underline{\boldsymbol{y}}^{(2)} = -\left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)^{-1}\mathbf{M}^{(21)}\underline{\boldsymbol{y}}^{(1)}$$

Plug into first equation:

$$\Rightarrow \underline{\boldsymbol{r}}^{(1)} = \left(\mathbf{M}^{(11)} - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)} + \mathbf{M}^{(21)\dagger}\underline{\boldsymbol{y}}^{(2)}$$

PP-ADC: Doubles folding (1)

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Plug into first equation:

$$\Rightarrow \underline{\boldsymbol{r}}^{(1)} = \left(\mathbf{M}^{(11)} - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)} - \underbrace{\mathbf{M}^{(21)\dagger}\left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)^{-1}\mathbf{M}^{(21)}}_{\equiv\mathbf{A}_\theta}\underline{\boldsymbol{y}}^{(1)}$$

$$= \left(\mathbf{M}^{(11)} - \mathbf{A}_\theta - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)}$$

PP-ADC: Doubles folding (2)

- Result of doubles folding:

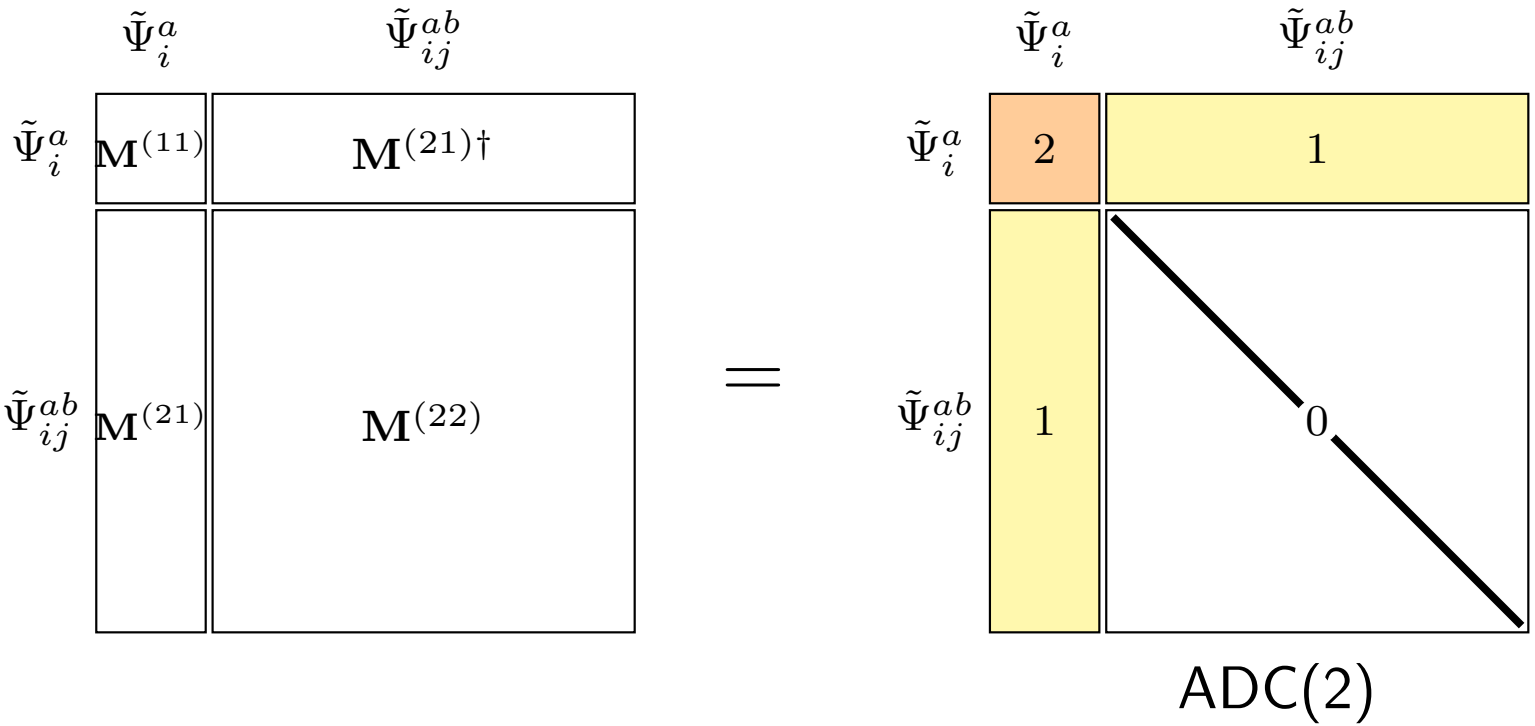
$$\underline{\boldsymbol{r}}^{(1)} = \left(\mathbf{M}^{(11)} - \mathbf{A}_\theta - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)}, \qquad \underline{\boldsymbol{r}}^{(2)} = \underline{\mathbf{0}}$$

$$\mathbf{A}_\theta = \mathbf{M}^{(21)\dagger}\left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)^{-1}\mathbf{M}^{(21)}$$

- Iterates are only $\underline{\boldsymbol{r}}^{(1)}$ and $\underline{\boldsymbol{y}}^{(1)}$

$\Rightarrow$ More memory-efficient

PP-ADC: Doubles folding (2)



ADC(2)

PP-ADC: Doubles folding (2)

- Result of doubles folding:

$$\underline{\boldsymbol{r}}^{(1)} = \left(\mathbf{M}^{(11)} - \mathbf{A}_\theta - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)}, \qquad \underline{\boldsymbol{r}}^{(2)} = \underline{\mathbf{0}}$$

$$\mathbf{A}_\theta = \mathbf{M}^{(21)\dagger}\left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)^{-1}\mathbf{M}^{(21)}$$

- Iterates are only $\underline{\boldsymbol{r}}^{(1)}$ and $\underline{\boldsymbol{y}}^{(1)}$

$\Rightarrow$ More memory-efficient

- For ADC(2) $\mathbf{M}^{(22)}$ is diagonal

$\Rightarrow$ Computing $\mathbf{A}_\theta$ trivial given expression for $\mathbf{M}^{(21)}$ and $\mathbf{M}^{(21)\dagger}$

Complex polarisation propagator (1)

- Complex polarisation propagator ansatz lead to

$$\Big(\mathbf{M} - (\omega_m - \imath\gamma_m)\mathbf{I}\Big)\underline{\boldsymbol{y}}_m = \underline{\boldsymbol{f}}$$

- γ_m: Half-width, stimulated emission
- $\underline{\boldsymbol{f}}$: modified transition moments (real)

$\Rightarrow$ $\underline{\boldsymbol{y}}_m$ becomes complex

- Assume same half-width: $\gamma_m = \gamma$ (empirically determined)
- Seek: $(\omega_m, \underline{\boldsymbol{y}}_m)$

Complex polarisation propagator (2)

- Separate $\underline{\boldsymbol{y}}_m = \underline{\boldsymbol{y}}_m^R + \imath \underline{\boldsymbol{y}}_m^I$:

$$\begin{pmatrix} \mathbf{M} - \omega\mathbf{I} & \gamma\mathbf{I} \\ -\gamma\mathbf{I} & \mathbf{M} - \omega\mathbf{I} \end{pmatrix} \begin{pmatrix} \underline{\boldsymbol{y}}_m^R \\ \underline{\boldsymbol{y}}_m^I \end{pmatrix} = \begin{pmatrix} \underline{\boldsymbol{f}} \\ 0 \end{pmatrix}$$

- Therefore

$$\begin{aligned} \underline{\boldsymbol{y}}_m^R &= -\frac{1}{\gamma} \left(\mathbf{M} - \omega\mathbf{I}\right) \underline{\boldsymbol{y}}_m^I \\ \gamma\underline{\boldsymbol{f}} &= \Big(\left(\mathbf{M} - \omega\mathbf{I}\right)^2 - \gamma^2\mathbf{I} \Big) \underline{\boldsymbol{y}}_m^I \\ &= \Big(\left(\mathbf{M} - 2\omega\mathbf{I}\right)\mathbf{M} + (\omega^2 + \gamma^2)\mathbf{I} \Big) \underline{\boldsymbol{y}}_m^I \end{aligned}$$

- Expensive linear system
- Doubles folding not so simple

Contents

General complications

- Index restrictions in expressions
- Conserving spin symmetry

- Doubles part $\underline{\boldsymbol{y}}^{(2)}$ is large vector

$\Rightarrow$ Storing the subspace can be memory bottleneck

- ADC(n) matrix expressions get a lot more involved with n
- Storage of ADC matrix is impossible

$\Rightarrow$ Doubles folding is very appealing

- Complex propagator:
  - Two ADC matrices needed
  - Need to solve for multiple ω / γ

Open questions

- Convergence properties of ADC(n) series for Π^+
- Convergence properties of ADC(n) eigenvalue problem

- Initial guess for ADC(n) from ADC($n-1$)
- Going beyond the Jacobi algorithm
- Better preconditioning techniques for
  - Solving by diagonalisation
  - Solving linear-response-like

- Doubles folding for PP-ADC(2)-x or PP-ADC(3)
- Doubles folding for CPP-ADC(2) and beyond
- Can one re-use some of the work for one ω for the next

Preconditioning PP-ADC

- Davidson, Sleijpen-van-der-Vorst preconditioning:

$$\mathbf{K}_\theta^+ \mathbf{M}_\theta \underline{\boldsymbol{t}}^{(j)} = -\mathbf{K}_\theta^+ \underline{\boldsymbol{r}}^{(j)}$$

  where

$$\mathbf{K}_\theta = \left(\mathbf{I} - \underline{\boldsymbol{v}}^{(j)} \underline{\boldsymbol{v}}^{(j)\,*}\right) \mathbf{K} \left(\mathbf{I} - \underline{\boldsymbol{v}}^{(j)} \underline{\boldsymbol{v}}^{(j)\,*}\right)$$

  and a cheaply invertible

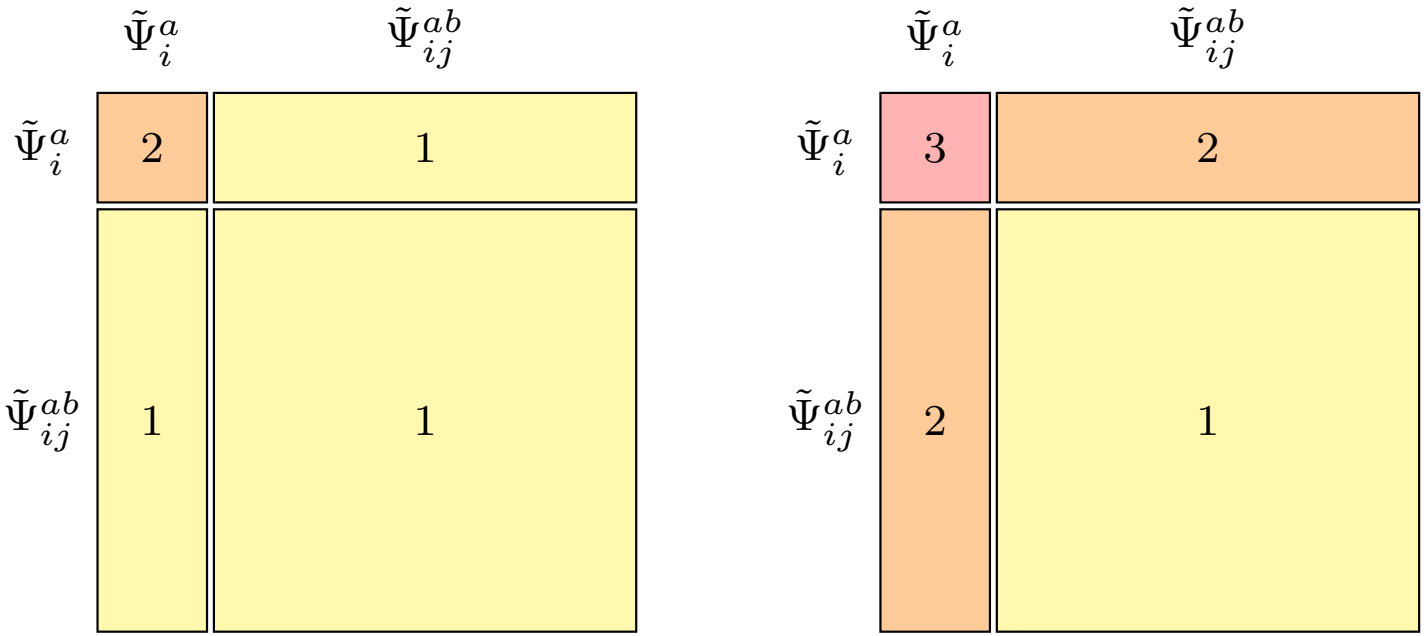
$$\mathbf{K} \approx \left(\mathbf{M} - \theta^{(j)} \mathbf{I}\right)$$

- Linear-response-like formalism

$$\underline{\boldsymbol{r}}^{(j)} = \mathbf{M} \underline{\boldsymbol{y}}^{(j)} - \theta^{(j)} \underline{\boldsymbol{y}}^{(j)}$$

- Preconditioner re-use for different ω?
- Going beyond Jacobi?

PP-ADC(2)x, PP-ADC(3): Doubles folding



$$\underline{\boldsymbol{r}}^{(1)} = \left(\mathbf{M}^{(11)} - \mathbf{A}_\theta - \theta\mathbf{I}\right)\underline{\boldsymbol{y}}^{(1)}$$

$$\mathbf{A}_\theta = \mathbf{M}^{(21)\dagger}\left(\mathbf{M}^{(22)} - \theta\mathbf{I}\right)^{-1}\mathbf{M}^{(21)}$$

CPP-ADC: Doubles folding

Let $$\widetilde{\mathbf{M}}_{\omega\gamma} \equiv (\mathbf{M} - 2\omega\mathbf{I})\,\mathbf{M} + (\omega^2 + \gamma^2)\mathbf{I}$$

$$\Rightarrow \begin{pmatrix} \underline{\boldsymbol{r}}^{(1)} \\ \underline{\boldsymbol{r}}^{(2)} \end{pmatrix} = \begin{pmatrix} \widetilde{\mathbf{M}}^{(11)}_{\omega\gamma} & \widetilde{\mathbf{M}}^{(21)\dagger}_{\omega\gamma} \\ \widetilde{\mathbf{M}}^{(21)}_{\omega\gamma} & \widetilde{\mathbf{M}}^{(22)}_{\omega\gamma} \end{pmatrix} \begin{pmatrix} \underline{\boldsymbol{y}}^{(1)} \\ \underline{\boldsymbol{y}}^{(2)} \end{pmatrix} - \begin{pmatrix} \gamma\underline{\boldsymbol{f}}^{(1)} \\ \gamma\underline{\boldsymbol{f}}^{(2)} \end{pmatrix}$$

Enforce zero doubles residual:

$$\underline{\mathbf{0}} \overset{!}{=} \underline{\boldsymbol{r}}^{(2)} = \widetilde{\mathbf{M}}^{(21)}_{\omega\gamma}\underline{\boldsymbol{y}}^{(1)} + \widetilde{\mathbf{M}}^{(22)}_{\omega\gamma}\underline{\boldsymbol{y}}^{(2)} - \gamma\underline{\boldsymbol{f}}^{(2)}$$

$$\Rightarrow \underline{\boldsymbol{y}}^{(2)} = \left(\widetilde{\mathbf{M}}^{(22)}_{\omega\gamma}\right)^{-1}\left(\gamma\underline{\boldsymbol{f}}^{(2)} - \widetilde{\mathbf{M}}^{(21)}_{\omega\gamma}\underline{\boldsymbol{y}}^{(1)}\right)$$

Plug into first equation:

$$\Rightarrow \underline{\boldsymbol{r}}^{(1)} = \widetilde{\mathbf{M}}^{(11)}_{\omega\gamma}\underline{\boldsymbol{y}}^{(1)} - \widetilde{\mathbf{M}}^{(21)\dagger}_{\omega\gamma}\left(\widetilde{\mathbf{M}}^{(22)}_{\omega\gamma}\right)^{-1}\widetilde{\mathbf{M}}^{(21)}_{\omega\gamma}\underline{\boldsymbol{y}}^{(1)} + \gamma\widetilde{\mathbf{M}}^{(21)\dagger}_{\omega\gamma}\left(\widetilde{\mathbf{M}}^{(22)}_{\omega\gamma}\right)^{-1}\underline{\boldsymbol{f}}^{(2)}$$