The CC2 Method: Parallel Implementation and Applications on Nanomolecules

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- Part I: Second-order Møller-Plesset Perturbation Theorie
  Using the Resolution-of-the-Identity (RI) Approximation
- Part II: Coupled-Cluster Response Theory for Energies
  and Structures of Excited States
- Part III: The approximate coupled-cluster singles-and-doubles
  model CC2 for investigations on excited states

Part I

Second-order Møller-Plesset Perturbation Theorie Using the Resolution-of-the-Identity (RI) Approximation

Part I

Second-order Møller-Plesset Perturbation Theorie Using the Resolution-of-the-Identity (RI) Approximation

- Electron Correlation: Physics, Wavefunction Ansätze
- MP2: Equations, Basis Sets, Accuracies, Diagonistics
- Bypassing Bottlenecks:
  The Resolution-of-the-identity Approximation for ERIs
- Parallel Implementation
- Large-scale MP2 Calculations

Electron-Electron Correlation

In wavefunction based ab initio methods...

- linear combination of Slater determinants:

$$\Psi = c_{\mathrm{HF}}\Phi_{\mathrm{HF}} + \sum_{ai} \Phi_i^a + \sum_{aibj} \Phi_{ij}^{ab} \ldots$$

  $\rightsquigarrow$ provides complete basis for N-electron Hilbert space

  if one-electron basis set is complete

- Example: minimal ansatz for H_2

$$\Psi = c_g \left| \phi_{1\sigma_g}^{\alpha} \phi_{1\sigma_g}^{\beta} \right| + c_u \left| \phi_{1\sigma_u}^{\alpha} \phi_{1\sigma_u}^{\beta} \right|$$

$\rightsquigarrow$ "*configuration interaction*"

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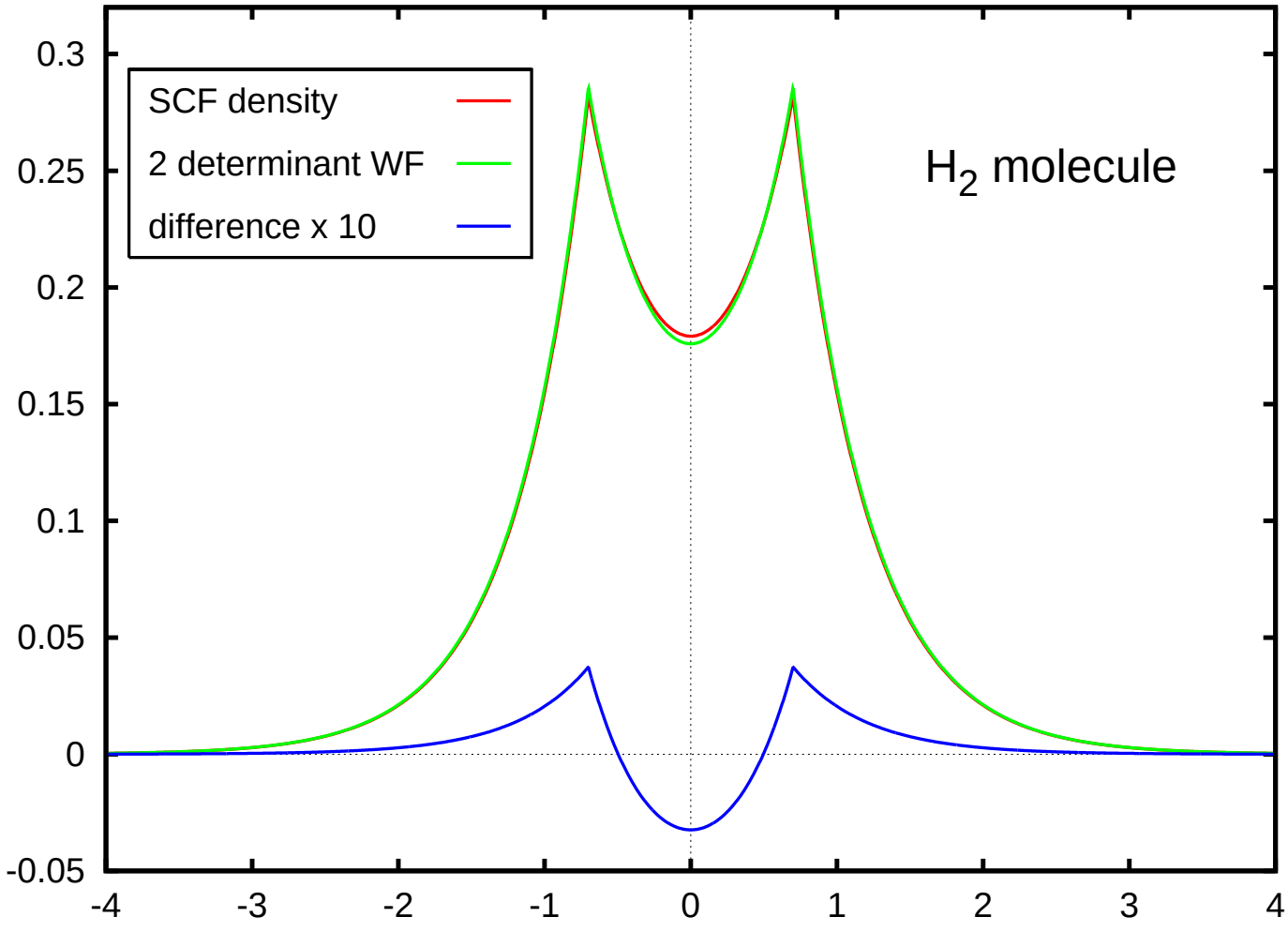
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antibonding configuration

$$\Psi = c_g\left|\phi_{1\sigma_g}^{\alpha}\phi_{1\sigma_g}^{\beta}\right| + c_u\left|\phi_{1\sigma_u}^{\alpha}\phi_{1\sigma_u}^{\beta}\right|$$

⇝ "*configuration interaction*"

Electron-Electron Correlation



- density along bonds is reduced ⇝ longer bonds/smaller force constants
- density is increased in outer regions ⇝ larger polarizabilities

Correlation Effects & Excitation Classes

Expansion of wavefunction in “excited” determinants...

- configuration interaction ansatz (linear parameterization)

$$\Psi = \left(1 + \sum_{ai} c_{ai} \hat{\tau}_i^a + \sum_{ai \geq bj} c_{aibj} \hat{\tau}_{ij}^{ab} + \sum_{ai \geq bj \geq ck} c_{aibjck} \hat{\tau}_{ijk}^{abc} + \ldots \right) \Phi_{\mathrm{HF}}$$

- coupled-cluster ansatz (exponential parameterization)

$$\Psi = \exp\left(\sum_{ai} t_a^i \hat{\tau}_i^a + \sum_{ai \geq bj} t_{ab}^{ij} \hat{\tau}_{ij}^{ab} + \sum_{ai \geq bj \geq ck} t_{abc}^{ijk} \hat{\tau}_{ijk}^{abc} + \ldots \right) \Phi_{\mathrm{HF}}$$

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Both expansions are equivalent, but the CC ansatz is more efficient for the single-reference methods.

Correlation Effects & Excitation Classes

largest contribution comes from double excitations...

- physical explanation: Coulomb interaction is a 2-particle interaction

  $\rightsquigarrow$ (near) collisions of two electrons most important incident
- mathematical explanation: only double excitations have non-vanishing matrix elements with Hartree-Fock wavefunction

$$\langle \Phi_i^a | \hat{H} | \Phi_{\mathrm{HF}} \rangle = 0 \qquad \text{(Brioullin theorem)}$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{\mathrm{HF}} \rangle = (ai|bj) - (aj|bi)$$

$$\langle \Phi_{ijk\ldots}^{abc\ldots} | \hat{H} | \Phi_{\mathrm{HF}} \rangle = 0 \qquad \text{(Slater rules)}$$

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$$\langle \Phi_{ijk\ldots}^{abc\ldots} | \hat{H} | \Phi_{\mathrm{HF}} \rangle = 0 \qquad \text{(Slater rules)}$$

$\rightsquigarrow$ **largest correlation contribution from double excitations**

(typically > 90 **%)**

Correlation Effects & Excitation Classes

- **Single excitations** describe mainly orbital relaxation:

$$\exp\left(\sum_{ai} t_{ai}\hat{\tau}_i^a\right)\Phi_{\mathrm{HF}} \qquad \exp\left(\sum_{ai} \kappa_{ai}(\hat{\tau}_i^a - \hat{\tau}_a^i)\right)\Phi_{\mathrm{HF}} = \hat{U}\Phi_{\mathrm{HF}}$$

single excitations in CC orbital transformations

- This accounts for the fact that the orbitals have been optimized for the Hartree-Fock and not for correlated wavefunction...

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- **Triple and higher excitations** describe various combinations of many-electron collisions and/or orbital relaxation.

Second Order Møller-Plesset Perturbation Theory — MP2

- First order amplitudes:

$$\langle {}^{ij}_{ab} | [\hat{F}, \hat{T}_2] + \hat{H} | \mathrm{HF} \rangle = 0 \quad \Longrightarrow \quad t^{ij}_{ab} = \frac{(ia|jb)}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b}$$

- Second order energy (closed shell case):

$$E_{\mathrm{MP2}} = \langle \mathrm{HF} | \hat{H} \hat{T}_2 | \mathrm{HF} \rangle = \sum_{aibj} \frac{[2(ia|jb) - (ib|ja)](ia|jb)}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b}$$

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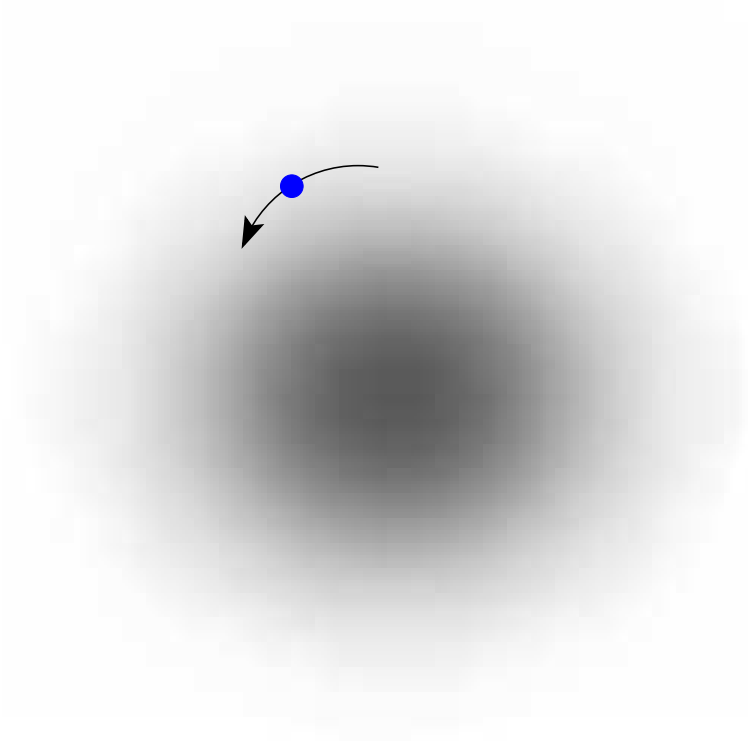
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- Simple implementation (. . . once $(ia|jb)$ is available):

```
do i = 1, nocc
  do j = i, nocc
   do a = 1, nvirt
    do b = b, nvirt
     tiajb = (ia|jb)/(εi-εa+εj-εb)
     EMP2 = EMP2 + (2-δij)[2(ia|jb)-(ib|ja)] * tiajb
    end do
   end do
  end do
end do
```

Electron Correlation & Basis Sets

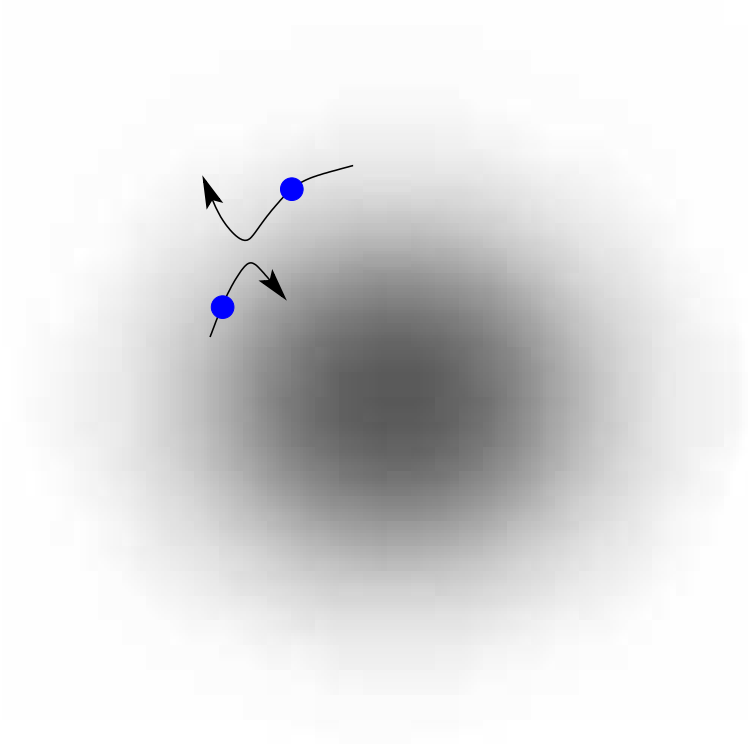


consider ground state of He atom $1s^2$:

- uncorrelated wavefunction (e.g. SCF):

  s functions sufficient to reach the basis set limit, no higher angular momenta contribute

Electron Correlation & Basis Sets

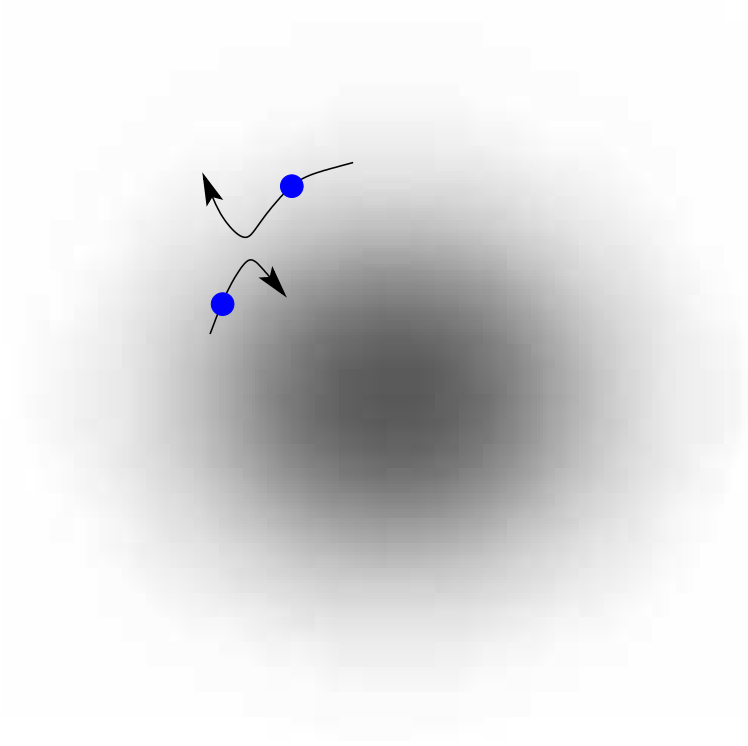


consider ground state of He atom $1s^2$:

- correlated wavefunction (e.g. CI):

  with determinants $|\phi^{\alpha}_{n_1 s}\phi^{\beta}_{n_2 s}|$ build only from s functions the angular position of electron 2 cannot depend on the position of electron 1 . . .

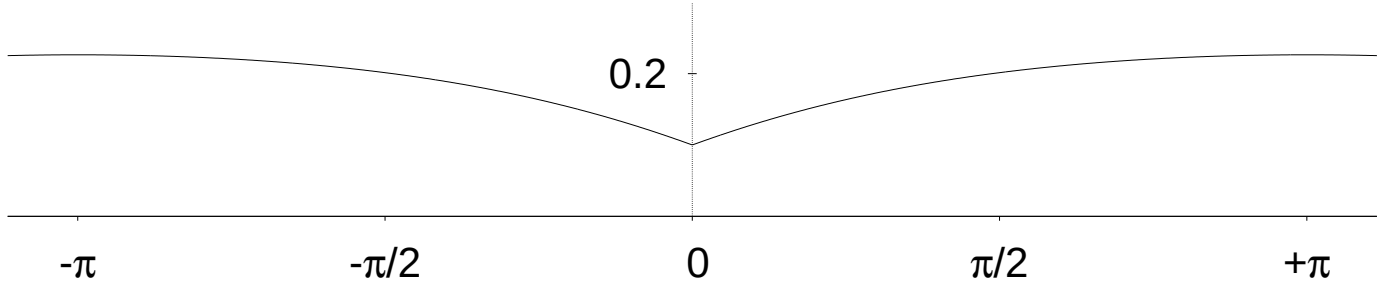
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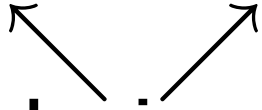
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- correlated calculations require higher angular momentum (correlation) functions p, d, f, . . . to describe the **Coulomb cusp**



Electron Correlation & Basis Sets

SCF, DFT		correlated wavefunction methods			
SVP	[3s2p1d]	SVP	[3s2p1d]	cc-pVDZ	[3s2p1d]
TZVP	[5s3p1d]	TZVPP	[5s3p1d1f]	cc-pVTZ	[4s3p2d1f]
		QZVPP	[7s4p3d2f1g]	cc-pVQZ	[5s4p3d2f1g]
				cc-pV5Z	[6s5p4d3f2g1h]
				cc-pV6Z	[7s6p5d4f3g2h1i]



Karlsruhe basis sets (row 1)
(segmented contracted)



Dunning basis sets (row 1)
(general contracted)

Electron Correlation & Basis Sets

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- Correlation energies converges approximately as

$$E_X = E_{lim} - a/X^3$$

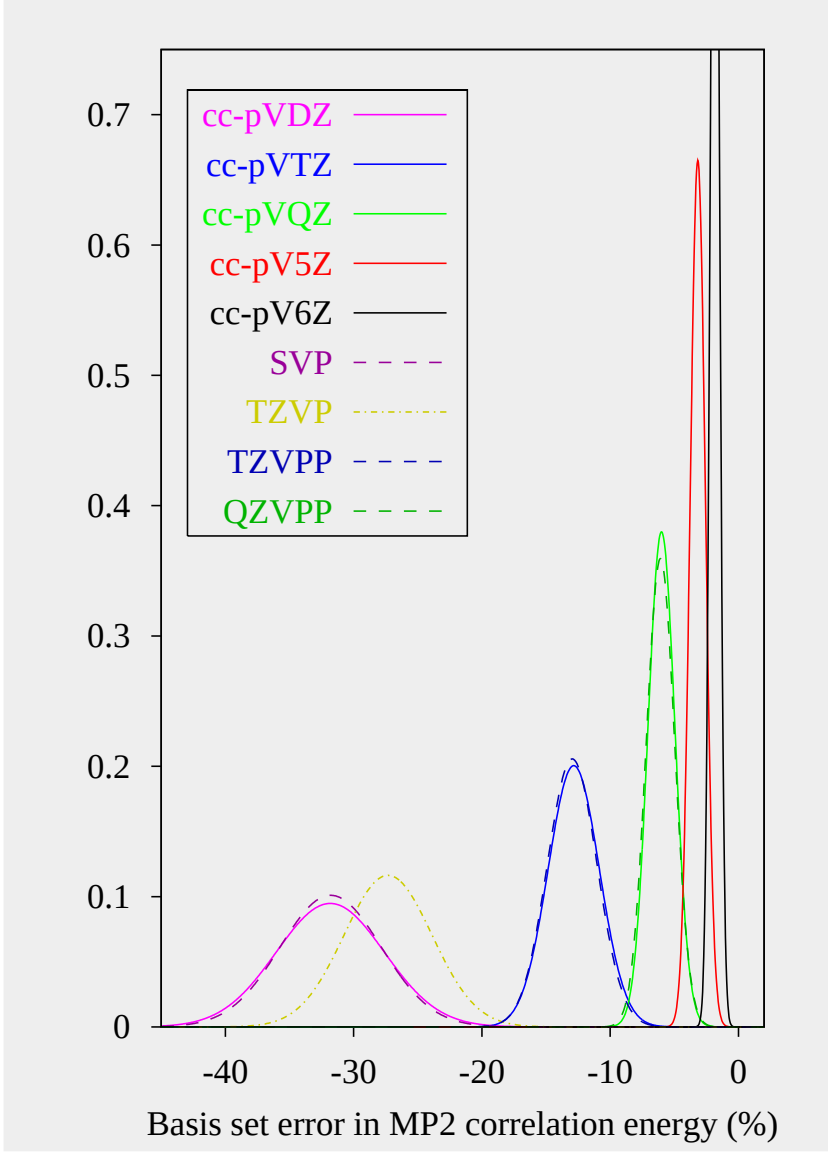
with cardinal number X = D (2), T (3), Q (4), 5, 6, ...

The basis set hierarchy cc-pVXZ

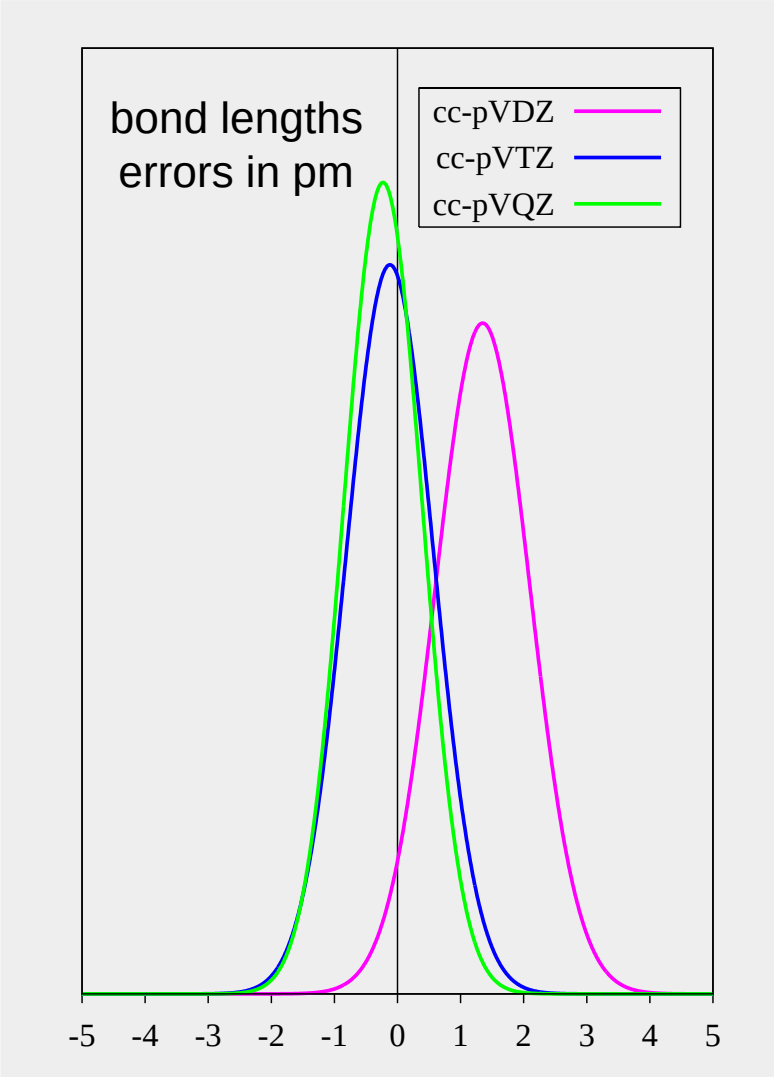
Error in MP2 correlation energy (in %) for 72 molecules containing first and second row atoms:

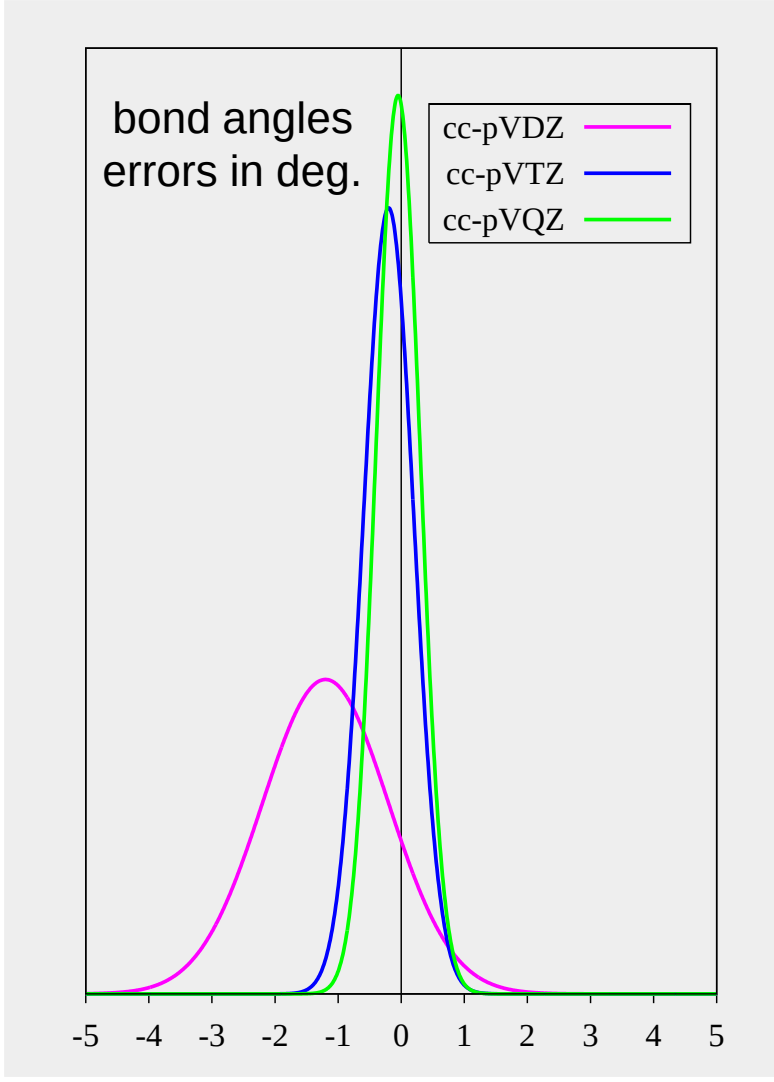
cc-pVDZ	$-32 \pm 4\%$
cc-pVTZ	$-13 \pm 2\%$
cc-pVQZ	$-6 \pm 1\%$
cc-pV5Z	$-3 \pm 0.6\%$
cc-pV6Z	$-1.8 \pm 0.4\%$

(Basis set limit estimated by extra-polation of the 5Z/6Z results using the empirical formula: $E_{lim} \approx E_X + a/X^3$)



The basis set hierarchy cc-pVXZ





- doubly polarized triple-ζ basis sets (TZVPP, cc-pVTZ) give usually the best accuracy/costs ratio for MP2.

Second Order Møller-Plesset Perturbation Theory — MP2

Typical accuracies obtained for single-reference cases:

bond lengths	-0.2 ± 0.7 pm
bond angles	± 0.5 degree
(harm.) vibrational frequencies	1–2%
(isogyric) reaction enthalphies	$\pm$5–10 kJ/mol per bond
atomization energies	$\approx 10 \pm 10$ kJ/mol per atom

Diagnostics

Individual amplitudes $t_{a\ldots}^{i\ldots}$ large $\Longrightarrow |\mathrm{HF}\rangle$ poor approximation for $|\mathrm{FCI}\rangle$

$\longrightarrow$ diagnostic: how adequate is a single-reference ansatz?

Problem: $t_{a\ldots}^{i\ldots}$ depends on choice for MOs (e.g. canonical/localized)

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$\mathscr{T}_1$ **norm for CC:** Lee, Taylor, *IJQC Symp.* 23 (1989) 199

$$\mathscr{T}_1 = ||t_{\mu_1}||/\sqrt{N_{e^-}} \qquad \text{should be } < 0.02$$

$\mathscr{S}_2$ **norm for MP2:** Lee, Head-Gordon, Rendell, *CPL* 243 (1995) 402

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$+$ invariant under same orbital transformations as $|\mathrm{HF}\rangle$

$-$ not size-intensive, because no maximum norm
$\Rightarrow$ threshold depends on number correlated electrons!

Diagnostics

$\mathbf{D_1}$ norm: (Janssen, Nielsen, *CPL* 290 (1998) 423)

$$D_1 = ||\mathbf{t}_{\mu_1}||_2 = \sqrt{\lambda_{max}\Big(\sum_a t_a^i t_a^j, \sum_i t_a^i t_b^i\Big)}$$

- measure for maximum contribution of a single excitation
  $\Longrightarrow$ tests for strong interaction with single excited determinants
- for MP2 it should be $D_1(t_{\mu_1}^{(2)}) \lesssim 0.025$

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D_2 norm: (Nielsen, Janssen, *CPL* 310 (1999) 568)

$$D_2 = ||\mathbf{t}_{\mu_2}||_2 = \sqrt{\lambda_{max}\Big(\sum_{ack} t_{ac}^{ik} t_{ac}^{jk}, \sum_{ick} t_{ac}^{ik} t_{bc}^{ik}\Big)}$$

- measure for maximum contribution of a double excitation
  $\Longrightarrow$ tests for strong interaction with double excited determinants
- for MP2 it should be $D_2(t_{\mu_2}^{(1)}) \lesssim 0.15$

MP2 calculations — bottlenecks

Transformation of 4-index AO integrals to MO basis

1. $(\mu\nu|\kappa j) = \sum_\lambda (\mu\nu|\kappa\lambda) C_{\lambda j}$ $\propto ON^4 \leftarrow$ usually most expensive step!
2. $(\mu i|\kappa j) = \sum_\nu C_{\nu i} (\mu\nu|\kappa j)$ $\propto O^2N^3$
3. $(\mu i|bj) = \sum_\kappa (\mu i|\kappa j) C_{\kappa b}$ $\propto O^2VN^2$
4. $(ai|bj) = \sum_\mu C_{\mu a} (\mu i|bj)$ $\propto O^2V^2N$

- requires storage of at least one array with a size of $\mathscr{O}(\mathscr{N}^4)$
  often half-transformed $(\mu i|\kappa j)$ integrals stored on disk $\propto O^2N^2$
  (typically already for 20 atoms several GByte).
- even more severe bottlenecks in gradient calculations!

The Resolution-of-the-Identity (RI) Approximation

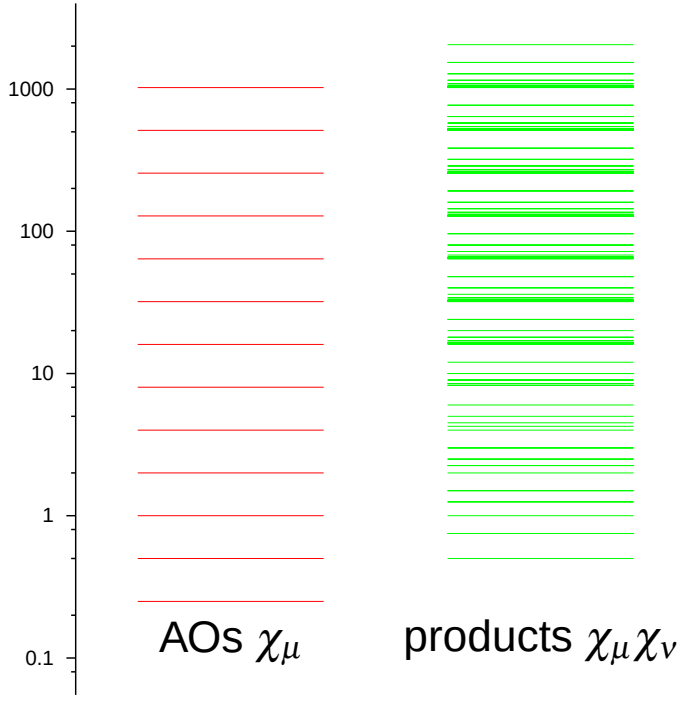
Idea: Exploit that many of the products $\chi_\mu \chi_\nu$ give very similar results (i.e. numerically linear dependent) and approximate:

auxiliary function

$$\chi_\mu(\vec{r}_1)\chi_\nu(\vec{r}_1) \approx \sum_Q Q(\vec{r}_1)\, c_{Q,\mu\nu}$$

expansion coefficient

Example: s orbitals at an atom: $\chi_\mu \chi_\nu = e^{-(\alpha_\mu+\alpha_\nu)r^2}$



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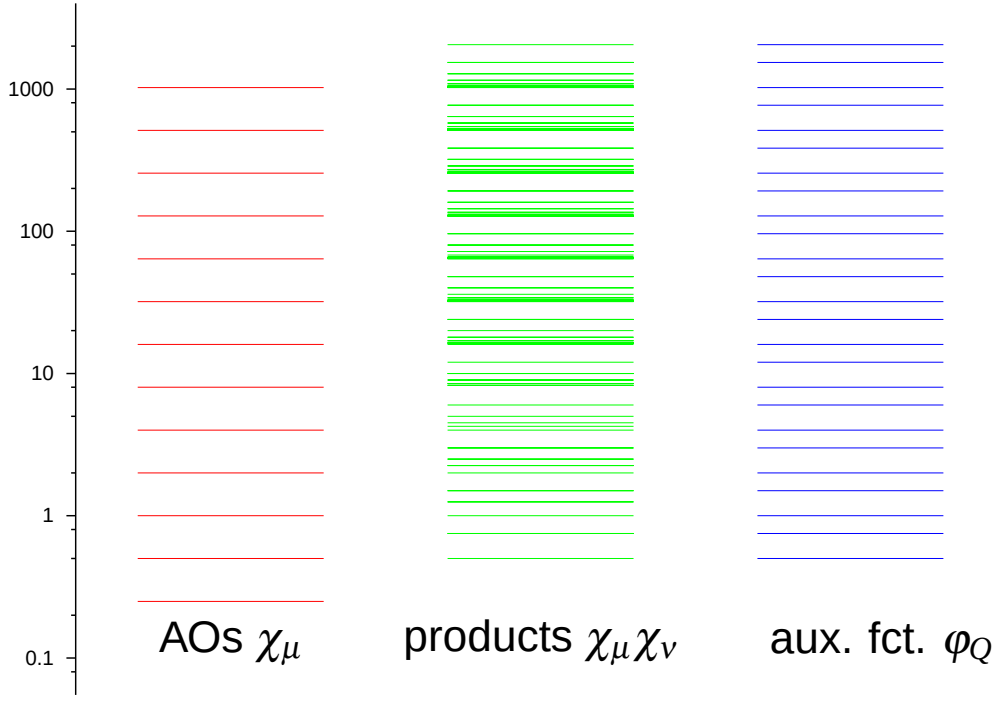
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instead of $N(N+1)/2$ products $\chi_\mu \chi_\nu$

N_X auxiliary functions φ_Q

where $N_X/N \approx const$ (usually < 4)

The Resolution-of-the-Identity (RI) Approximation

errors in products: $$R_{\mu\nu} = \chi_\mu \chi_\nu - \sum_Q Q c_{Q,\mu\nu}$$

quadratic error in integrals: $$(R_{\mu\nu}|R_{\mu\nu}) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} R_{\mu\nu}(1)\frac{1}{r_{12}}R_{\mu\nu}(2)d\tau_1 d\tau_2$$

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Minimization of $(R_{\mu\nu}|R_{\mu\nu})$ gives: $$c_{Q,\mu\nu} = \sum_P (\mu\nu|P)[\mathbf{V}^{-1}]_{PQ}$$

where: $$V_{PQ} = (Q|P)$$

$$(Q|P) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} Q(1)\frac{1}{r_{12}}P(2)d\tau_1 d\tau_2 \qquad \text{2-index ERIs}$$

$$(\mu\nu|P) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}P(2)d\tau_1 d\tau_2 \qquad \text{3-index ERIs}$$

The Resolution-of-the-Identity (RI) Approximation

errors in products: $R_{\mu\nu} = \chi_\mu \chi_\nu - \sum_Q Q c_{Q,\mu\nu}$

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$$(\mu\nu|\kappa\lambda) \approx \sum_{PQ} (\mu\nu|P)\, V_{PQ}^{-1}\, (Q|\kappa\lambda) \quad \text{with} \quad V_{PQ} = (P|Q)$$

(Whitten 1973; Dunlap, Connelly, Sabin 1979; Vahtras, Almlöf, Feiereisen 1993; . . .)

MP2 & CC2 for Large Systems: Approximating the 4-Index-ERIs

- time-determining step:

$$(ai|bj) = \sum_{\mu} C_{\mu a} \sum_{\nu} C_{\nu i} \sum_{\kappa} C_{\kappa b} \sum_{\lambda} C_{\lambda j} (\mu\nu|\kappa\lambda) \qquad \propto ON^4$$

occupied orbitals

MP2 & CC2 for Large Systems: Approximating the 4-Index-ERIs

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- Acceleration through RI approximation:

1. $$B_{Q,ai} = \sum_{\mu} C_{\mu a} \sum_{\nu} C_{\nu i} \sum_{P} (\mu\nu|P)\, [\mathbf{V}^{-1/2}]_{PQ} \qquad \propto ONN_X^2$$

2. $$(ai|bj) \approx \sum_{Q} B_{Q,ai}\, B_{Q,bj} \qquad \propto O^2V^2N_X$$

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reduction by a factor of $\approx N^2/(ON_X)$ (typically $10-100$)

Scheme for an RI-MP2 energy calculation

1. evaluate $V_{PQ} = (Q|P)$ and $\mathbf{V}^{-1/2}$ $\propto N_x^3$
2. $B_{Q,ai} = C_{\mu a} C_{\nu i} (\mu\nu|P) V_{PQ}^{-1/2}$ and save on file $\propto N^2 N_x + 2ON^2 N_x + ONN_x^2$
3. do i

   read $B_{Q,ai}$

   do $j \leq i$

   - read $B_{Q,bj}$
   - $(ai|bj) = B_{Q,ai} B_{Q,bj}$ $\propto \frac{1}{2} O^2 N^2 N_x$
   - $t_{ab}^{ij} = (ai|bj) / \{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\propto \frac{1}{2} O^2 N^2$
   - $E_{\mathrm{MP2}} = E_{\mathrm{MP2}} + (2 - \delta_{ij})[2(ai|bj) - (aj|bi)] t_{ab}^{ij}$ $\propto \frac{1}{2} O^2 N^2$

   end do j

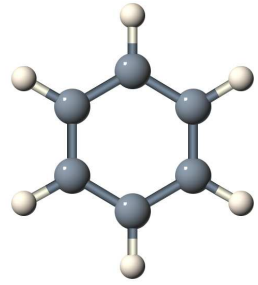
end do i

- memory (RAM) demands: $\propto N_x^2 + NN_x$
- disc space demands: $\propto ONN_x$

Computational Savings of RI-MP2 ↔ MP2

Benzol:

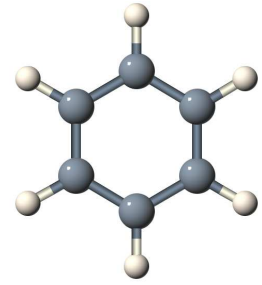
Basis	# Fkt.	MP2	RI-MP2
QZVPP	522	28 min	24 sec
aug-cc-pVQZ	756	3.8 h	1.2 min



Computational Savings of RI-MP2 ↔ MP2

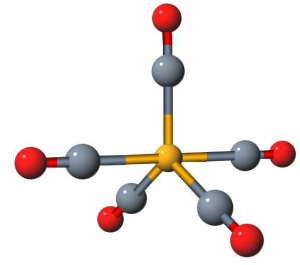
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Basis	# Fkt.	MP2	RI-MP2
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$Fe(CO)_5$:

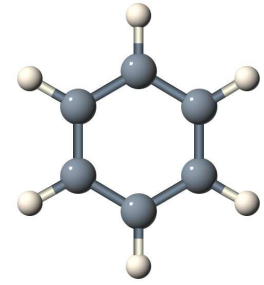
Basis	# Fkt.	MP2	RI-MP2
QZVPP	670	11.3 h	8.7 min



Computational Savings of RI-MP2 ↔ MP2

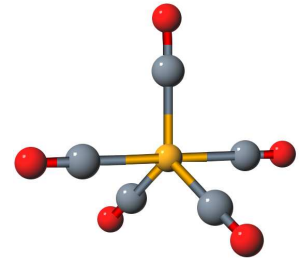
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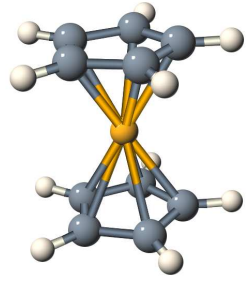
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QZVPP	670	11.3 h	8.7 min



Ferrocen:

Basis	# Fkt.	MP2	RI-MP2
QZVPP	970	843 h	45 min
		10 Gb	<1 Gb



Requirements for auxiliary basis sets for atoms

$$\phi_a(\vec{r})\phi_i(\vec{r}) \approx \sum_P c_{ai,P}\, \chi_P(\vec{r})$$

- maximum angular momentum:

  $$l_{aux} = l_{orb} + l_{occ}$$

  – importance will decrease with l

- range of exponents:

  $$"\alpha_{min}" + "\alpha_{min,occ}" \leq \alpha_{aux} \leq "\alpha_{max}" + "\alpha_{max,occ}"$$

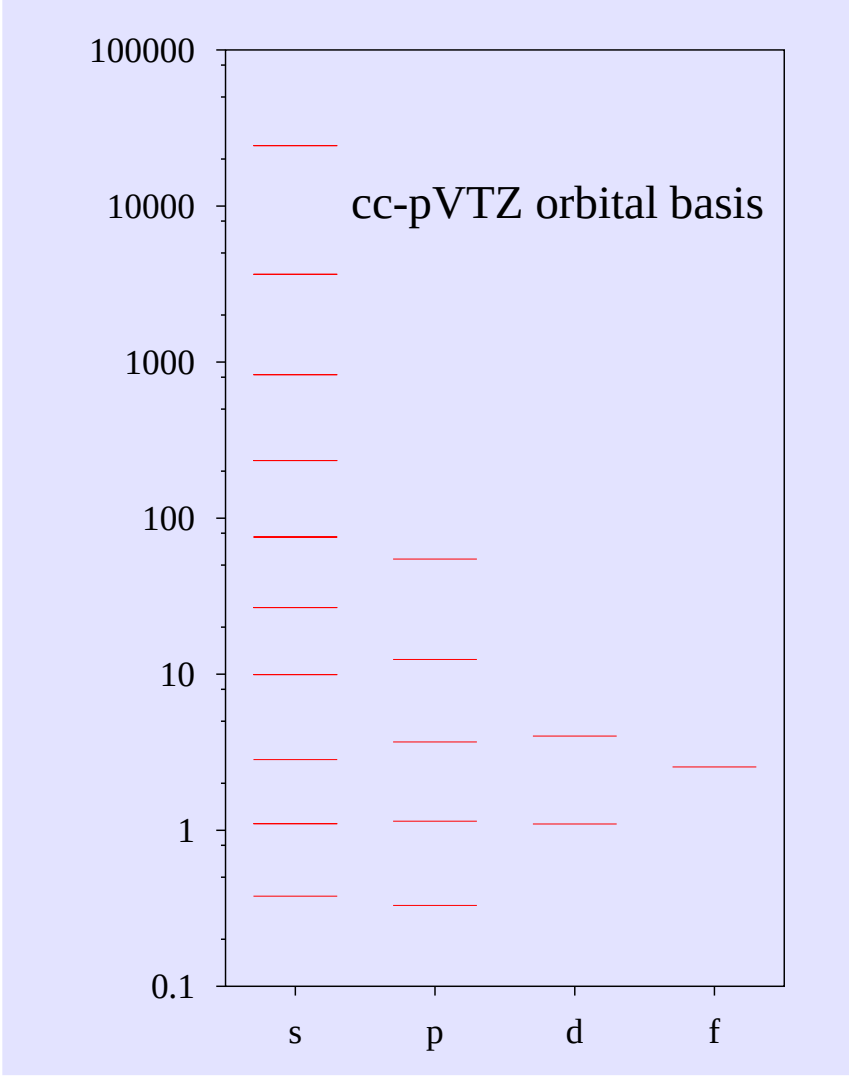
  – exponents have to be larger than for the orbital basis,

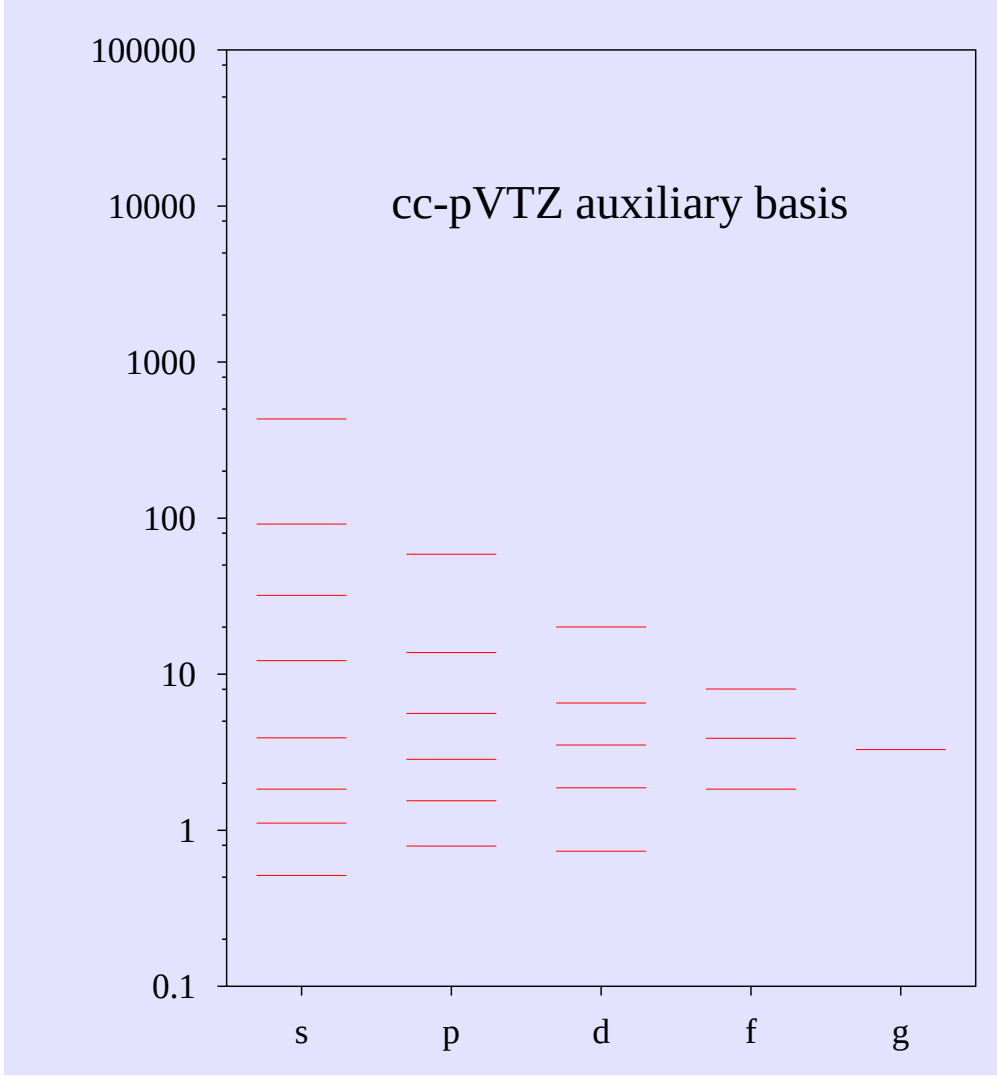
  but: importance of very tight functions damped

  by orbital energy denominators

Requirements for auxiliary basis sets for atoms

Example: Neon atom, cc-pVTZ basis





Optimization of Auxiliary Basis Sets for RI-MP2

RI error in MP2 correlation energy (for UHF):

$$\Delta_{\text{RI}} = E_{\text{RI-MP2}} - E_{\text{MP2}}$$

$$= -\frac{1}{2}\sum_{aibj}\frac{\langle ab||ij\rangle\left(\langle ab||ij\rangle_{RI} - \langle ab||ij\rangle\right)}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}$$

linear,

positive or negative

$$- \frac{1}{4}\sum_{aibj}\frac{\left(\langle ab||ij\rangle_{RI} - \langle ab||ij\rangle\right)^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}$$

quadratic,

negative semi-definite

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δ_{RI} error functional minimized in optimization of auxiliary basis sets for RI-MP2, RI-CC2, etc.

Optimized Auxiliary Basis Sets For RI-MP2

- Optimized auxiliary basis set already available for:
  - correlation-consistent basis families:

    (aug-)cc-pVXZ & (aug-)cc-pwCVXZ for X = D, T, Q, 5 (H–Ar)
  - Karlsruhe basis sets (segmented contr.):

    SVP, TZVP, TZVPP, QZVPP (H–Rn)

$\Longrightarrow$ `ftp://ftp.chemie.uni-karlsruhe.de`

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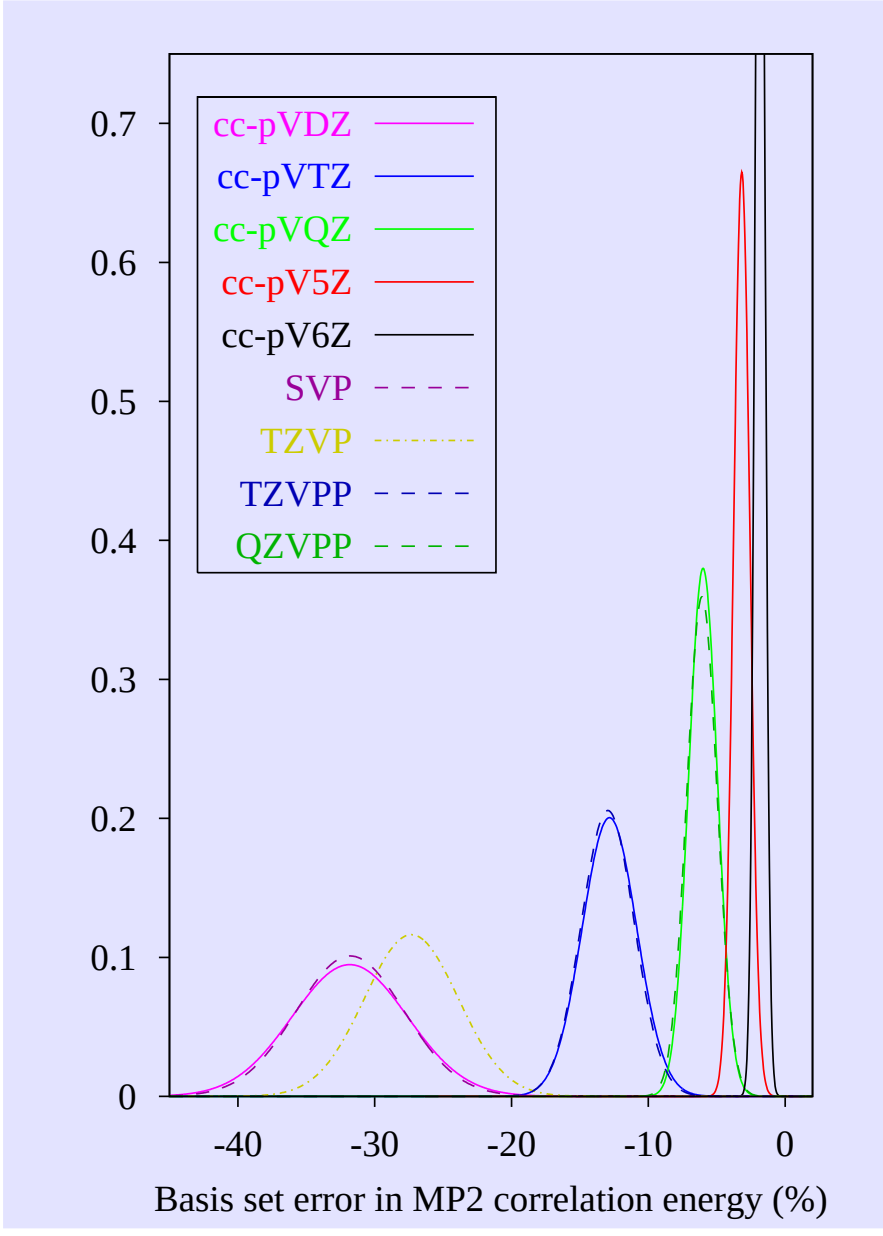
- Optimized and tested for similar conditions as the corresponding orbital basis sets

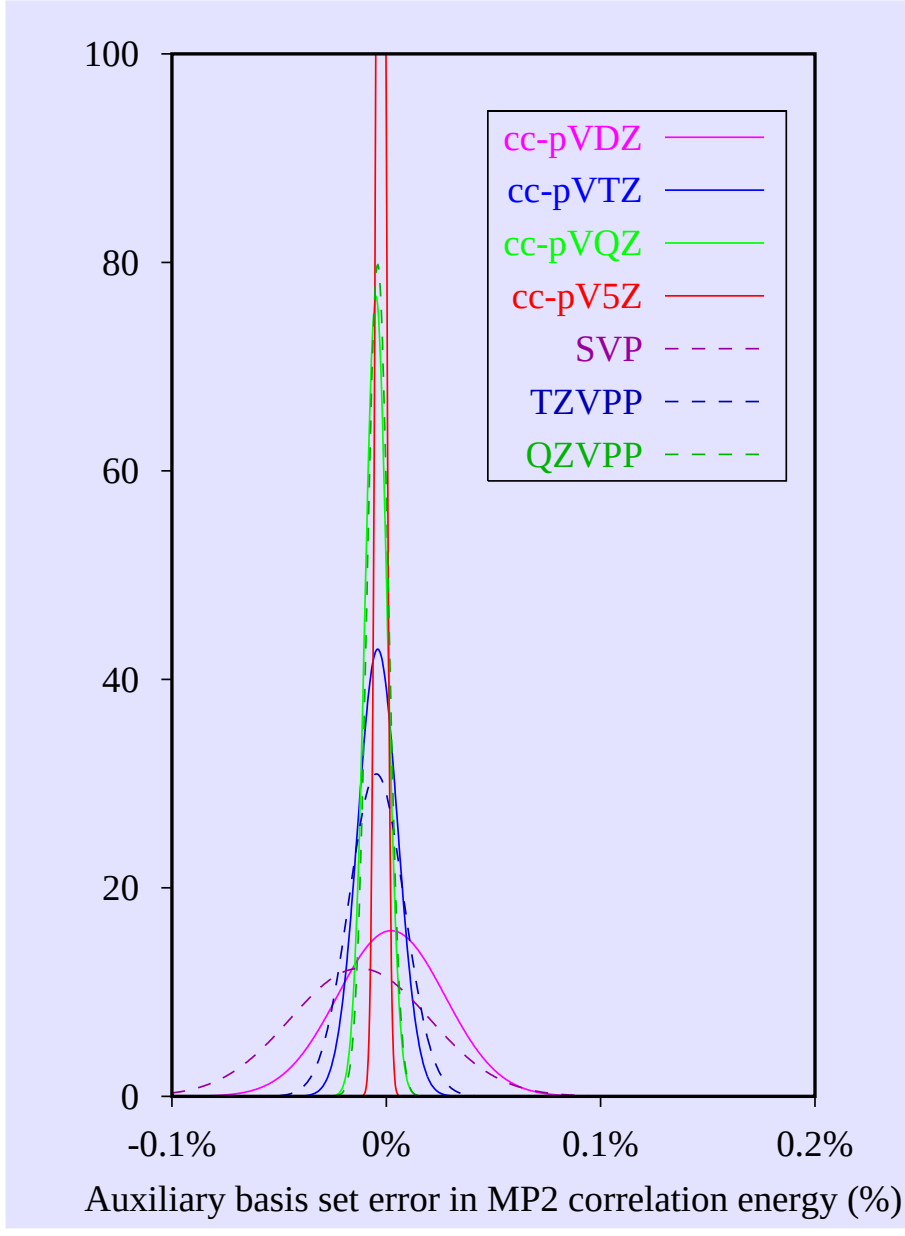
Auxiliary basis sets for the hierarchy cc-pVXZ

Error in MP2 correlation energy (in %) for 72 molecules containing first and second row atoms:

	basis set error		RI error	
	$\bar{\Delta} \pm \Delta_{std}$	Δ_{max}	$\bar{\Delta} \pm \Delta_{std}$	Δ_{max}
cc-pVDZ	$-32 \pm 4\%$	45%	$0.003 \pm 0.04\%$	0.15%
cc-pVTZ	$-13 \pm 2\%$	19%	$-0.004 \pm 0.01\%$	0.05%
cc-pVQZ	$-6 \pm 1\%$	10%	$-0.005 \pm 0.006\%$	0.03%
cc-pV5Z	$-3 \pm 0.6\%$	6%	$-0.003 \pm 0.002\%$	0.01%

Auxiliary basis sets for the hierarchy cc-pVXZ





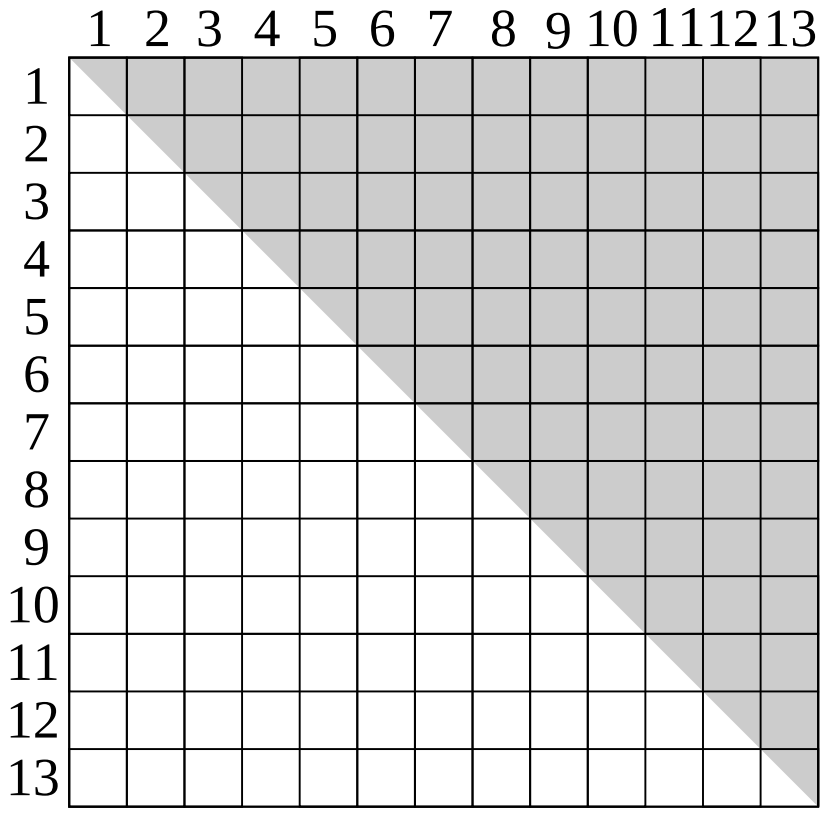
Optimized Auxiliary Basis Sets For RI-MP2

- Rules for optimizing auxiliary basis sets:

1. **start from auxiliary basis for a similar orbital basis** and modify analogous to changes in orbital basis:
   - add/remove higher angular momentum functions
   - add/remove diffuse/tight functionss
2. **reoptimize exponents** in atomic calculation (analytic gradient & optimization script available in TM)
3. **check accuracy** on small model systems

Parallel Implementation of RI-MP2

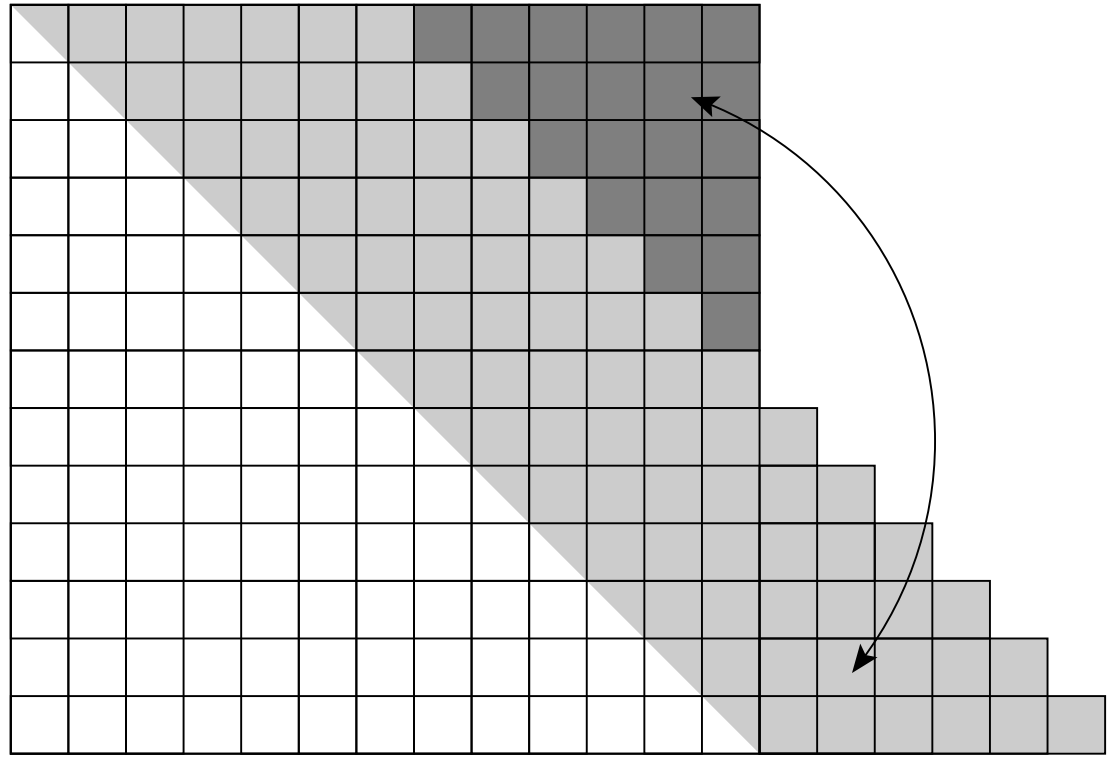
- loop (IJ)
  - loop $i \geq j \in (IJ)$
    - $(ai|bj) = B_{ai}^{Q} B_{bj}^{Q}$
    - $t_{ab}^{ij} = \frac{(ai|bj)}{\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b}$
    - $E_{\mathrm{MP2}} = E_{\mathrm{MP2}} + (2 - \delta_{ij}) \times \{2(ai|bj) - (aj|bi)\} t_{ab}^{ij}$
  - end loop
- end loop



- occupied orbitals are partitioned into as many blocks I as computer nodes used (n_{nodes}).

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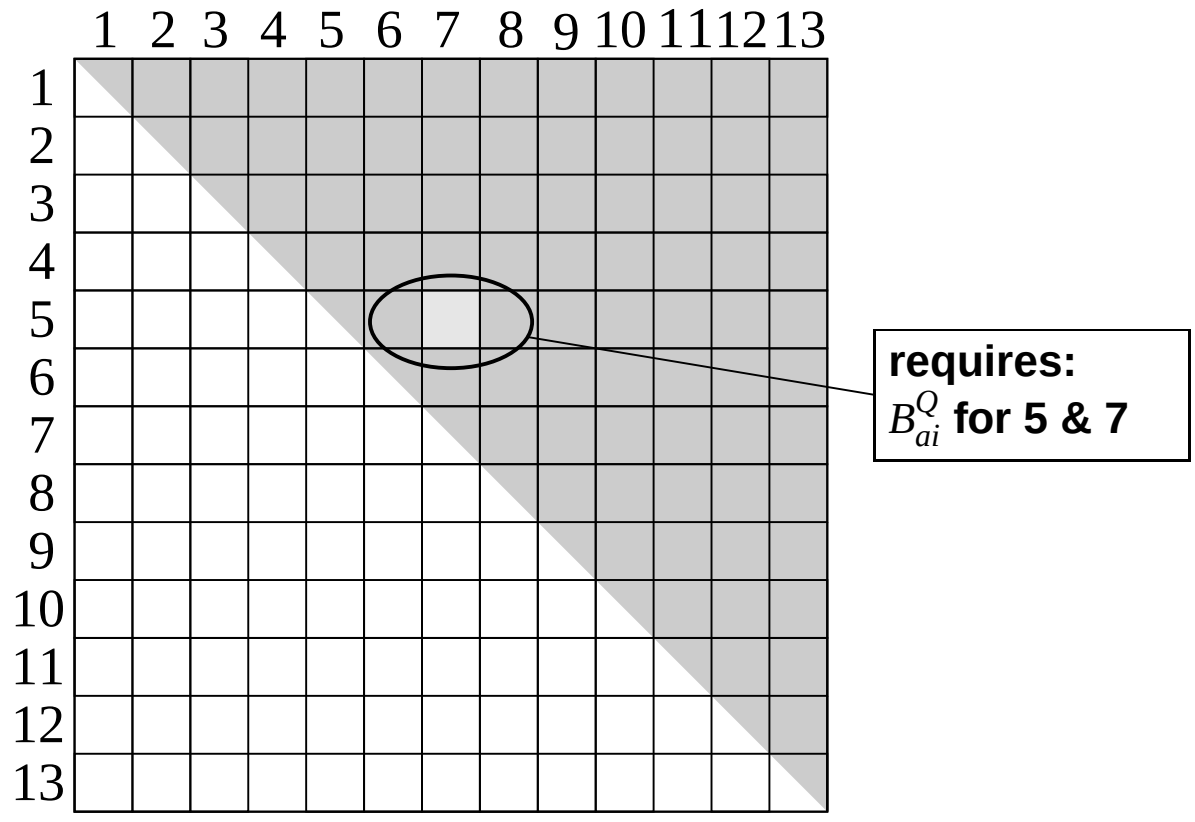
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- pairs of blocks (IJ) are arranged on $(n_{nodes}+1)/2$ diagonals each node gets one block of each diagonal assigned (load balance!)

Parallel Implementation of RI-MP2

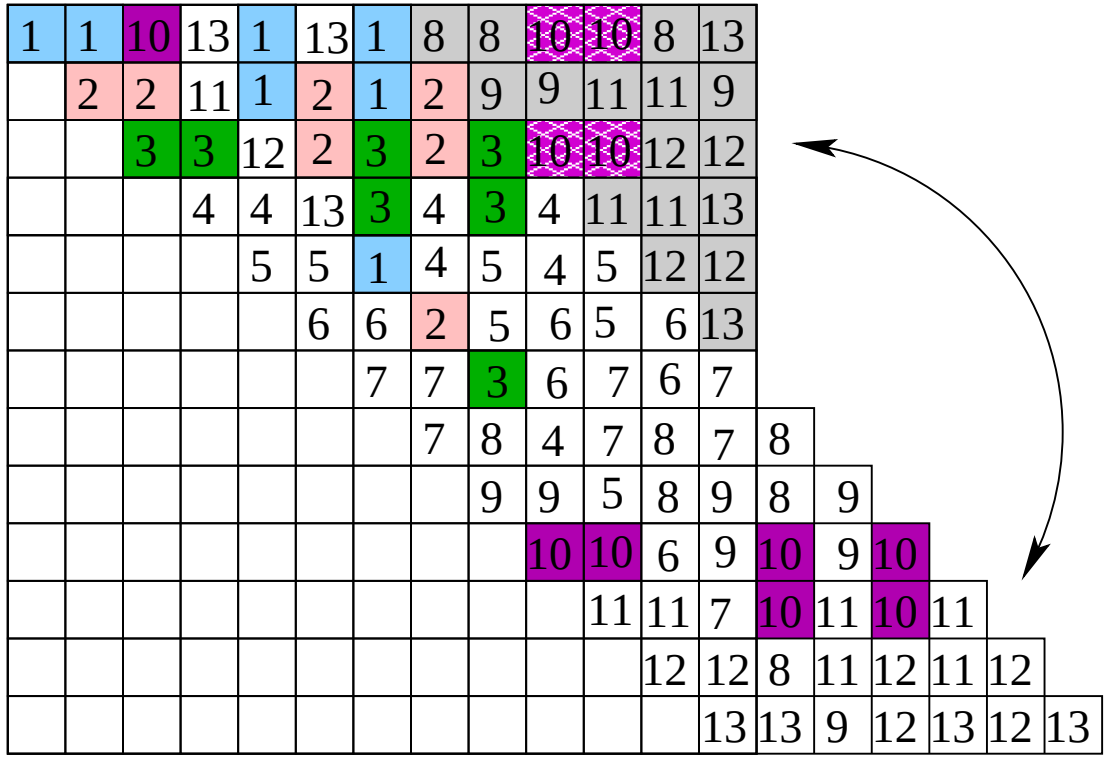
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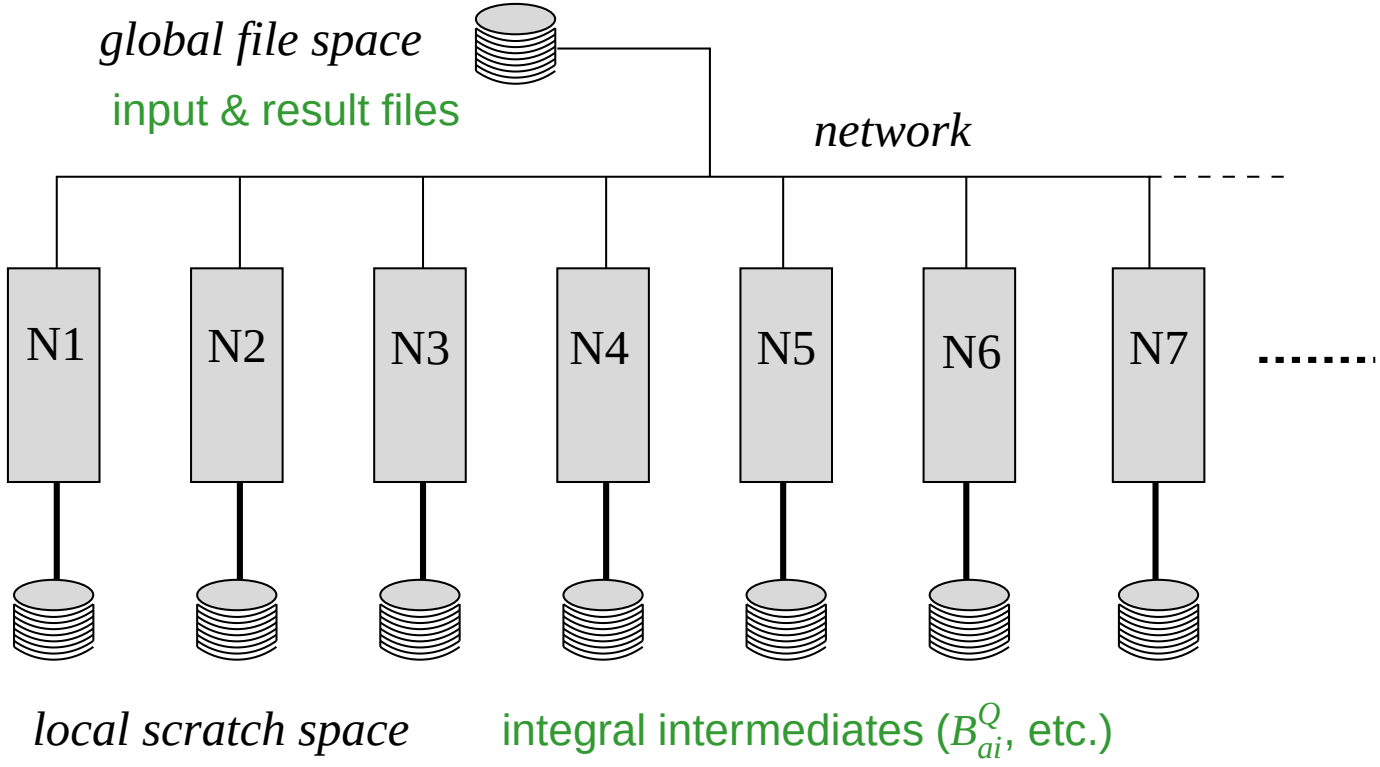
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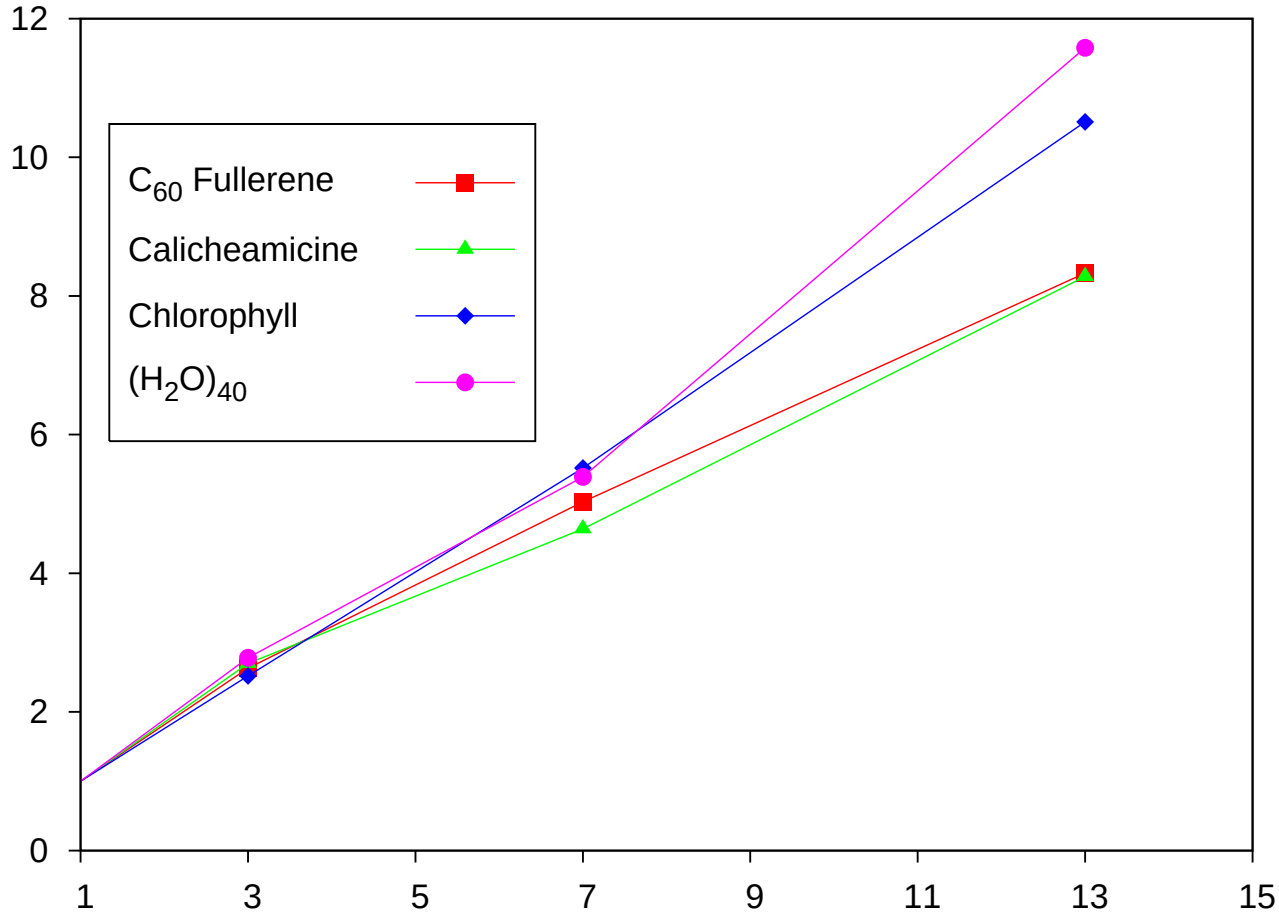
- positions on diagonals chosen such that each node needs to acces only a minimal number ($\propto \mathcal{O}(\sqrt{n_{nodes}})$) of blocks of B^Q_{ai}

Typical Architecture of PC Clusters



- small input & result files in global file system
- large files with integrals & intermediates in local scratch file systems

Parallel Implementation of RI-MP2: Performance



molecule	symmetry	# e^-	basis	# bf.	# aux. bf.
C_{60}	D_{2h}	240	cc-pVTZ	1800	4860
Calicheamicine	C_1	124	cc-pVTZ	934	2429
Chlorophyll	C_1	264	cc-pVDZ	918	3436
$(H_2O)_{40}$	C_1	320	6-31G$*$	760	3840

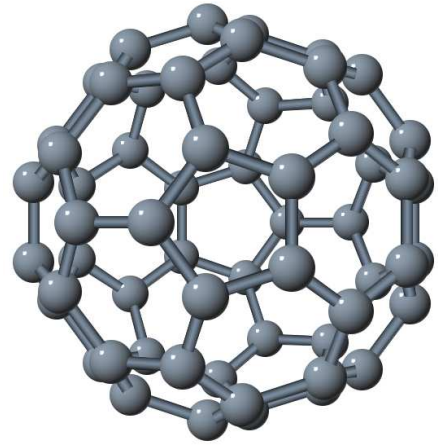
Parallel Implementation of RI-MP2: Fullerenes

C_{60}: *cc-pVTZ*, 1800 Bf.

RI-MP2:	1 CPU	33 min
	3 CPUs	12 min
	7 CPUs	6.5 min

cc-pVQZ, 3300 Bf.

RI-MP2:	7 CPUs	59 min



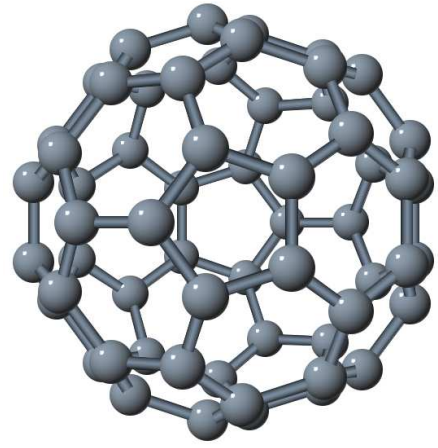
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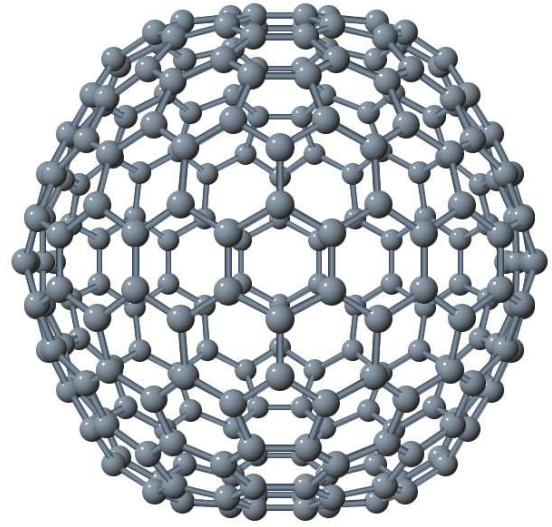


Method	d_{C-C}/Å	$d_{C=C}$/Å
SCF/TZP	1.448	1.370
MP2/TZP	1.446	1.406
MP2/cc-pVTZ	1.443	1.404
MP2/cc-pVQZ	1.441	1.402
Exp.	1.423-1.464	1.383-1.411

Parallel Implementation of RI-MP2: Fullerenes

C_{240}: *cc-pVTZ*, 7200 Bf.

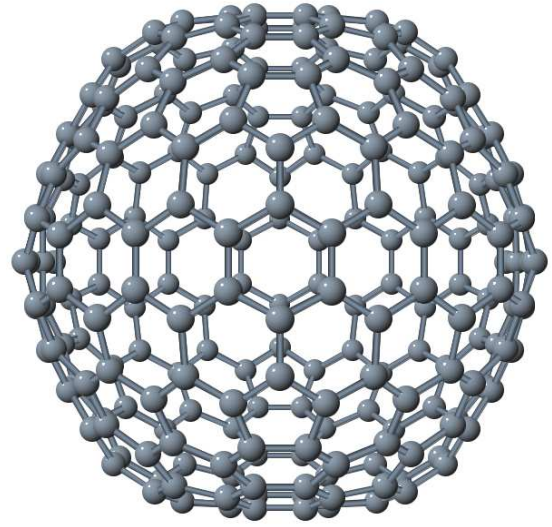
RI-MP2: 19 CPUs 16 h 6 min



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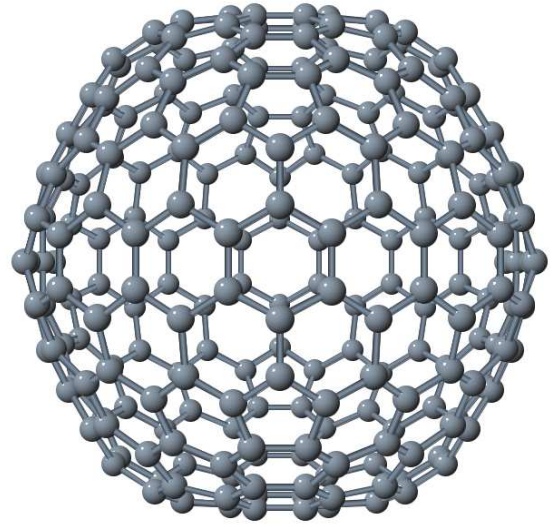
- 6×10^{11} four-index MO integrals

  ($\approx$ 4.8 TByte in conventional calculation)

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- 6×10^{11} four-index MO integrals

  ($\approx$ 4.8 TByte in conventional calculation)

- $4 \times C_{60} \rightarrow C_{240}$ $\Delta H = -25 \mathrm{kJ/mol}$ per C atom

- $\Delta_f H^0$ of C_{60} is 39.25$\pm$0.25 kJ/mol per C atom

  $\rightsquigarrow \Delta_f H^0$ of $C_{240} \approx$ 15 kJ/mol per C atom

RI-MP2 — Summary

- **RI approximation extends significantly the applicability of second-order Møller-Plesset perturbation theory to larger systems**

$\approx$ 20–30 $\longrightarrow >$ 50 atoms

(with parallelization $>$100 atoms)

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  (with parallelization $>$100 atoms)

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    $\rightsquigarrow$ excited states in response theory

- **With optimized auxiliary basis sets RI errors negligible compared to one-electron basis set error**

Part II

Coupled-Cluster Response Theory for Energies and Structures of Excited States

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Coupled-Cluster Response Theory for Energies and Structures of Excited States

- Single-reference coupled-cluster methods
- Response theory for CC methods
- Energies, structures, and vibr. freqs. of excited states

Standard Single-Reference Coupled-Cluster Ansatz

Parameterization of wavefunction:

$$|\mathrm{CC}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots)|\mathrm{Ref}\rangle \qquad \text{with} \quad \hat{T}_n = \sum_{ai \geq bj \geq ck \ldots} t^{ijk\ldots}_{abc\ldots} \hat{\tau}^{abc\ldots}_{ijk\ldots}$$

reference determinant
usually $|\mathrm{HF}\rangle$

amplitudes (coefficients)
number $\sim \frac{1}{n!} O^n V^n$

excitation operators:
$\hat{\tau}^{ijk}_{abc} |\phi_i \phi_j \phi_k\rangle \rightarrow |\phi_a \phi_b \phi_c\rangle$

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- $|\mathrm{Ref}\rangle$: reference determinant, usually $|\mathrm{HF}\rangle$
- $t^{ijk\ldots}_{abc\ldots}$: amplitudes (coefficients), number $\sim \frac{1}{n!} O^n V^n$
- $\hat{\tau}^{abc\ldots}_{ijk\ldots}$: excitation operators, $\hat{\tau}^{ijk}_{abc}|\phi_i\phi_j\phi_k\rangle \rightarrow |\phi_a\phi_b\phi_c\rangle$

Formula for energy:

$$E = \langle \mathrm{HF}|\hat{H}|\mathrm{CC}\rangle = \langle \mathrm{HF}|\hat{H} + [\hat{H}, \hat{T}_1] + [\hat{H}, (\hat{T}_2 + \hat{T}_1\hat{T}_1)]|\mathrm{HF}\rangle \qquad (\text{note that } \langle \mathrm{HF}|\mathrm{CC}\rangle = 1)$$

$[\hat{H}, \hat{T}_1] \neq 0$ only if Brillouin theorem not fulfilled (e. g. for ROHF)

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Equation determining the cluster amplitudes:

$$\Omega^{ijk\ldots}_{abc\ldots} = \langle \mathrm{HF}|(\hat{\tau}^{ijk\ldots}_{abc\ldots})^\dagger \exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle = \langle \mu^{ijk\ldots}_{abc\ldots}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle = 0$$

vector function / residuum

Standard Single-Reference Coupled-Cluster Ansatz

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projected Schrödinger equation:

$$\langle \mu|\exp(-\hat{T})\hat{H}|\mathrm{CC}\rangle = \langle \mu|\exp(-\hat{T})E|\mathrm{CC}\rangle$$

Standard Single-Reference Coupled-Cluster Ansatz

Advantages:

- size consistent
- faster convergent than CI and MPn

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Advantages:

- size consistent
- faster convergent than CI and MPn

Disadvantages:

- not variational
  - $\rightsquigarrow$ more complicated derivatives/response theory
  - $\rightsquigarrow E \ngeq E_{FCI}$
- non-linear parameterization
  - problems in spin-adaptation for open-shell systems
  - generalization to multi-reference theory difficult

“Truncated” Coupled-Cluster Methods

- Restriction of cluster operator $\hat{T}$ to lowest excitation classes (but at this point no other approximations)

hierarchy of “truncated” CC methods:

Model	Operator $\hat{T}$	Order MPn	Scaling
CCS [a]	$\hat{T}_1$	1	$\mathcal{O}(N^4)$
CCSD	$\hat{T}_1 + \hat{T}_2$	3	$\mathcal{O}(O^2N^4)$
CCSDT	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3$	4	$\mathcal{O}(O^3N^5)$
CCSDTQ	$\hat{T}_1 + \ldots + \hat{T}_4$	6	$\mathcal{O}(O^4N^6)$
⋮	⋮	⋮	⋮
CCn	$\hat{T}_1 + \ldots + \hat{T}_n$	[3n/2]	$\mathcal{O}(O^nN^{n+2})$

[a] if Brillouin theorem fulfilled CCS ≡ CIS ≡ SCF (for G.S.)

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for comparison:

Model	Order MPn
CIS [a]	1
CISD	3
CISDT	3
CISDTQ	5
⋮	⋮
CIn	2[n/2]+1

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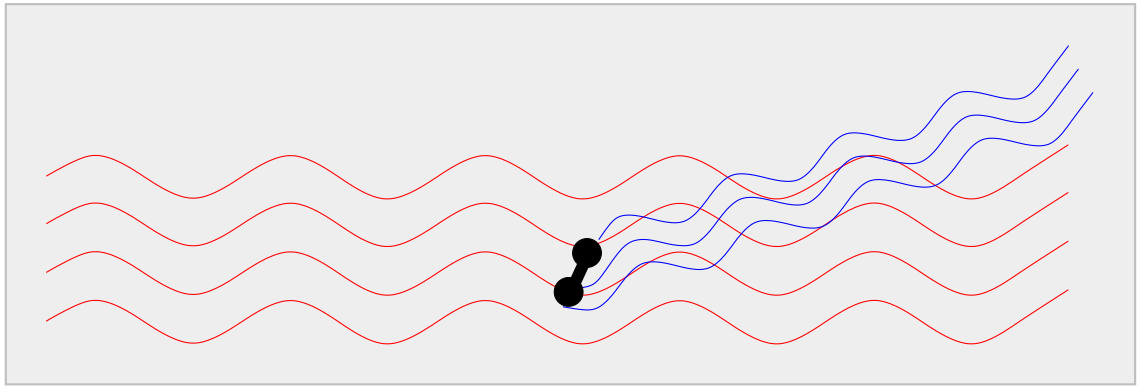
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- improving low-order method with perturbative correction:
  SCF/CCS → MP2 and CCSD → CCSD[T], CCSD(T), etc.
- reducing costs by approximating cluster equations:
  CCSD → CC2 and CCSDT → CC3, CCSDT-n, etc.

What is Response Theory?

Consider a molecule perturbed by oscillating electromagnetic fields:

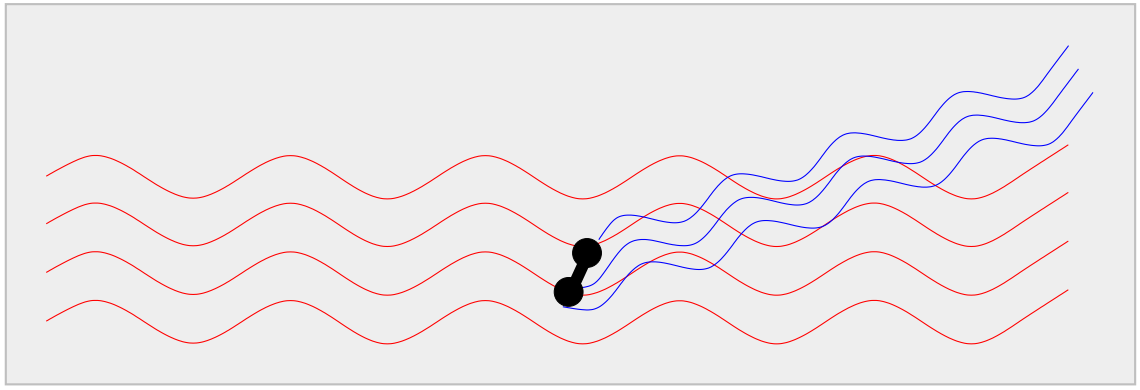


$$H(t) = H^{(0)} + \sum_j V_j \boxed{f_j(\omega_j) e^{-i\omega_j t}}$$

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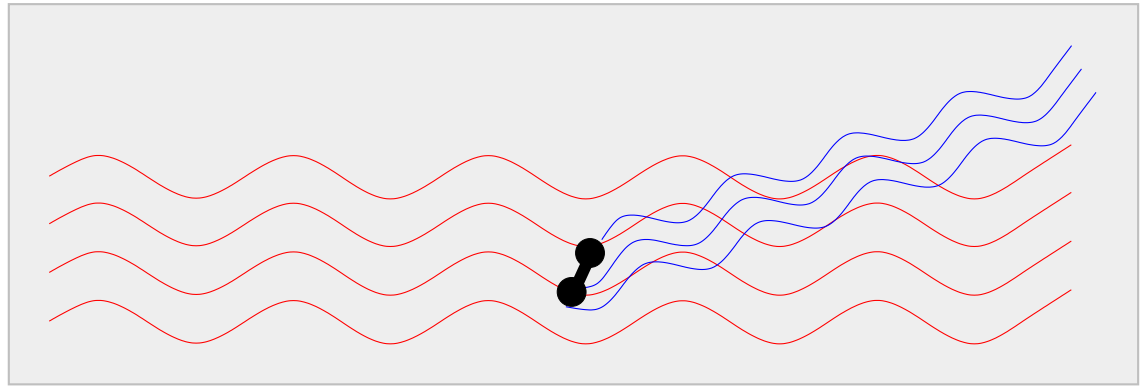
Investigate wavefunction, properties, etc. as function of the frequency:

$$\Psi(t) \;=\; \left[\Psi^{(0)} + \textstyle\sum_j \Psi_j^{(1)}(\omega_j)\; f_j(\omega_j) e^{-i\omega_j t} + \ldots\right] e^{-i\int_{t_0}^{t} dt' \langle \widetilde{\Psi} | H(t') - i\frac{\partial}{\partial t'} | \widetilde{\Psi} \rangle}$$

phase-isolated wavefunction $\widetilde{\Psi}$

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$$\langle \mu_i \rangle(t) \;=\; \mu_i^{(0)} + \sum_j \boxed{\langle\langle \mu_i ; V_j \rangle\rangle_{\omega_j}} \; f_j(\omega_j) e^{-i\omega_j t} + \ldots$$

response functions

Response Theory for Exact States

- Apply time-dependent perturbation theory, i.e. insert

$$H(t) = H^{(0)} + \sum_j V_j \, f_j(\omega_j) e^{-i\omega_j t}$$

$$\Psi(t) = \left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(\omega_j) \, f_j(\omega_j) e^{-i\omega_j t} + \ldots \right] e^{-i \int_{t_0}^{t} dt' \langle \widetilde{\Psi} | H(t') - i \frac{\partial}{\partial t'} | \widetilde{\Psi} \rangle}$$

into time-dependent Schrödinger equation,

$$H(t)\Psi(t) = i \frac{\partial}{\partial t} \Psi(t)$$

expand in orders of the field strengths, and solve order by order ...

- Obtain response functions by expansion of

$$\langle \mu_i \rangle(t) = \langle \widetilde{\Psi}(t) | \mu_i | \widetilde{\Psi}(t) \rangle = \mu_i^{(0)} + \sum_j \langle\langle \mu_i ; V_j \rangle\rangle_{\omega_j} \, f_j(\omega_j) e^{-i\omega_j t} + \ldots$$

Response Theory for Variational Methods

- Apply time-dependent perturbation theory, i.e. insert

$$H(t) = H^{(0)} + \sum_j V_j f_j(\omega_j) e^{-i\omega_j t}$$

$$\Psi(t) = \left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(\omega_j) f_j(\omega_j) e^{-i\omega_j t} + \ldots\right] e^{-i\int_{t_0}^{t} dt' \langle\widetilde{\Psi}|H(t') - i\frac{\partial}{\partial t'}|\widetilde{\Psi}\rangle}$$

into Frenkels variation principle,

$$\langle \delta\widetilde{\Psi}^{\perp}(t)|H(t) - i\frac{\partial}{\partial t}|\widetilde{\Psi}(t)\rangle = 0$$

expand in orders of the field strengths, and solve order by order ...

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Symmetries of Response Functions

- symmetric with respect to permutation of perturbing fields:

$$\langle\langle A;B,C,\ldots\rangle\rangle_{\omega_B,\omega_C,\ldots} = \langle\langle A;C,B,\ldots\rangle\rangle_{\omega_C,\omega_B,\ldots} = \langle\langle B;A,C,\ldots\rangle\rangle_{\omega_A,\omega_C,\ldots} = \ldots$$

- hermitian:

$$\langle\langle A;B,C,\ldots\rangle\rangle_{-\omega_B,-\omega_C,\ldots} = \langle\langle A;B,C,\ldots\rangle\rangle^*_{\omega_B,\omega_C,\ldots}$$

compare with static limit:

$$\langle\langle A;B,C,\ldots\rangle\rangle_{0,0,\ldots} = -\left.\frac{d^n E}{d f_A\, d f_B\, d f_C \ldots}\right|_0$$

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Problem:

- only fulfilled if Hellmann-Feynman theorem is obeyed
- $\langle \delta\widetilde{\Psi}^{\perp}(t)|H(t) - i\frac{\partial}{\partial t}|\widetilde{\Psi}(t)\rangle = 0$ not of the form $\delta F\left[\widetilde{\Psi}\right] = 0$

The Quasienergy of Floquet States

combine perturbation theory with Floquet theory for periodic systems:

- extended Hilbert space including time integration:

$$\langle\langle \widetilde{\Psi}_i | \widetilde{\Psi}_j \rangle\rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \langle \widetilde{\Psi}_i | \widetilde{\Psi}_j \rangle dt$$

- quasienergy of Floquet state:

$$Q = \langle\langle \widetilde{\Psi} | H - i\frac{\partial}{\partial t} | \widetilde{\Psi} \rangle\rangle$$

- variation principle:

$$\delta Q\left[\widetilde{\Psi}\right] = 0$$

- response functions obtained as derivatives of the quasienergy:

$$\langle\langle A; B, C, \ldots \rangle\rangle_{\omega_B, \omega_C, \ldots} = -\frac{d^n Q}{d f_A d f_B d f_C \ldots}\bigg|_0$$

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Response Theory for Nonvariational Methods

variational $\longrightarrow$ nonvariational

$$Q \longrightarrow \{L\}_T = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} L\,dt$$

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quasienergy Lagrangian for coupled-cluster methods:

$$L = \mathrm{Re}\left\{ \left\langle \mathrm{HF}\middle| \left(H - i\frac{\partial}{\partial t}\right)\exp(T)\middle|\mathrm{HF}\right\rangle + \sum_{\mu_i} \bar{t}_{\mu_i} \left\langle \mu_i\middle| \exp(-T)\left(H - i\frac{\partial}{\partial t}\right)\exp(T)\middle|\mathrm{HF}\right\rangle \right\}$$

quasienergy — Lagrangian multiplier — cluster equations as constraints

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  $\rightsquigarrow$ requires only minor changes in a code for static properties!

Coupled-Cluster Response Theory

- Hamiltonian: $H(t) = H^{(0)} + V\, f(\omega) e^{-i\omega t}$

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$$A_{\mu_i \nu_j} = \left. \frac{d\Omega_{\mu_i}}{dt_{\nu_j}} \right|_{f=0}$$ Jacoby matrix

$$S_{\mu_i \nu_j} = i \left. \frac{d\Omega_{\mu_i}}{dt_{\nu_j}} \right|_{f=0}$$ overlap matrix

$$\xi_{\mu_i}(V,\omega) = \left. \frac{\partial \Omega_{\mu_i}}{\partial f(\omega)} \right|_{f=0}$$ r.h.s. vector

Coupled-Cluster Response Theory

Coupled-cluster methods:

$$\left[\mathbf{A} - \omega\,\mathbf{S}\right] \vec{t}^{\,(1)}(\omega) \;=\; -\vec{\xi}(V,\omega)$$

Exact wavefunctions:

$$\left[H^{(0)} - E_0 - \omega\right] \Psi^{(1)}(\omega) \;=\; -\left[V\, f(\omega) e^{-i\omega t}\right] \Psi^{(0)}$$

$\rightsquigarrow$ Poles occur at eigenvalues of the Jacoby matrix:

$$\left[\mathbf{A} - \omega\,\mathbf{S}\right] \vec{E}(\omega) \;=\; 0$$

$\rightsquigarrow$ Jacoby matrix provides a model for $H^{(0)} - E_0$

Excitation Energies in Response Theory

The stability matrix for the quantum mechanical Lagrange functional:

$$L = \left\langle H - i\frac{\partial}{\partial t} \right\rangle \quad \underbrace{+ \quad \sum_i \bar{t}_i \Omega_i}$$

constraints for
non-variational methods

variational methods:

symmetric electronic Hesse matrix

$$H_{ij} = \left(\frac{d^2 L}{dt_i\, dt_j}\right)_0$$

$$\left(\mathbf{H} - \omega_k \mathbf{S}\right)\vec{c}^{(k)} = 0$$

non-variational methods:

asymmetric electronic Jacoby matrix

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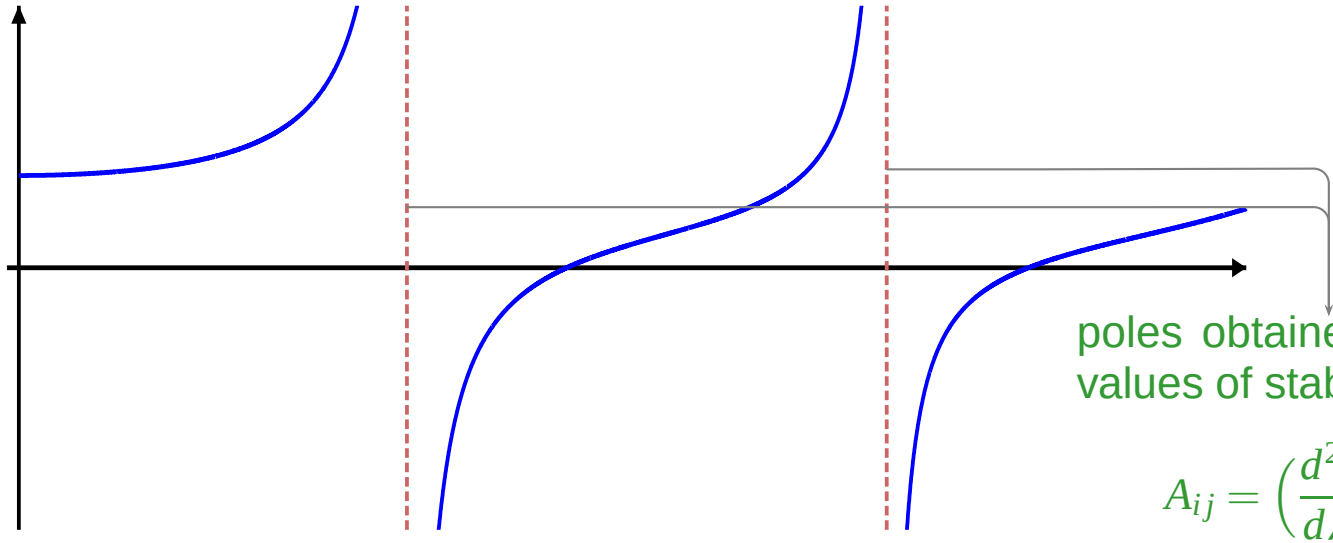
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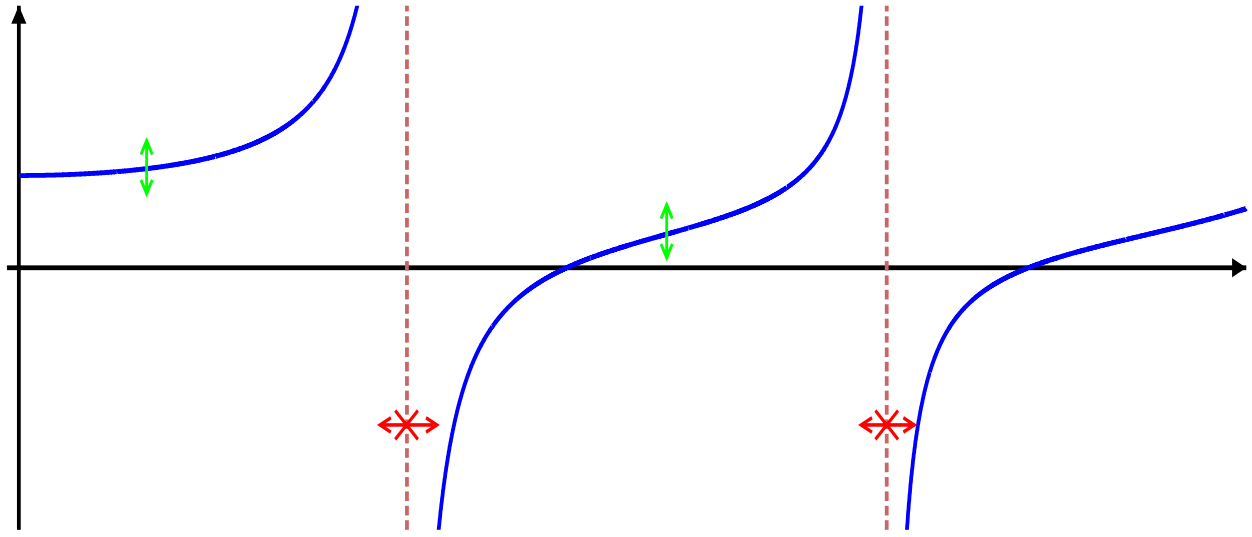
secular matrices

Requirements for Wavefunction Ansatz



- consistent pole structure $\Longleftrightarrow$ consistent spectrum
  - single step methods (SCF, DFT, MCSCF, not SCF+CI)
  - CC response based on unperturbed Hartree-Fock determinant

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- consistent pole structure $\Longleftrightarrow$ consistent spectrum
  - single step methods (SCF, DFT, MCSCF, not SCF+CI)
  - CC response based on unperturbed Hartree-Fock determinant
- perturbative corrections cannot shift singularities
  - MP2, CCSD(T), etc. not suitable for $\langle\langle A; B, \ldots \rangle\rangle_{\omega_B,\ldots}$
  - CIS(D), CCSDR(3) only for excitation energies

The Coupled-Cluster Jacobian & Excited States

$$A_{\mu\nu} = \langle \mu | e^{-\hat{T}} [\hat{H}, \hat{\tau}_\nu] e^{\hat{T}} | \mathrm{HF} \rangle = \langle \mu | e^{-\hat{T}} (\hat{H} - E_0) \hat{\tau}_\nu e^{\hat{T}} | \mathrm{HF} \rangle$$

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$$\hat{\tau}_\nu e^{\hat{T}} | \mathrm{HF} \rangle = \hat{\tau}_\nu | \mathrm{CC} \rangle \qquad \text{and} \qquad \langle \mu | e^{-\hat{T}}$$

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$$\hat{\tau}_\nu e^{\hat{T}} | \mathrm{HF} \rangle = \hat{\tau}_\nu | \mathrm{CC} \rangle \qquad \text{and} \qquad \langle \mu | e^{-\hat{T}}$$

- Eigenvectors represent excited states (contrib. $\perp$ to $|\mathrm{CC}\rangle$) in this basis

e.g. from right eigenvectors:

$$|\Psi_f\rangle = (c_0^f + \sum_{\mu_1} E_{\mu_1}^f \hat{\tau}_{\mu_1} + \sum_{\mu_2} E_{\mu_2}^f \hat{\tau}_{\mu_2} + \ldots) | \mathrm{CC} \rangle$$

The Coupled-Cluster Jacobian & Excited States

Excited state in coupled-cluster response theory:

$$|\Psi_f\rangle = c_0^f|\mathrm{HF}\rangle + \left(\sum_{\mu_1} E_{\mu_1}^f \hat{\tau}_{\mu_1} + \sum_{\mu_2} E_{\mu_2}^f \hat{\tau}_{\mu_2} + \ldots\right)|\mathrm{CC}\rangle$$

Advantages:

- excited state inherits many correlation effects from $|\mathrm{CC}\rangle$ ground state
- response calculation needs only to account for differential correlation effects
- multi-reference character of excited state is automatically accounted for

The Coupled-Cluster Jacobian & Excited States

Excited state in coupled-cluster response theory:

$$|\Psi_f\rangle = c_0^f|\mathrm{HF}\rangle + \left(\sum_{\mu_1} E_{\mu_1}^f \hat{\tau}_{\mu_1} + \sum_{\mu_2} E_{\mu_2}^f \hat{\tau}_{\mu_2} + \ldots\right)|\mathrm{CC}\rangle$$

Advantages:

- excited state inherits many correlation effects from $|\mathrm{CC}\rangle$ ground state
- response calculation needs only to account for differential correlation effects
- multi-reference character of excited state is automatically accounted for

Disadvantages:

- doubly (and higher) excited states are difficult to treat
- not applicable for conical intersections with the ground state
- relies on accurate description of the ground state

Single-Reference Methods for Excited States

	Comput. Costs	Ground State	Single Excit. Energy / Structure	Double Excitations	Oscillator Strengths
(TD) SCF	N^4(iter.)	1	1 / √	—	1
CIS/CCS	N^4(iter.)	(SCF)	1 / √	—	0
(TD) DFT	N^4(iter.)	√	√ / √	—	√
CCSD	n^2N^4(iter.)	3	2 / √	1	2
CCSDT	n^4N^4(iter.)	4	3 / √	2	3
⋮	⋮	⋮	⋮	⋮	⋮

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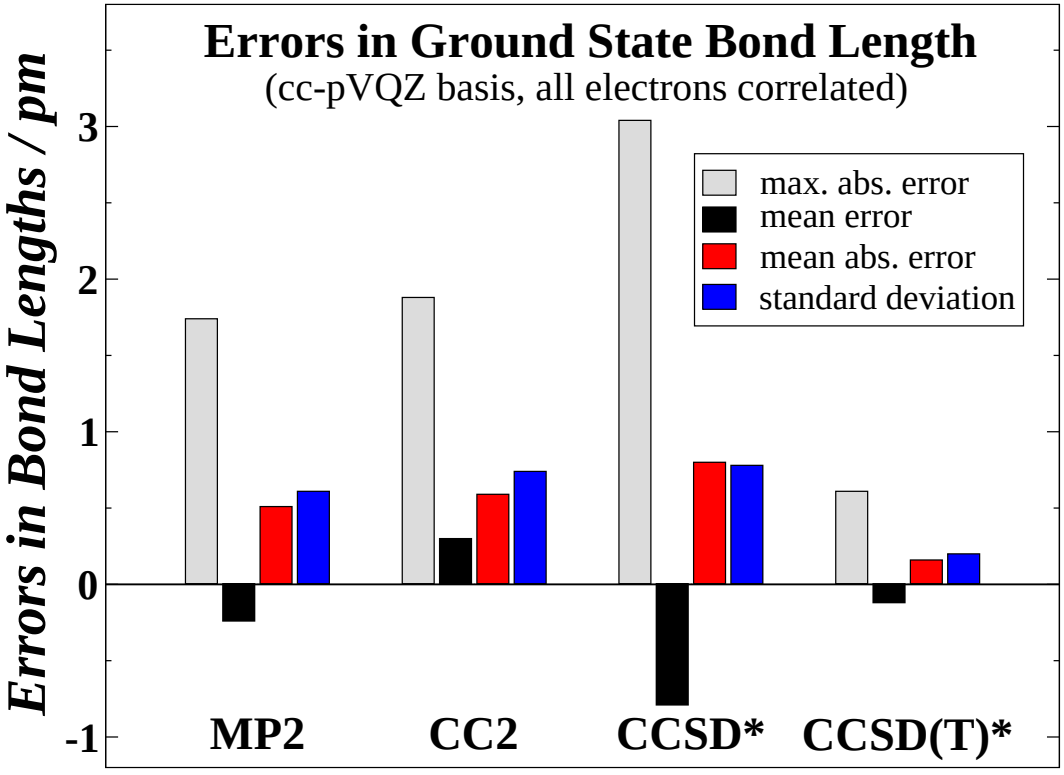
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CIS/CCS	N^4(iter.)	(SCF)	1 / √	—	0
(TD) DFT	N^4(iter.)	√	√ / √	—	√
CC2	nN^4(iter.)	2	2 / √	0	1
CCSD	n^2N^4(iter.)	3	2 / √	1	2
CC3	n^3N^4(iter.)	4	3 / √	2	3
CCSDT	n^4N^4(iter.)	4	3 / √	2	3
⋮	⋮	⋮	⋮	⋮	⋮

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CIS/CCS	N^4(iter.)	(SCF)	1 / √	—	0
(TD) DFT	N^4(iter.)	√	√ / √	—	√
CIS(D)	nN^4	(MP2)	2 / ?	—	—
CC2	nN^4(iter.)	2	2 / √	0	1
CCSD	n^2N^4(iter.)	3	2 / √	1	2
CCSDR(3)	n^3N^4	4	3 / ?	2	3
CC3	n^3N^4(iter.)	4	3 / √	2	3
CCSDT	n^4N^4(iter.)	4	3 / √	2	3
⋮	⋮	⋮	⋮	⋮	⋮

Performance for Ground State Equilibrium Structures

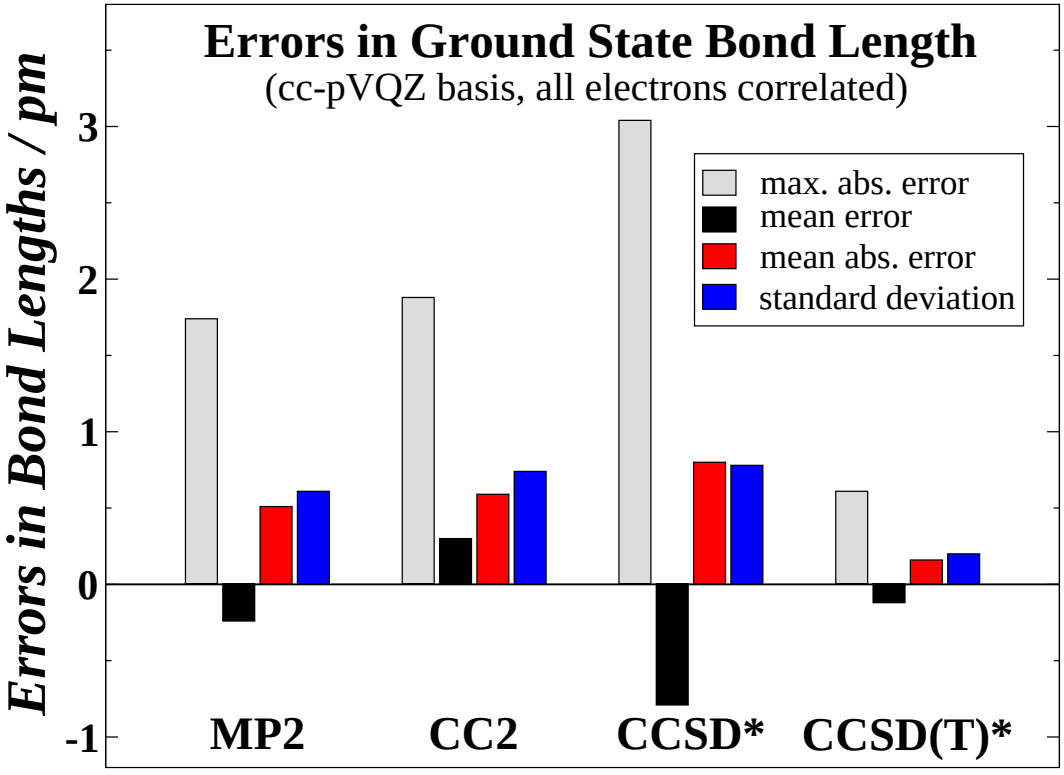


(*Test set for CCSD and CCSD(T) included in addition Ozon)

Test set: H_2, HF, H_2O, HOF, H_2O_2, HNC, NH_3, N_2H_2, C_2H_2, HNO, HCN, C_2H_4, CH_4, N_2, CH_2O, CH_2, CO, CO_2, F_2

* CCSD(T) results from: Helgaker, Jørgensen, Olsen, Modern Electronic-Structure Theory, Wiley 2000.

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	MP2	CC2	CCSD(T)
SiH_4	147.7	147.8	148.3
N≡N	111.4	112.1	110.4
HO-OH	144.9	146.4	145.9

cc-pVTZ, only valence electrons correlated

- strong correlation effects ⇒ bond lengths in CC2 longer than in MP2
- CCSD underestimates bond lengths

Equilibrium Structures of Excited States

Comparison of response methods:

CIS	1. order
CIS(D)	2. order perturbative
CC2, CCSD	2. order iterative
CCSDR(3)	3. order perturbative
CC3	3. order iterative

19 single-excitation dominated states:

N_2 : $A\ ^3\Sigma_g^+$, $B\ ^3\Pi_g$, $B'\ ^3\Sigma_u^-$, $a'\ ^1\Sigma_u^-$, $a\ ^1\Pi_g$, $w^1\Delta_u$, $C^3\Pi_u$

CO: $a\ ^3\Pi$, $A\ ^1\Pi$, $B\ ^1\Sigma^+$, $C\ ^1\Sigma^+$

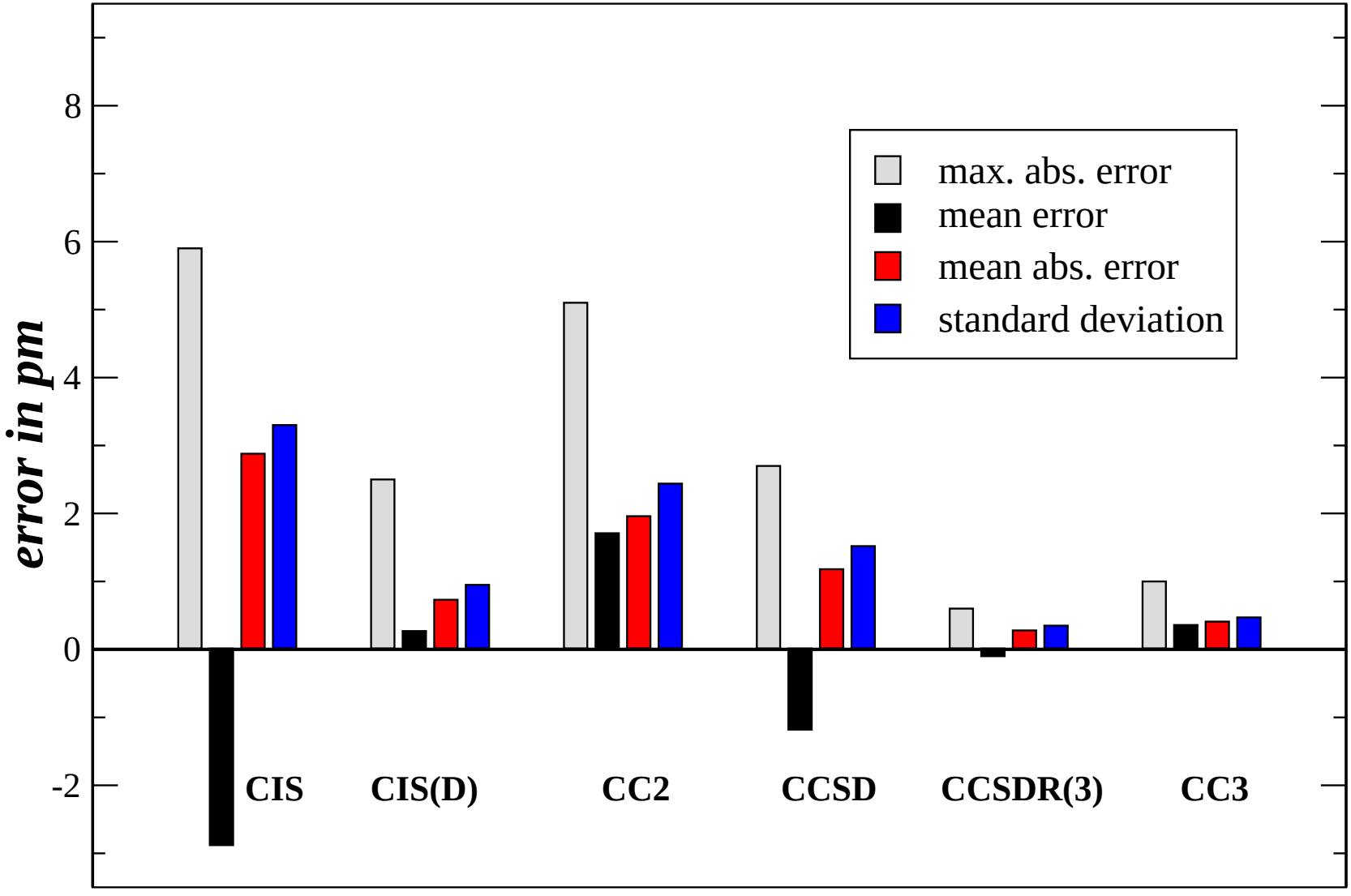
BF : $a\ ^3\Pi$, $A\ ^1\Pi$, $B\ ^1\Sigma^+$, $C\ ^1\Sigma^+$, $b\ ^3\Sigma^+$, $d\ ^3\Pi$

BH: $A\ ^1\Pi$, $B\ ^1\Sigma^+$

Technical details:

- aug-cc-pwCVQZ basis
- all electrons correlated

Bond Lengths of Excited States



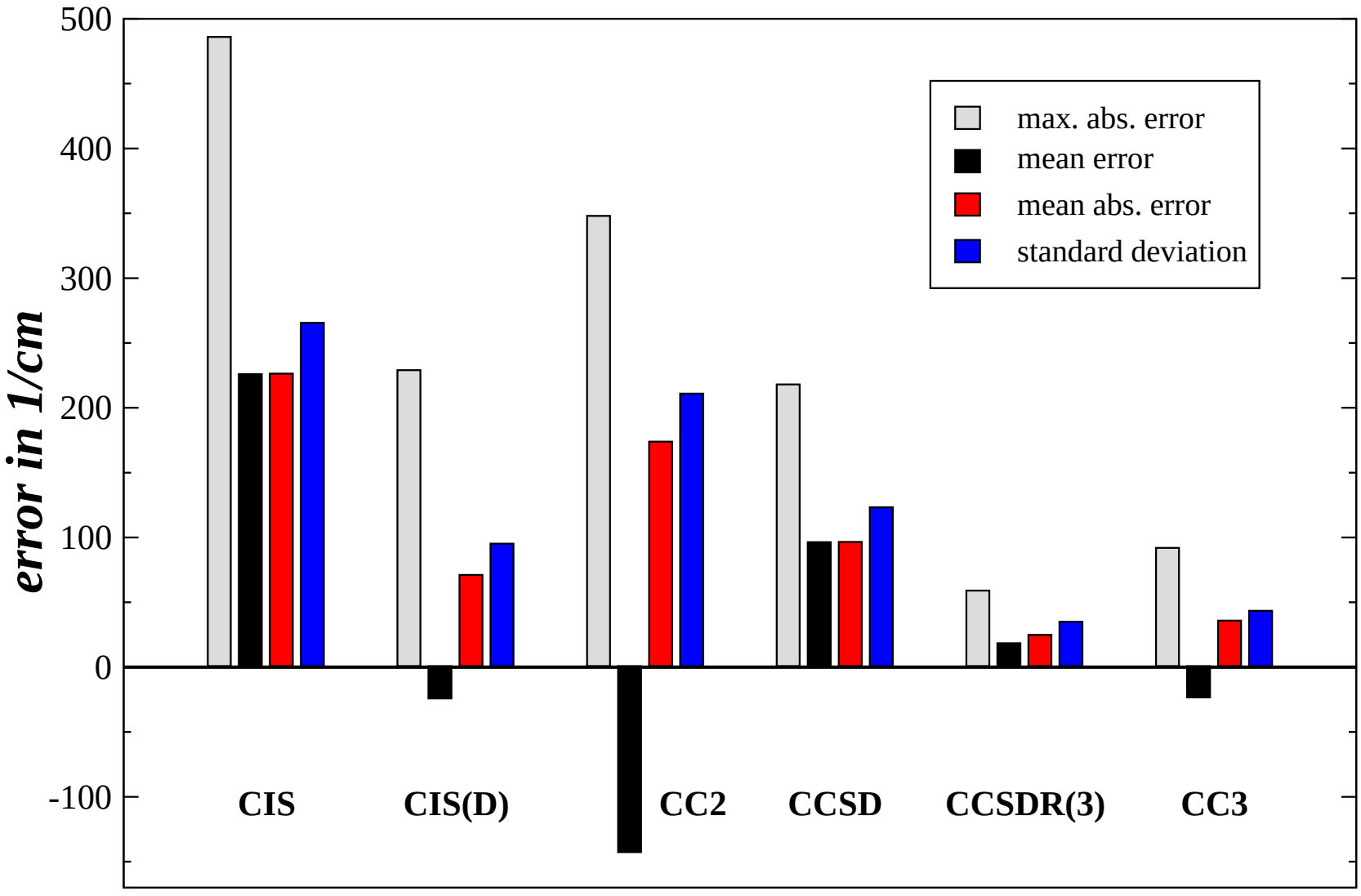
- bond lengths of excited states follow similar trends as in ground state

Selected Bond Lenghts of Excited States (in pm)

(basis set: aug-cc-pVQZ; frozen core)

Molecule/State		Bond	CC2	Exp.
SO_2	$1\,^3B_1$	r_{S-O}	155	149
SiF_2	$1\,^1B_1$	r_{Si-F}	163	160
HC≡CH	$1\,^1A_u$	r_{C-C}	138	138
CH_2O	$1\,^3A''$	r_{C-O}	134	131
CH_2S	$2\,^1A''$	r_{C-S}	171	168
CHO-CHO	$2\,^1A_u$	r_{C-C}	148	146
HC≡C-CHO	$2\,^1A''$	r_{C-O}	141	133

Harmonic Frequencies of Excited States



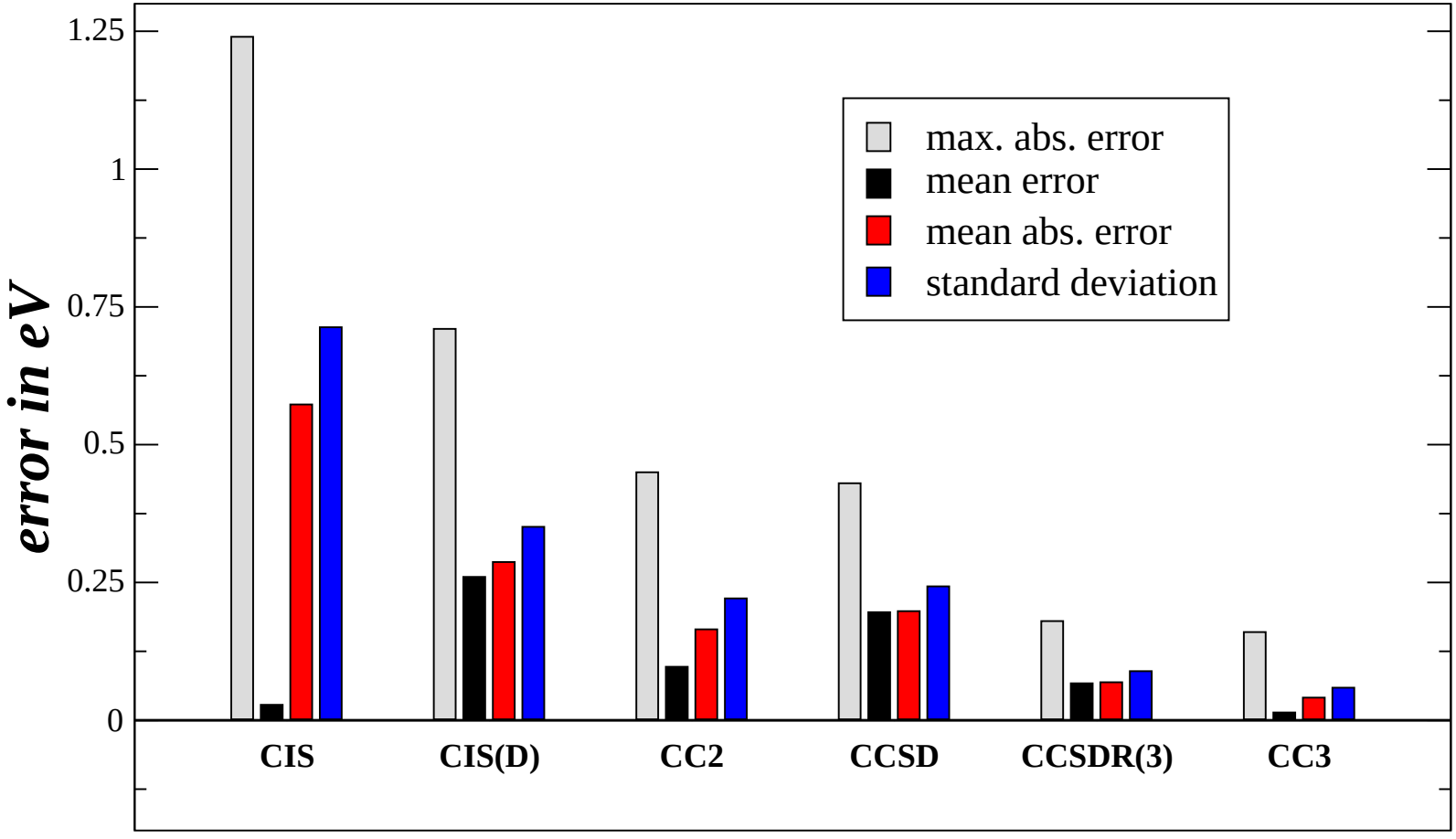
- harmonic frequencies follow the trends found for bond lengths

Selected Vibrational Frequencies of Excited States (in cm^{-1})

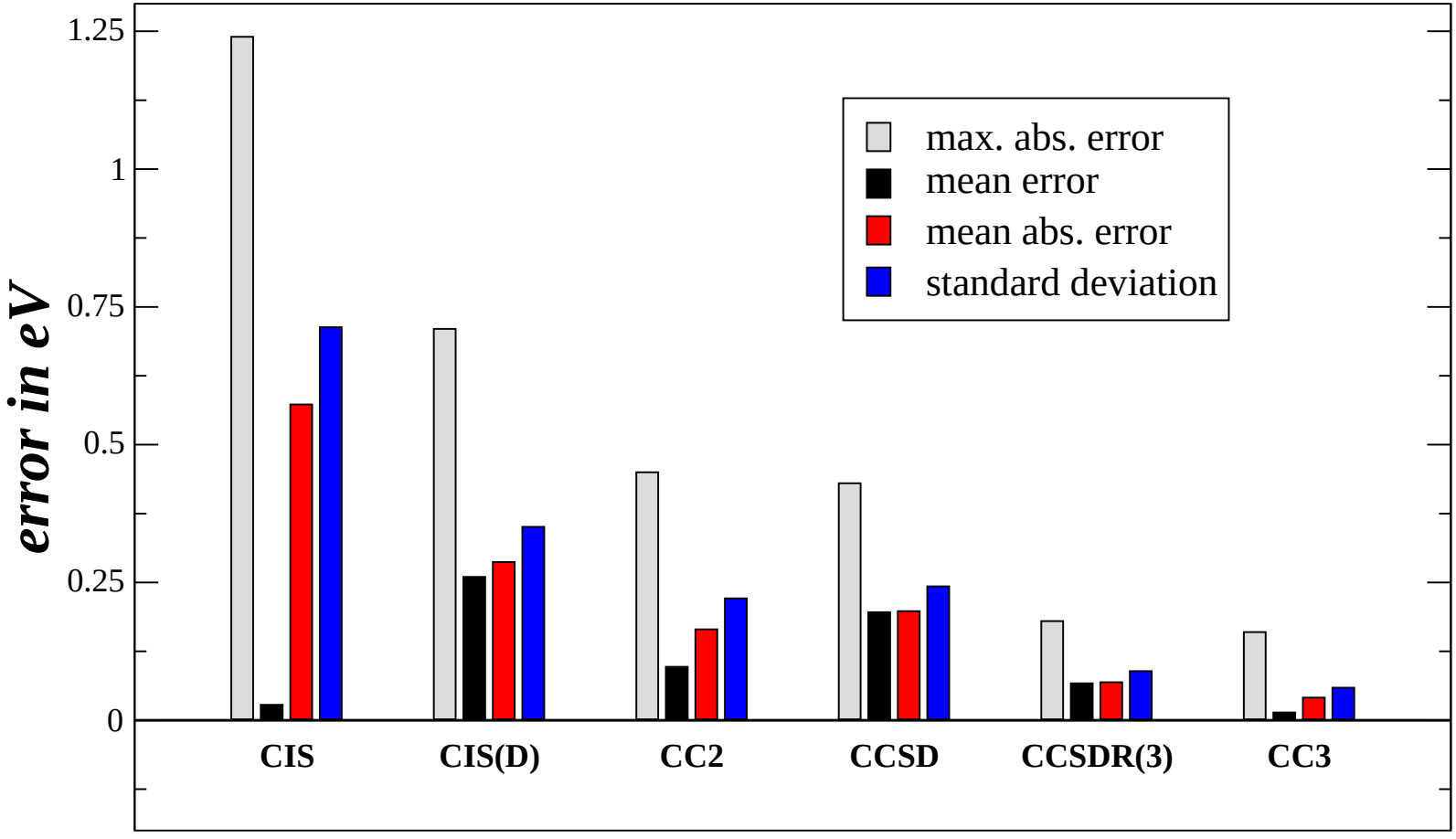
(calculated in the harmonic approximation; aug-cc-pVQZ basis; frozen core)

Molecule/State		CC2	Exp.
SO_2	$1\,^3B_1$	673	906
SiF_2	$1\,^1B_1$	705	598
$HC{\equiv}CH$	$1\,^1A_u$	1368	1385
CH_2O	$1\,^3A''$	1298	1283
CH_2S	$2\,^1A''$	1343	1320
CHO-CHO	$2\,^1A_u$	1369	1391
		1233	1195
$HC{\equiv}C$-CHO	$2\,^1A''$	1218	1304
		1898	1946

Adiabatic Excitation Energies



Adiabatic Excitation Energies



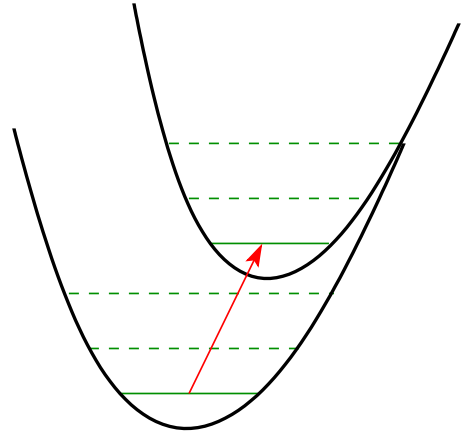
- **errors in adiabatic excitation energies decrease in the order:**

CIS > CIS(D) > CCSD > CC2 > CCSDR(3) > CC3

0-0 Transition Energies of Polyatomic Molecules (in eV)

(calculated in the harmonic approximation; aug-cc-pVQZ basis; frozen core)

Molecule/State		CC2	Exp.
SO_2	$1\,^3B_1$	2.92	3.19
SiF_2	$1\,^1B_1$	5.49	5.34
HC≡CH	$1\,^1A_u$	5.33	5.23
CH_2O	$1\,^3A''$	3.05	3.12
CH_2S	$2\,^1A''$	2.15	2.03
CHO-CHO	$2\,^1A_u$	2.70	2.72
HC≡C-CHO	$2\,^1A''$	3.17	3.24



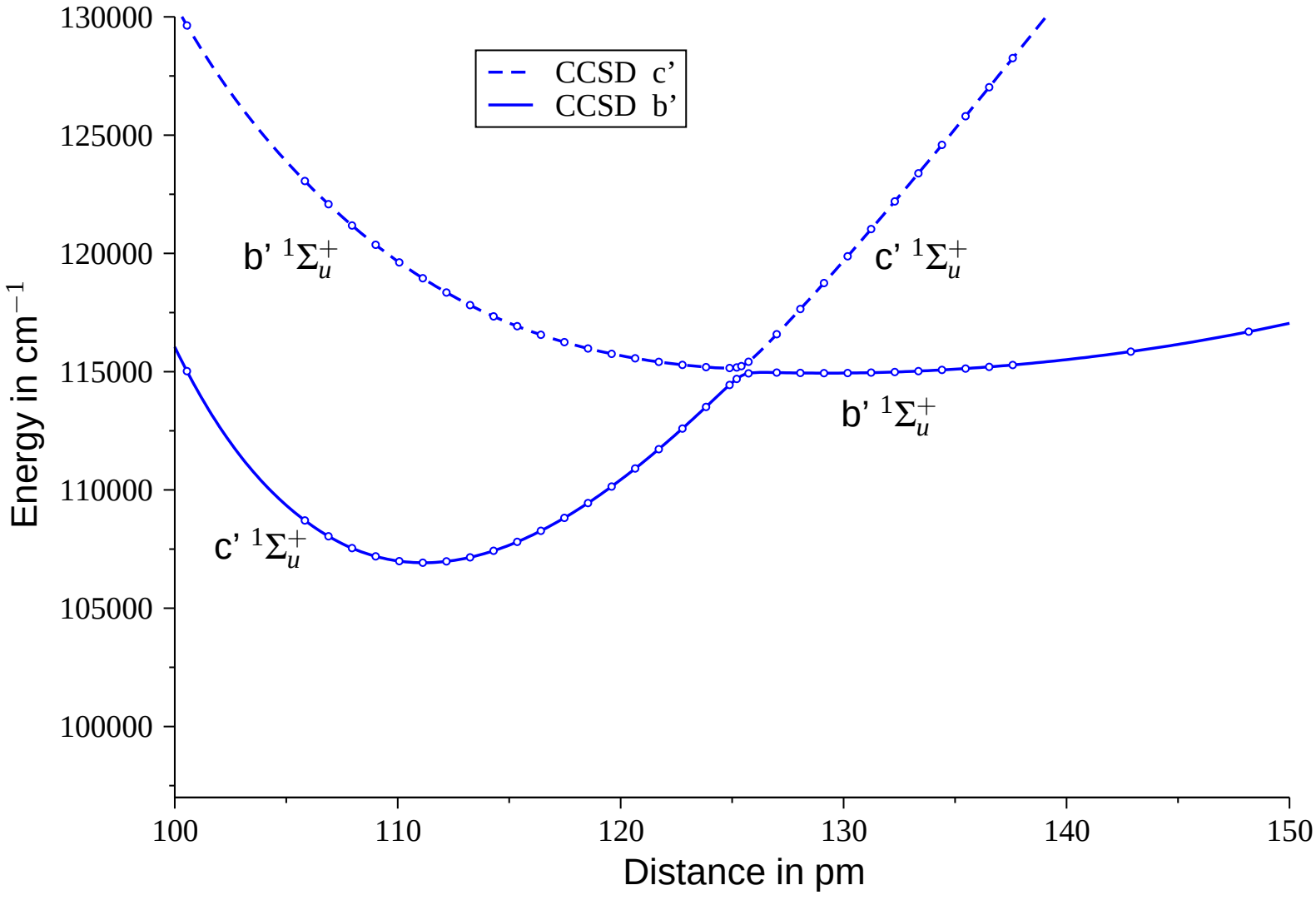
Breakdown of Perturbation Theory: (Avoided) Crossings

Valence-Rydberg Crossing in N_2:

(aug-cc-pVTZ basis set)

c' $^1\Sigma_u^+$: $\sigma_g \rightarrow 3p_z$ (Rydberg)

b' $^1\Sigma_u^+$: $\pi_u \rightarrow \pi_g^*$ (Valence)



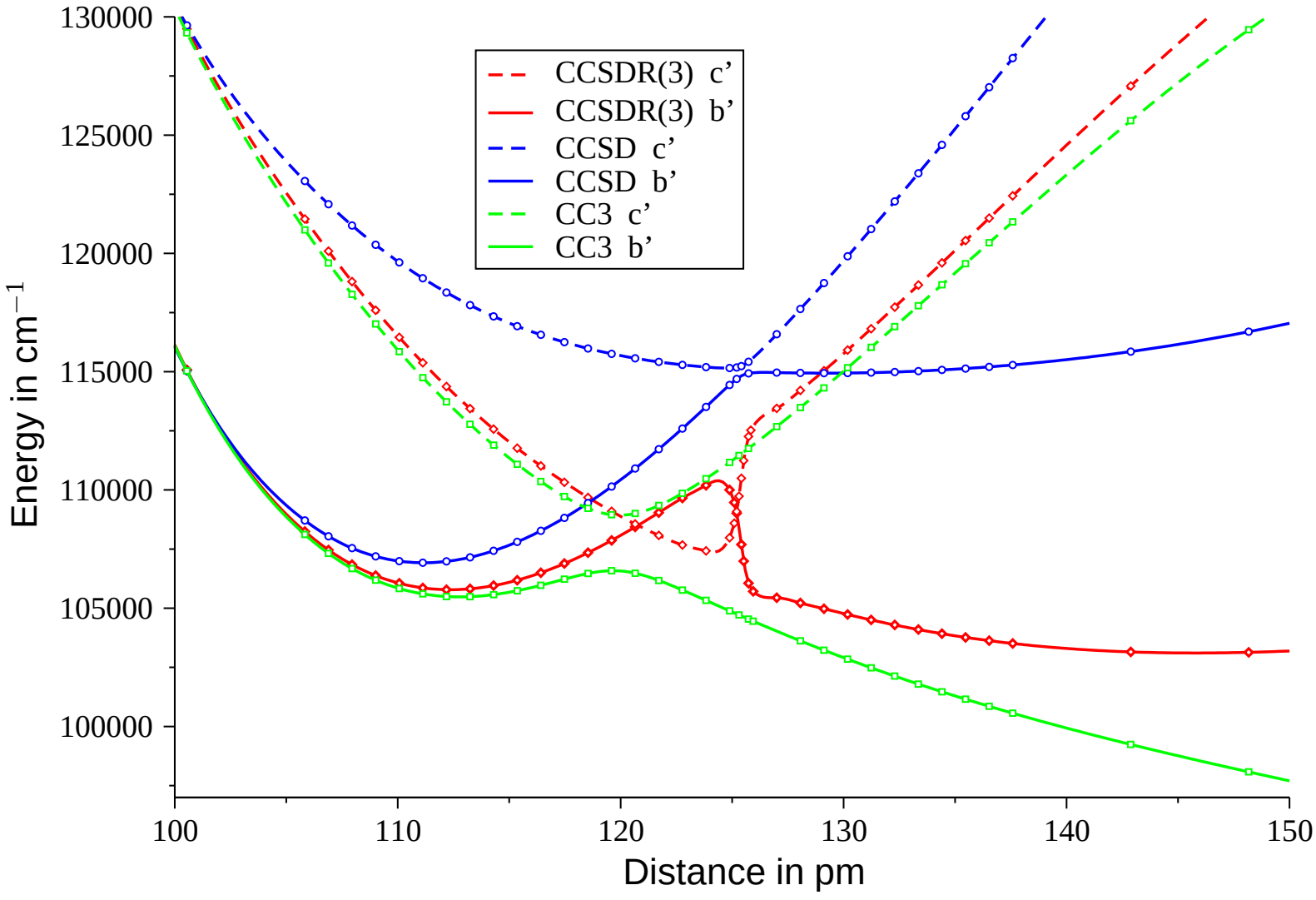
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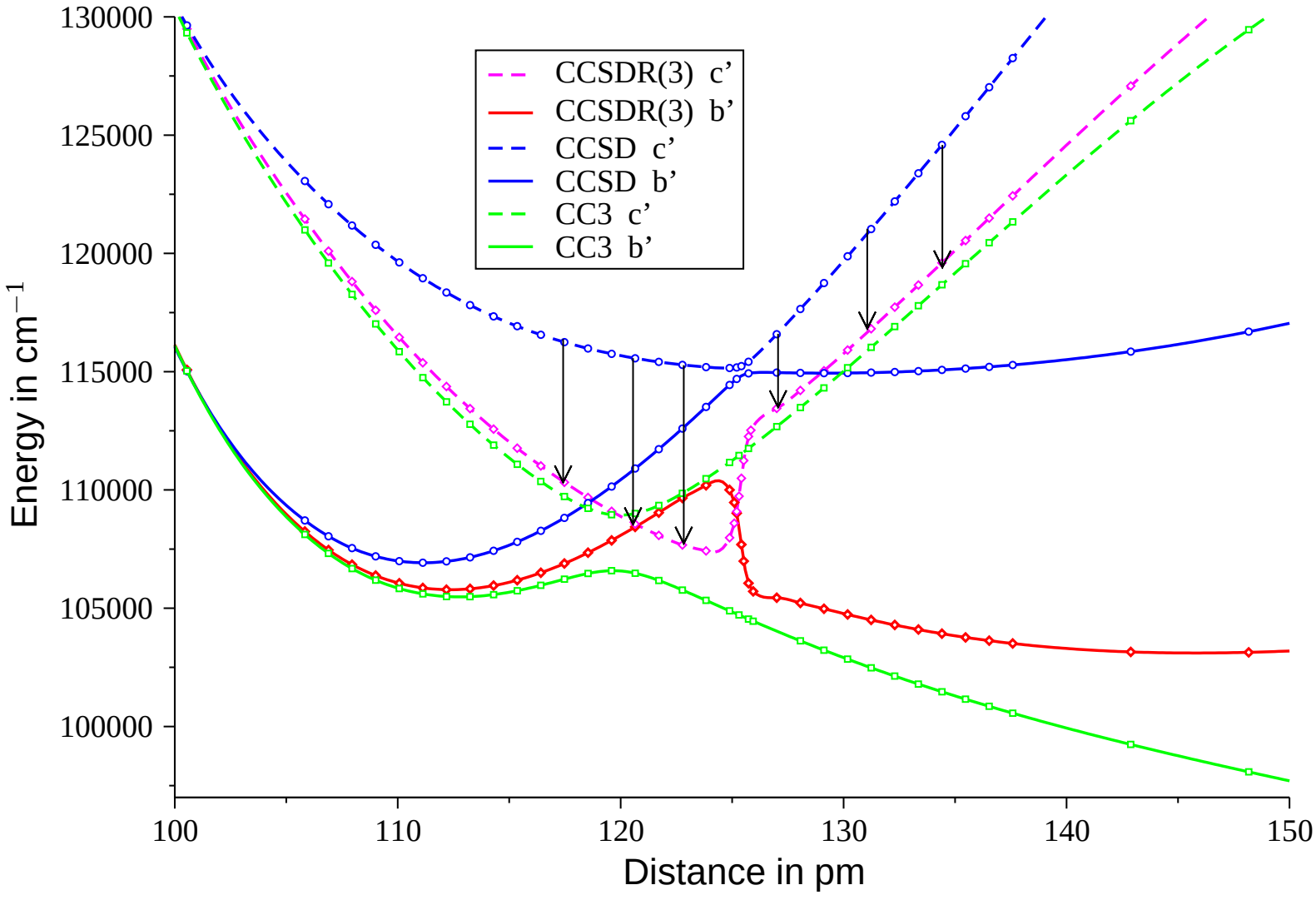
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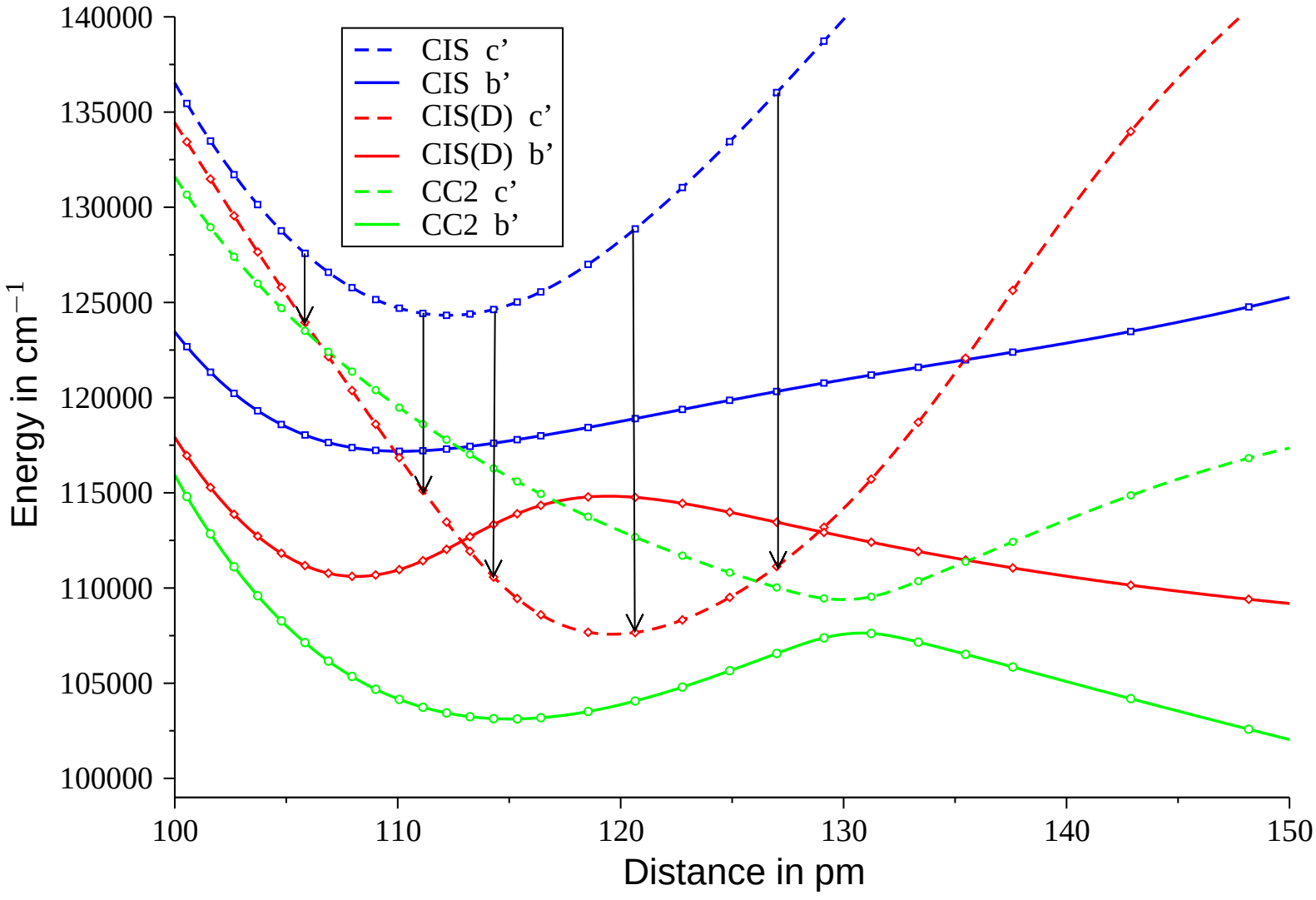
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CC Response Theory — Summary

- coupled-cluster response theory is an efficient and systematic approach to structures and energies of excited states
  - excited state should be dominated by single excitations
  - ground state must be a single-reference case
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- perturbative corrections can be an economical alternative,
  - but are only applicable for isolated states!

Part III

The approximate coupled-cluster singles-and-doubles model CC2 for investigations on excited states

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The approximate coupled-cluster singles-and-doubles model CC2 for investigations on excited states

- What is CC2?
- Related approximate doubles methods
- Diagnostics
- Implementation with RI approximation
- Applications

Approximate Coupled-Cluster Models: CC2

perturbation expansion of the cluster equations to 2. order starting from an SCF done *without* time-dependent field (Christiansen, Koch, Jørgensen, CPL, 1996):

MP2	**CC2**
$\hat{H} = \hat{F} + \hat{U}$	$\hat{H}(t) = \hat{F} + \hat{V}(t) + \hat{U}$
0.th order $\hat{T}^{(0)} = 0$	0.th order $\hat{T}^{(0)} = \hat{T}_1^{(0)}$
1.th order $\hat{T}^{(1)} = \hat{T}_2^{(1)}$	1.th order $\hat{T}^{(1)} = \hat{T}_1^{(1)} + \hat{T}_2^{(1)}$
—	$\left\langle {}_{i}^{a} \middle\vert \tilde{H} + [\tilde{H}, \hat{T}_2] \middle\vert \mathrm{HF} \right\rangle = 0$
$\left\langle {}_{ij}^{ab} \middle\vert \hat{H} + [\hat{F}, \hat{T}_2] \middle\vert \mathrm{HF} \right\rangle = 0$	$\left\langle {}_{ij}^{ab} \middle\vert \tilde{H} + [\hat{F}, \hat{T}_2] \middle\vert \mathrm{HF} \right\rangle = 0$
noniterative N^5	iterative N^5

$\hat{F}$: Fock operator

$\tilde{H} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$

The CC2 Jacobian

$$\begin{pmatrix} \left\langle {}^{a}_{i} \right| \left[\left(\tilde{H} + \left[\tilde{H}, \hat{T}_2 \right] \right), \tau^{c}_{k} \right] \left| \mathrm{HF} \right\rangle & \left\langle {}^{a}_{i} \right| \left[\tilde{H}, \hat{\tau}^{cd}_{kl} \right] \left| \mathrm{HF} \right\rangle \\ \text{correct through 2. order} & \text{correct through 1. order} \\ \hline \left\langle {}^{ab}_{ij} \right| \left[\tilde{H}, \hat{\tau}^{c}_{k} \right] \left| \mathrm{HF} \right\rangle & \left\langle {}^{ab}_{ij} \right| \left[\hat{F}, \hat{\tau}^{cd}_{kl} \right] \left| \mathrm{HF} \right\rangle \\ \text{correct through 1. order} & \text{correct through 0. order} \end{pmatrix}$$

(with: $\hat{F}$ = Fock operator and $\tilde{H} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$)

Jacobian for Approximate Doubles Models

$$\mathbf{A}(t_1,t_2) = \left(\begin{array}{c|c} \left\langle {}^{a}_{i}\middle|\left[\left(\tilde{H}+\left[\tilde{H},\hat{T}_2\right]\right),\tau_k^c\right]\middle|\mathrm{HF}\right\rangle & \left\langle {}^{a}_{i}\middle|\left[\tilde{H},\hat{\tau}_{kl}^{cd}\right]\middle|\mathrm{HF}\right\rangle \\ \text{correct through 2. order} & \text{correct through 1. order} \\ \hline \left\langle {}^{ab}_{ij}\middle|\left[\tilde{H},\hat{\tau}_k^c\right]\middle|\mathrm{HF}\right\rangle & \left\langle {}^{ab}_{ij}\middle|\left[\hat{F},\hat{\tau}_{kl}^{cd}\right]\middle|\mathrm{HF}\right\rangle \\ \text{correct through 1. order} & \text{correct through 0. order} \end{array}\right)$$

(with: $\hat{F}$ = Fock operator and $\tilde{H} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$)

- CIS(D$_\infty$): (Head-Gordon, Oumi, Maurice, *MP*, 96 (1999) 593)

$$\mathbf{A}\left(0,t_2^{(\mathrm{MP1})}\right)E = \omega^{\mathrm{CIS}(\mathrm{D}_\infty)}E$$

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$$\mathbf{A}\left(0,t_2^{(\mathrm{MP1})}\right)E = \omega^{\mathrm{CIS}(\mathrm{D}_\infty)}E$$

- ADC(2): (Schirmer, *PRA*, 26 (1981) 2395)

$$\frac{1}{2}\left(\mathbf{A}\left(0,t_2^{(\mathrm{MP1})}\right)+\mathbf{A}\left(0,t_2^{(\mathrm{MP1})}\right)^{T}\right)E = \omega^{\mathrm{ADC}(2)}E$$

The Eigenvalue Problem for Approximate Doubles Models

$$\begin{pmatrix} \mathbf{A}\mu_1\nu_1 & \mathbf{A}\mu_1\nu_2 \\ \mathbf{A}\mu_2\nu_1 & \delta\mu_2\nu_2\varepsilon\nu_2 \end{pmatrix} \begin{pmatrix} E\nu_1 \\ E\nu_2 \end{pmatrix} = \omega \begin{pmatrix} E\mu_1 \\ E\mu_2 \end{pmatrix}$$

μ_1, ν_1 single replacements

μ_2, ν_2 double replacements

$\varepsilon_{\nu_2} = \varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j$

The Eigenvalue Problem for Approximate Doubles Models

$$\begin{pmatrix} \mathbf{A}_{\mu_1\nu_1} & \mathbf{A}_{\mu_1\nu_2} \\ \mathbf{A}_{\mu_2\nu_1} & \delta_{\mu_2\nu_2}\varepsilon_{\nu_2} \end{pmatrix} \begin{pmatrix} E_{\nu_1} \\ E_{\nu_2} \end{pmatrix} = \omega \begin{pmatrix} E_{\mu_1} \\ E_{\mu_2} \end{pmatrix}$$

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$\varepsilon_{\nu_2} = \varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j$

- The Eigenvalue can be partitioned: $E_{\mu_2} = (\omega - \varepsilon_{\mu_2})^{-1}\left(\sum_{\nu_1} \mathbf{A}_{\mu_2\nu_1} E_{\nu_1}\right)$

  ↷ *nonlinear* eigenvalue problem only in the singles space:

$$\left[\mathbf{A}_{\mu_1\nu_1} - \frac{\mathbf{A}_{\mu_1\mu_2}\mathbf{A}_{\mu_2\nu_1}}{\varepsilon_{\mu_2} - \omega}\right] E_{\nu_1} = \mathbf{A}^{eff}_{\mu_1\nu_1}(t_1, \omega) E_{\nu_1} = \omega E_{\nu_1}$$

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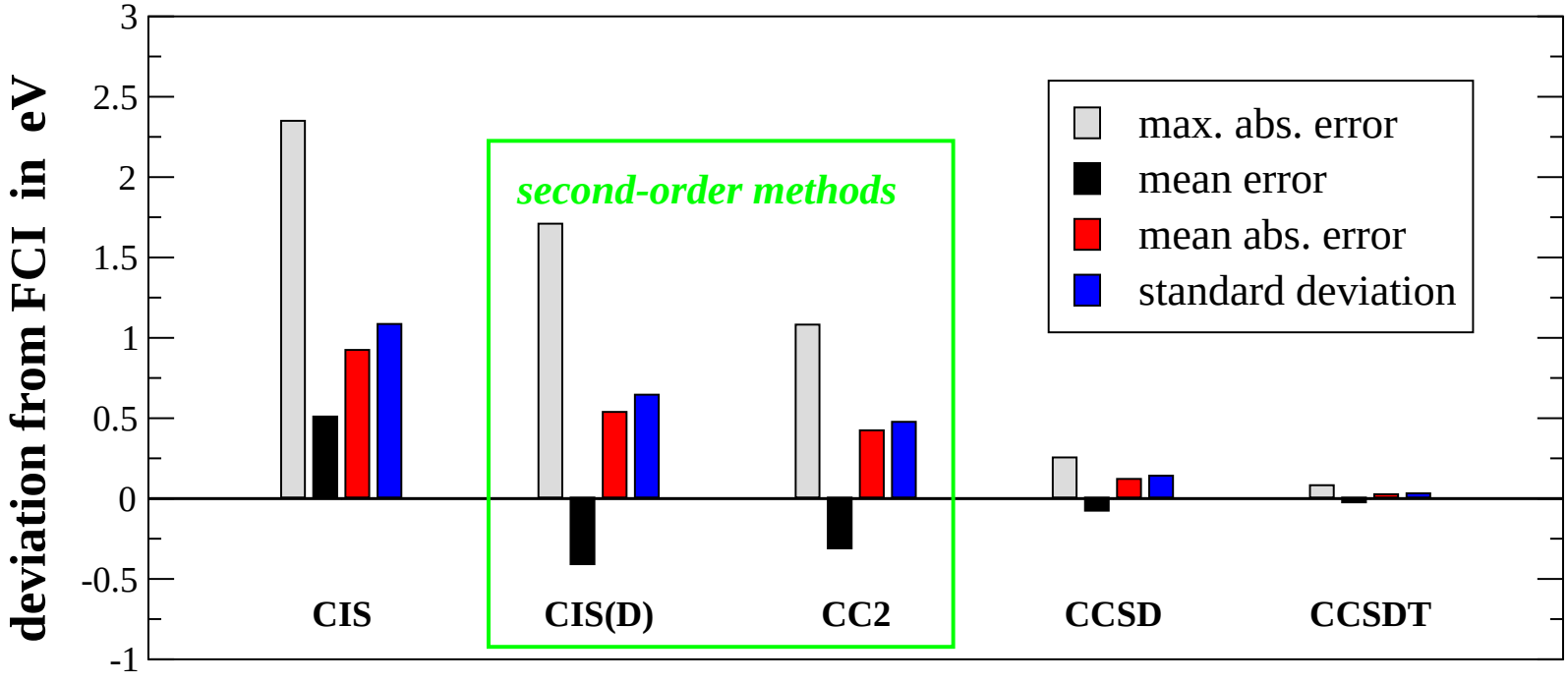
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- Non-iterative approximation with $t_{\mu_1} = 0$ and $E_{\mu_1} = E^{\mathrm{CIS}}$ gives CIS(D):

$$\omega^{\mathrm{CIS(D)}} = E^{\mathrm{CIS}}_{\mu_1} \mathbf{A}^{eff}_{\nu_1\mu_1}(0, \omega^{\mathrm{CIS}}) E^{\mathrm{CIS}}_{\nu_1}$$

Accuracy of CC Models for Vertical Excitation Energies

49 States (21 Singlet & 28 Triplet) in Ne, H_2O, BH, N_2, HF



data taken from:

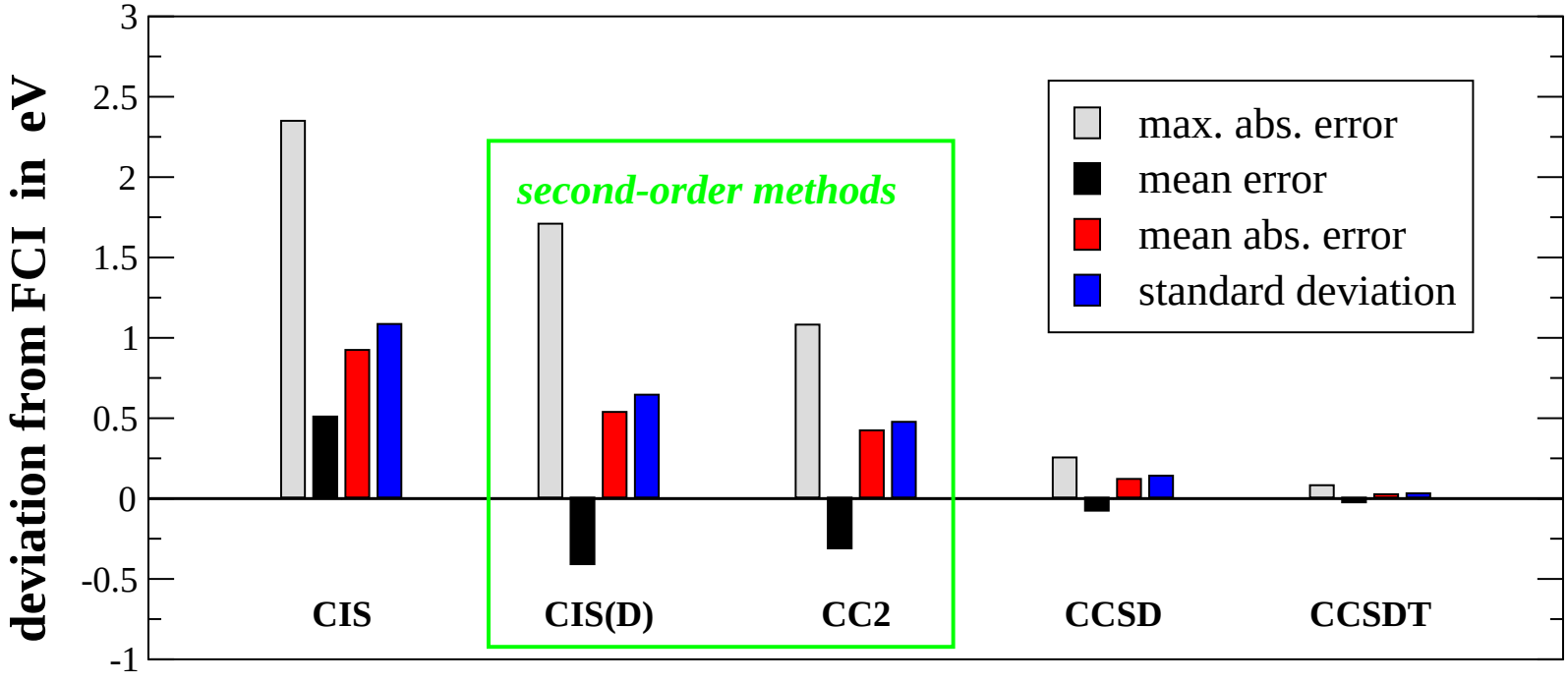
Koch *et. al.*,
CPL 244 (1995) 75;

Christiansen *et. al.*,
CPL 256 (1996) 185;

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- *Typical errors in vertical excitation energies for second-order methods:*

1. correlation error (method) CIS(D), CC2 $\approx$ 0.2 – 0.4 eV
2. one-electron basis set error aug-cc-pVTZ $\approx$ 0.02 – 0.04 eV

Diagnostics — Ground State

D_1 norm: (Janssen, Nielsen, *CPL* 290 (1998) 423)

$$D_1 = ||\mathbf{t}_{\mu_1}||_2 = \sqrt{\lambda_{max}\Big(\sum_a t_a^i t_a^j, \sum_i t_a^i t_b^i\Big)}$$

- for CC2 it should be $D_1(t_{\mu_1}) \lesssim 0.04$

D_2 norm: (Nielsen, Janssen, *CPL* 310 (1999) 568)

$$D_2 = ||\mathbf{t}_{\mu_2}||_2 = \sqrt{\lambda_{max}\Big(\sum_{ack} t_{ac}^{ik} t_{ac}^{jk}, \sum_{ick} t_{ac}^{ik} t_{bc}^{ik}\Big)}$$

- for CC2 it should be $D_2(t_{\mu_2}) \lesssim 0.17$

Diagnostics — Excited States

$||\mathbf{T_1}||$ **norm**: $$||T_1|| = \frac{\sum_{\mu_1} E^2_{\mu_1}}{\sum_i \sum_{\mu_i} E^2_{\mu_1}} \times 100\%$$

(where E right eigenvector)

- problem: depends on definition/normalization of excitation manifold!
  $\rightsquigarrow$ results depend on spin-coupling, different results for left eigenvectors
- for CC2 $||T_1||$ should be

singlet excitations (spin-coupled formulation)	$\gtrsim 90\%$
triplet excitations (spin coupled formulation)	$\gtrsim 95\%$
spin-orbital formulation (UHF based calculations)	$\gtrsim 95\%$

Diagnostics — Excited States

$||\mathbf{T_1}||$ **norm**: $$||T_1|| = \frac{\sum_{\mu_1} E_{\mu_1}^2}{\sum_i \sum_{\mu_i} E_{\mu_1}^2} \times 100\%$$

(where E right eigenvector)

- problem: depends on definition/normalization of excitation manifold!
  $\rightsquigarrow$ results depend on spin-coupling, different results for left eigenvectors
- for CC2 $||T_1||$ should be

  singlet excitations (spin-coupled formulation) $\gtrsim 90\%$
  triplet excitations (spin coupled formulation) $\gtrsim 95\%$
  spin-orbital formulation (UHF based calculations) $\gtrsim 95\%$

$\langle \bar{\mathbf{E}}_\mathbf{1} | \mathbf{E_1} \rangle$ **norm**: $$\langle \bar{E}_1 | E_1 \rangle = \frac{\sum_{\mu_1 \nu_1} \bar{E}_{\mu_1} \langle \mu_1 | \hat{\tau}_{\nu_1} | \mathrm{HF} \rangle E_{\nu_1}}{\sum_i \sum_{\mu_i \nu_i} \bar{E}_{\mu_i} \langle \mu_i | \hat{\tau}_{\nu_i} | \mathrm{HF} \rangle E_{\nu_i}} \times 100\%$$

(where $\bar{E}$, E left & right eigenvectors)

- for CC2 it should be $\langle \bar{E}_1 | E_1 \rangle \gtrsim 85\%$

Implementation of CC2 for Excitation Energies

Needed for iterative solution of eigenproblem:

$$\sigma_{\mu_1}(b_{\nu_1},\omega) = \sum_{\nu_1} \mathbf{A}^{eff}_{\mu_1\nu_1}(t_1,\omega) b_{\nu_1} = \sum_{\nu_1} \mathbf{A}_{\mu_1\nu_1} b_{\nu_1} - \sum_{\mu_2} \mathbf{A}_{\mu_1\mu_2} \frac{\sum_{\nu_1} \mathbf{A}_{\mu_2\nu_1} b_{\nu_1}}{\varepsilon_{\mu_2} - \omega}$$

Implementation of CC2 for Excitation Energies

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```
do i = 1, nocc
 do j = 1, nocc
  do a = 1, nvirt
   do b = 1, nvirt
```

$b^{ij}_{ab} = (ai|\bar{b}j)/(\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b + \omega)$

$\sigma_{ci} = \sigma_{ci} + \sum_{abj}(2b^{ij}_{ab} - b^{ij}_{ba})(jb|\tilde{c}a)$

$\vdots$

$t^{ij}_{ab} = (ai|\tilde{b}j)/(\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b)$

$\sigma_{ai} = \sigma_{ai} + \sum_{bj}(2t^{ij}_{ab} - t^{ij}_{ba}) \sum_{ck}[2(jb|kc) - (jc|kb]\ b_{ck}$

```
   end do
  end do
 end do
end do
```

where $(ai|\tilde{b}j)$ and $(ai|\bar{b}j)$ one-index transformed ERIs

Implementation of CC2 for Excitation Energies

Needed for iterative solution of eigenproblem:

$$\sigma_{\mu_1}(b_{\nu_1},\omega) = \sum_{\nu_1} \mathbf{A}^{eff}_{\mu_1\nu_1}(t_1,\omega) b_{\nu_1} = \sum_{\nu_1} \mathbf{A}_{\mu_1\nu_1} b_{\nu_1} - \sum_{\mu_2} \mathbf{A}_{\mu_1\mu_2} \frac{\sum_{\nu_1} \mathbf{A}_{\mu_2\nu_1} b_{\nu_1}}{\varepsilon_{\mu_2} - \omega}$$

```
do i = 1, nocc
 do j = 1, nocc
  do a = 1, nvirt
   do b = 1, nvirt
```

$b^{ij}_{ab} = (ai|\bar{b}j)/(\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b + \omega)$

$\sigma_{ci} = \sigma_{ci} + \sum_{abj}(2b^{ij}_{ab} - b^{ij}_{ba})(jb|\tilde{c}a)$

$\vdots$

$t^{ij}_{ab} = (ai|\tilde{b}j)/(\varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b)$

$\sigma_{ai} = \sigma_{ai} + \sum_{bj}(2t^{ij}_{ab} - t^{ij}_{ba}) \sum_{ck}[2(jb|kc) - (jc|kb]\ b_{ck}$

```
   end do
  end do
 end do
end do
```

where $(ai|\tilde{b}j)$ and $(ai|\bar{b}j)$ one-index transformed ERIs

- Similar bottlenecks as in MP2! $\Longrightarrow$ RI approximation

CC2 for Large Systems: Approximating the 4-Index-ERIs

- time-determining step:

$$(ai|\tilde{b}j) = \sum_{\mu}\Lambda^{p}_{\mu a}\sum_{\nu}\Lambda^{h}_{\nu i}\sum_{\kappa}\Lambda^{p}_{\kappa b}\sum_{\lambda}\Lambda^{h}_{\lambda j}(\mu\nu|\kappa\lambda) \qquad \propto ON^4$$

occupied orbitals

with $\Lambda^p = \mathbf{C}(\mathbf{1} - \mathbf{t}_1^T)$ and $\Lambda^h = \mathbf{C}(\mathbf{1} + \mathbf{t}_1)$

- Acceleration through RI approximation:

1. $$\tilde{B}_{Q,ai} = \sum_{\mu}\Lambda^{p}_{\mu a}\sum_{\nu}\Lambda^{h}_{\nu i}\sum_{P}(\mu\nu|P)\,[\mathbf{V}^{-1/2}]_{PQ} \qquad \propto ONN_X^2$$

2. $$(ai|\tilde{b}j) \approx \sum_{Q}\tilde{B}_{Q,ai}\,\tilde{B}_{Q,bj} \qquad \propto O^2V^2N_X$$

CC2 with 3-index-RI-integrals

1. $\tilde{B}_{Q,pi} = \Lambda^{p}_{\mu p}\,\Lambda^{h}_{\nu i}\,(\mu\nu|P)\,V^{-1/2}_{PQ}$ $\quad \approx pN^2N_x + 2ON^2N_x + ONN_x^2$
2. $\bar{B}_{Q,pi} = \Lambda^{p}_{\mu p}\,\bar{\Lambda}^{h}_{\nu i}\,(\mu\nu|P)\,V^{-1/2}_{PQ} - b_{ak}\tilde{B}_{Q,ki}$ $\quad \approx pN^2N_x + 3ON^2N_x + ONN_x^2$

   ⋮
3. loop $i,\ j \le i$
   - read $\tilde{B}_{Q,ai}$, $\tilde{B}_{Q,bj}$, ...
   - $(ai\tilde{|}bj) = \tilde{B}_{Q,ai}\tilde{B}_{Q,bj}$ $\quad \approx \frac{1}{2}O^2N^2N_x$
   - $t^{ij}_{ab} = (ai\tilde{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\quad \approx \frac{1}{2}O^2N^2N_x$
   - $\sigma_{ai} = \sigma_{ai} + t^{ij}_{ab}\bar{F}_{jb}$ and for $j \ne i$ also $\sigma_{bj} = \sigma_{bj} + t^{ij}_{ab}\bar{F}_{ia}$ $\quad \approx \frac{1}{2}O^2N^2$

   ⋮
   - $(ai|\bar{b}j) = \bar{B}_{Q,ai}\tilde{B}_{Q,bj} + \tilde{B}_{Q,ai}\bar{B}_{Q,bj}$ $\quad \approx O^2N^2N_x$
   - $b^{ij}_{ab} = (ai|\bar{b}j)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\quad \approx \frac{1}{2}O^2N^2$
   - $\bar{Y}_{Q,ai} += b^{ij}_{ab}B_{Q,bj}$ and for $j \ne i$ also $\bar{Y}_{Q,bj} += b^{ij}_{ab}B_{Q,ai}$ $\quad \approx O^2N^2N_x$

   ⋮

   end loop $i,\ j$

   ⋮
4. $\sigma_{ai} = \sigma_{ai} + \bar{Y}^{Q}_{ak}\tilde{B}_{Q,ki}$ $\quad \approx O^2NN_x$

   ⋮

CC2 with 3-index-RI-integrals

1. $\tilde{B}_{Q,pi} = \Lambda^{p}_{\mu p}\,\Lambda^{h}_{\nu i}\,(\mu\nu|P)\,V^{-1/2}_{PQ}$ $\quad \approx pN^2N_x + 2ON^2N_x + ONN_x^2$
2. $\bar{B}_{Q,pi} = \Lambda^{p}_{\mu p}\,\bar{\Lambda}^{h}_{\nu i}\,(\mu\nu|P)\,V^{-1/2}_{PQ} - b_{ak}\tilde{B}_{Q,ki}$ $\quad \approx pN^2N_x + 3ON^2N_x + ONN_x^2$

   ⋮
3. loop $i,\ j \le i$
   - read $\tilde{B}_{Q,ai},\ \tilde{B}_{Q,bj},\ \ldots$
   - $(ai\tilde{|}bj) = \tilde{B}_{Q,ai}\tilde{B}_{Q,bj}$ $\quad \approx \frac{1}{2}O^2N^2N_x$
   - $t^{ij}_{ab} = (ai\tilde{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\quad \approx \frac{1}{2}O^2N^2N_x$
   - $\sigma_{ai} = \sigma_{ai} + t^{ij}_{ab}\bar{F}_{jb}$ and for $j \ne i$ also $\sigma_{bj} = \sigma_{bj} + t^{ij}_{ab}\bar{F}_{ia}$ $\quad \approx \frac{1}{2}O^2N^2$

   ⋮
   - $(ai|\bar{b}j) = \bar{B}_{Q,ai}\tilde{B}_{Q,bj} + \tilde{B}_{Q,ai}\bar{B}_{Q,bj}$ $\quad \approx O^2N^2N_x$
   - $b^{ij}_{ab} = (ai|\bar{b}j)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\quad \approx \frac{1}{2}O^2N^2$
   - $\bar{Y}_{Q,ai} += b^{ij}_{ab}B_{Q,bj}$ and for $j \ne i$ also $\bar{Y}_{Q,bj} += b^{ij}_{ab}B_{Q,ai}$ $\quad \approx O^2N^2N_x$

   ⋮

   end loop $i,\ j$

   ⋮
4. $\sigma_{ai} = \sigma_{ai} + \bar{Y}^{Q}_{ak}\tilde{B}_{Q,ki}$ $\quad \approx O^2NN_x$

   ⋮

- one-index & AO-to-MO transformation done for 3-index integrals

CC2 with 3-index-RI-integrals

1. $\tilde{B}_{Q,pi} = \Lambda^{p}_{\mu p}\Lambda^{h}_{\nu i}(\mu\nu|P)V^{-1/2}_{PQ}$ $\approx pN^2N_x + 2ON^2N_x + ONN_x^2$
2. $\bar{B}_{Q,pi} = \Lambda^{p}_{\mu p}\bar{\Lambda}^{h}_{\nu i}(\mu\nu|P)V^{-1/2}_{PQ} - b_{ak}\tilde{B}_{Q,ki}$ $\approx pN^2N_x + 3ON^2N_x + ONN_x^2$

⋮

3. loop $i,\ j \le i$

   t^{ij}_{ab} *reevaluated whenever needed!*

   – read $\tilde{B}_{Q,ai}$, $\tilde{B}_{Q,bj}$, ...
   – $(ai\tilde{|}bj) = \tilde{B}_{Q,ai}\tilde{B}_{Q,bj}$ $\approx \frac{1}{2}O^2N^2N_x$
   – $t^{ij}_{ab} = (ai\tilde{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2N_x$
   – $\sigma_{ai} = \sigma_{ai} + t^{ij}_{ab}\bar{F}_{jb}$ and for $j \ne i$ also $\sigma_{bj} = \sigma_{bj} + t^{ij}_{ab}\bar{F}_{ia}$ $\approx \frac{1}{2}O^2N^2$

   ⋮

   – $(ai\bar{|}bj) = \bar{B}_{Q,ai}\tilde{B}_{Q,bj} + \tilde{B}_{Q,ai}\bar{B}_{Q,bj}$ $\approx O^2N^2N_x$
   – $b^{ij}_{ab} = (ai\bar{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2$
   – $\bar{Y}_{Q,ai} += b^{ij}_{ab}B_{Q,bj}$ and for $j \ne i$ also $\bar{Y}_{Q,bj} += b^{ij}_{ab}B_{Q,ai}$ $\approx O^2N^2N_x$

   ⋮

   end loop $i,\ j$

   ⋮

4. $\sigma_{ai} = \sigma_{ai} + \bar{Y}^{Q}_{ak}\tilde{B}_{Q,ki}$ $\approx O^2NN_x$

⋮

- doubles amplitudes are not saved on disc

CC2 with 3-index-RI-integrals

1. $\tilde{B}_{Q,pi} = \Lambda^{p}_{\mu p}\Lambda^{h}_{\nu i}(\mu\nu|P)V^{-1/2}_{PQ}$ $\approx pN^2N_x + 2ON^2N_x + ONN_x^2$
2. $\bar{B}_{Q,pi} = \Lambda^{p}_{\mu p}\bar{\Lambda}^{h}_{\nu i}(\mu\nu|P)V^{-1/2}_{PQ} - b_{ak}\tilde{B}_{Q,ki}$ $\approx pN^2N_x + 3ON^2N_x + ONN_x^2$

   ⋮
3. loop $i,\ j \le i$
   - read $\tilde{B}_{Q,ai}$, $\tilde{B}_{Q,bj}$, ...
   - $(ai\tilde{|}bj) = \tilde{B}_{Q,ai}\tilde{B}_{Q,bj}$ $\approx \frac{1}{2}O^2N^2N_x$
   - $t^{ij}_{ab} = (ai\tilde{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2N_x$
   - $\sigma_{ai} = \sigma_{ai} + t^{ij}_{ab}\bar{F}_{jb}$ and for $j \ne i$ also $\sigma_{bj} = \sigma_{bj} + t^{ij}_{ab}\bar{F}_{ia}$ $\approx \frac{1}{2}O^2N^2$

   ⋮
   - $(ai\bar{|}bj) = \bar{B}_{Q,ai}\tilde{B}_{Q,bj} + \tilde{B}_{Q,ai}\bar{B}_{Q,bj}$ $\approx O^2N^2N_x$
   - $b^{ij}_{ab} = (ai\bar{|}bj)/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2$
   - $\bar{Y}_{Q,ai} += b^{ij}_{ab}B_{Q,bj}$ and for $j \ne i$ also $\bar{Y}_{Q,bj} += b^{ij}_{ab}B_{Q,ai}$ $\approx O^2N^2N_x$

   ⋮

   end loop $i,\ j$

   ⋮
4. $\sigma_{ai} = \sigma_{ai} + \bar{Y}^{Q}_{ak}\tilde{B}_{Q,ki}$ $\approx O^2NN_x$

   ⋮

- disc space $\propto ONN_x$, core memory $\propto NN_x$

CC2 with 3-index-RI-integrals

1. $\tilde{B}_{Q,pi} = \Lambda^{p}_{\mu p}\Lambda^{h}_{\nu i}(\mu\nu|P)V^{-1/2}_{PQ}$ $\approx pN^2N_x + 2ON^2N_x + ONN_x^2$
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   ⋮
3. loop i, $j \leq i$
   - read $\tilde{B}_{Q,ai}$, $\tilde{B}_{Q,bj}$, ...
   - $(ai|\tilde{bj}) = \tilde{B}_{Q,ai}\tilde{B}_{Q,bj}$ $\approx \frac{1}{2}O^2N^2N_x$
   - $t^{ij}_{ab} = (ai|\tilde{bj})/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2N_x$
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   ⋮
   - $(ai|\bar{bj}) = \bar{B}_{Q,ai}\tilde{B}_{Q,bj} + \tilde{B}_{Q,ai}\bar{B}_{Q,bj}$ $\approx O^2N^2N_x$
   - $b^{ij}_{ab} = (ai|\bar{bj})/\{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j\}$ $\approx \frac{1}{2}O^2N^2$
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   ⋮

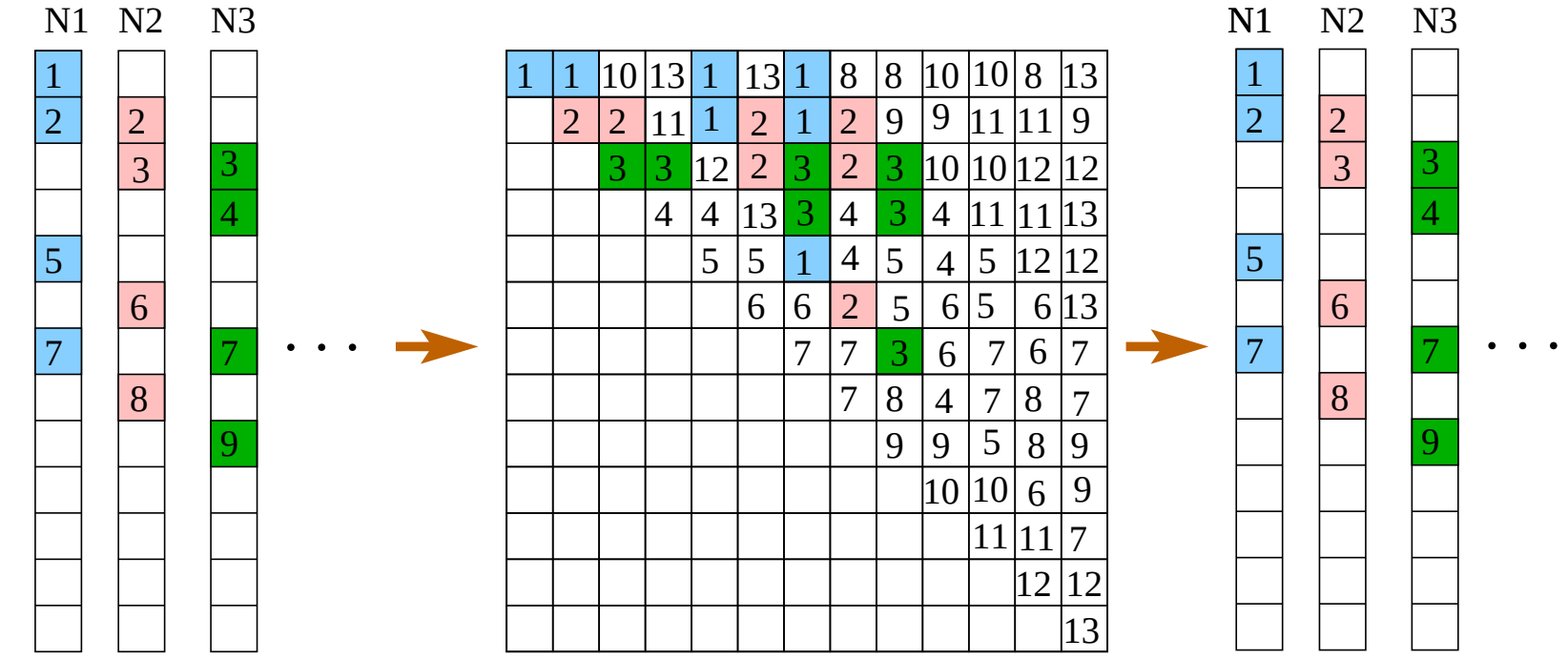
   end loop i, j

   ⋮
4. $\sigma_{ai} = \sigma_{ai} + \bar{Y}^{Q}_{ak}\tilde{B}_{Q,ki}$ $\approx O^2NN_x$

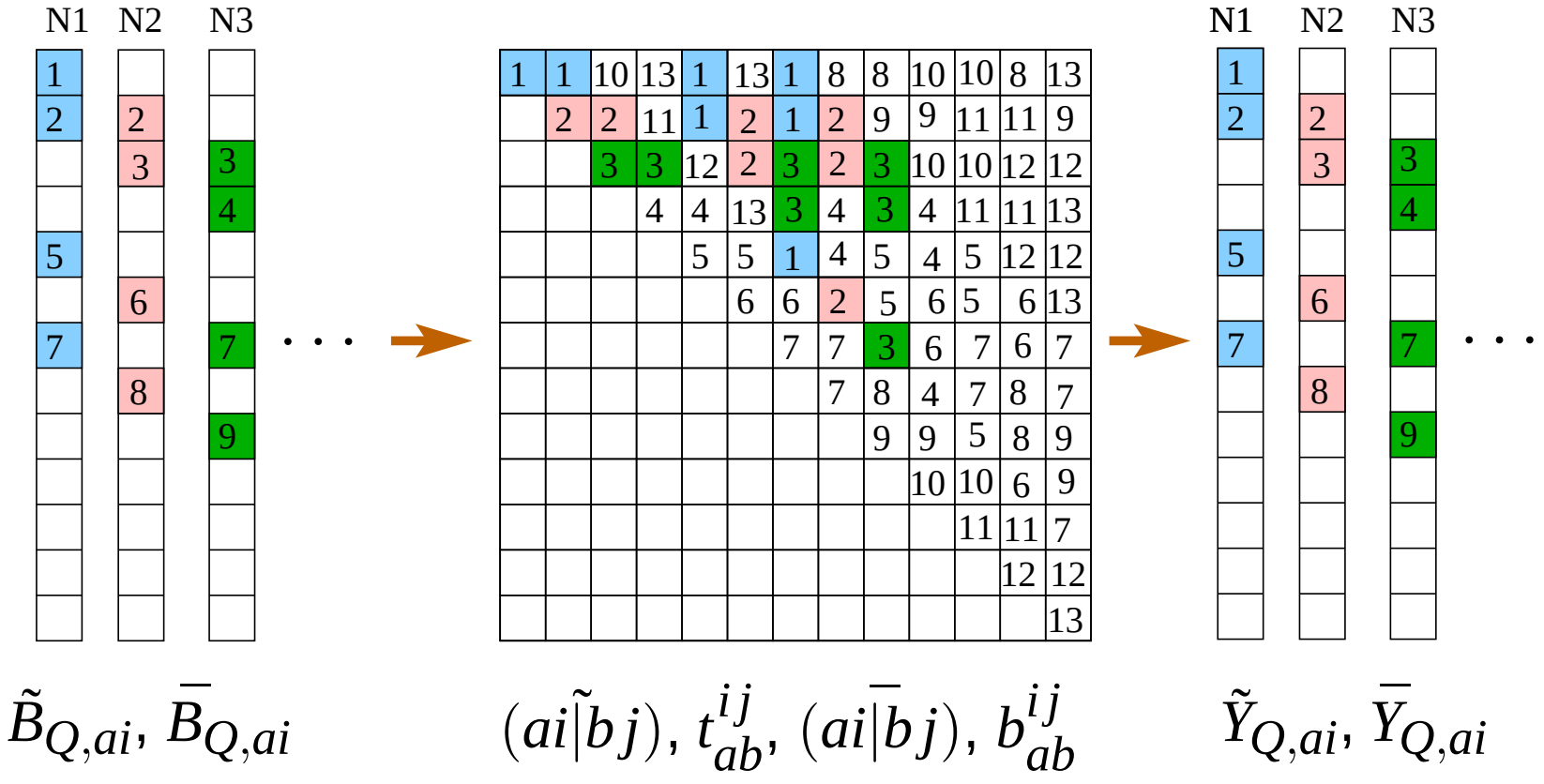
   ⋮

- same parallelization concepts as for RI-MP2 can be applied

Parallel Evaluation of $\mathcal{N}^5$ Expressions



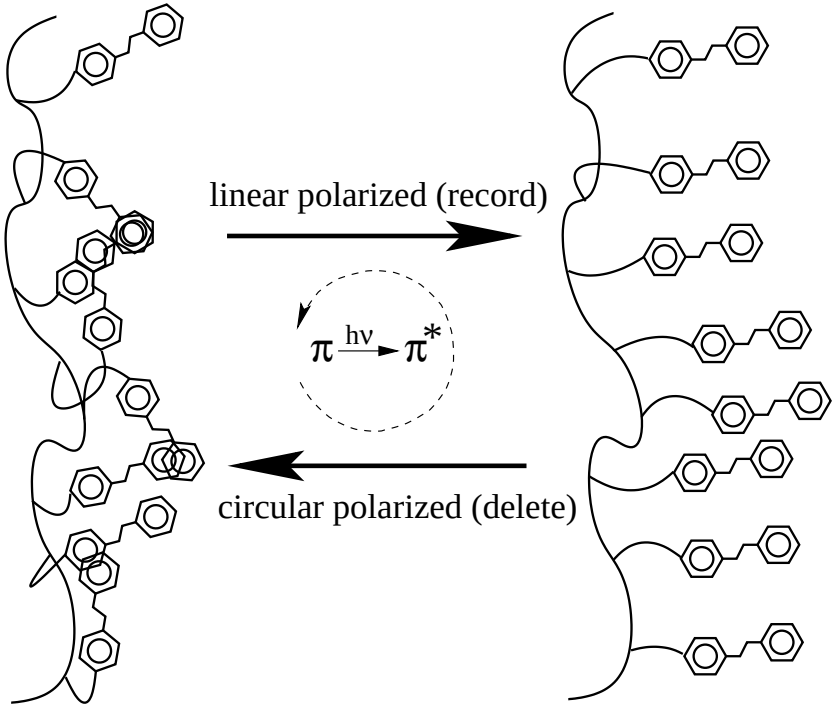
Parallel Evaluation of $\mathcal{N}^5$ Expressions



- more complicated, since more terms/intermediates than in RI-MP2
- but the same concepts for parallelization apply

$\pi - \pi^*$-Transitions in Azobenzenes

Optical data storage in polymers containing azobenzene dyes:

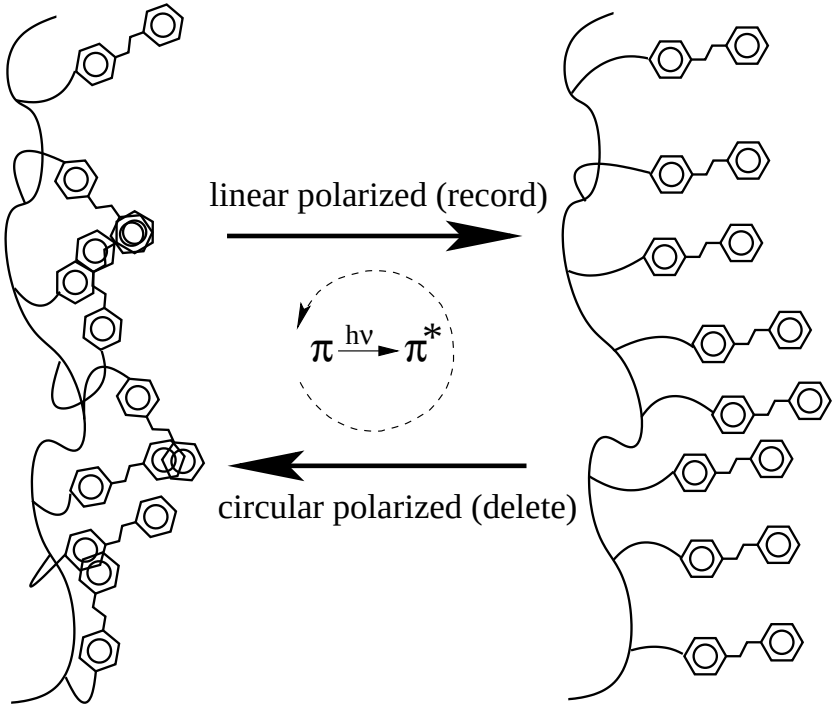


$\Rightarrow$ motivated a SOPPA study:

P.-O. Åstrand et al., JACS 2000, 122, 3482

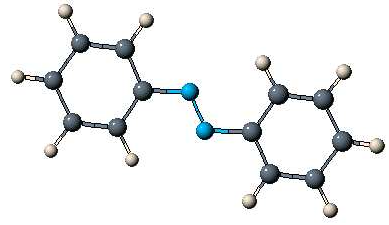
$\pi - \pi^*$-Transitions in Azobenzenes

Optical data storage in polymers containing azobenzene dyes:

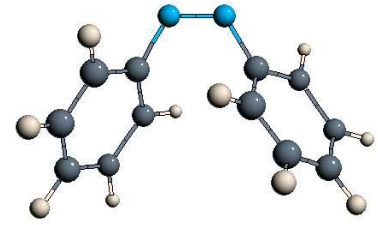


$\Rightarrow$ motivated a SOPPA study:

P.-O. Åstrand et al., JACS 2000, 122, 3482



trans



cis

- aug-cc-pVTZ basis [5s4p3d2f/4s3p2d]
- auxiliary basis (10s8p7d5f3g/5s4p3d2f)
- geometries optimized at MP2/cc-pVTZ level

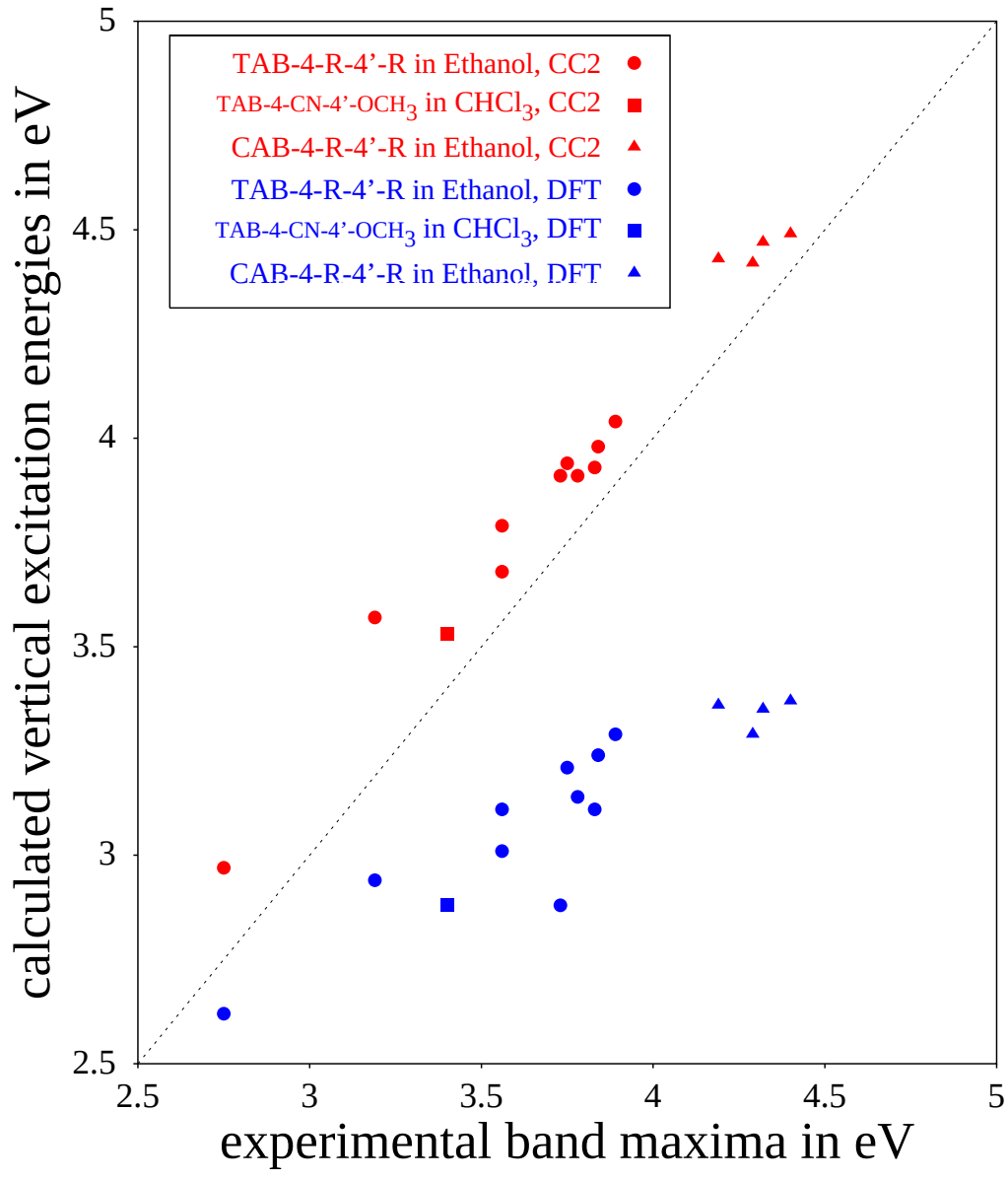
config.	State	SOPPA*	CC2	Exp.
trans	$1\ ^1B_g$	2.49	2.84	2.82
trans	$1\ ^1B_u$	3.90	4.04	4.12
trans	$3\ ^1B_u$	5.82	5.79	(5.64)
cis	$1\ ^1B$	2.52	3.00	2.92
cis	$1\ ^3B$		4.79	(4.68)

*[3s2p(1d)/2s], from: Åstrand et al., JACS 2000, 122, 3482

$\pi - \pi^*$-Transitions in Azobenzenes

- CC2: aug-cc-pVTZ basis; MP2/cc-pVTZ geometry
- DFT: BP86, aug-cc-pVDZ basis; BP86/cc-pVDZ geometry

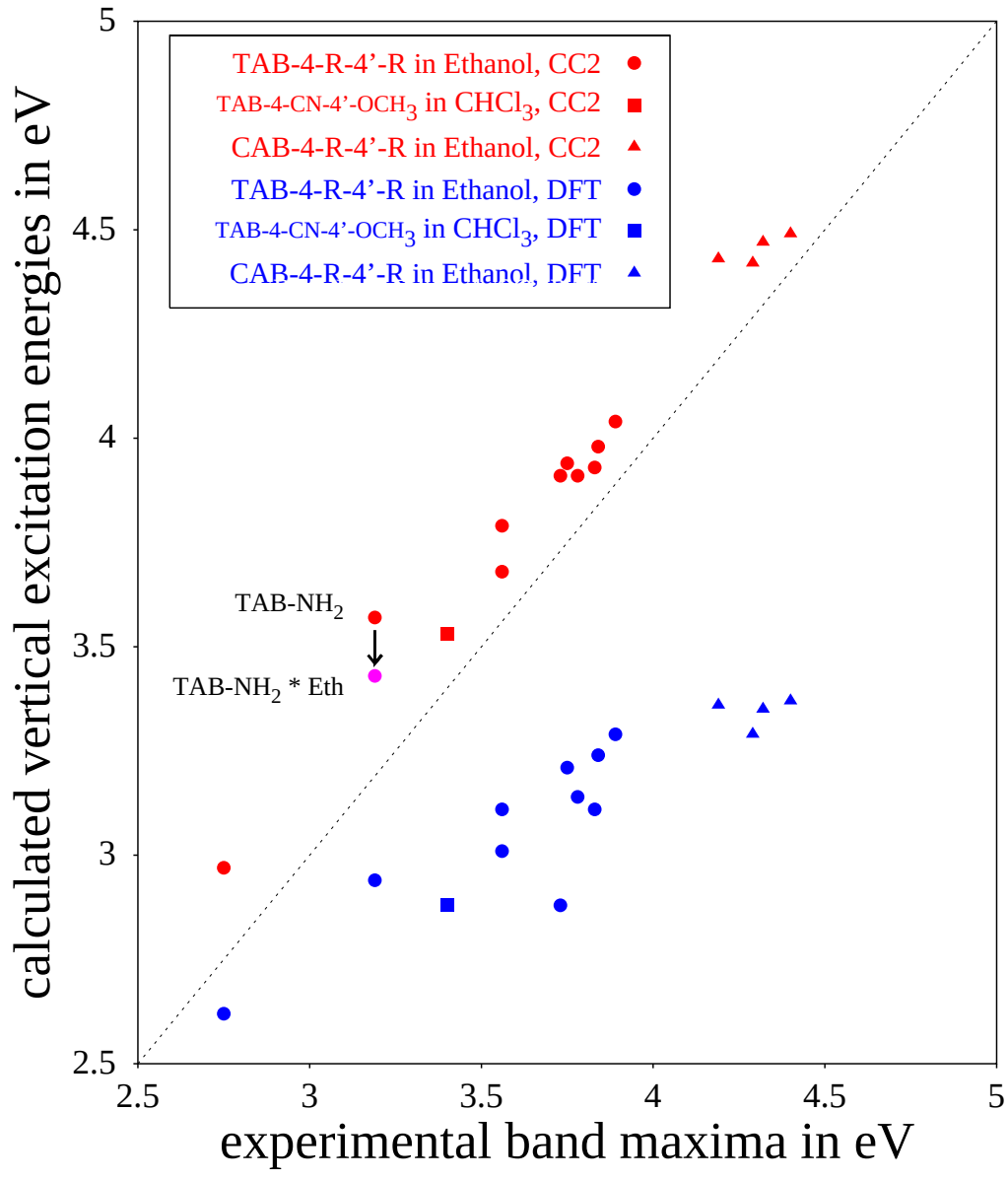
Substitution	*trans*-AB		*cis*-AB	
	CC2	Exp.	CC2	Exp.
-4-CN	3.93	3.83	4.41	
-4-CH_3	3.94	3.75	4.43	4.19
-4-NH_2	3.57	3.19	4.09	
-4-OH	3.79	3.56	4.29	3.94
-4-OCH_3	3.68	3.56	4.23	
-4-NO_2	3.91	3.73	4.34	
-4-F	3.98	3.84	4.47	4.32
-4-Cl	3.91	3.73	4.42	4.29
-4-CHO	3.91		3.77	
-4-COOH	3.94		4.40	
-4-CN-4'-OCH_3	3.53	3.40	4.02	
-4-CN-4'-$N(CH_3)_2$	2.97	2.75	3.59	



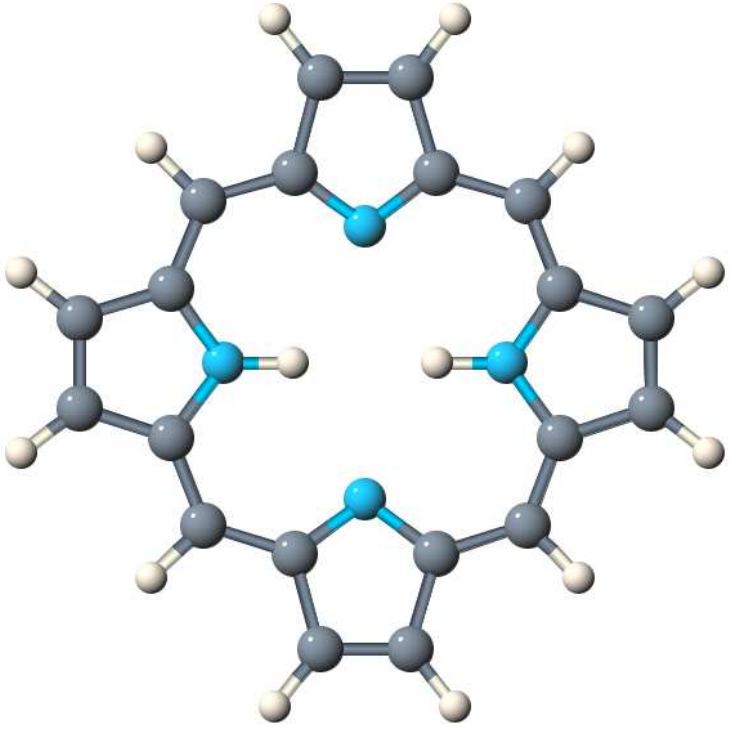
$\pi - \pi^*$-Transitions in Azobenzenes

- CC2: aug-cc-pVTZ basis; MP2/cc-pVTZ geometry
- DFT: BP86, aug-cc-pVDZ basis; BP86/cc-pVDZ geometry

Substitution	*trans*-AB		*cis*-AB	
	CC2	Exp.	CC2	Exp.
-4-CN	3.93	3.83	4.41	
-4-CH_3	3.94	3.75	4.43	4.19
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-4-Cl	3.91	3.73	4.42	4.29
-4-CHO	3.91		3.77	
-4-COOH	3.94		4.40	
-4-CN-4'-OCH_3	3.53	3.40	4.02	
-4-CN-4'-$N(CH_3)_2$	2.97	2.75	3.59	



The UV/VIS Spectrum of Free-Base Porphyrin



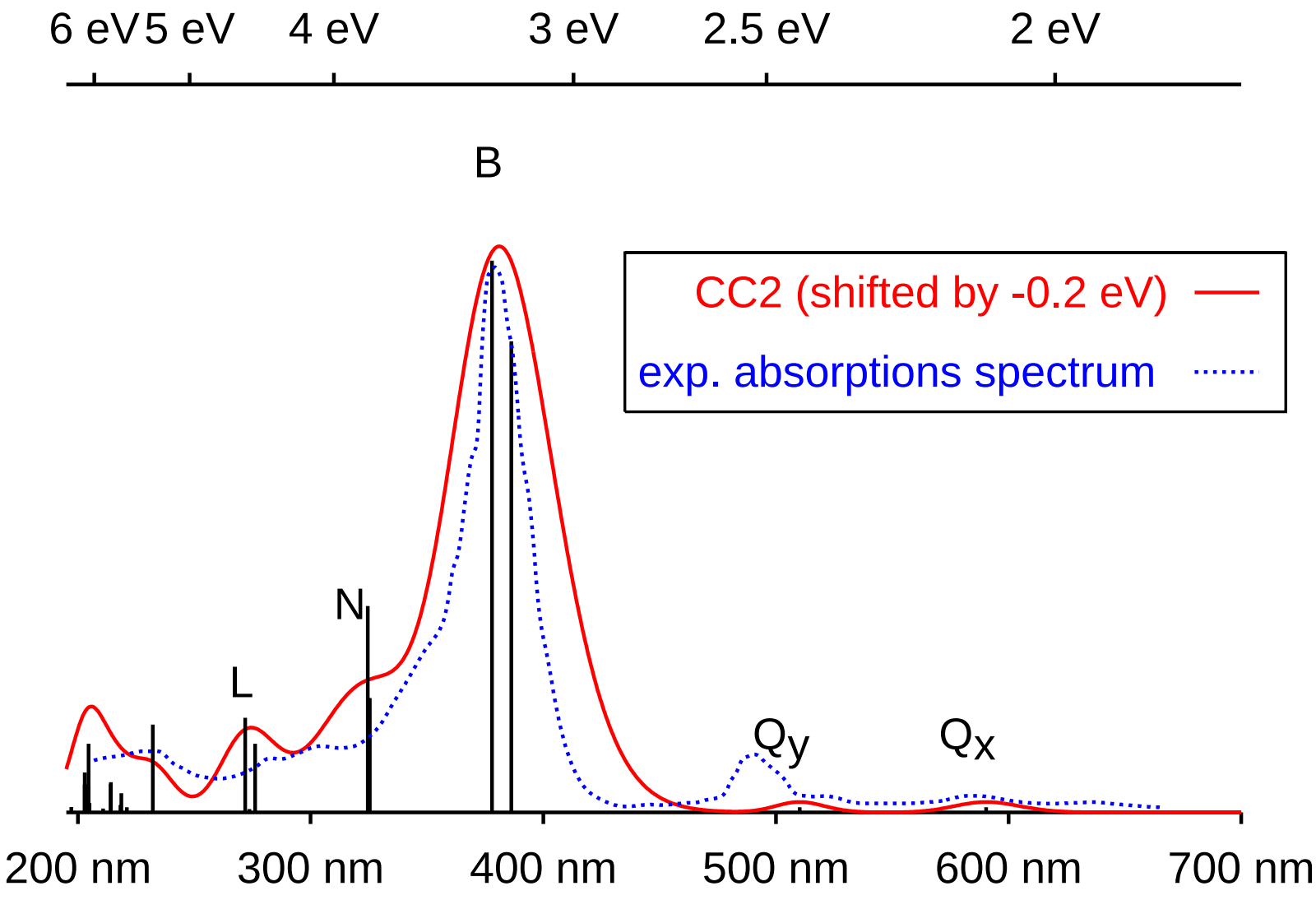
(almost D_{4h} symmetry)

State	Excit. Energ. CC2	Excit. Energ. Exp	Band	Oscill. Str. Exp	Oscill. Str. CC2
$1\ ^1B_{3u}$	2.30	1.98	Q_x	0.01	<0.01
$1\ ^1B_{2u}$	2.63	2.42	Q_y	0.06	<0.01
$2\ ^1B_{3u}$	3.41	3.33	B	1.15	0.98
$2\ ^1B_{2u}$	3.48				1.10
$3\ ^1B_{2u}$	4.01	3.63	N	<0.1	0.17
$3\ ^1B_{3u}$	4.02				0.33
$4\ ^1B_{2u}$	4.69	4.25	L	≈ 0.1	0.13
$4\ ^1B_{3u}$	4.76				0.18

Computational Details:

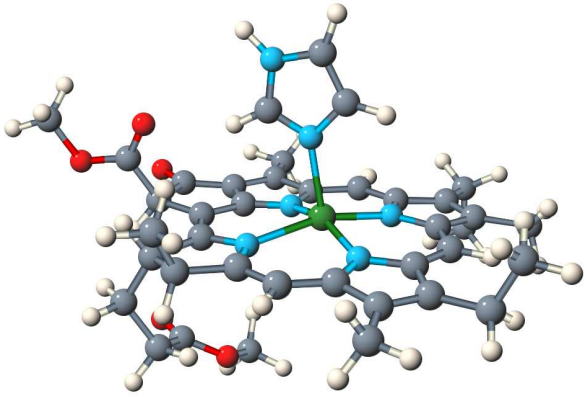
- CC2/cc-pVTZ optimized geometry
- aug-cc-pVTZ basis for the vertical excitation energies

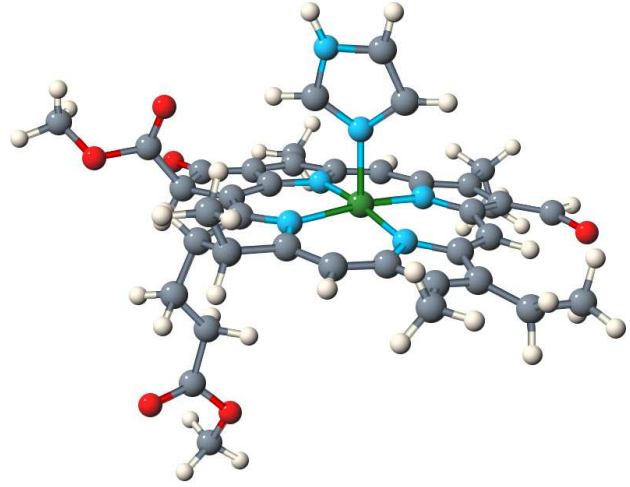
The UV/VIS Spectrum of Free-Base Porphyrin



UV/VIS Spectra of Chlorophylls

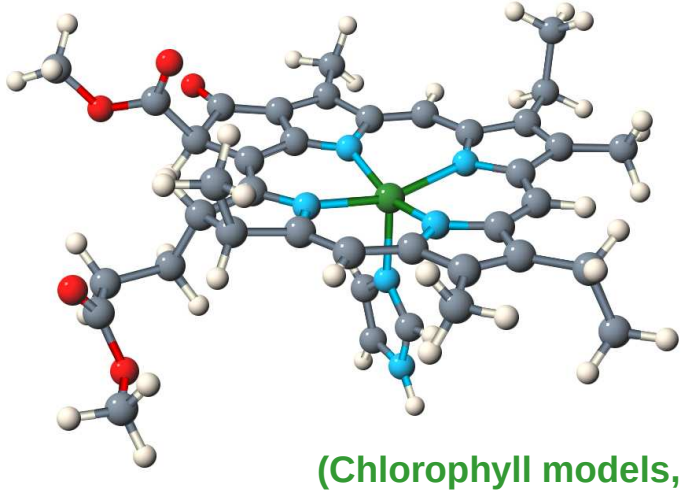
Chlorophyll a anti

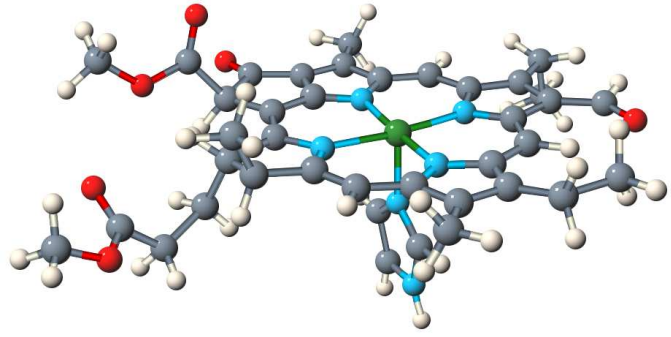




Chlorophyll b anti

Chlorophyll a syn





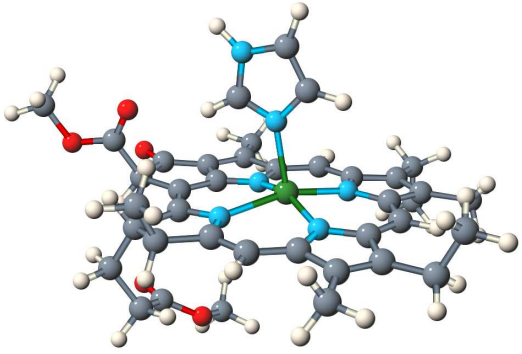
Chlorophyll b syn

(Chlorophyll models, Silviu Balaban, INT)

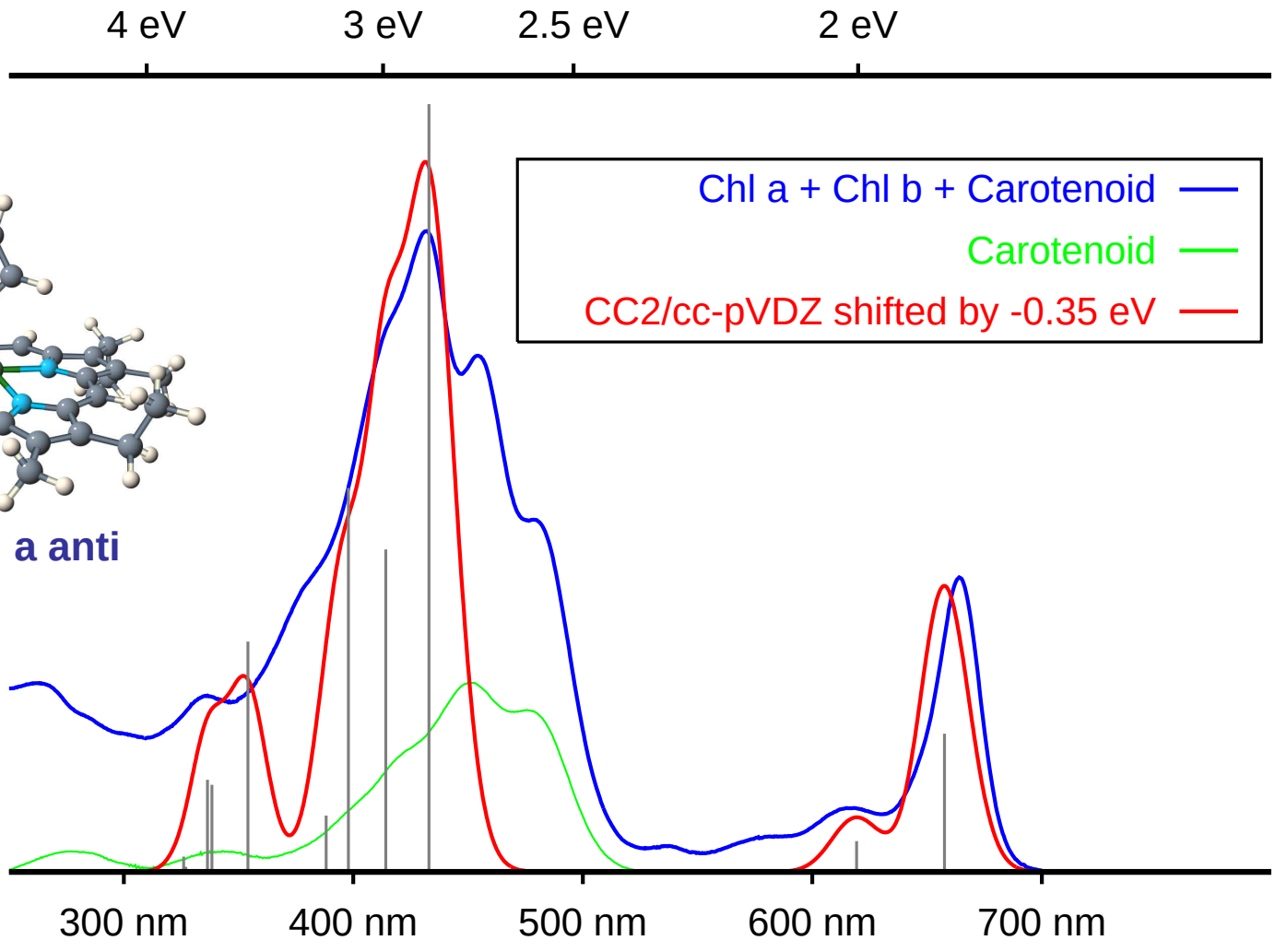
Computational Details:

- 93/92 atoms (51/49 non-hydrogen), $> 260\ e^-$ correlated
- DFT/B3LYP/TZVP optimized geometry
- CC2/cc-pVDZ (938 bf, 3464 aux. bf) for vertical excit. energies

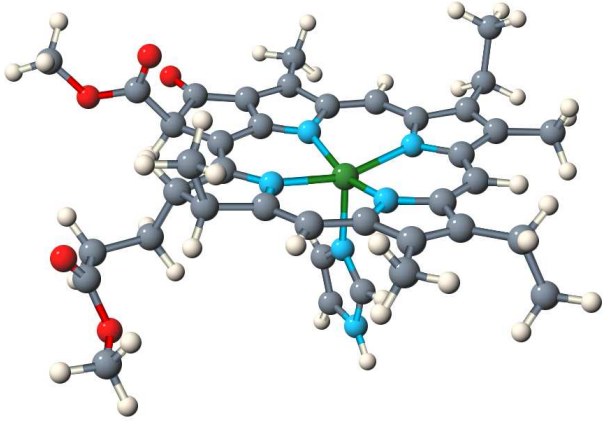
UV/VIS Spectra of Chlorophylls



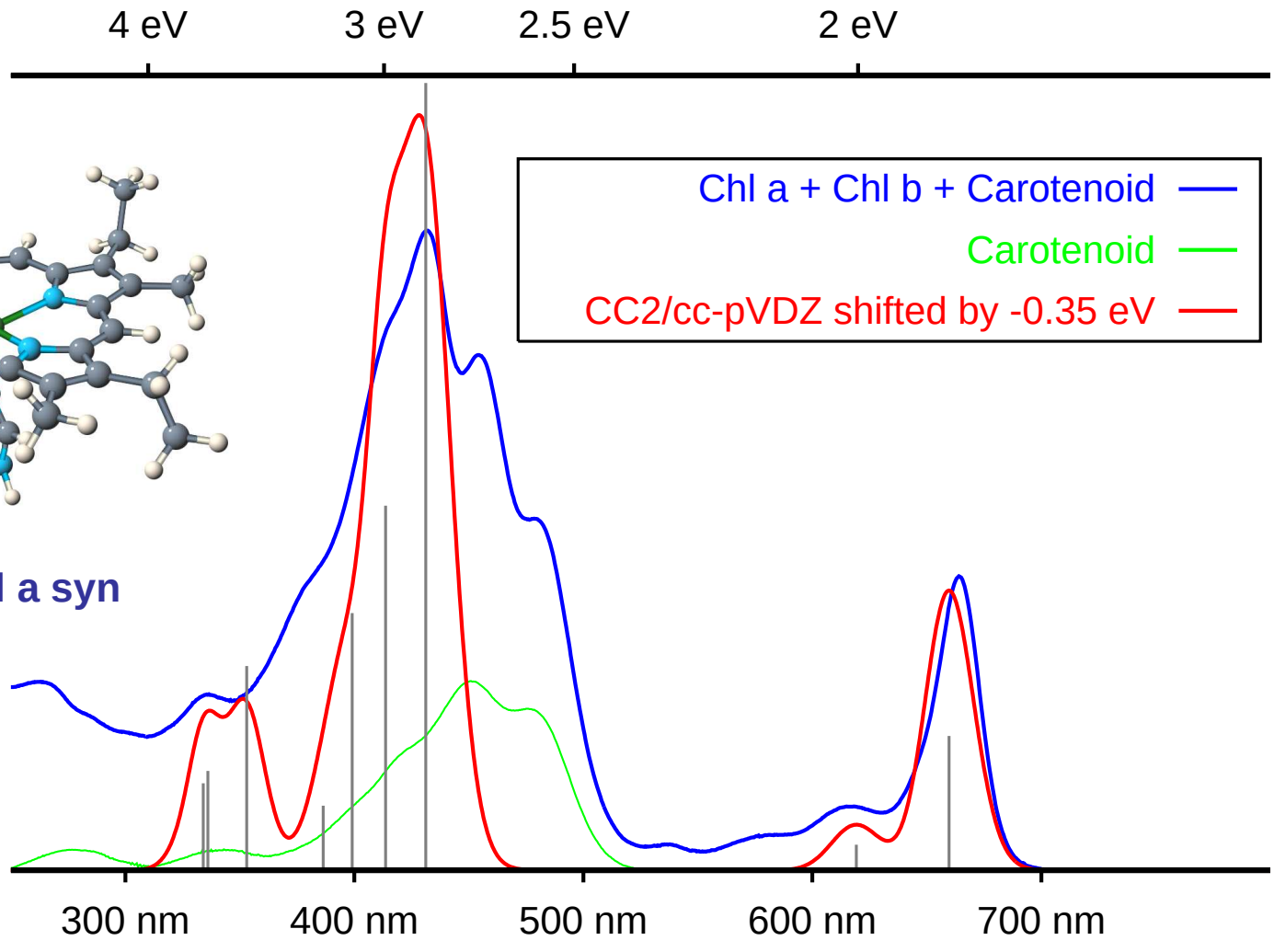
Chlorophyll a anti



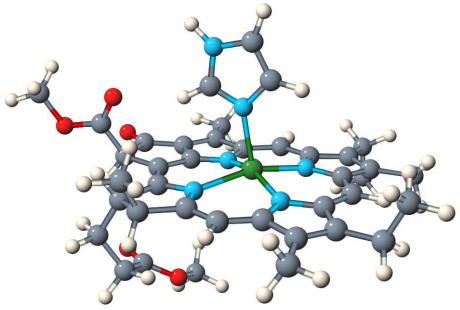
UV/VIS Spectra of Chlorophylls



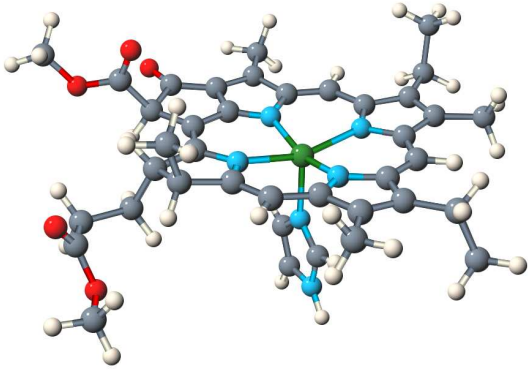
Chlorophyll a syn



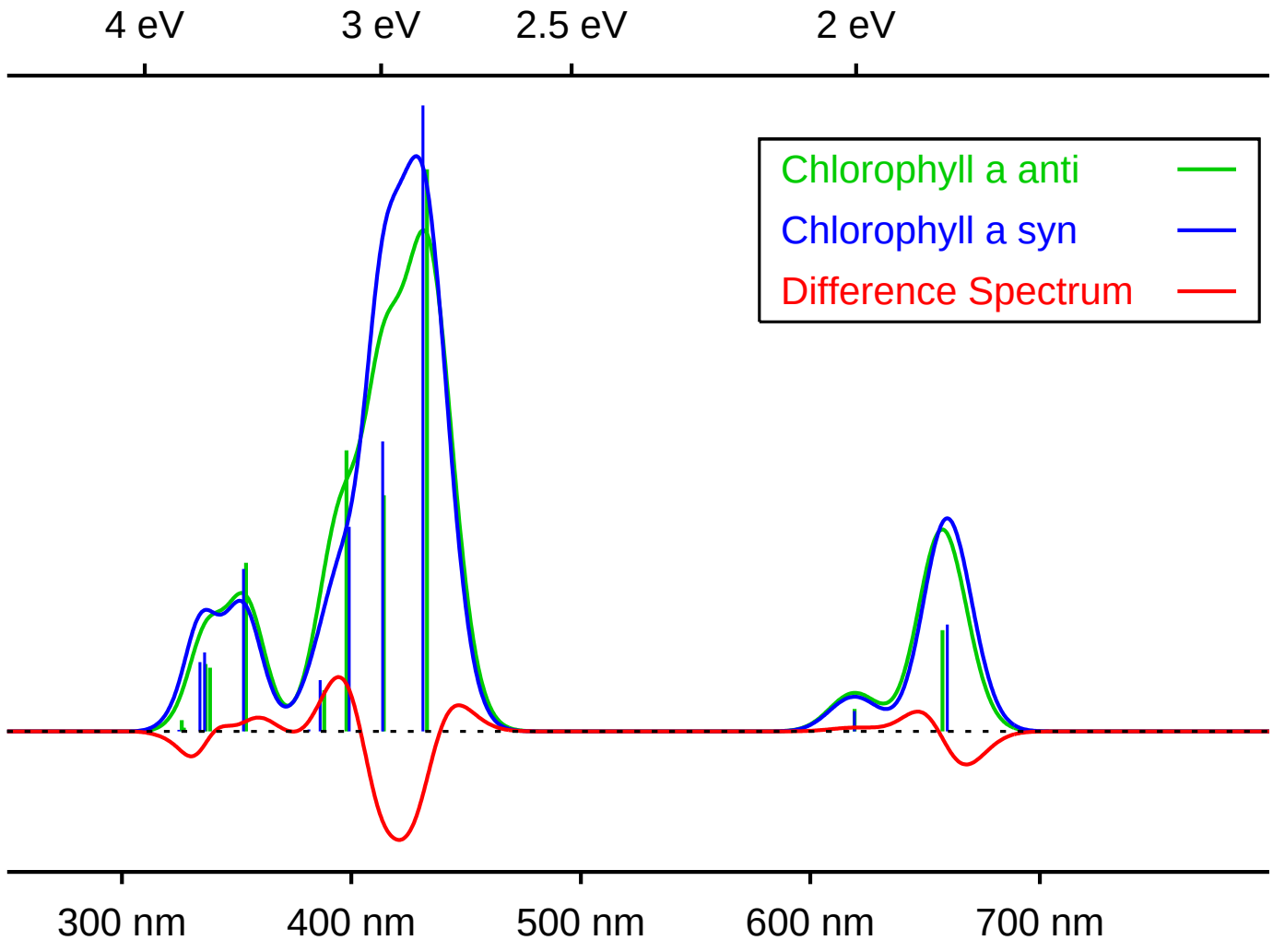
UV/VIS Spectra of Chlorophylls



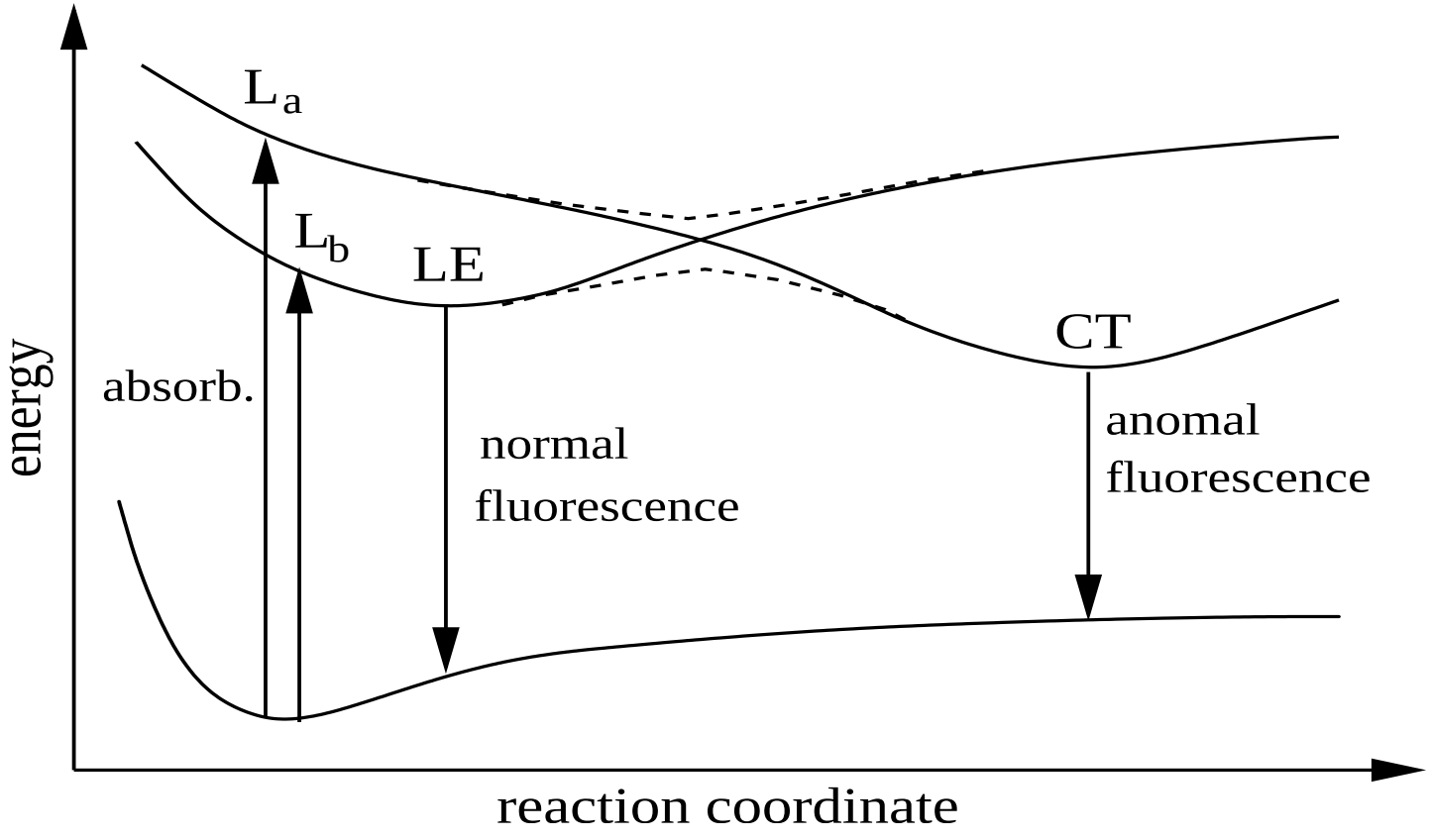
Chlorophyll a anti

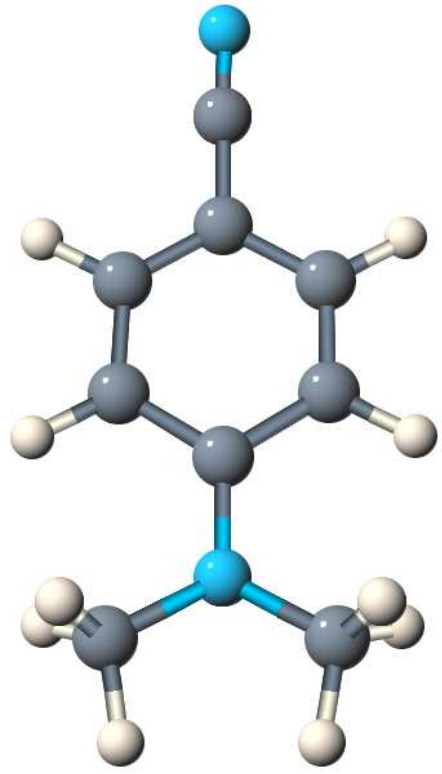


Chlorophyll a syn



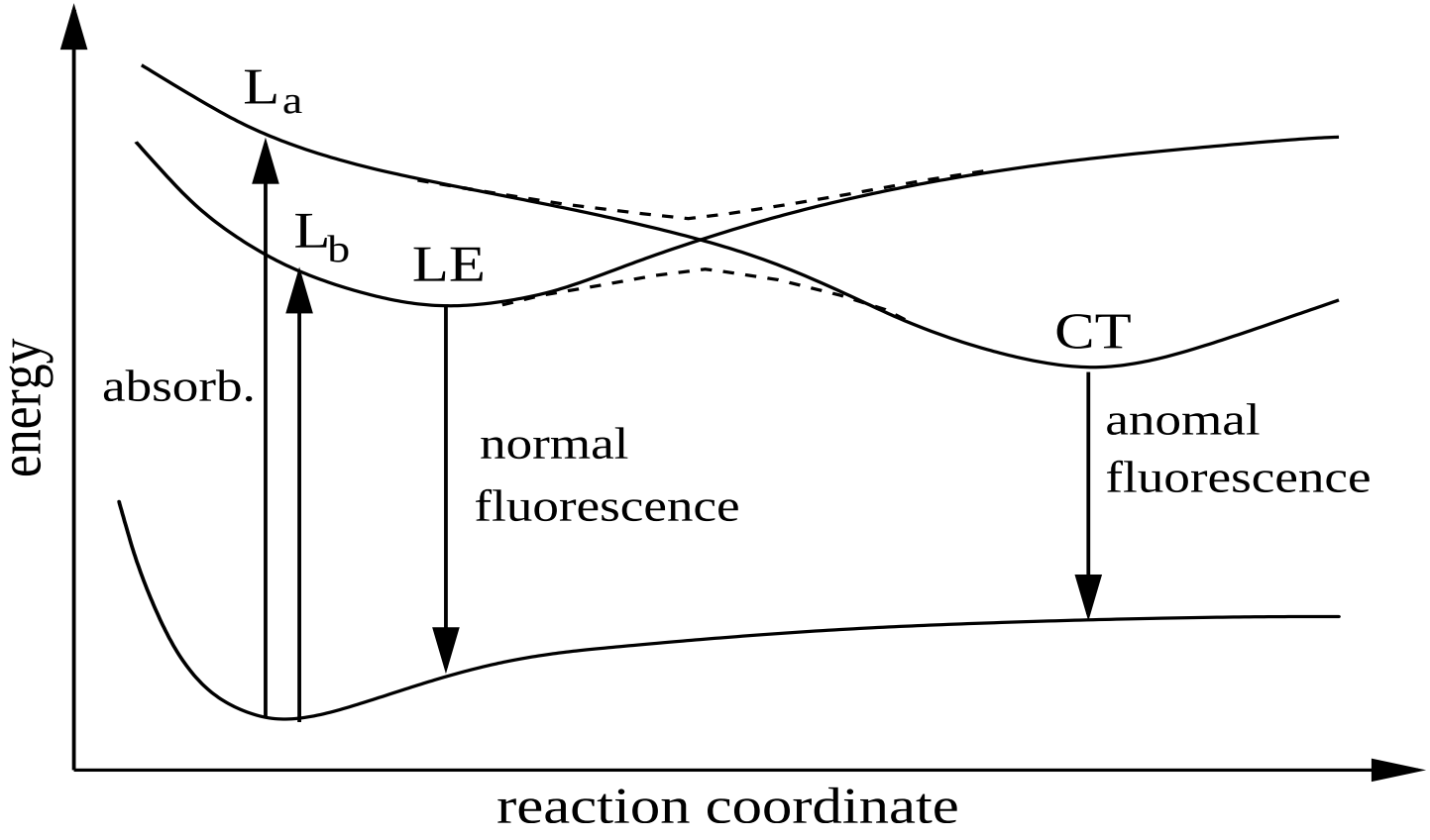
Dual Fluorescence in Dimethylaminobenzonitril (DMABN)

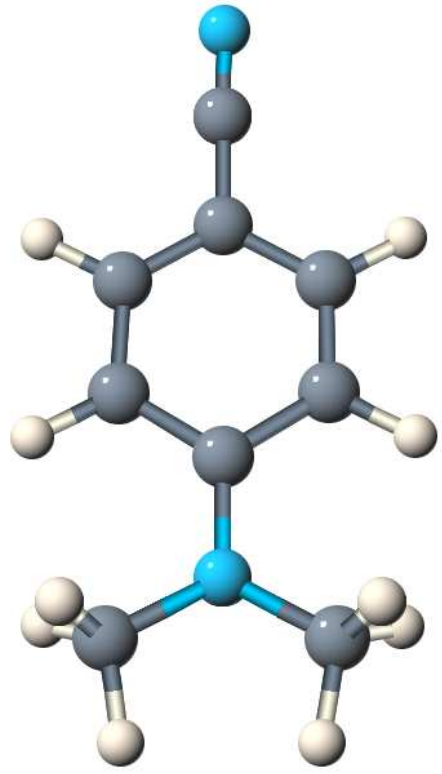




C_S symmetry

Dual Fluorescence in Dimethylaminobenzonitril (DMABN)





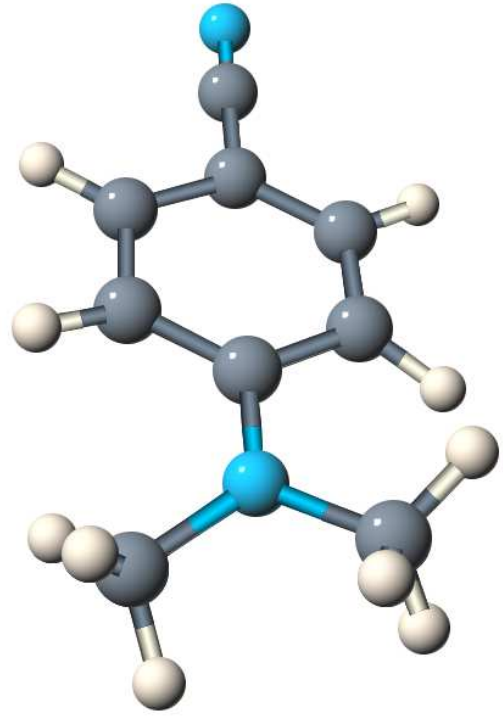
C_S symmetry

vertical excitation energies at the S_0 equilibrium geometry:

State	CC2/TZVPP		CC2/aug-cc-pVTZ		Exp
	ΔE	TS	ΔE	TS	
$^1A''$ (L_b, LE)	4.41 eV	0.029	4.37 eV	0.030	4.25 eV
$^1A'$ (L_a, CT)	4.77 eV	0.615	4.64 eV	0.407	4.56 eV

The Locally Excited State in Dimethylaminobenzonitril (DMABN)

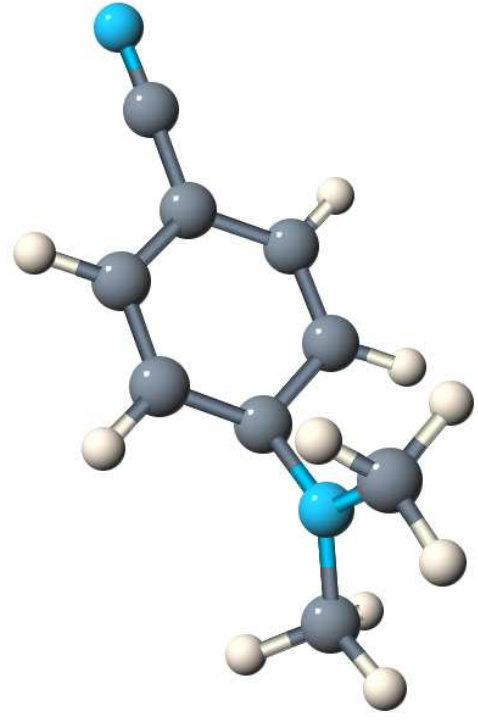
	CC2/TZVPP	Exp.
μ	10.1 D	9.7 D
ΔE	3.78 eV	
ν_{00}	3.96 eV	3.998 eV
torsion	19°	0–30° (?)
$\nu(\mathrm{Ph-NMe_2})$	1353 (-37) cm^{-1}	1423 cm^{-1} (?)
$\nu(\mathrm{Ph-CN})$	1181 (-55) cm^{-1}	
$\nu(\mathrm{C{\equiv}N})$	2074 (-30) cm^{-1}	2181 (-38) cm^{-1}



C_2 symmetry

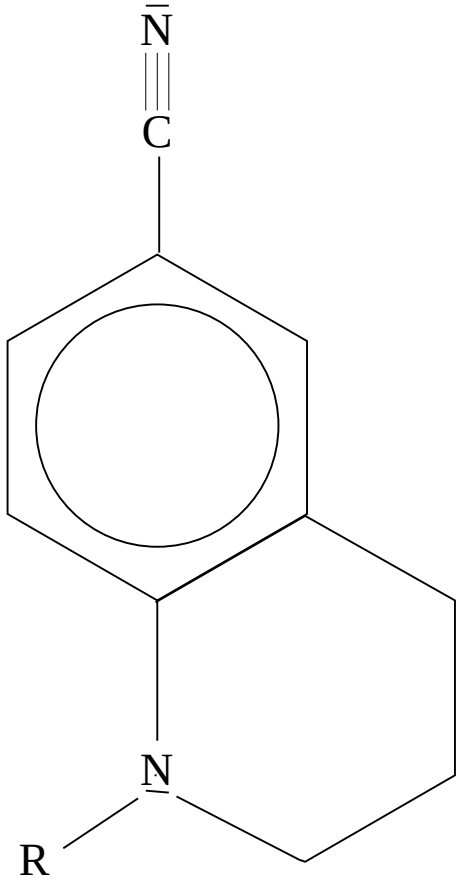
The Charge Transfer State in Dimethylaminobenzonitril (DMABN)

	CC2/TZVPP	Exp.
μ	13.3 D	15.1 D
ΔE	2.49 eV	2.8 – 3.2 eV
ν_{00}	3.91 eV	
torsion	90°	
$\nu(\mathrm{Ph-NMe_2})$	1274 (-116) cm^{-1}	1281 (-91) cm^{-1}
$\nu(\mathrm{Ph-CN})$	1224 (-11) cm^{-1}	1221 (-6) cm^{-1}
$\nu(\mathrm{C{\equiv}N})$	2043 (-61) cm^{-1}	2095 (-124) cm^{-1}



(almost) C_S symmetry

Dual Fluorescence in Sterically Hindered Aminobenzonitrils



Expected:

- aliphatic 6-ring hinders rotation of amino group

  $\Longrightarrow$ if mechanism for anomal fluorescence involves a TICT structure it should be blocked

Experimental observation:

- **no dual fluorescence** observed for
  - R = methyl, $-CH_3$: NMC6

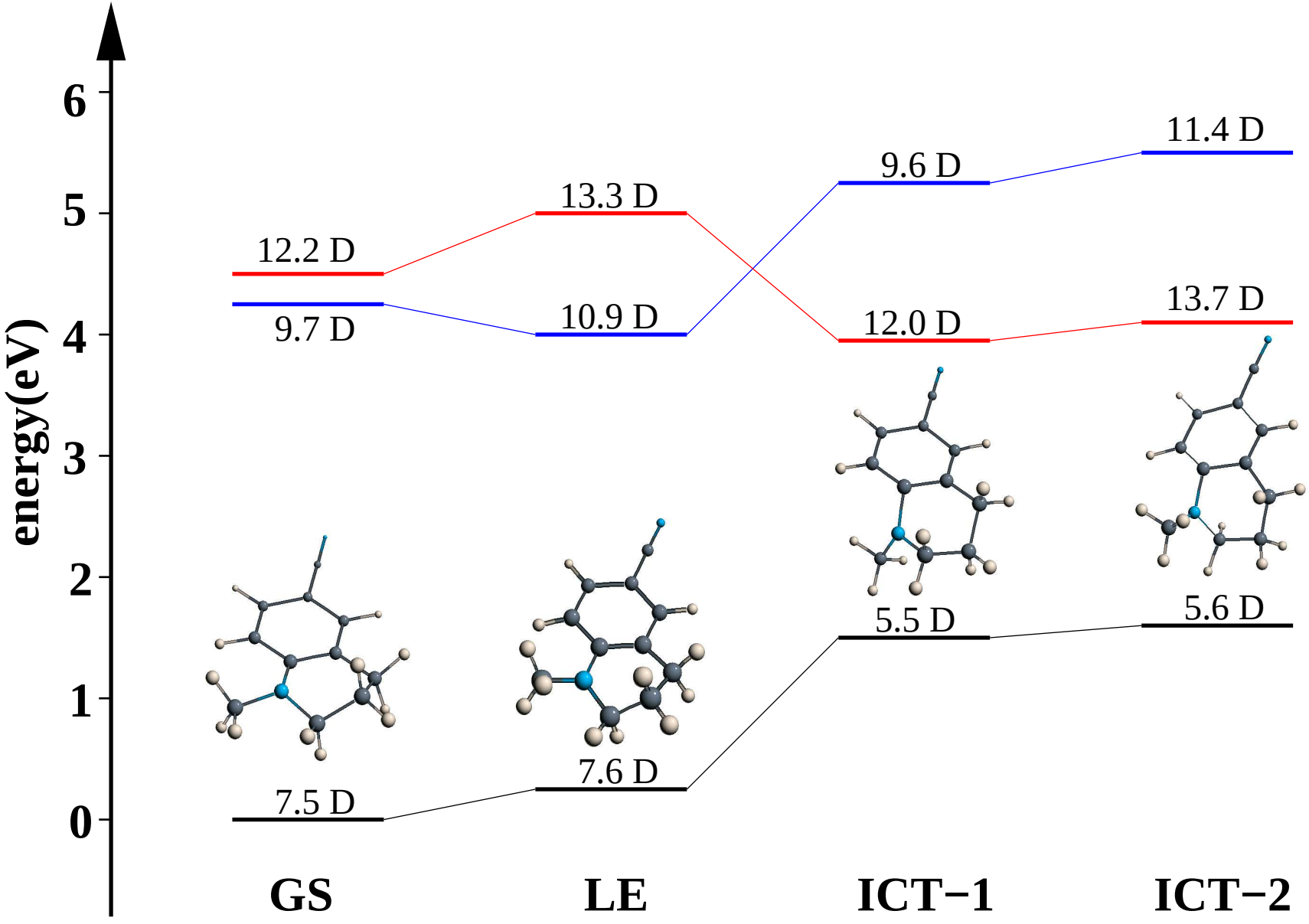
    (1-Methyl-6-cyano-1,2,3,4-tetrahydroquinoline)
  - R = ethyl, $-CH_2-CH_3$: NEC6

    (1-Ethyl-6-cyano-1,2,3,4-tetrahydroquinoline)
- **dual fluorescence is** observed for
  - R = *tert*-butyl, $-C(CH_3)_3$: NTC6

    (1-*tert*-Butyl-6-cyano-1,2,3,4-tetrahydroquinoline)

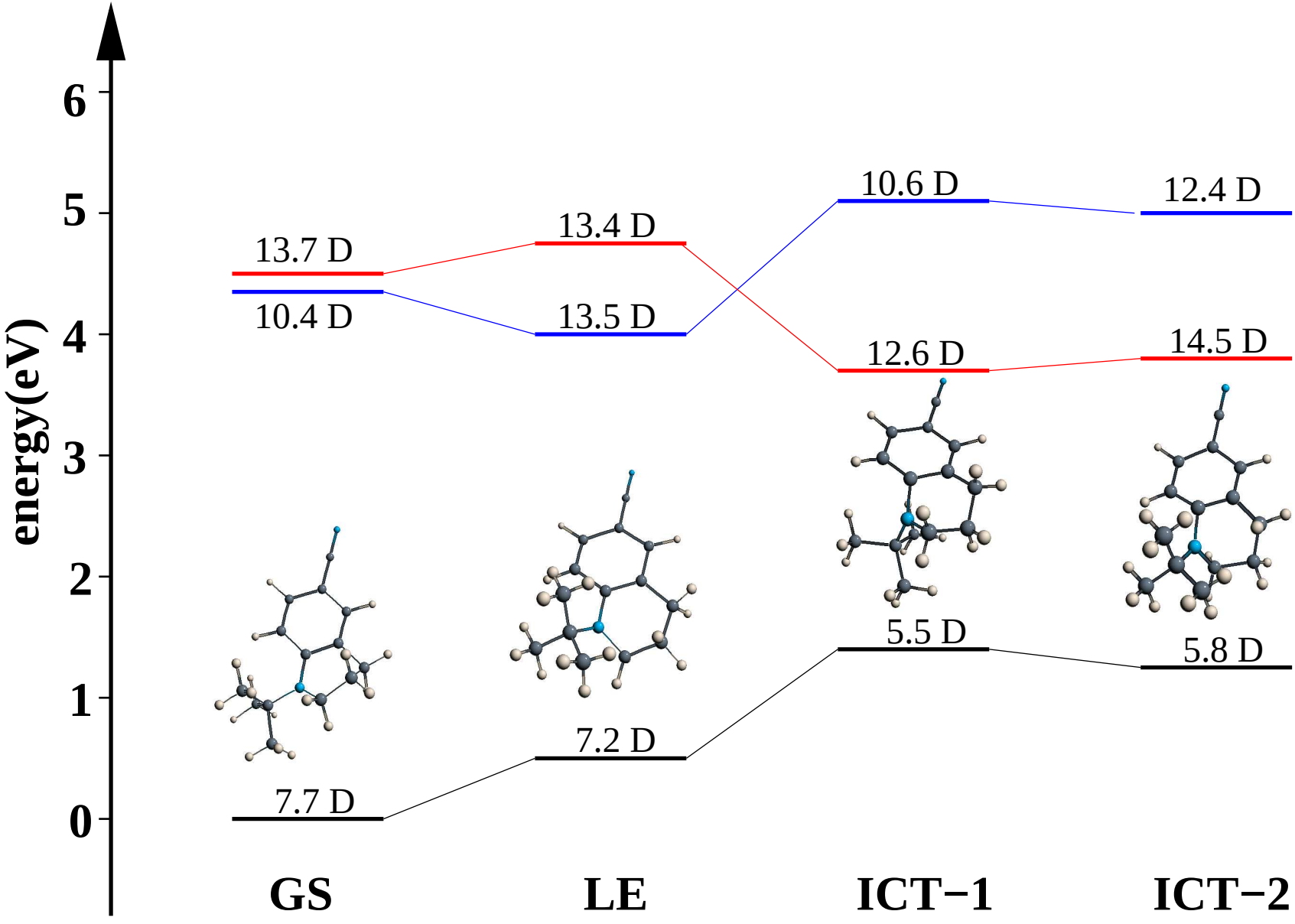
Lowest Excited States of NMC6

(1-Methyl-6-cyano-1,2,3,4-tetrahydroquinoline)

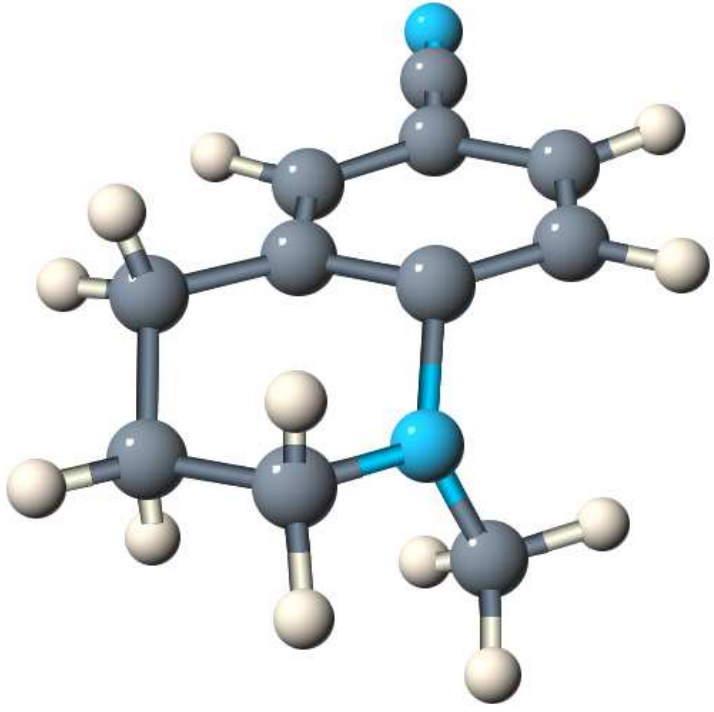


Lowest Excited States of NTC6

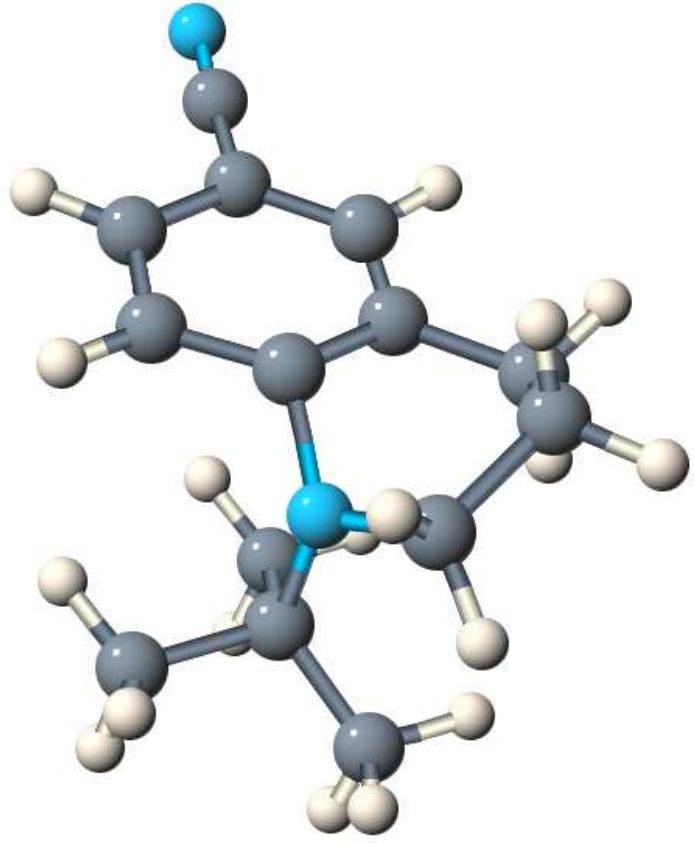
(1-*tert*-Butyl-6-cyano-1,2,3,4-tetrahydroquinoline)



TICT States in Sterically Hindered Aminobenzonitrils

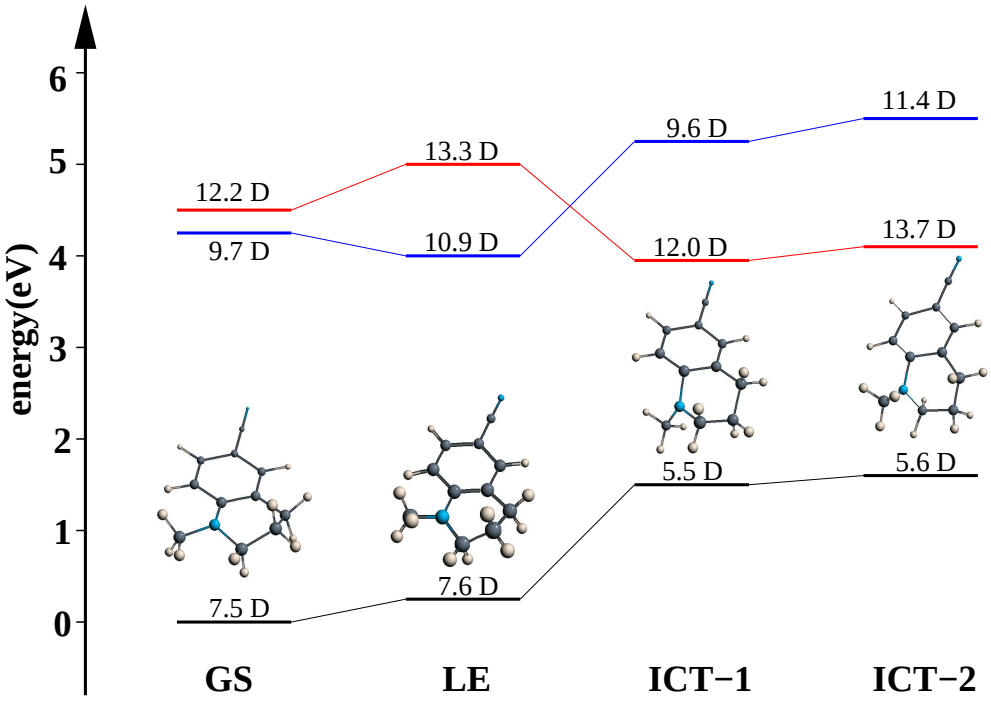


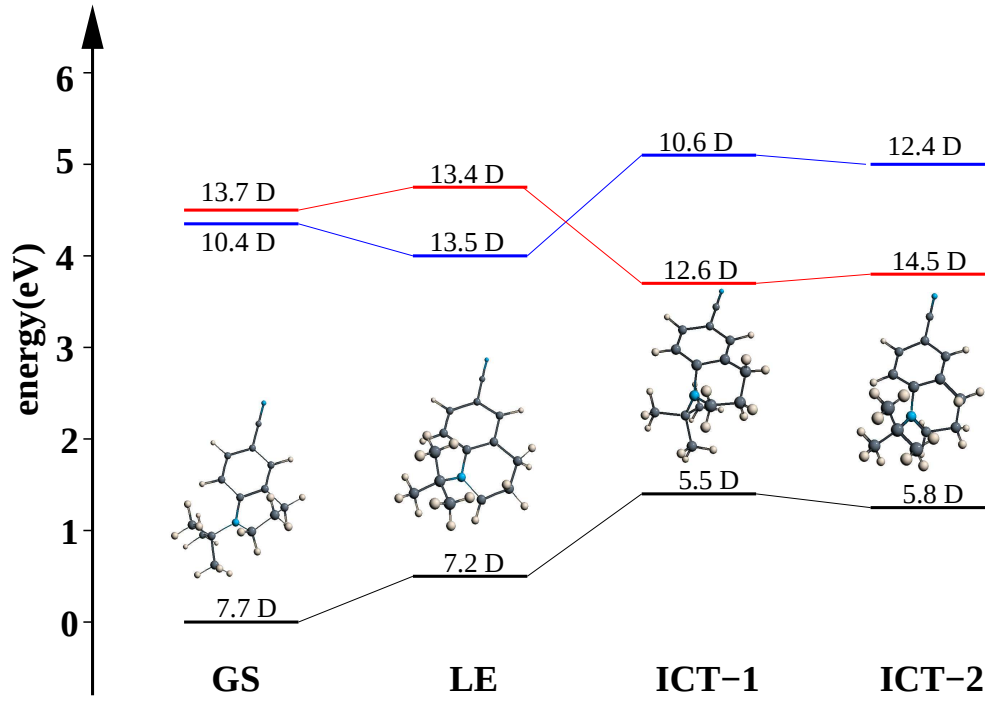
1-Methyl-6-cyano-
1,2,3,4-tetrahydroquinoline



1-*tert*-Butyl-6-cyano-
1,2,3,4-tetrahydroquinoline

Lowest Excited States of NMC6 and NTC6





- aliphatic 6-ring hinders the rotation of the amino group only slightly
- bulky substituents destabilize the planar (non-twisted) geometries of the ground and the locally excited states

$\Longrightarrow$ calculations and experimental findings in agreement with TICT hypotheses!

Summary

- **CC2 provides an "extension" of MP2 to excited states:**
  - excitation energies: vertical $\approx \pm$ 0.3 eV, adiabatic $\approx \pm$ 0.2 eV
  - $\Delta r_e \approx \pm 1 - 2\text{pm}$; $\Delta \omega_e \approx \pm 50 - 100\text{cm}^{-1}$

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  max. $\approx$. 12 atoms $\longrightarrow$ 40 – 60 atoms

  together with parallelization: $\longrightarrow$ 60 – 100 atoms

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- **Alternative to TDDFT calculations**
  - for: charge-transfer, valence-Rydberg mixing, anions
  - if: single excited states out of single-reference ground state