The Algebraic Diagrammatic Construction - a versatile approach to excited electronic states, ionization potentials and electron affinities

Motivation: QM methods for excited states of large molecules

Wish list of properties:

- balanced treatment of all states:
  reliable excitation energies

- direct comparison with experiment:
  error of 0.1–0.2 eV
  0.5 eV more realistic
  reliable transition moments
  reliable geometries
  predictable errors

- "black-box" method

- computationally cheap

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Available methods:

- wavefunction based:
  CIS, ADC, CC2, CASSCF, SAC-CI....
- density based:
  TDDFT and variants
- semi-empirical methods:
  INDO/S, AM1/MRCI, OM2/MRCI....

None of the available methods fulfills all points of our wish list.

Even worse:
No thorough evaluation possible:
no benchmarks, no experiments

ADC: general introduction

Algebraic diagrammatic construction (ADC) scheme

- based on many-body Green's function (propagator) theory
- uses diagrammatic perturbation theory to construct algebraic expressions from propagator approximations
- applicable to "all" propagators

ADC scheme for the polarization propagator

- gives access to excitation energies and transition moments

ADC scheme for the single particle propagator

- gives access to ionization energies and electron affinities

Intermediate state representation (ISR)

- gives access to excited state properties and transition moments
- intuitive derivation of ADC matrix equations

Overview I

Theory

- many-body Green's functions (propagators)
  - Green's functions
  - Green's functions in quantum mechanics (single particle)
  - propagators and quasi-particles
  - many-body single-particle and two-particle propagator
  - polarization propagator
- Algebraic diagrammatic construction for the polarization propagator
  - derivation of ADC(0) and ADC(1) matrix expressions
  - uniqueness of the ADC procedure

Green's functions

What are Green's functions?

Considering:

$$\hat{D}\,f(x) = I(x)$$

Green's function defined by:

$$\hat{D}G(x,x') = \delta(x-x')$$

Integrating with the inhomogeneity yields:

$$\int dx'\,\hat{D}G(x,x')I(x') = \int dx'\,\delta(x-x')I(x') = I(x)$$

Green's functions

$$\int dx' \hat{D}G(x,x')I(x') = \int dx' \delta(x-x')I(x') = I(x)$$

Using this expression for the inhomogeneity:

$$\hat{D}f(x) = I(x) = \int dx' \hat{D}G(x,x')I(x')$$

and rewriting

$$\hat{D}f(x) = \hat{D}\left(\int dx' G(x,x')I(x')\right)$$

we find

$$f(x) = \int dx' G(x,x')I(x')$$

Single particle Green's function

Green's function for the time-dependent Schrödinger equation:

$$\left(i\frac{\partial}{\partial t} - \hat{H}\right) G(\mathbf{x}, t; \mathbf{x}', t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')$$

gives access to the time-dependent wave-function

$$\psi(\mathbf{x}, t) = i \int d^3x' G(\mathbf{x}, t; \mathbf{x}', t')\psi(\mathbf{x}', t')$$

Single particle Green's function

How does the Green's function look like?

Considering a single particle at initial time t' described by:

$$|Q, t'\rangle$$

at $t > t'$:

$$|Q, t'; t\rangle = e^{-i\hat{H}(t-t')}|Q, t'\rangle$$

according to

$$i\frac{\partial}{\partial t}|Q, t'; t\rangle = \hat{H}e^{-iH(t-t')}|Q, t'\rangle = \hat{H}|Q, t'; t\rangle$$

Single particle Green's function

How does the Green's function look like?

The time-dependent wave-function is found as:

$$\psi(\mathbf{x},t) = \langle \mathbf{x}|Q,t';t\rangle = \langle \mathbf{x}|e^{-iH(t-t')}|Q,t'\rangle$$

which we rewrite using $\int d^3x'|\mathbf{x}'\rangle\langle\mathbf{x}'| = \mathbf{1}$

$$\psi(\mathbf{x},t) = \int d^3x' \underbrace{\langle \mathbf{x}|e^{-iH(t-t')}|\mathbf{x}'\rangle}_{i\tilde{G}(\mathbf{x},t;\mathbf{x}',t')} \underbrace{\langle \mathbf{x}'|Q,t'\rangle}_{\psi(\mathbf{x}',t')}$$

Single particle Green's function

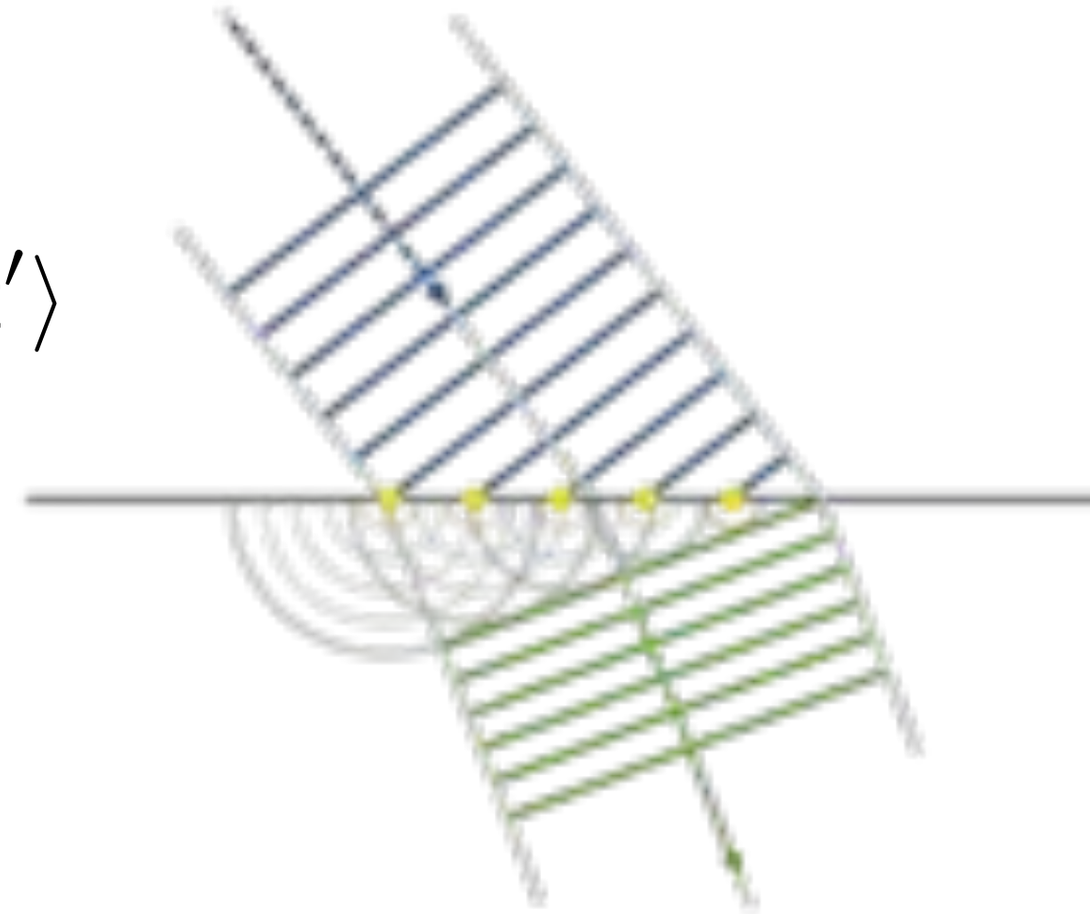
Physical interpretation (Huygens' principle)

$$\psi(\mathbf{x},t) = i\int d^3x' \tilde{G}(\mathbf{x},t;\mathbf{x}',t')\psi(\mathbf{x}',t')$$

Probability amplitude

$$\tilde{G}(\mathbf{x},t;\mathbf{x}',t') = -i\langle \mathbf{x}|e^{-iH(t-t')}|\mathbf{x}'\rangle$$

$$= -i\langle \mathbf{x},t|\mathbf{x}',t'\rangle$$



Single particle Green's function

"actual" Green's function

$$\left(i\frac{\partial}{\partial t} - \hat{H}\right) G(\mathbf{x}, t; \mathbf{x}', t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')$$

Step function

$$\theta(t - t') = \begin{cases} e^{-i\eta}, & t - t' \geq 0 \quad , \eta \downarrow 0 \\ 0, & t - t' < 0 \end{cases}$$

$$G(\mathbf{x}, t; \mathbf{x}', t') = \theta(t - t')\tilde{G}(\mathbf{x}, t; \mathbf{x}', t')$$

Single particle Green's function

Analysis of the single particle propagator

Spectrum of the Hamiltonian $\hat{H}|n\rangle = E_n|n\rangle$, with $\sum_n |n\rangle\langle n| = \mathbf{1}$

$$i\tilde{G}(\mathbf{x},t;\mathbf{x}',t') = \langle 0|\hat{c}_x e^{-iH(t-t')}\hat{c}^\dagger_{x'}|0\rangle$$

$$= \sum_n \langle 0|\hat{c}_x|n\rangle\langle n|e^{-iH(t-t')}|n\rangle\langle n|\hat{c}^\dagger_{x'}|0\rangle$$

$$= \sum_n \langle 0|\hat{c}_x|n\rangle\langle n|\hat{c}^\dagger_{x'}|0\rangle e^{-iE_n(t-t')}$$

Single particle Green's function

Analysis of the single particle propagator

Fourier transform with $\tau = t - t'$

$$G(\mathbf{x}, \mathbf{x}; \omega) = \int d\tau e^{i\omega\tau} G(\mathbf{x}, \mathbf{x}'; \tau)$$

$$= \sum_n \frac{\langle 0|\hat{c}_x|n\rangle\langle n|\hat{c}^\dagger_{x'}|0\rangle}{\omega - E_n + i\eta}$$

denominator has poles at the spectrum of $\hat{H}$

$$= \langle 0|\hat{c}_x \frac{1}{\omega - \hat{H} + i\eta} \hat{c}^\dagger_{x'}|0\rangle$$

can be represented in any single-particle basis

Single particle Green's function

Perturbation expansion of the propagator

Using a splited Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$ for $G(\mathbf{x},\mathbf{x};\omega) = \langle 0|\hat{c}_x \underbrace{\frac{1}{\omega - \hat{H} - i\eta}}_{\hat{G}} \hat{c}^\dagger_{x'}|0\rangle$

$$\hat{G} = \frac{1}{\omega - \hat{H} + i\eta} = \frac{1}{A - \hat{H}_1}$$

$$\hat{G}_0 = \frac{1}{\omega - \hat{H}_0 + i\eta} = \frac{1}{A}$$

we can find the recursion formula:

$$\frac{1}{A - \hat{H}_1} = \frac{1}{A} + \frac{1}{A}\hat{H}_1 \frac{1}{A - \hat{H}_1}$$

Single particle Green's function

Perturbation expansion of the propagator

Recursion formula: $$\frac{1}{A-\hat{H}_1} = \frac{1}{A} + \frac{1}{A}\hat{H}_1\frac{1}{A-\hat{H}_1}$$

$$G(\omega) = G^{(0)}(\omega) + G^{(0)}(\omega)\hat{H}_1 G(\omega)$$

$$= G^{(0)}(\omega) + G^{(0)}(\omega)H_1 G^{(0)}(\omega) + G^{(0)}(\omega)H_1 G^{(0)}(\omega)H_1 G^{(0)}(\omega) + \ldots$$

0th order in spectrum of $\hat{H}_0|i\rangle = \epsilon_i|i\rangle, i \in \{p,q,r,\ldots\}$

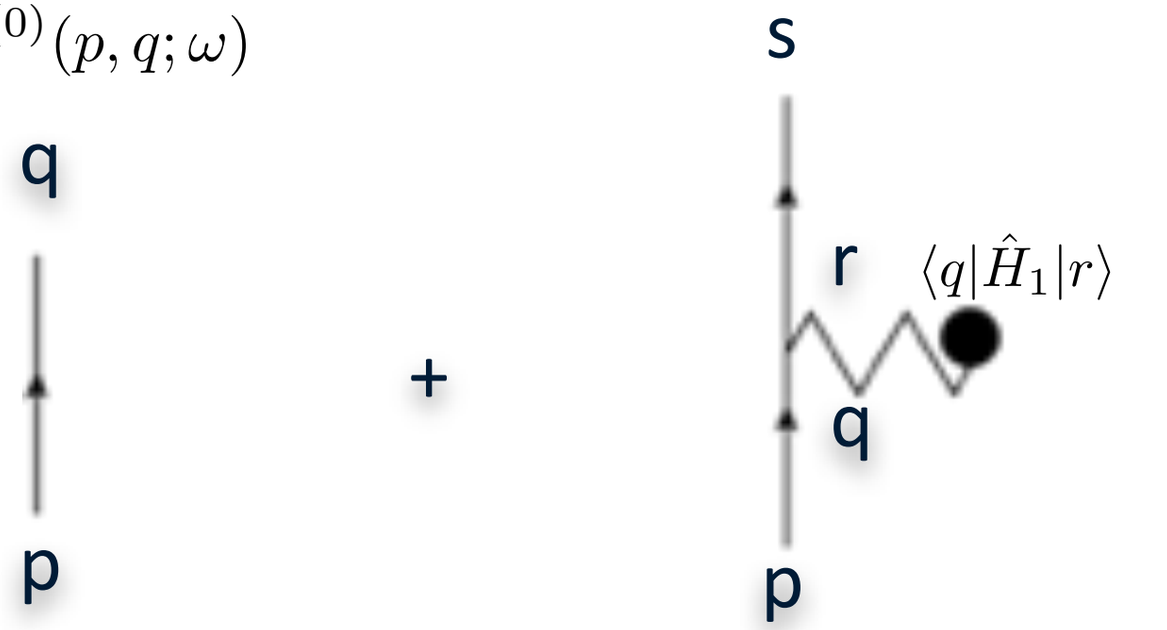
$$G^{(0)}(p,q;\omega) = \langle p|\frac{1}{\omega - \hat{H}_0 + i\eta}|q\rangle = \frac{\delta_{pq}}{\omega - \epsilon_p + i\eta}$$

Single particle Green's function

Diagrammatic expansion of the propagator

$G^{(0)}(p,q;\omega)$

$G(p,q;\omega) =$



$$= \frac{\delta_{pq}}{\omega - \epsilon_p + i\eta} + \sum_{qr} \frac{\delta_{pq}}{\omega - \epsilon_p + i\eta} \langle q|\hat{H}_1|r\rangle \frac{\delta_{rs}}{\omega - \epsilon_r + i\eta} + \ldots$$

$$= G^{(0)}(\omega) + G^{(0)}(\omega) H_1 G^{(0)}(\omega) + G^{(0)}(\omega) H_1 G^{(0)}(\omega) H_1 G^{(0)}(\omega) + \ldots$$

Green's function summary

Checklist	Single particle propagator	Many-body propagators
Describes time propagation	Yes	Yes
FT: poles spectrum of Hamiltonian	Yes	Yes
0th order propagator looks like	$\frac{\delta_{pq}}{\omega - \epsilon_p + i\eta}$	identical/similar
Has recursive PT expansion	Yes	Yes
Has diagrammatic expansion	Yes (trivial)	Yes (not trivial)

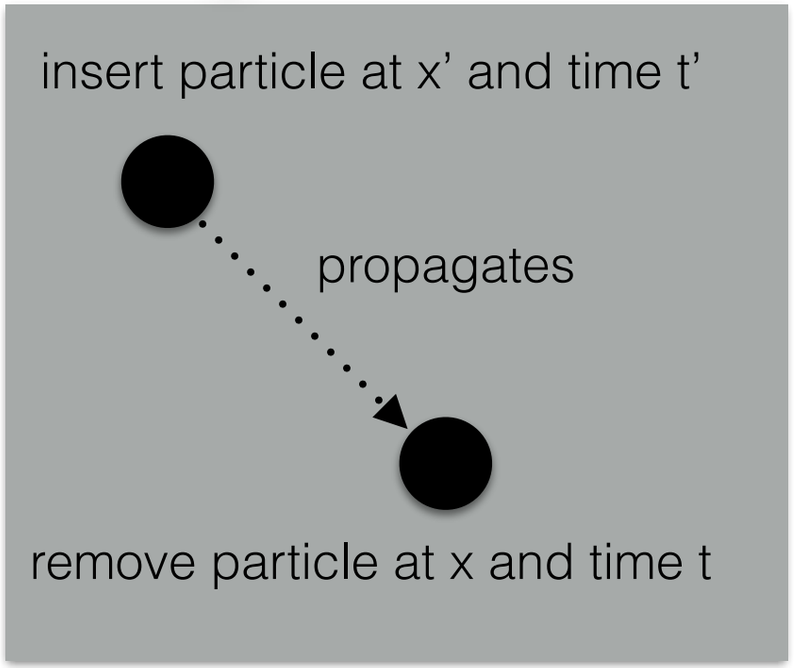
Quasi particle

Some more physical interpretation

Quasi particles:

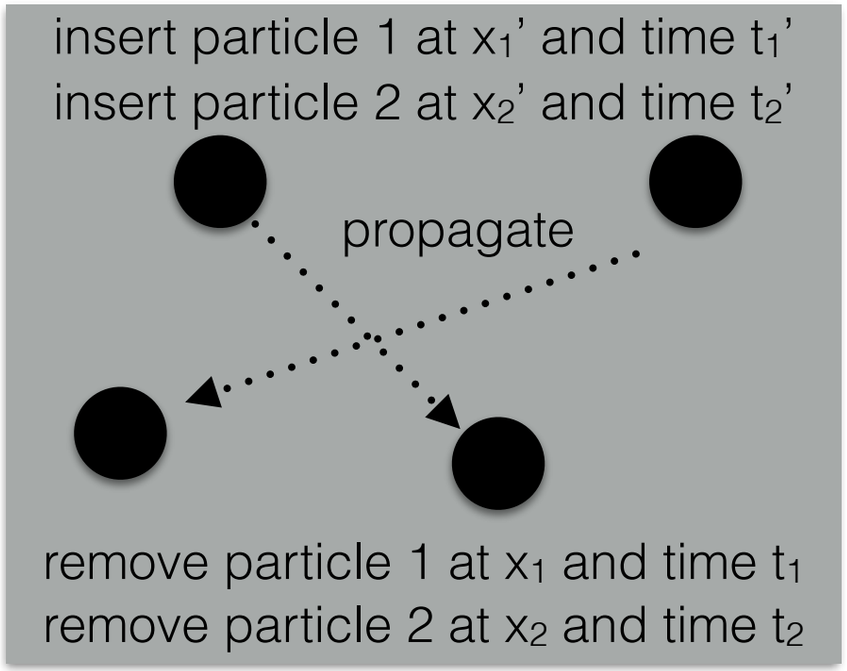
- ion in solvatation shell
- electron and shell in uniform electron gas

} weakly interacting



$$G(\mathbf{x}, t; \mathbf{x}', t')$$

Probability amplitude



$$G(\mathbf{x}_1, t_1; \mathbf{x}_1', t_1'; \mathbf{x}_2, t_2; \mathbf{x}_2', t_2')$$

Probability amplitude

Many-body propagators

Single-particle propagator

$$G_{p,q}\left(t_p, t_q\right) = -\imath \left\langle \Psi_0 \left| \hat{T}\left[\hat{c}_{H\,p}\left(t_p\right) \hat{c}^{\dagger}_{H\,q}\left(t_q\right)\right] \right| \Psi_0 \right\rangle$$

$$\hat{c}_{H\,p}\left(t\right) = e^{\imath \hat{\mathcal{H}} t}\ \hat{c}_p\ e^{-\imath \hat{\mathcal{H}} t}$$

$$\hat{c}^{\dagger}_{H\,p}\left(t\right) = e^{\imath \hat{\mathcal{H}} t}\ \hat{c}^{\dagger}_p\ e^{-\imath \hat{\mathcal{H}} t}$$

Two-particle propagator

$$G_{p,q;r,s}\left(t_p, t_q; t_r, t_s\right) = (-\imath)^2 \left\langle \Psi_0 \left| \hat{T}\left[\hat{c}_{H\,p}\left(t_p\right) \hat{c}_{H\,q}\left(t_q\right) \hat{c}^{\dagger}_{H\,s}\left(t_s\right) \hat{c}^{\dagger}_{H\,r}\left(t_r\right)\right] \right| \Psi_0 \right\rangle$$

Time-ordering operator operator

$$\hat{T}\left[\hat{A}_H(t)\hat{B}_H(t')\right] = \hat{A}_H(t)\underbrace{\hat{B}_H(t')\theta(t-t')}_{\text{“+” or retarded}} - \hat{B}_H(t')\underbrace{\hat{A}_H(t)\theta(t'-t)}_{\text{“-” or advanced}}$$

Many-body propagators

Polarization propagator

$$\Pi_{pq,rs}\left(t,t'\right) = \lim_{t_q \searrow t} \lim_{t_s \searrow t'} \imath \left\{ G_{p,s;q,r}\left(t,t_s;t_q,t'\right) - G_{p,q}\left(t,t_q\right) G_{s,r}\left(t_s,t'\right) \right\}$$

$$= -\imath \left\langle \Psi_0 \left| \hat{T}\left[\hat{c}^{\dagger}_{H\,q}\left(t\right) \hat{c}_{H\,p}\left(t\right) \hat{c}^{\dagger}_{H\,r}\left(t'\right) \hat{c}_{H\,s}\left(t'\right) \right] \right| \Psi_0 \right\rangle$$

$$+ \imath \left\langle \Psi_0 \left| \hat{c}^{\dagger}_{H\,q}\left(t\right) \hat{c}_{H\,p}\left(t\right) \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \hat{c}^{\dagger}_{H\,r}\left(t'\right) \hat{c}_{H\,s}\left(t'\right) \right| \Psi_0 \right\rangle$$

Spectral representation

$$\Pi_{pq,rs}\left(\omega\right) = \int d\tau e^{\imath\omega\tau}\, \Pi_{pq,rs}\left(\tau\right)$$

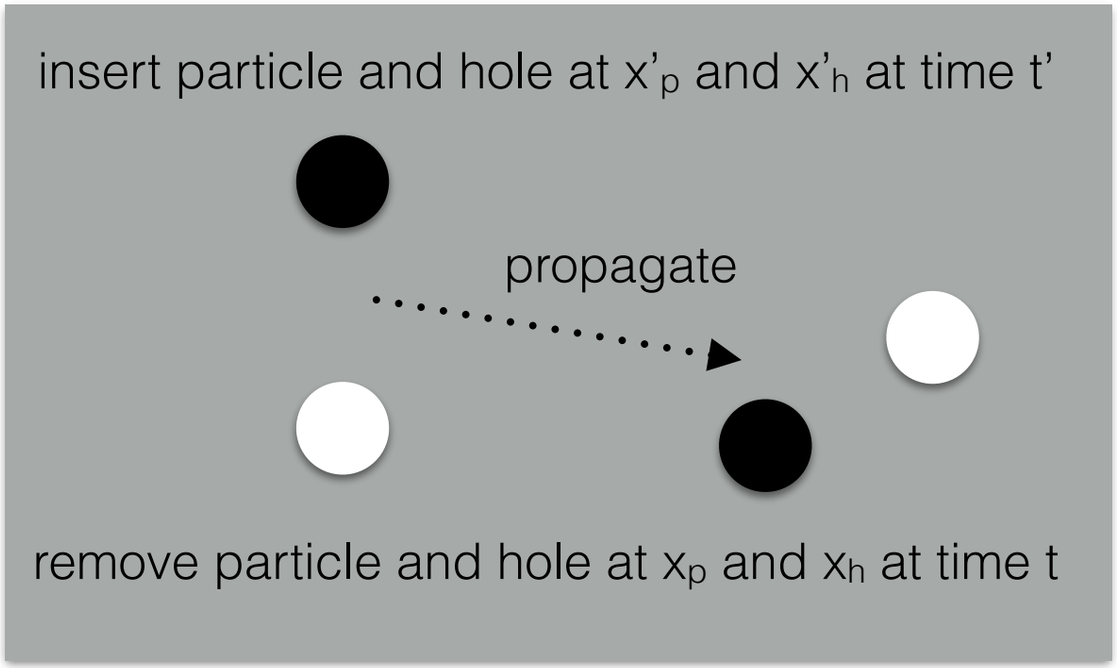
$$= \underbrace{\sum_{n\neq 0} \frac{\left\langle \Psi_0 \left| \hat{c}^{\dagger}_q \hat{c}_p \right| \Psi_n \right\rangle \left\langle \Psi_n \left| \hat{c}^{\dagger}_r \hat{c}_s \right| \Psi_0 \right\rangle}{\omega - \left(E_n - E_0\right) + \imath\eta}}_{\Pi_+(\omega)} + \underbrace{\sum_{n\neq 0} \frac{\left\langle \Psi_0 \left| \hat{c}^{\dagger}_r \hat{c}_s \right| \Psi_n \right\rangle \left\langle \Psi_n \left| \hat{c}^{\dagger}_q \hat{c}_p \right| \Psi_0 \right\rangle}{-\omega - \left(E_n - E_0\right) + \imath\eta}}_{\Pi_-(\omega)}$$

Quasi particle

Some more physical interpretation

Polarization propagator

- propagation of particle-hole pair
- linear response with respect to time-dependent field



corresponds to moving polarization

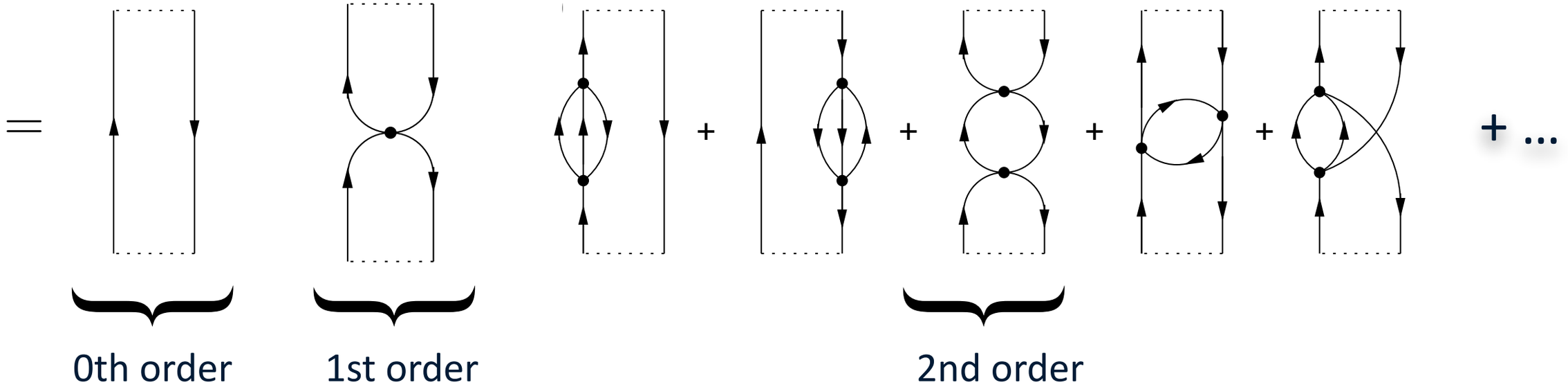
$$G(\mathbf{x}_p, \mathbf{x}_h, t; \mathbf{x}'_p, \mathbf{x}'_h, t')$$

Probability amplitude

Algebraic diagrammatic construction

Diagrammatic perturbation expansion of the polarization propagator in Feynman Diagrams

$$\Pi^{+}_{pq,rs}(\omega) = \sum_{n\neq 0} \frac{\langle\Psi_0|\hat{c}_p^\dagger \hat{c}_q|\Psi_n\rangle\langle\Psi_n|\hat{c}_p^\dagger \hat{c}_q|\Psi_0\rangle}{\omega - (E_n - E_0)} = \mathbf{x}^\dagger_{pq}\,(\underbrace{\mathbb{1}\omega - \mathbf{\Omega}}_{\text{diagonal form}})^{-1}\,\mathbf{x}_{rs}$$



Algebraic diagrammatic construction

Transition function

$$T(\omega) = \mathbf{D}^\dagger \mathbf{\Pi}(\omega) \mathbf{D}$$

$\mathbf{D}$: vector of operator representation in single-particle basis

Postulation of non-diagonal form

$$T(\omega) = \mathbf{F}^\dagger \left(\mathbb{1}\omega - \mathbf{M}\right)^{-1} \mathbf{F}$$

$$\mathbf{Y}^t \mathbf{M} \mathbf{Y} = \mathbf{\Omega}$$

Postulation of perturbation expansion for so-called ADC matrix $\mathbf{M}$ and so-called modified transition moments $\mathbf{F}$

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \dots$$

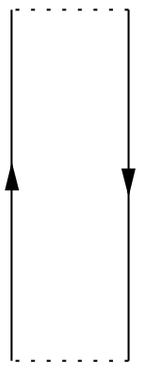
$$\mathbf{F} = \mathbf{F}^{(0)} + \mathbf{F}^{(1)} + \mathbf{F}^{(2)} + \dots,$$

Using Møller-Plesset Hamiltonian splitting $\hat{H} = \hat{H}_0 + \hat{H}_1$

ADC(0)

Perturbation expansion of the transition function using Goldstone (FT) diagrams

0th order:



$$T^{(0)}(\omega) = \sum_{ia} D^*_{ia} \frac{1}{\omega + \epsilon_a - \epsilon_i} D_{ia}$$

$$\Pi^{(0)}_{ia,jb} = \frac{\delta_{(ia),(jb)}}{\omega + \epsilon_a - \epsilon_i} = \frac{\delta_{ab}\delta_{ij}}{\omega + \epsilon_a - \epsilon_i}$$

$$= \mathbf{F}^{(0)\dagger} \left(\mathbb{1}\omega - \mathbf{M^{(0)}} \right)^{-1} \mathbf{F}^{(0)}$$

$$\Rightarrow M^{(0)}_{ia,jb} = \delta_{ab}\delta_{ij} \left(\epsilon_a - \epsilon_i \right)$$

$$\mathbf{F}^{(0)}_{ia} = D_{ia}$$

ADC(1)

Perturbation expansion of the Transition function using Goldstone diagrams

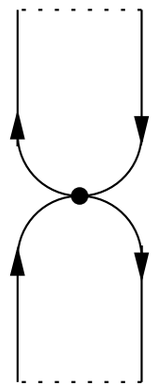
Remembering from the single particle propagator

$$G(\omega) = G^{(0)}(\omega) + G^{(0)}(\omega)H_1G^{(0)}(\omega) + G^{(0)}(\omega)H_1G^{(0)}(\omega)H_1G^{(0)}(\omega) + \dots$$

Rewrite

$$(\mathbb{1}\omega - \mathbf{M})^{-1} = \left(\mathbb{1}\omega - \mathbf{M^{(0)}}\right)^{-1} + \left(\mathbb{1}\omega - \mathbf{M^{(0)}}\right)^{-1}\mathbf{M^{(1)}}\left(\mathbb{1}\omega - \mathbf{M^{(0)}}\right)^{-1} + \dots$$

1st order (one contribution):



$$T_1^A(\omega) = \sum_{ia,jb} D^*_{ia}\frac{1}{\omega + \epsilon_a - \epsilon_i}(-\langle aj||bi\rangle)\frac{1}{\omega + \epsilon_b - \epsilon_j}D_{jb}$$

$$\Rightarrow M^{(1)}_{ia,jb} = -\langle aj||bi\rangle$$

Uniqueness of the ADC procedure

Considering

$$T_1^A(\omega) = \sum_{ia,jb} D_{ia}^* \frac{1}{\omega + \epsilon_a - \epsilon_i}(-\langle aj||bi\rangle)\frac{1}{\omega + \epsilon_b - \epsilon_j} D_{jb}$$

Rewriting

$$\frac{1}{\omega - \epsilon_a - \epsilon_i}\frac{1}{\omega - \epsilon_b - \epsilon_j} = \frac{1}{(\epsilon_i - \epsilon_a + \epsilon_b - \epsilon_j)}\left(\frac{1}{\omega + \epsilon_a - \epsilon_i} - \frac{1}{\omega + \epsilon_b - \epsilon_j}\right) \quad \begin{matrix} i \neq j \\ a \neq b \end{matrix}$$

$$\Rightarrow \tilde{M}_{ia,jb}^{(1)} = -\delta_{ab}\delta_{ij}\langle ai||ai\rangle \neq M_{ia,jb}^{(1)}$$

ADC: maximum possible number of contributions in ADC matrix

How does the ADC matrix look like?

$$M^{(0)}_{ia,jb} = (\epsilon_a - \epsilon_i)\,\delta_{ab}\delta_{ij}$$

$$M^{(1)}_{ia,jb} = -\langle aj||bi\rangle$$

$$M^{(2)\,A}_{ia,jb} = \frac{1}{4}\delta_{ij}\sum_{ckl}\left(\frac{\langle ac||kl\rangle\langle kl||bc\rangle}{\epsilon_a+\epsilon_c-\epsilon_k-\epsilon_l} + \frac{\langle ac||kl\rangle\langle kl||bc\rangle}{\epsilon_b+\epsilon_c-\epsilon_k-\epsilon_l}\right)$$

$$M^{(2)\,B}_{ia,jb} = \frac{1}{4}\delta_{ab}\sum_{cdk}\left(\frac{\langle cd||ik\rangle\langle jk||cd\rangle}{\epsilon_c+\epsilon_d-\epsilon_i-\epsilon_k} + \frac{\langle cd||ik\rangle\langle jk||cd\rangle}{\epsilon_c+\epsilon_d-\epsilon_j-\epsilon_k}\right)$$

$$M^{(2)\,C}_{ia,jb} = -\frac{1}{2}\sum_{ck}\left(\frac{\langle ac||ik\rangle\langle jk||bc\rangle}{\epsilon_a+\epsilon_c-\epsilon_i-\epsilon_k} + \frac{\langle ac||ik\rangle\langle jk||bc\rangle}{\epsilon_b+\epsilon_c-\epsilon_j-\epsilon_k}\right)$$

$$M^{(1)}_{ia,kcld} = \langle kl||id\rangle\delta_{ac} - \langle kl||ic\rangle\delta_{ad} - \langle al||cd\rangle\delta_{ik} + \langle ak||cd\rangle\delta_{il}$$

$$M^{(1)}_{iajb,kc} = \langle kb||ij\rangle\delta_{ac} - \langle ka||ij\rangle\delta_{bc} - \langle ab||cj\rangle\delta_{ik} + \langle ab||ci\rangle\delta_{jk}$$

$$M^{(0)}_{iajb,kcld} = (\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j)\,\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl}.$$

Overview II

Theory

- Intermediate state representation
  - derivation
  - linear and non-linear properties

Implementation

- How to code in `adcman`

Applications

- UADC
- SOS-ADC
- ADC(3)
- Spin-flip ADC
- wave-function analysis
- IP-ADC and EA-ADC
- ADC geometry optimizations

Introduction

CISD...

$$\begin{array}{c|ccc} \hat{H} & |\Psi_{HF}\rangle & |\Psi_i^a\rangle & |\Psi_{ij}^{ab}\rangle \\ \hline \langle\Psi_{HF}| & & 0 & \\ \langle\Psi_i^a| & 0 & & \\ \langle\Psi_{ij}^{ab}| & & & \end{array} \quad \cdots \rightarrow \quad \vdots$$

- arbitrary truncation
- not size consistent

Diagonalization

Exact solution

$$\begin{array}{c|cccc} \hat{H} & |\Psi_0\rangle & |\Psi_1\rangle & \dots & |\Psi_N\rangle \\ \hline \langle\Psi_0| & E_0 & & & 0 \\ \langle\Psi_1| & & \omega_1 & & \\ \vdots & & & \ddots & \\ \langle\Psi_N| & 0 & & & \omega_N \end{array}$$

Reinterpretation of ADC

ADC(N)

$\hat{H}$ | $-E_0|\tilde{\Psi}_{ia}\rangle$ | $|\tilde{\Psi}_{ijab}\rangle$ | ...

consistent to N-th order perturbation theory

$\langle\tilde{\Psi}_{ia}|$	M (0..N)	M (0..(N-1))
$\langle\tilde{\Psi}_{ijab}|$	M h.c.	M (0..(N-2))
⋮		

- size consistent
- systematically improvable
- hermitian (compared to CC)

Diagonalization

Algebraic Diagrammatic Construction

(Exact) solution

$\hat{H}$ | $|\Psi_1\rangle$ | ... | $|\Psi_N\rangle$

$\langle\Psi_1|$	ω_1		0
⋮		⋱	
$\langle\Psi_N|$	0		ω_N

Intermediate State Representation

Excitation operators

$$\{\hat{C}_I\} \equiv \{\hat{c}_a^\dagger c_i, \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_i \hat{c}_j, \dots\}$$

$$\hat{c}_a^\dagger c_i |\Psi_{HF}\rangle = |\Psi_i^a\rangle$$

Applying to the exact ground state

$$|\Psi_0^I\rangle = \hat{C}_I |\Psi_0\rangle$$

Intermediate State Representation

Orthonormalization

$$|\tilde{\Psi}_I\rangle$$ Intermediate State

ADC: “Configuration interaction” in correlated states

Intermediate State Representation

Formal construction of ADC in Intermediate States

I: Orthogonalize with respect to ground state

$$|\Psi_I^\#\rangle = \hat{C}_I|\Psi_0\rangle - |\Psi_0\rangle\langle\Psi_0|\hat{C}_I|\Psi_0\rangle$$

Precursor states

II: Orthonormalization

$$|\tilde{\Psi}_I\rangle = \sum_J |\Psi_J^\#\rangle (S^{-\frac{1}{2}})_{I,J}$$

Overlap matrix

$$S_{I,J} = \langle\Psi_I^\#|\Psi_J^\#\rangle$$

III: Matrix representation of shifted Hamiltonian

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

$$\mathbf{Y}^t\mathbf{M}\mathbf{Y} = \mathbf{\Omega}$$

Hermitian eigenvalue problem

IV: Approximate E_0 and $|\Psi_0\rangle$

Approximate ISR

Approximation: Møller-Plesset PT

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \qquad \hat{H}_0 |\Psi_0^{(0)}\rangle = E_I^{(0)} |\Psi_0^{(0)}\rangle$$

Expansion of the energy and wave-function

$$E_0 = \sum_{n=0}^{\infty} \lambda^n E_0^{(n)} \qquad |\Psi_0\rangle = \sum_{n=0}^{\infty} \lambda^n |\Psi_0^{(n)}\rangle$$

Expansion of the ADC matrix

$$M_{I,J}^{(k+l+m)} \lambda^{k+l+m} = \sum_{K,L} \left(S_{I,K}^{-\frac{1}{2}} \right)^{(k)} \lambda^k \left(\langle \Psi_K^{\#} | \hat{H} - E_0 | \Psi_L^{\#} \rangle \right)^{(l)} \lambda^l \left(S_{L,J}^{-\frac{1}{2}} \right)^{(m)} \lambda^m$$

Truncation of ISR

0th-order: $$M^{(0)}_{I,J} = \sum_{K,L} \underbrace{\left(S^{-\frac{1}{2}}_{I,K}\right)^{(0)}}_{\delta_{IK}} \underbrace{\left(\langle \Psi^{\#}_K | \hat{H} - E_0 | \Psi^{\#}_L \rangle\right)^{(0)}}_{\langle \Psi^{(0)}_K | \hat{H}_0 - E^{(0)}_0 | \Psi^{(0)}_L \rangle} \underbrace{\left(S^{-\frac{1}{2}}_{L,J}\right)^{(m)}}_{\delta_{JL}}$$

$$\Rightarrow M^{(0)}_{ia,jb} = \delta_{ab}\delta_{ij}\left(\epsilon_a - \epsilon_i\right)$$

How to truncate the expansion?

=> use PT order structure from ADC

	p-h	2p-2h
p-h	M	M
2p-2h	M	M

	ADC1	ADC2	ADC2-x	ADC3
M	0..1	0..2	0..2	0..3
M	-	1	1	1..2
M	-	0	0..1	0..1

Dipole and transition moments

Representation of arbitrary operator

$$D_{IJ} = \langle \tilde{\Psi}_I | \hat{D} - D_0 | \tilde{\Psi}_J \rangle$$

Gives access to excited-state static and transition moments:

$$\langle \Psi_n | \hat{D} | \Psi_m \rangle = \mathbf{y}_n^\dagger \tilde{\mathbf{D}} \mathbf{y}_m \qquad \tilde{D}_{IJ} = D_{IJ} + D_0 \delta_{IJ}$$

Uses the same PT order structure from the ADC matrix

	p-h	2p-2h
p-h	D	D
2p-2h	D	D

	ISR(1)	ISR(2)	ISR(3)
D	0..1	0..2	0..3
D	-	1	1..2
D	-	0	0..1

Absolute energies

Representation of unshifted Hamiltonian

$$\tilde{M}_{IJ} = \langle \tilde{\Psi}_I | H | \tilde{\Psi}_J \rangle = M_{IJ} + \delta_{IJ} E_0$$

gives formal access to absolute energies:

$$E_n = \mathbf{y}_n^\dagger \tilde{\mathbf{M}} \mathbf{y}_n = \mathbf{y}_n^\dagger \mathbf{M} \mathbf{y}_n + E_0 = \omega_n + E_0$$

Important for ADC gradients!

Non-linear properties

Two-photon absorption (TPA) matrix

$$\mathbf{S} = \{S_{\alpha\beta}\} \qquad \alpha, \beta \in \{x, y, z\}$$

$$S_{\alpha\beta} = \langle \Psi_0 | \hat{\mu}^{\alpha} \left[\hat{H} - \frac{\omega_f}{2} \right]^{-1} \hat{\mu}^{\beta} | \Psi_f \rangle + \langle \Psi_0 | \hat{\mu}_{\beta} \left[\hat{H} - \frac{\omega_f}{2} \right]^{-1} \hat{\mu}_{\alpha} | \Psi_f \rangle$$

Resolution of identity yields sum over states:

$$\sum_{n}^{\infty} |\Psi_n\rangle\langle\Psi_n| \quad \Rightarrow \quad S_{\alpha\beta} = \sum_{n}^{\infty} \frac{\langle \Psi_0 | \hat{\mu}^{\alpha} | \Psi_n \rangle \langle \Psi_n | \hat{\mu}^{\beta} | \Psi_f \rangle}{\omega_n - \frac{\omega}{2}} + \alpha \leftrightarrow \beta$$

Resolution of identity yields ISR expression:

$$\sum_{I}^{\infty} |\tilde{\Psi}_I\rangle\langle\tilde{\Psi}_I| \quad \Rightarrow \quad S_{\alpha\beta} = \mathbf{F}_{\alpha}^{\dagger} \left(\mathbf{M} - \mathbb{1}\omega \right)^{-1} \mathbf{B}_{\beta} \mathbf{Y}_{\mathbf{f}} + \frac{\mu_{00}^{\alpha} \mu_{0f}^{\beta}}{E_0 - \frac{\omega}{2}} + \alpha \leftrightarrow \beta$$

TPA probabilities are obtained by contraction of S-matrix with ADC vector.

Comparison to CC and CI

	CI(n)	ADC(n)	CC(n)
size-consistency	no	yes	yes
hermiticity	yes	yes	no
compactness	n	even (n=2m) : m+1 odd (n=2m+1): m+1	even (n=2m) : m+1 odd (n=2m+1): m+2
ground state	CI(n)	MPn	CC(n)

Coding in adcman

Block tensor contraction library: libtensor

- C++ template library (open source)
- create tensors of arbitrary rank and size and perform linear algebra operations
- parallelisation of tensor operations in a shared memory environment
- fully supports symmetry, in particular spin and point group symmetry
- allows for the direct translation of equations into code

Michael Wormit
† 14.3.2015

$$
\begin{aligned}
w_{ijab} = & \sum_c (v_{ijac} f_{bc} - f_{ac} v_{ijbc}) \\
& - \sum_k (f_{ik} v_{kjab} - f_{jk} v_{kiab}) \\
& - \frac{1}{2} \sum_k (\langle ij||ka\rangle v_{kb} - \langle ij||kb\rangle v_{ka}) \\
& + \frac{1}{2} \sum_c (v_{ic} \langle jc||ab\rangle - v_{jc} \langle ic||ab\rangle)
\end{aligned}
$$

```
w(i|j|a|b) = asymm(a, b,
      contract(c, v_oovv(i|j|a|c), f_vv(b|c)))

  - asymm(i, j,
      contract(k, f_oo(i|k), v_oovv(k|j|a|b)))

  - 0.5 * asymm(a, b,
      contract(k, i_ooov(i|j|k|a), v_ov(k|b)))

  + 0.5 * asymm(i, j,
      contract(c, v_ov(i|c), i_ovvv(j|c|a|b)));
```

E. Epifanovsky, M. Wormit, T. Kus, A. Landau, D. Zuev, K. Khistyaev, P. Manohar, I. Kaliman, A. Dreuw, A. I. Krylov J. Comp. Chem. 34, 2293 (2013)

How to use ADC within Q-Chem 4.4

adcman (rem variables):

METHOD
Controls the order in perturbation theory of ADC.
TYPE:
STRING
DEFAULT:
None
OPTIONS:

ADC(1)	Perform ADC(1) calculation.
ADC(2)	Perform ADC(2)-s calculation.
ADC(2)-x	Perform ADC(2)-x calculation.
ADC(3)	Perform ADC(3) calculation.
SOS-ADC(2)	Perform spin-opposite scaled ADC(2)-s calculation.
SOS-ADC(2)-x	Perform spin-opposite scaled ADC(2)-x calculation.
CVS-ADC(1)	Perform ADC(1) calculation of core excitations.
CVS-ADC(2)	Perform ADC(2)-s calculation of core excitations.
CVS-ADC(2)-x	Perform ADC(2)-x calculation of core excitations.

RECOMMENDATION:
None

EE_STATES
Controls the number of excited states to calculate.
TYPE:
INTEGER
DEFAULT:
0 Do not perform an ADC calculation
OPTIONS:

$n > 0$	Number of states to calculate for each
$[n_1, n_2, ...]$	Compute n_1 states for the first irrep, n

EE_SINGLETS
Controls the number of singlet excited states to calculate.
TYPE:
INTEGER
DEFAULT:
0 Do not perform an ADC calculation of singlet excited
OPTIONS:

$n > 0$	Number of singlet states to calculate for eac
$[n_1, n_2, ...]$	Compute n_1 states for the first irrep, n_2 state

EE_TRIPLETS
Controls the number of triplet excited states to calculate.
TYPE:
INTEGER/INTEGER ARRAY
DEFAULT:
0 Do not perform an ADC calculation of triplet excited
OPTIONS:

$n > 0$	Number of triplet states to calculate for each
$[n_1, n_2, ...]$	Compute n_1 states for the first irrep, n_2 state

ADC_PROP_ES
Controls the calculation of excited state properties (currently only dipole mom
TYPE:
LOGICAL
DEFAULT:
FALSE
OPTIONS:

TRUE	Calculate excited state properties.
FALSE	Do not compute state properties.

RECOMMENDATION:
Set to TRUE, if properties are required or attachment/detachment densities of states should be plotted.

ADC_PROP_ES2ES
Controls the calculation of transition properties between excited states (curr transition dipole moments and oscillator strengths).
TYPE:
LOGICAL
DEFAULT:
FALSE
OPTIONS:

TRUE	Calculate state-to-state transition properties.
FALSE	Do not compute transition properties between excited states.

RECOMMENDATION:
Set to TRUE, if state-to-state properties are required.

CC_SYMMETRY
Activates point-group symmetry in the ADC calcu
TYPE:
LOGICAL
DEFAULT:
TRUE If the system possesses any point-group
OPTIONS:

TRUE	Employ point-group symmetry
FALSE	Do not use point-group symmetry

RECOMMENDATION:
None

Open-shell molecules with UADC(2)

Jan-Hendrik Starcke

Derivation via Intermediate State Representation

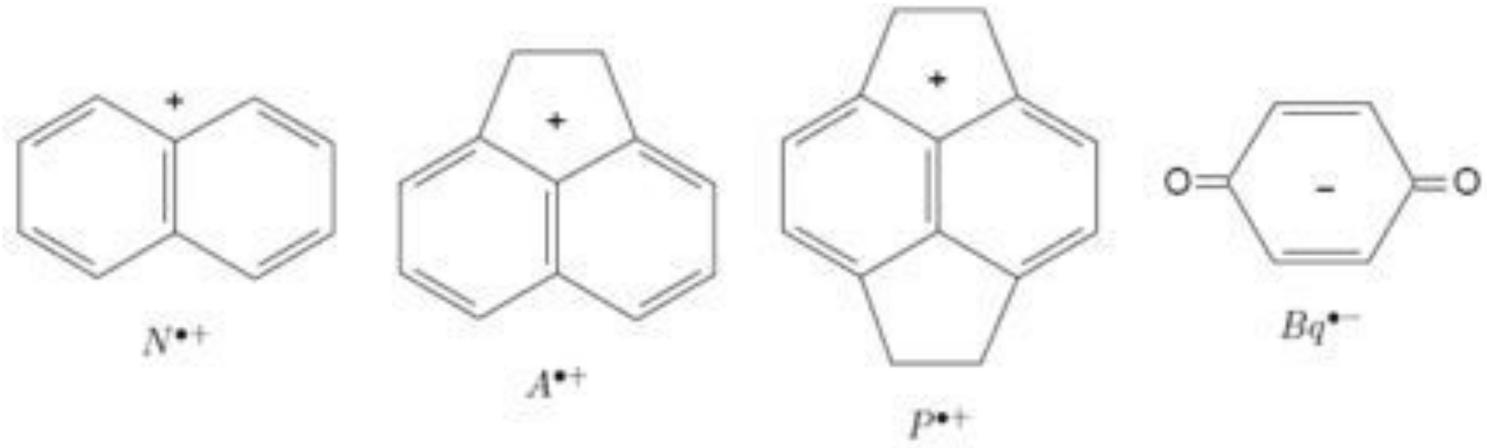
- analogous to closed-shell, but excitation operator needs spin:

$$\{\hat{C}_J\} = \{\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}, \hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}\hat{c}^\dagger_{b\tau}\hat{c}_{j\tau}, \dots\}$$

⇒ Subsequent annihilation and creation operators must act on the same spin

J.-H. Starcke, M. Wormit, A. Dreuw, J. Chem. Phys. 130, 024104 (2009)
J.-H. Starcke, M. Wormit, A. Dreuw, J. Chem. Phys. 131, 144311 (2009)

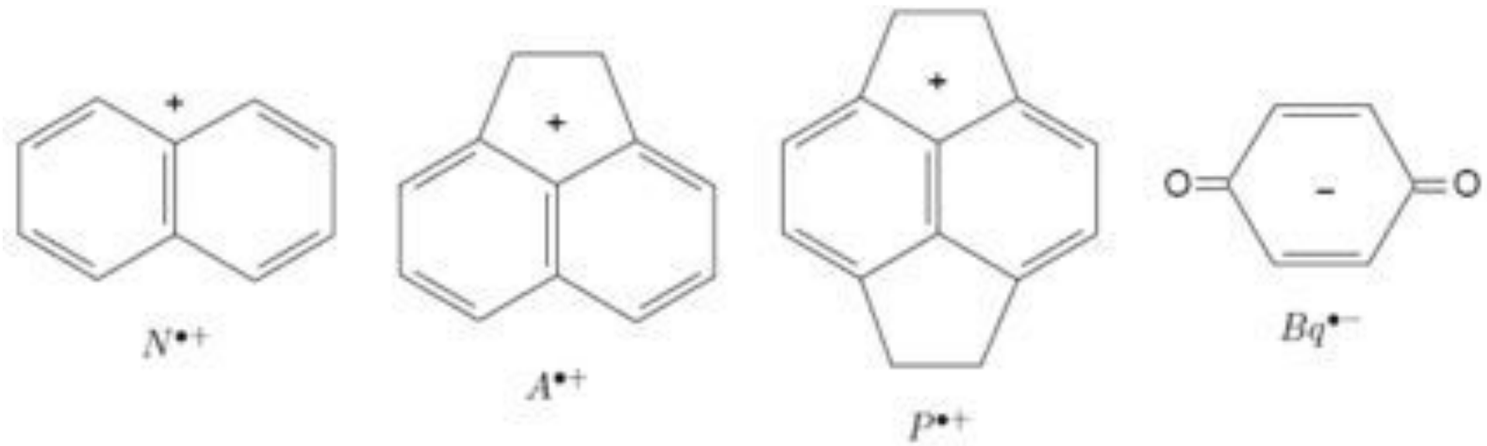
Unrestricted ADC(2)-x – some results



It is nearly impossible to find experimental data for comparison.

Symmetry	UADC(2)-x	EOM-CCSD	Experiment
$N^{\bullet+}$ ($\langle S^2 \rangle = 0.84$), GS: 1^2A_u			
1^2B_{3u}	0.62 (0.00)	1.30 (0.00)	0.73
1^2B_{1g}	1.76 (0.09)	2.48 (0.08)	1.84, 1.84
1^2B_{2g}	2.75 (0.02)	3.67 (0.01)	2.69, 2.72
1^2A_u	2.85 (0.00)	3.71 (0.00)	-
1^2B_{3g}	3.03 (0.00)	3.89 (0.00)	-
2^2B_{2g}	3.48 (0.15)	4.34 (0.10)	3.25, 3.29
2^2B_{1g}	3.89 (0.01)	4.90 (0.07)	4.02, 4.02
1^2B_{1u}	4.07 (0.00)	4.97 (0.00)	-
2^2B_{3u}	4.37 (0.00)	5.19 (0.00)	-
3^2B_{1g}	4.37 (0.18)	5.38 (0.01)	4.55, 4.89
Δ_{Jellium}	0.23	1.09	
$\overline{\lvert\Delta_\omega\rvert}$, $\overline{\Delta_\omega}$	0.13, -0.04	0.83, 0.83	
σ	0.06	0.20	

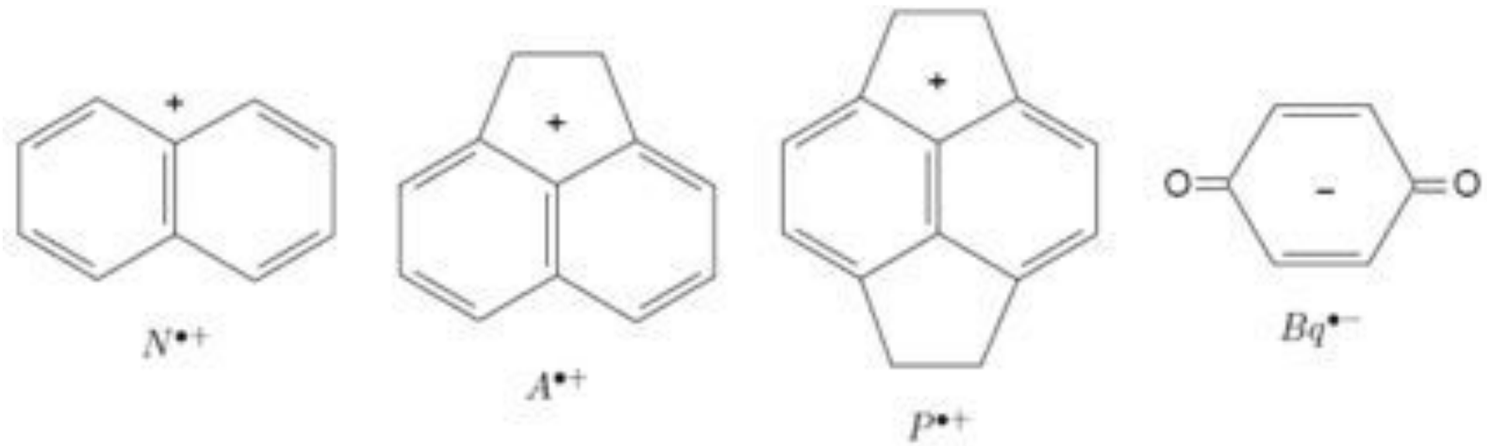
Unrestricted ADC(2)-x – some results



It is nearly impossible to find experimental data for comparison.

$\mathbf{A}^{\bullet+}$, $\langle S^2 \rangle = 0.98$, GS: 1^2A_2			*
1^2B_1	0.71 (0.00)	1.48 (0.00)	-
2^2B_1	1.37 (0.09)	2.15 (0.07)	1.89
2^2A_2	2.39 (0.01)	3.38 (0.00)	2.76
3^2A_2	2.88 (0.17)	3.85 (0.15)	3.23
1^2B_2	3.03 (0.00)	3.91 (0.00)	-
1^2A_1	3.21 (0.00)	4.12 (0.00)	-
3^2B_1	3.50 (0.07)	4.49 (0.02)	-
4^2B_1	3.66 (0.01)	4.58 (0.05)	-
5^2B_1	3.75 (0.02)	4.87 (0.00)	4.56
$\Delta\omega_{max}$	-0.52	0.62	
$\overline{\lvert\Delta\omega\rvert}$, $\overline{\Delta\omega}$	0.43, -0.43	0.45, 0.45	
σ	0.08	0.19	

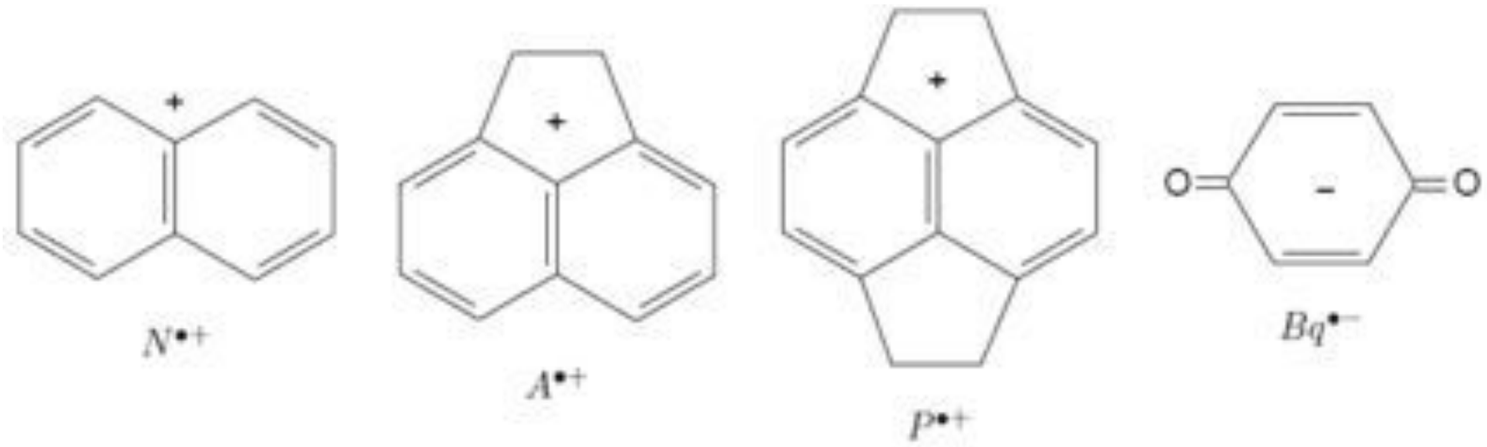
Unrestricted ADC(2)-x – some results



It is nearly impossible to find experimental data for comparison.

$P^{\bullet+}$, $\langle S^2 \rangle = 0.85$, GS: 1^2A_u			
1^2B_{3u}	0.81 (0.00)	1.59 (0.00)	-
1^2B_{2g}	1.46 (0.08)	2.26 (0.06)	1.99
1^2B_{1g}	2.32 (0.01)	3.23 (0.00)	2.79
2^2B_{1g}	2.66 (0.22)	3.56 (0.19)	3.15
1^2B_{3g}		3.95 (0.00)	-
2^2B_{3g}	3.49 (0.01)	4.44 (0.01)	≈3.75[c]
3^2B_{3g}	3.56 (0.01)	4.67 (0.05)	≈4.20[c]
2^2B_{3u}	3.58 (0.00)	4.45 (0.00)	-
3^2B_{1g}	4.22 (0.01)	5.23 (0.08)	4.65
$\Delta\omega_{max}$	-0.53	0.69	
$\overline{\lvert\Delta\omega\rvert}$, $\overline{\Delta\omega}$	0.43, -0.43	0.48, 0.48	
σ	0.11	0.16	

Unrestricted ADC(2)-x – some results

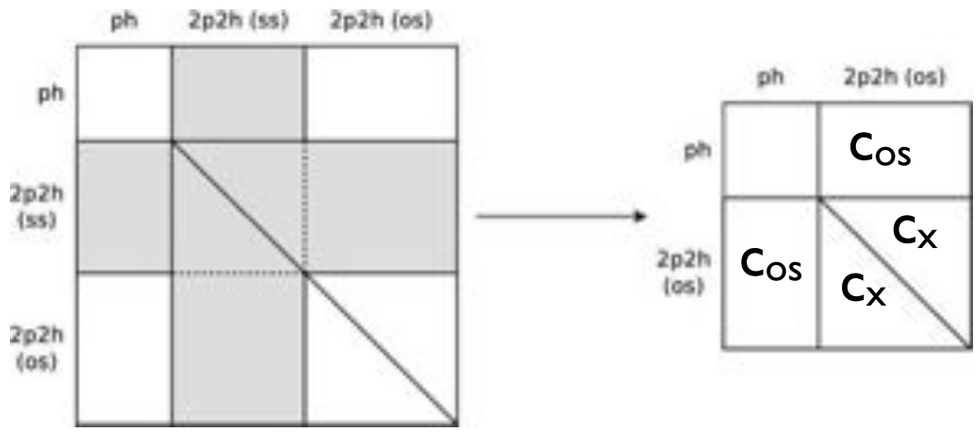


It is nearly impossible to find experimental data for comparison.

Symmetry	UADC(2)-x	EOM-CCSD	Experiment
$Bq^{\bullet-}$ $\langle S^2\rangle = 0.86$, GS: 1^2B_{2g}			[a]
1^2B_{2g}	1.85 (0.00)	2.71 (0.00)	-
1^2B_{2u}	1.86 (0.00)	2.73 (0.00)	-
1^2A_u	2.39 (0.08)	3.31 (0.07)	≈2.76[b]
1^2B_{3u}	2.52 (0.07)	3.34 (0.07)	2.95
1^2B_{1g}	2.97 (0.00)	3.85 (0.00)	-
2^2B_{3u}	3.69 (0.47)	4.47 (0.20)	3.88
$\Delta\omega_{max}$	-0.44	0.59	
$\overline{\lvert\Delta\omega\rvert}$, $\overline{\Delta\omega}$	0.33, -0.33	0.51, 0.51	
σ	0.12	0.11	

SOS-ADC(2)-x

- Semi-empirical method for doubly excited states.
- rigorous ISR-SOS-ADC(2) possible (no gain)
- two empirical scaling factors required, c_{os} and c_x
- fitted to Thiel's benchmark set!



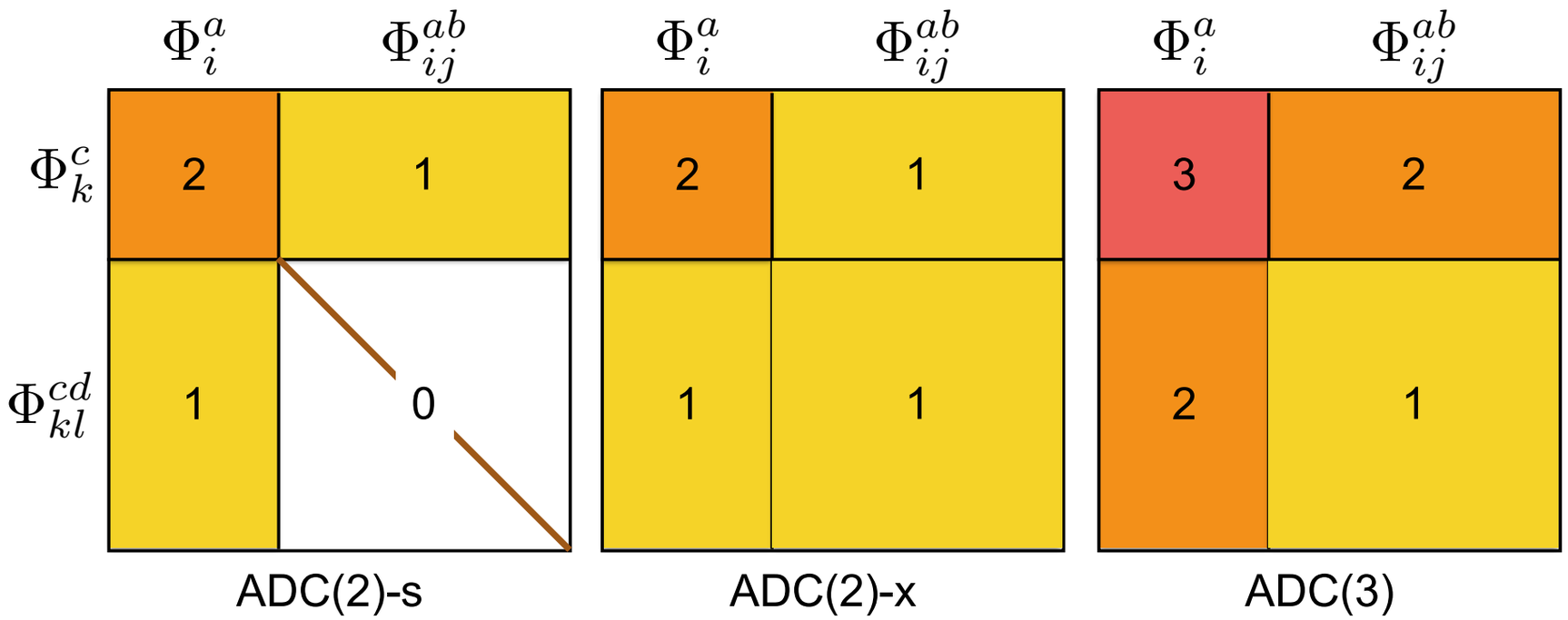
c_{os} influences the excitation energy of both singly and doubly excited states

c_x shifts essentially only doubles (weight of doubles in brackets)

	State	TBE-2	DFT/ MRCI	SOS-ADC(2)-s	ADC(2)-x	SOS-ADC(2)-x	SOS-ADC(2)-x	SOS-ADC(2)-x
$c^{os}_{coupling}$				1.17	...	1.17	1.0	1.0
c^{os}_{x}				...	...	...	0.85	0.9
				Singlet states with high double excitation character				
Butadiene	$2A_g$	6.55	6.18	7.17 (0.08)	5.12 (0.55)	4.71 (0.50)	6.39 (0.40)	6.19 (0.47)
Hexatriene	$2A_g$	5.09	4.92	6.65 (0.10)	4.06 (0.58)	3.77 (0.58)	5.40 (0.55)	5.16 (0.60)
Octatetraene	$2A_g$	4.47	4.01	6.04 (0.12)	3.36 (0.61)	3.12 (0.61)	4.69 (0.60)	4.45 (0.66)
Cyclopentadiene	$2A_1$	6.28	6.15	6.93 (0.10)	5.10 (0.49)	4.60 (0.43)	6.20 (0.37)	6.05 (0.42)
				Singlet states with high single excitation character				
Butadiene	$1B_u$	6.18	6.02	6.16 (0.06)	5.56 (0.10)	5.26 (0.12)	6.21 (0.09)	6.19 (0.09)
Hexatriene	$1B_u$	5.10	4.95	5.24 (0.07)	4.60 (0.14)	4.29 (0.13)	5.34 (0.10)	5.33 (0.10)
Octatetraene	$1B_u$	4.66	4.25	4.62 (0.08)	3.96 (0.12)	3.65 (0.14)	4.77 (0.11)	4.75 (0.11)
Cyclopentadiene	$1B_2$	5.55	5.42	5.48 (0.06)	4.91 (0.09)	4.56 (0.09)	5.55 (0.08)	5.54 (0.10)

C. Krauter, M. Pernpointner, A. Dreuw, J. Chem. Phys. 138, 044107 (2013)

ADC(3)



Philipp Harbach

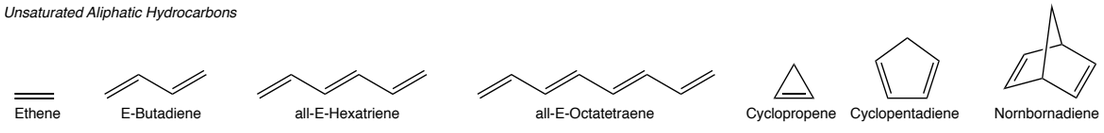
ADC(3) stays within the 2p2h-excitation manifold, and scales like $O(N^6)$!
Every molecule, for which ADC(2)-x is possible, also ADC(3) is doable!

P. H. P. Harbach, M. Wormit, A. Dreuw, J. Chem. Phys. 141, 064113 (2014)

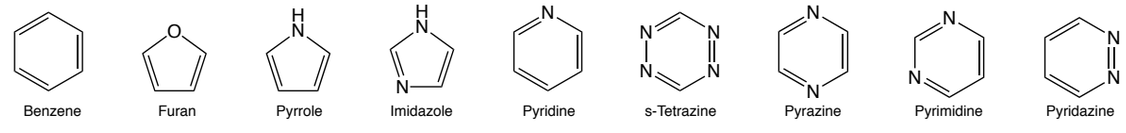
Potential of ADC(3)

Thiel's benchmark set

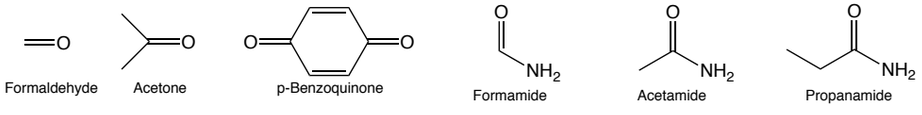
Unsaturated Aliphatic Hydrocarbons



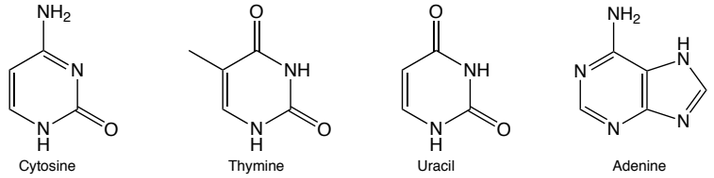
Aromatic Hydrocarbons and Heterocycles



Aldehydes, Ketons and Amides



Nucleobases



singlets

TBE as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	103	103	84	104	104	104
Min	-0.30	-2.92	-0.11	-1.43	-1.86	-0.78
Max	1.58	1.58	1.15	2.05	0.93	0.90
Mean	0.29	0.43	0.23	0.22	-0.70	0.12
Std. Dev	0.28	0.44	0.21	0.38	0.37	0.28

CC3 as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	114	114	–	114	114	114
Min	-0.22	-3.75	–	-2.95	-3.47	-2.41
Max	2.17	2.26	–	2.16	0.76	1.10
Mean	0.14	0.27	–	-0.03	-0.99	-0.20
Std. Dev	0.29	0.48	–	0.54	0.48	0.46

ADC3 as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	141	141	114	141	141	–
Min	-1.15	-2.96	-1.10	-1.29	-1.80	–
Max	2.62	2.68	2.41	2.19	0.24	–
Mean	0.24	0.41	0.20	0.08	-0.83	–
Std. Dev.	0.55	0.59	0.46	0.50	0.38	–

[b]Total number of considered states.

triplets

TBE as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	63	63	63	63	63	63
Min	-0.09	-0.28	-0.04	-0.27	-0.96	-0.49
Max	0.48	0.39	0.32	0.48	-0.24	0.44
Mean	0.17	0.06	0.04	0.12	-0.55	-0.18
Std. Dev	0.13	0.14	0.08	0.16	0.20	0.16

CC3 as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	71	71	–	71	71	71
Min	-0.11	-0.28	–	-0.27	-1.33	-1.29
Max	0.56	0.51	–	0.48	-0.22	0.26
Mean	0.14	0.05	–	0.09	-0.63	-0.22
Std. Dev	0.14	0.15	–	0.14	0.24	0.20

ADC3 as reference						
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[b]	71	71	71	71	71	–
Min	-0.37	-0.96	-0.26	-0.38	-1.41	–
Max	1.58	1.39	1.29	1.53	0.08	–
Mean	0.37	0.27	0.22	0.32	-0.41	–
Std. Dev.	0.29	0.21	0.20	0.30	0.33	–

[b]Total number of considered states.

Comparison CC3 vs. ADC(3)?

non-CC3 TBEs only!

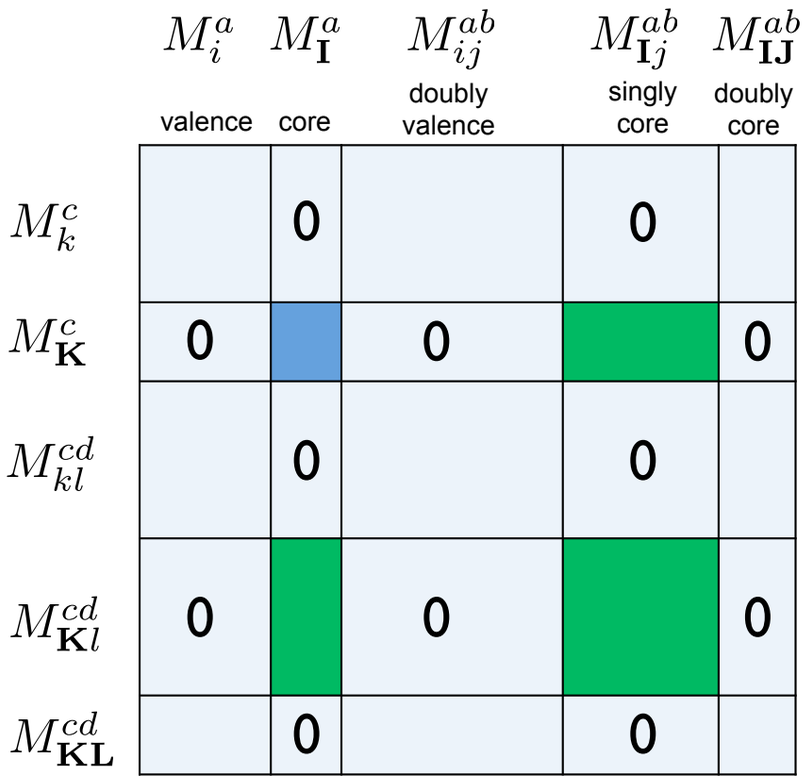
CC3:	0.23 ± 0.21 eV	0.04 ± 0.08 eV
ADC(3):	0.08 ± 0.27 eV	-0.10 ± 0.13 eV

P. H. P. Harbach, M. Wormit, A. Dreuw, J. Chem. Phys. 141, 064113 (2014)

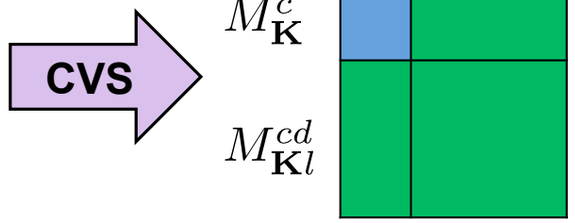
core-excited states with ADC

Core-Valence Separation (CVS) Approximation

- valence state couple only very weakly to core-excited states
- set coupling to exactly zero:



ADC Matrix



CVS-ADC Matrix

Jan Wenzel

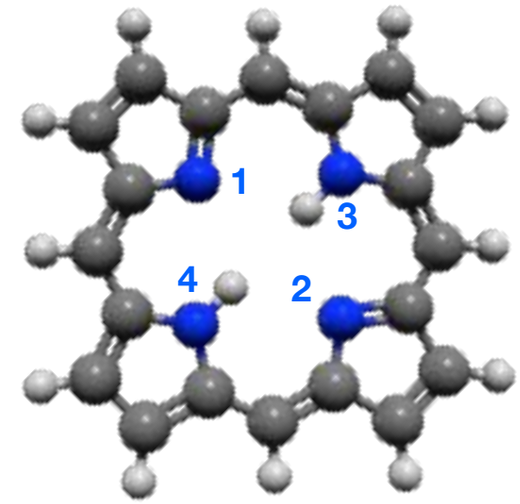
L. S. Cederbaum, W. Domcke, J. Schirmer, Phys. Rev. A 22, 206–222 (1980)
A. Barth, L. S. Cederbaum, Phys. Rev. A 23, 1038-1061 (1981)
A. Barth, J. Schirmer, J. Phys. B: Atom. Mol. Phys. 18, 867-885 (1985)

core-excited states with ADC

Efficient implementation:

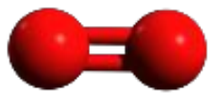
- up to ADC(3)
- restricted as well as unrestricted
- point group symmetry
- singlet and triplet core-excited states
- oscillator strengths
- properties: densities, dipole moments, excited state absorption
- fully parallelized

Porphin



N 1s (6-311++G**)			
Transition	**fosc**	**Energy [eV]**	**Experiment**
N1,N2 → π*	0.0351	398.07	398.2
N3,N4 → π*	0.0280	400.35	400.3
N1,N2 → π*	0.0257	401.18	402.3
N1,N2 → π*	0.0178	403.37	403.9

triplet O_2 diradical



O 1s (6-311++G**)			
Transition	**fosc**	**Energy [eV]**	**Experiment**
→ π*(SOMO)	0.106	529.82	530.7
→ diffuse	0.071	538.69	538.8
→ diffuse	0.019	541.55	541.7

J. Wenzel, M. Wormit, A. Dreuw J. Comp. Chem. 35, 1900 (2014)
J. Wenzel, M. Wormit, A. Dreuw J. Chem. Theo. Comp. in press (2014)

Spin-Flip ADC for “few-reference” systems

Daniel Lefrancois

Adapting regular ADC to spin-flip is straightforward via ISR

Creation operator regular ADC

$$\{\hat{C}_J\} = \{\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}, \hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}\hat{c}^\dagger_{b\tau}\hat{c}_{j\tau}, \dots\}$$

Creation operator spin-flip ADC

$$\{\hat{C}_J\} = \{\hat{c}^\dagger_{a\beta}\hat{c}_{i\alpha}, \hat{c}^\dagger_{a\beta}\hat{c}_{i\alpha}\hat{c}^\dagger_{b\tau}\hat{c}_{j\tau}, \dots\}$$

Excitations with $\Delta m_S = -1/+1$

SF-ADC requires a single-reference triplet ground state!

Structure of the open-shell ADC matrix:

	$i_\alpha a_\alpha$	$i_\alpha a_\beta$	$i_\beta a_\alpha$	$i_\beta a_\beta$
$i_\alpha a_\alpha$	αα-ADC	0	0	αα-ADC
$i_\alpha a_\beta$	0	α –> β	0	0
$i_\beta a_\alpha$	0	0	β –> α	0
$i_\beta a_\beta$	ββ-ADC	0	0	ββ-ADC

X

αα-ADC
α –> β
β –> α
ββ-ADC

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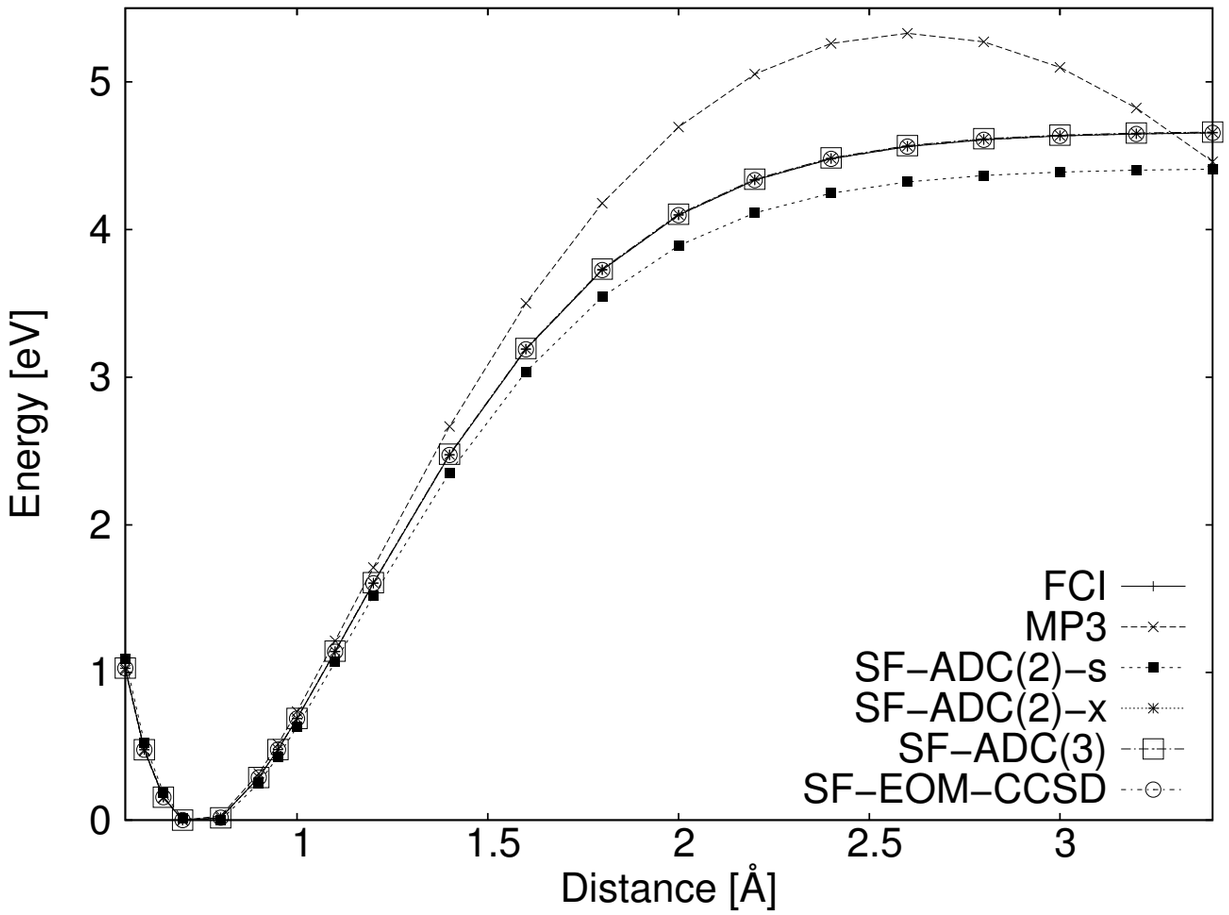
$i_\beta a_\alpha$	0	0	β –> α	0
$i_\beta a_\beta$	ββ-ADC	0	0	ββ-ADC

X

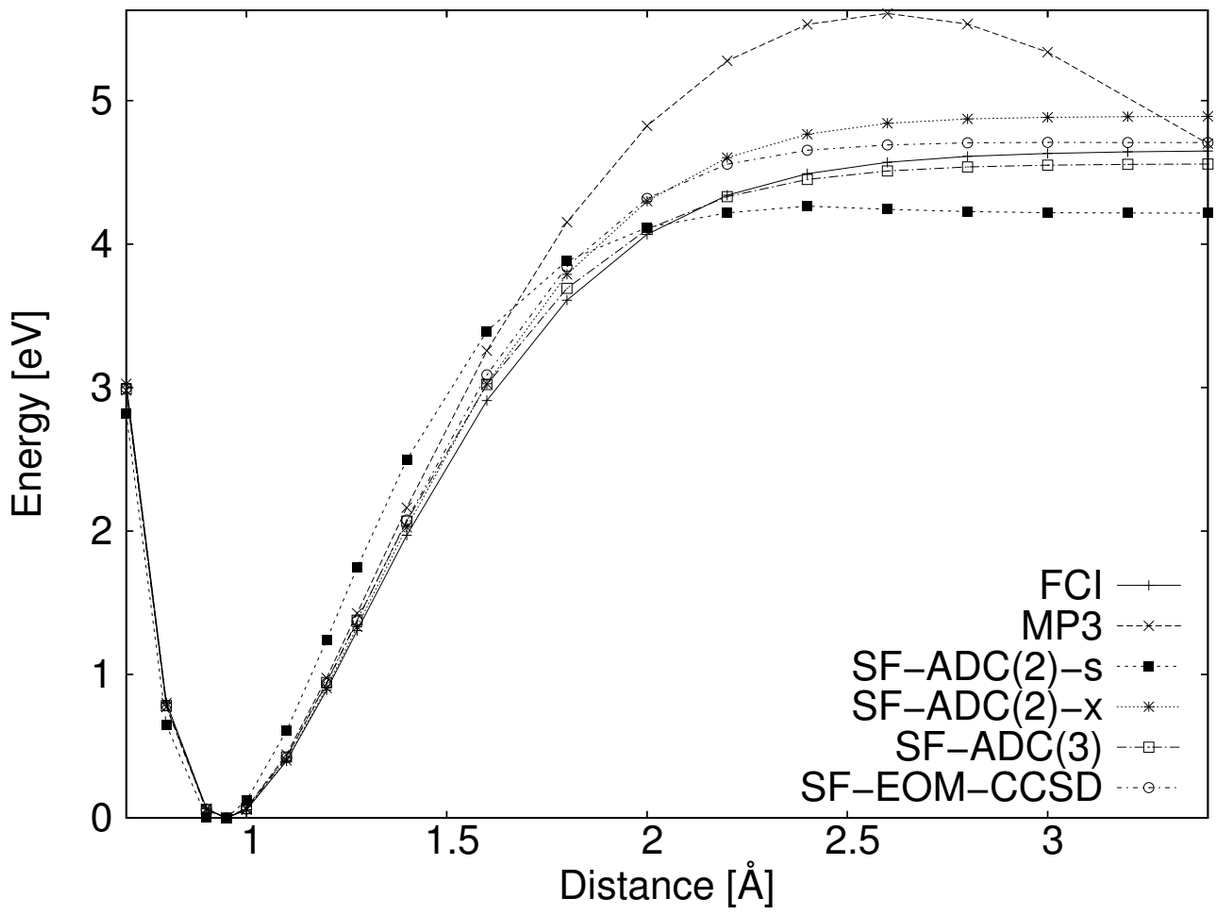
αα-ADC
α –> β
β –> α
ββ-ADC

Dissociation of a single bond

Let's start easy: H_2



More than two electrons: HF



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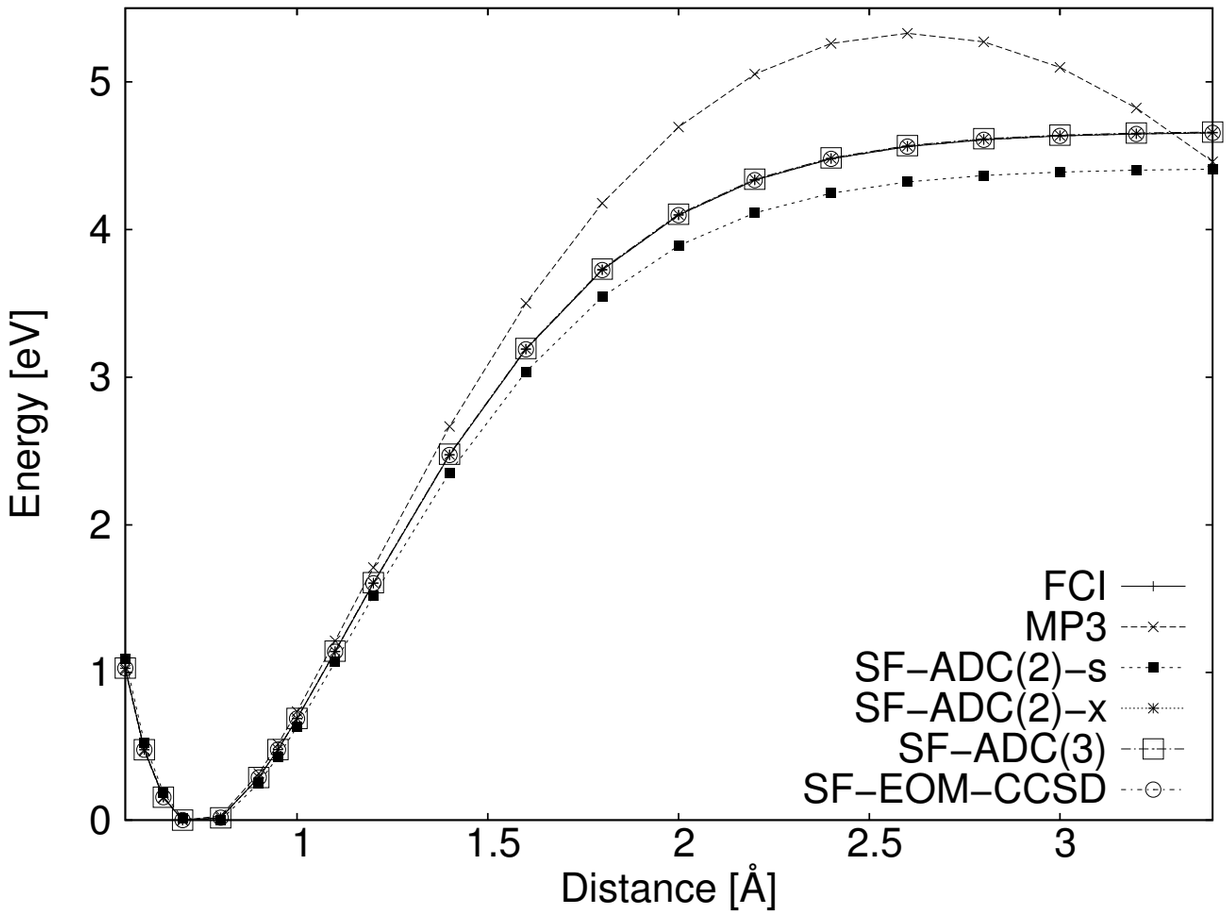
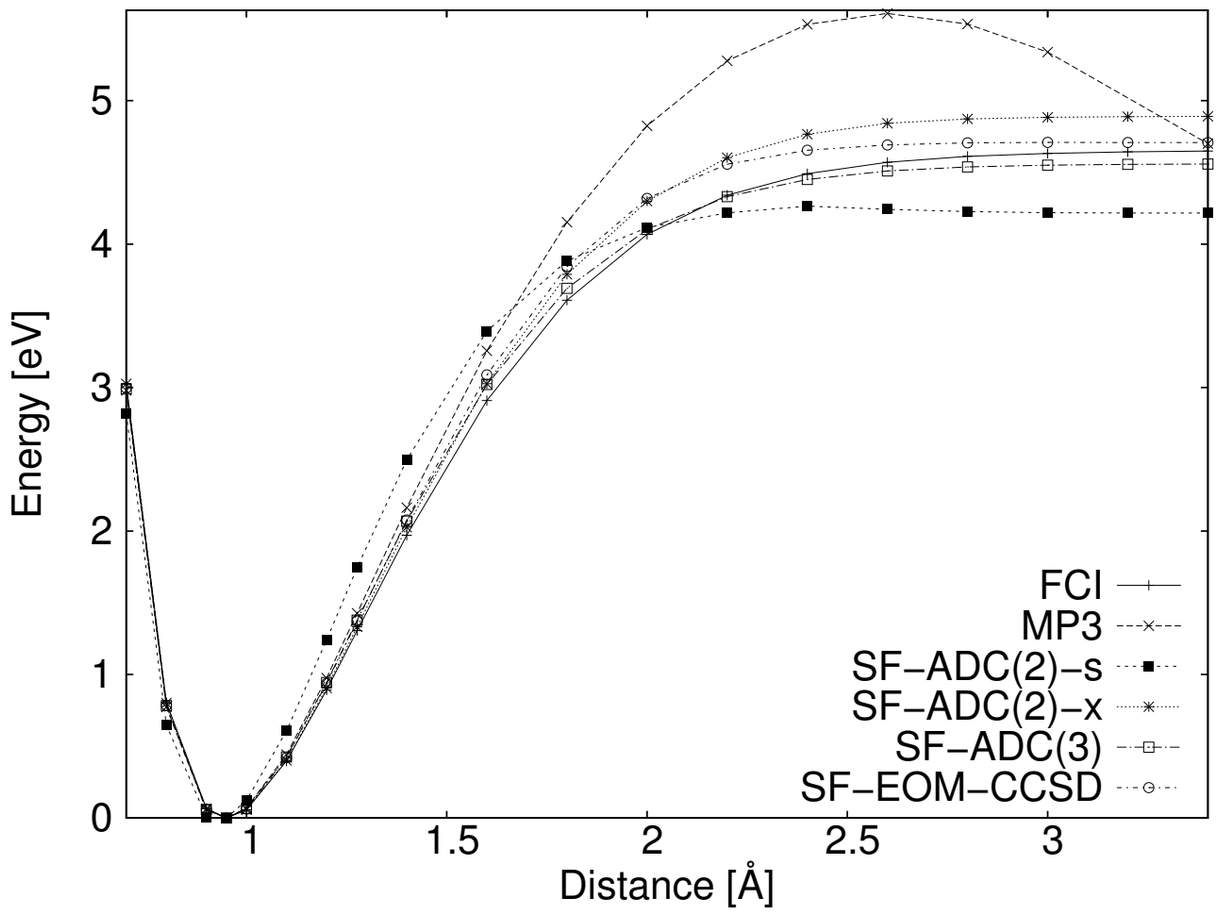
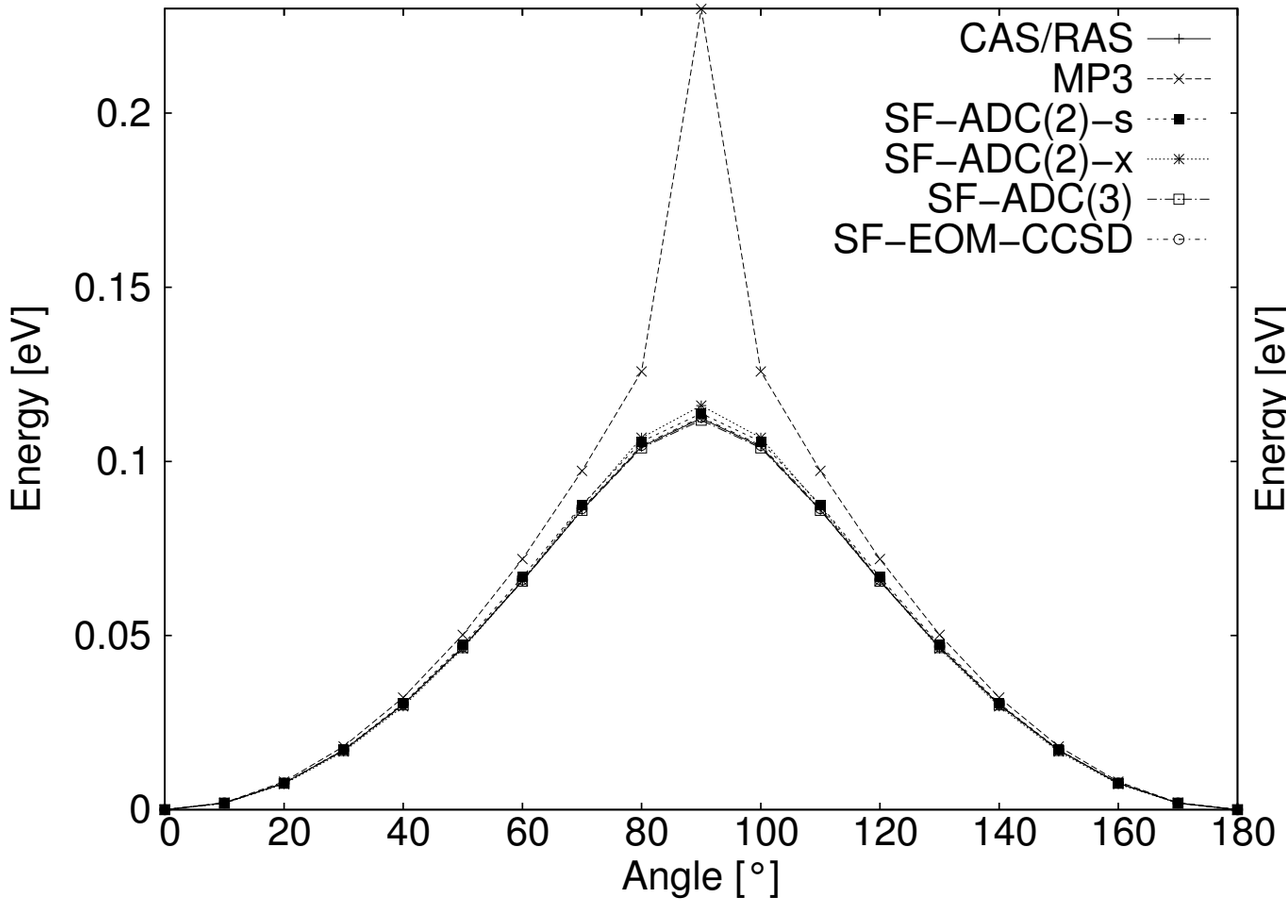


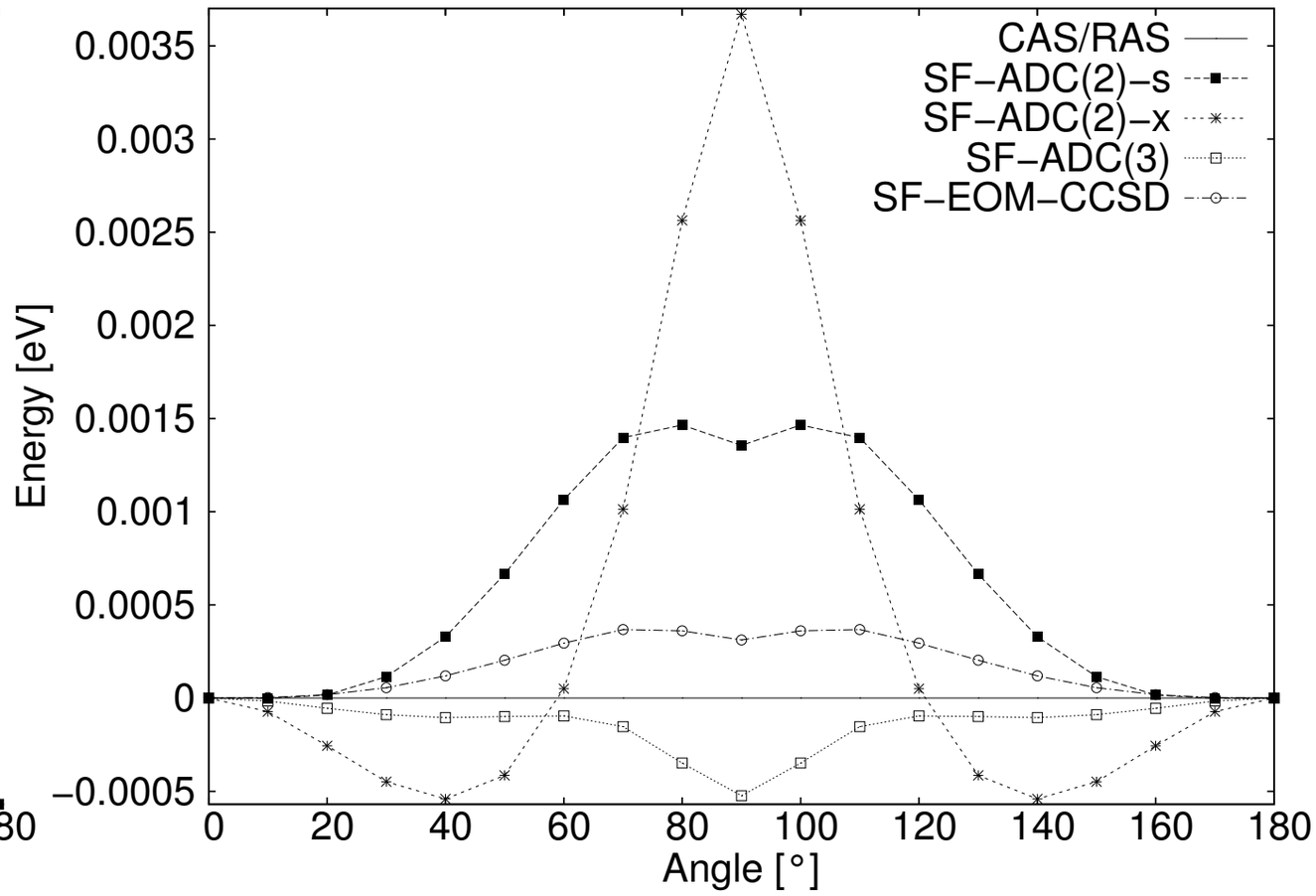
More than two electrons: HF



Rotating a double bond: ethylene

Errors compared to CAS reference

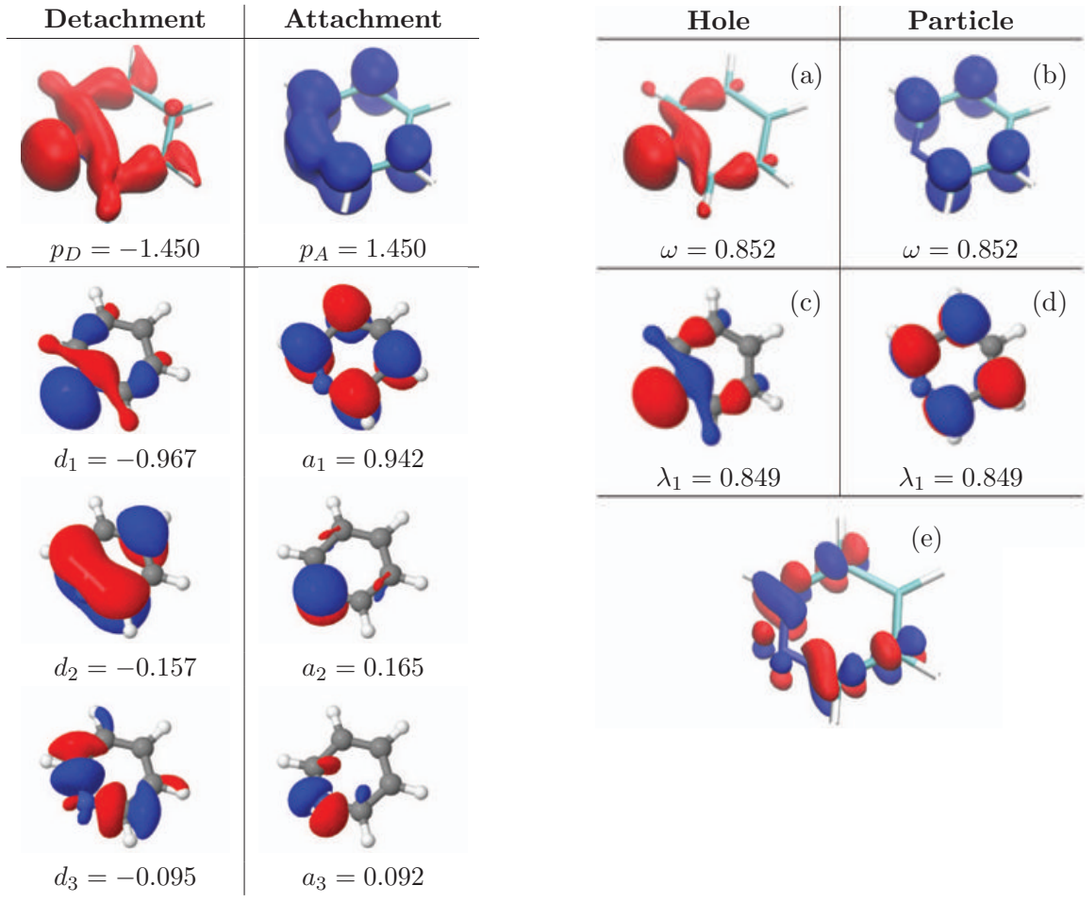




Density Analysis of ADC states

- Electron density of each state
- Difference density/ Natural difference density orbitals (NDDOs)
- Attachment/Detachment densities
- Transition density/ Natural transition orbitals (NTOs)

Felix Plasser



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F. Plasser, S. A. Bäppler M. Wormit, A. Dreuw, J. Chem. Phys. 141, 024107 (2014)
F. Plasser, B. Thomitzni, S. Bäppler, J. Wenzel, D. Rehn, M. Wormit and A. Dreuw J. Comp. Chem., 2015, 36, 1609

Ionization Potential and Electron attachment

non-Dyson IP-ADC and EA-ADC

$O(N^5)$ for IP-ADC and EA-ADC;
with N number of basis functions

different "excitation" operator ISR construction

EE-ADC

$$\{C_I\} = \{c_a^\dagger c_i, c_a^\dagger c_b^\dagger c_i c_j, c_a^\dagger c_b^\dagger c_c^\dagger c_i c_j c_k, ...\}$$

IP-ADC

$$\{C_I\} = \{c_i, c_a^\dagger c_i c_j, c_a^\dagger c_b^\dagger c_i c_j c_k, ...\}$$

EA-ADC

$$\{C_I\} = \{c_a^\dagger, c_a^\dagger c_b^\dagger c_i, c_a^\dagger c_b^\dagger c_c^\dagger c_i c_j, ...\}$$

Matthias Schneider

Structure of the ADC matrix

	$\lvert\tilde{\Psi}_i\rangle$	$\lvert\tilde{\Psi}^a_{ij}\rangle$
$\lvert\tilde{\Psi}_i\rangle$	$M^{(a)}_{11}$	$M^{(b)}_{12}$
$\lvert\tilde{\Psi}^a_{ij}\rangle$	$M^{(b)}_{21}$	$M^{(c)}_{22}$

	a	b	c
IP/EA-ADC(2)	***0,2***	***1***	***0***
IP/EA-ADC(3)	***0,2-3***	***1-2***	***0-1***

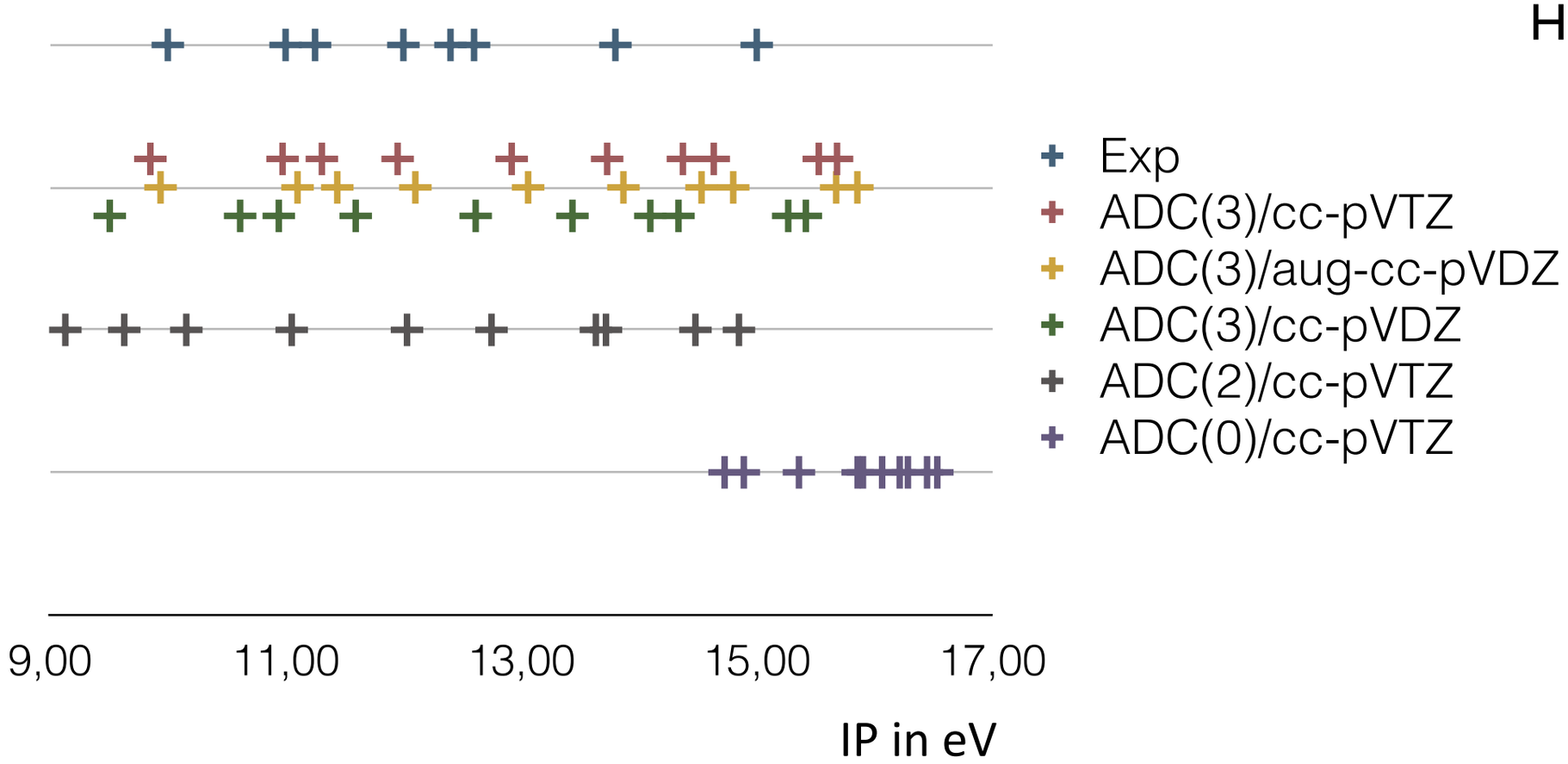
J. Schirmer, Phys. Rev. A. **26**, 2395 (1982).

Ionization Potential

Serine

- geometry: MP2/def2-tzvpp
- ADC(0) too high
- ADC(2) too low
- ADC(3) with cc-pVTZ and aug-cc-pVDZ:
  error < 0.2 eV for 3 lowest states

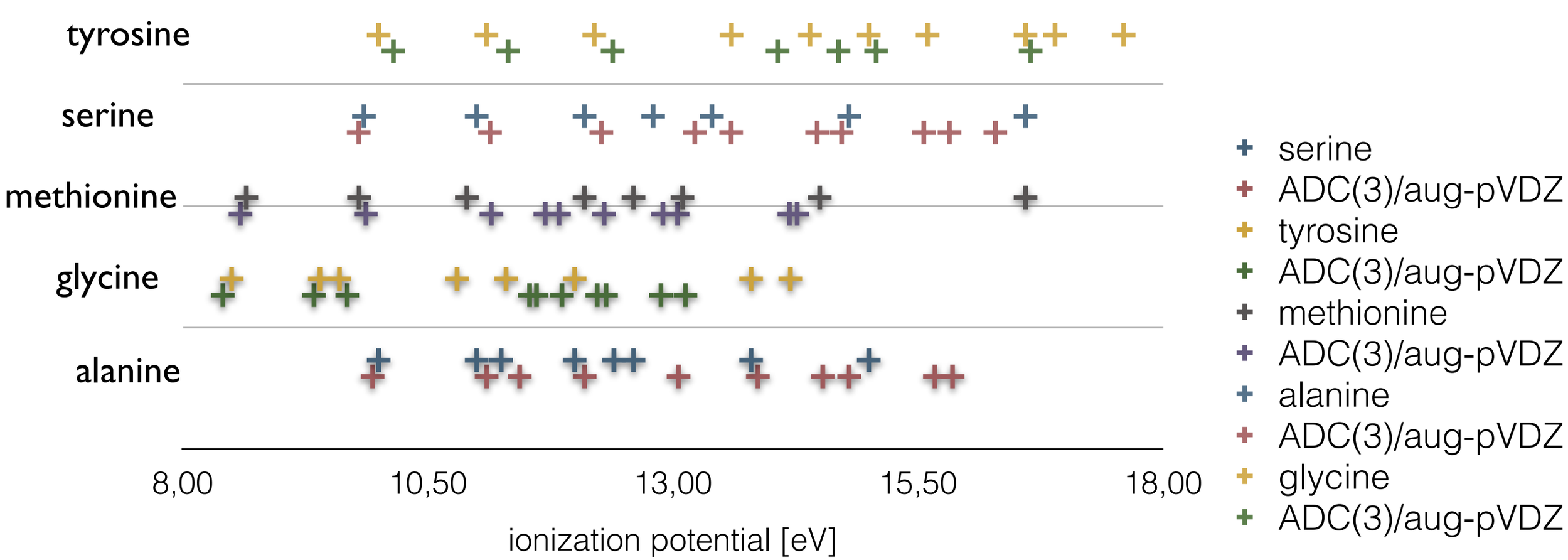
HOMO (Serine)



Ionization Potential

Amino acids

- geometry: MP2/def2-tzvpp
- error less than 0.25 eV for first 3 IPs

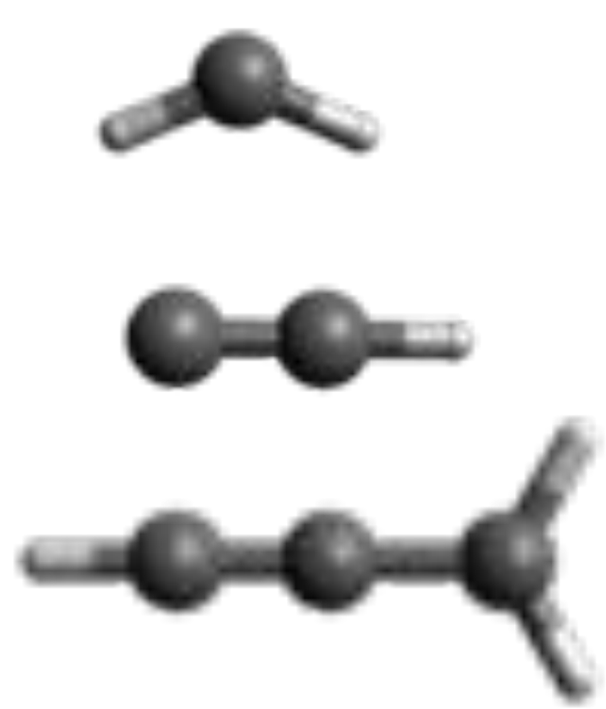


Ionization Potentials of Radicals

Hydrocarbon Radicals

- geometry: MP2/cc-pVTZ
- alpha and beta states computed independently
- 3 lowest IP

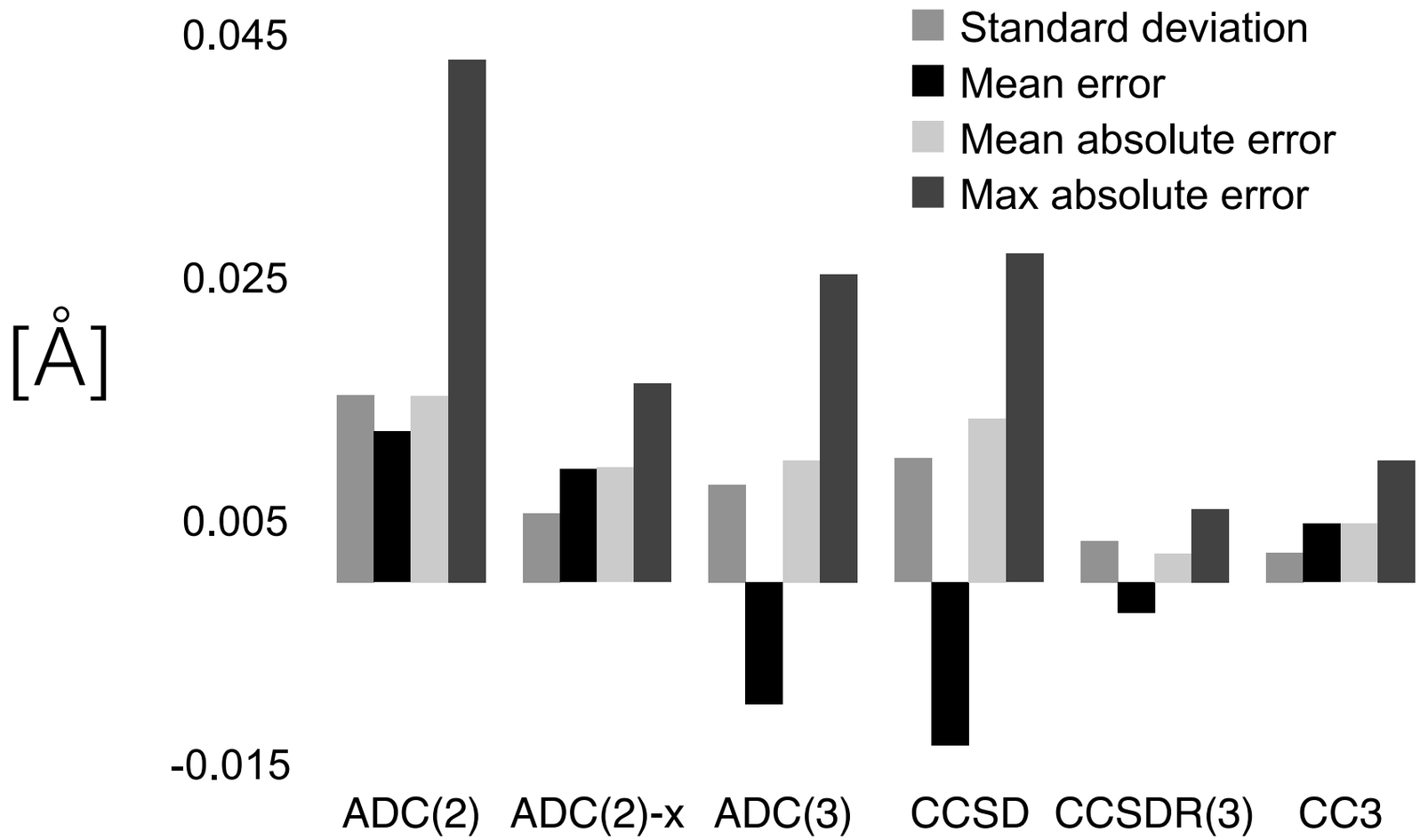
	State	Exp.	ADC(2)	ADC(3)	EOM-CC	MP2	B3LYP
					cc-pVTZ		
Methylene	1	10.39	10.30	10.35	10.38	10.35	
	2		11.44	11.47	11.49		
	3		16.39	15.66	16.37		
Ethynyl	1	11.65	12.18	11.77	12.39	14.10	14.03
	2		12.18	11.77	12.39		
	3		14.57	13.15	14.46		
Propargyl	1	8.67	8.64	8.66	8.78	8.46	8.70
	2		10.67	10.73	11.00		
	3		11.98	11.30	12.36		



ADC geometry optimizations

Dirk Rehn

Diatomic molecules (BH,CO,N_2,BF)
singlet and triplet states



Weak spot: MP ground state

Summary

- ADC(n) is an alternative to EOM-CC and CC-LR approaches
- ADC(2)-s/x and ADC(3) available
- impressive accuracy of ADC(3)
- Excited state properties via ISR accessible: excited-state absorption, excited-state dipoles, two-photon absorption, spin-orbit coupling elements
- CVS-ADC(2)-s/x
- SOS-ADC(2)
- spin-flip ADC
- density analyses for all ADC variants
- nuclear gradients for ADC(2) and ADC(3)
- polarizable continuum model for all ADC variants

adcman: general purpose black-box computational tool for photochemistry based on ADC.

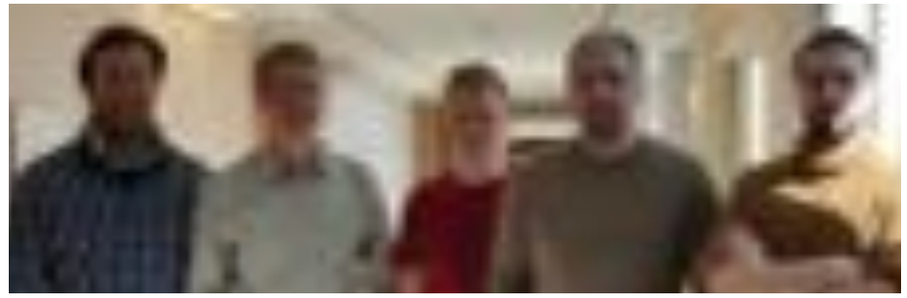
Outlook

Future developments:

- CVS-ADC TPA
- CVS-ADC Gradients
- CVS-CPP ADC

GATOR:

- free quantum chemistry program
- based on:
  - CPP-solver library (DALTON) (Patrick Norman)
  - `adcman` (Andreas Dreuw)
  - independent SCF (Jaime Axel Rosal)



Acknowledgements

adcman developers
Dr. Michael Wormit
Dr. Dirk R. Rehn
Dr. Jan Wenzel
Dr. Matthias Schneider
Dr. Jan-M. Mewes
Stefan Prager
Dr. Caroline Krauter
Dr. Philipp H. P. Harbach
Dr. Jan Hendrik Starcke

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Emmy Noether-Programm
Deutsche Forschungsgemeinschaft DFG

Heisenberg-Programm
Deutsche Forschungsgemeinschaft

Knut och Alice Wallenbergs Stiftelse

HGS MathComp

Alexander von Humboldt Stiftung/Foundation