Response Theory, Excitation Energies & Frequency-dependent Properties for Coupled-Cluster Wavefunctions

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- Part I: Response-Theory for Nonvariational Wavefunctions
- Part II: Accurate Frequency-dependent Properties
- Part III: Energies & Structures for Excited States

Part I

Response Theory for Nonvariational Wavefunctions

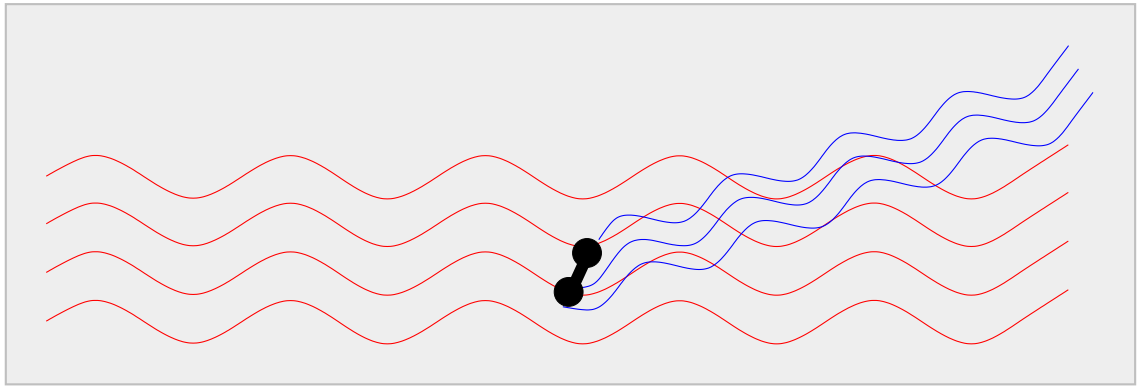
Part I

Response Theory for Nonvariational Wavefunctions

- Response theory for variational & nonvariational methods
- Requirements for wavefunctions in response theory
- Hierarchy of coupled-cluster response methods

What is Response Theory?

Consider a molecule perturbed by oscillating electromagnetic fields:

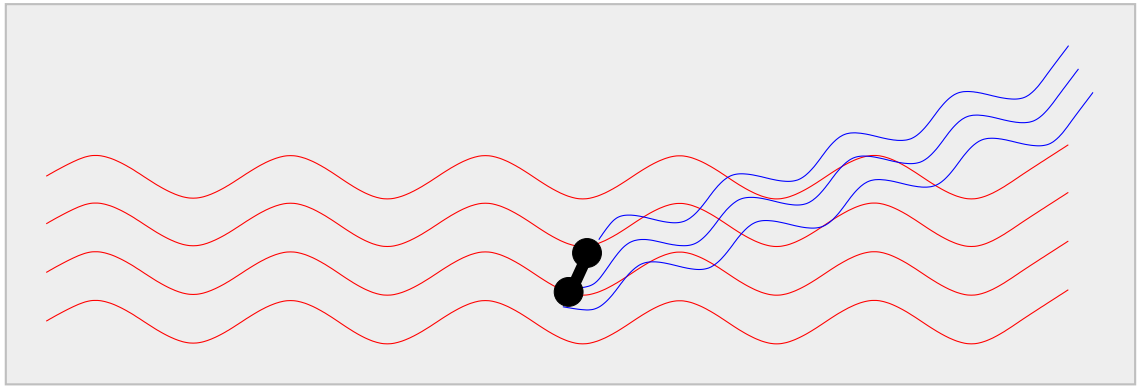


$$H(t) = H^{(0)} + \sum_j V_j \boxed{f_j(\omega_j) e^{-i\omega_j t}}$$

field strengths

What is Response Theory?

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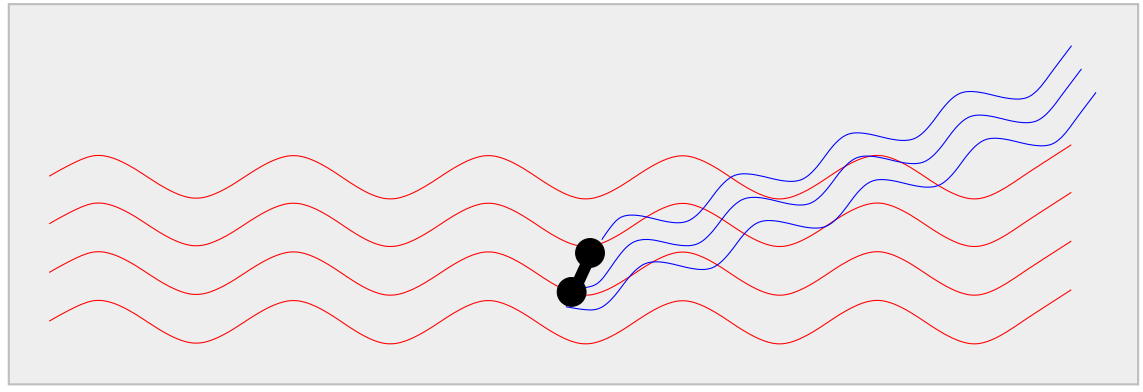
Investigate wavefunction, properties, etc. as function of the frequency:

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

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

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

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

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

response functions

Properties Accessible Through Response Theory

Response functions $\langle\langle V_1; V_2 \rangle\rangle_\omega$, $\langle\langle V_1; V_2, V_3 \rangle\rangle_{\omega_2,\omega_3}$, . . . :

- freq.-dep. polarizabilities $\alpha_{ij}(\omega) = \langle\langle \mu_i; \mu_j \rangle\rangle_\omega$
- freq.-dep. hyperpolarizabilities (Kerr, ESHG, THG, etc.)
  $\beta_{ijk}(\omega) = \langle\langle \mu_i; \mu_j, \mu_k \rangle\rangle_{\omega_j,\omega_k}$, $\gamma_{ijkl}(\omega) = \langle\langle \mu_i; \mu_j, \mu_k, \mu_l \rangle\rangle_{\omega_j,\omega_k,\omega_l}$, . . .
- nonlinear magneto-optical properties

Poles of $\langle\langle V_1; V_2 \rangle\rangle_\omega$:

- excitation and ionization energies

Residues of $\langle\langle V_1; V_2 \rangle\rangle_\omega$, $\langle\langle V_1; V_2, V_3 \rangle\rangle_{\omega_2,\omega_3}$, . . . :

- oscillator and rotatory strengths
- two-, three-, etc. photon transition strengths
- intensities for magnetic circular dichroism

Response Functions, Poles & Residues

sum-over-states expression for frequency-dependent polarizability:

$$\alpha_{ij}(\omega) = \sum_{n \neq 0} \left\{ \frac{\langle 0|\mu_i|n\rangle\langle n|\mu_j|0\rangle}{E_n - E_0 - \omega} + \frac{\langle 0|\mu_i|n\rangle\langle n|\mu_j|0\rangle}{E_n - E_0 + \omega} \right\}$$

- **Poles:** at $\omega = \pm(E_n - E_0)$

  $\rightsquigarrow$ excitation energies

- **Residues:**

$$\lim_{\omega \to \pm(E_n - E_0)} (E_n + E_0 \pm \omega)\alpha_{ij}(\omega) = \langle 0|\mu_i|f\rangle\langle f|\mu_j|0\rangle$$

  $\rightsquigarrow$ transition strengths

The Phase-isolated Wavefunction

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

$$\Downarrow \qquad \text{static limit } \omega \to 0 \qquad \Downarrow$$

$$\Psi(t) \;=\; \boxed{\left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(0)\; f_j(0) + \ldots\right]} e^{-i(t-t_0)\langle \widetilde{\Psi} | H | \widetilde{\Psi}\rangle}$$

time-independ. wavefunction

The Phase-isolated Wavefunction

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

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time-independ. wavefunction

Taylor series expansion of $\Psi(t)$:

$$\Psi(t) \;=\; \Psi^{(0)}(t) + \sum_j \Psi_j^{(1)}(t, \omega_j)\; f_j(\omega_j) e^{-i\omega_j t} + \ldots$$

The Phase-isolated Wavefunction

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

$\Downarrow$ static limit $\omega \to 0$ $\Downarrow$

$$\Psi(t) = \boxed{\left[\Psi^{(0)} + \sum_j \Psi_j^{(1)}(0)\, f_j(0) + \ldots\right]} e^{-i(t-t_0)\langle\widetilde{\Psi}|H|\widetilde{\Psi}\rangle}$$

time-independ. wavefunction

~~Taylor series expansion of $\Psi(t)$:~~

$$\Psi(t) = \Psi^{(0)}(t) + \sum_j \Psi_j^{(1)}(t, \omega_j)\, f_j(\omega_j) e^{-i\omega_j t} + \ldots$$

singular in the static limit!

The Phase-isolated Wavefunction

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

$F(t)$ real for normalized $\widetilde{\Psi}(t)$

phase-isolated wavefunction $\widetilde{\Psi}(t)$

- Phase factor does not contribute to expectation values:

$$\langle V\rangle(t) \;=\; \langle\widetilde{\Psi}(t)e^{-i\int_{t_0}^{t} dt' F(t)}|V|\widetilde{\Psi}(t)e^{-i\int_{t_0}^{t} dt' F(t)}\rangle = \langle\widetilde{\Psi}(t)|V|\widetilde{\Psi}(t)\rangle$$

(assuming that V does not contain differentation w.r.t to time $\frac{\partial}{\partial t}$)

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 ...

- Obtain response functions by expansion of

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

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:

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

Symmetries of Response Functions

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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:

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

The Quasienergy of Floquet States

combine perturbation theory with Floquet theory for periodic systems:

- extended Hilbert space including time integration:

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

- quasienergy of Floquet state:

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

- variation principle:

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

- response functions obtained as derivatives of the quasienergy:

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

The Quasienergy of Floquet States

Advantages for periodic time-dependence:

- variational formulation analogous to time-indep. theory:

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

- simple generalization of time-**in**dependent theory:

$$\begin{aligned} \widetilde{\Psi} = \Psi^{(0)} + \Sigma_j \Psi_j^{(1)} f_j \quad &\longrightarrow \quad \widetilde{\Psi}(t) = \Psi^{(0)} + \Sigma_j \Psi_j^{(1)}(\omega_j) f_j(\omega_j) e^{-i\omega_j t} \\ H \quad &\longrightarrow \quad H - i\frac{\partial}{\partial t} \end{aligned}$$

- leads to correct symmetries:

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

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

Lagrange Functional for Nonvariational Methods

- time-independent Lagrange functional for energy:

variational $\longrightarrow$ nonvariational

$$E \longrightarrow L = \mathrm{Re}\{E + \underbrace{\sum_{\mu} \bar{t}_{\mu}\, \Omega_{\mu}}\}$$

constraints/equations for non-variational methods

Lagrange Functional for Nonvariational Methods

- time-independent Lagrange functional for energy:

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constraints/equations for non-variational methods

- mathematical framework for efficient formulation of derivatives:

$$\frac{\partial L}{\partial t} = 0 \qquad \frac{\partial L}{\partial \bar{t}} = 0$$

2n+1 rule for wavefunctions variables t

2n+2 rule for Lagrange multipliers $\bar{t}$

e.g. $t^{(0)}, \bar{t}^{(0)}, t^{(1)}$ sufficient for 2. derivatives (hessian, polarizability, etc.)

$t^{(0)}, \bar{t}^{(0)}, t^{(1)}, \bar{t}^{(1)}$ sufficient for 3. derivatives (1. hyperpolarizability)

Response Theory for Nonvariational Methods

variational $\longrightarrow$ nonvariational

$$Q \longrightarrow \{L\}_T = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} \mathrm{Re}\left\{\left\langle H - i\frac{\partial}{\partial t}\right\rangle + \overline{t}_\mu \,\Omega_\mu\right\} dt$$

Response Theory for Nonvariational Methods

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$$Q \longrightarrow \{L\}_T = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} \mathrm{Re}\left\{\left\langle H - i\frac{\partial}{\partial t}\right\rangle + \bar{t}_\mu\,\Omega_\mu\right\} dt$$

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

Response Theory for Nonvariational Methods

variational $\longrightarrow$ nonvariational

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- variation principle: $\delta\int_{t_0}^{t_0+\tau} L\,dt = 0$

Response Theory for Nonvariational Methods

variational $\longrightarrow$ nonvariational

$$Q \longrightarrow \{L\}_T = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} \mathrm{Re}\left\{\left\langle H - i\frac{\partial}{\partial t}\right\rangle + \bar{t}_\mu\,\Omega_\mu\right\} dt$$

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- variation principle: $\delta\int_{t_0}^{t_0+\tau} L\,dt = 0 \quad \Rightarrow \quad \frac{d\{L\}_T}{d\bar{t}_{\mu_i}} = 0 \qquad \frac{d\{L\}_T}{dt_{\mu_i}} = 0$

Response Theory for Nonvariational Methods

variational $\longrightarrow$ nonvariational

$$Q \longrightarrow \{L\}_T = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} \mathrm{Re}\left\{\left\langle H - i\frac{\partial}{\partial t}\right\rangle + \bar{t}_\mu\,\Omega_\mu\right\} dt$$

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- response functions: $\langle\langle A;B,C,\ldots\rangle\rangle_{\omega_B,\omega_C,\ldots} = -\left.\frac{d^n\{L\}_T}{df_A\,df_B\,df_C\ldots}\right|_0$

Lagrange Functional & Time-dependent Theory

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

- quantum mechanical Lagrange functional for phase-isolated wavefunction:
- variation principle

$$\delta \int_{t_1}^{t_2} L(t) dt = 0$$

- Euler-Lagrange equations of motion

$$\delta L(t) + i\frac{\partial}{\partial t} \langle \tilde{\Lambda}(t) | \delta \widetilde{\mathrm{CC}}(t) \rangle = 0$$

Coupled-Cluster Response Theory

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

- 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 Ω_{μ_i}

- variation principle: $\delta \int_{t_0}^{t_0+\tau} L\, dt = 0 \quad \Rightarrow \quad \frac{d\{L\}_T}{d\bar{t}_{\mu_i}} = \Omega_{\mu_i} = 0$ and $\frac{d\{L\}_T}{dt_{\mu_i}} = 0$

Coupled-Cluster Response Theory

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

- quasienergy Lagrangian for coupled-cluster methods:

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- **ansatz for cluster amplitudes:** $t_{\mu_i} = t_{\mu_i}^{(0)} + t_{\mu_i}^{(1)}\, f(\omega) e^{-i\omega t} + \ldots$

Coupled-Cluster Response Theory

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

- quasienergy Lagrangian for coupled-cluster methods:

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

- variation principle: $\delta \int_{t_0}^{t_0+\tau} L\, dt = 0$

- **ansatz for cluster amplitudes:** $t_{\mu_i} = t_{\mu_i}^{(0)} + t_{\mu_i}^{(1)} f(\omega) e^{-i\omega t} + \ldots$

- **"response" equations for $\mathbf{t}_{\mu_i}^{(1)}$:** $\left. \frac{d\Omega_{\mu_i}}{d f(\omega)} \right|_{f=0} = 0$

Coupled-Cluster Response Theory

- 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 Ω_{μ_i}

- ansatz for cluster amplitudes: $t_{\mu_i} = t_{\mu_i}^{(0)} + t_{\mu_i}^{(1)} f(\omega) e^{-i\omega t} + \ldots$

- "response" equations for $t_{\nu_j}^{(1)}$: $\left.\frac{d\Omega_{\mu_i}}{df(\omega)}\right|_{f=0} = 0$

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

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

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

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

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

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:

$$L = \left\langle H - i\frac{\partial}{\partial t} \right\rangle + \underbrace{\sum_{\mu} \bar{t}_{\mu}\,\Omega_{\mu}}$$

constraints for
non-variational methods

variational methods:

symmetric electronic Hesse matrix

$$H_{\mu\nu} = \left(\frac{d^2 L}{dt_{\mu}\, dt_{\nu}}\right)_0$$

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

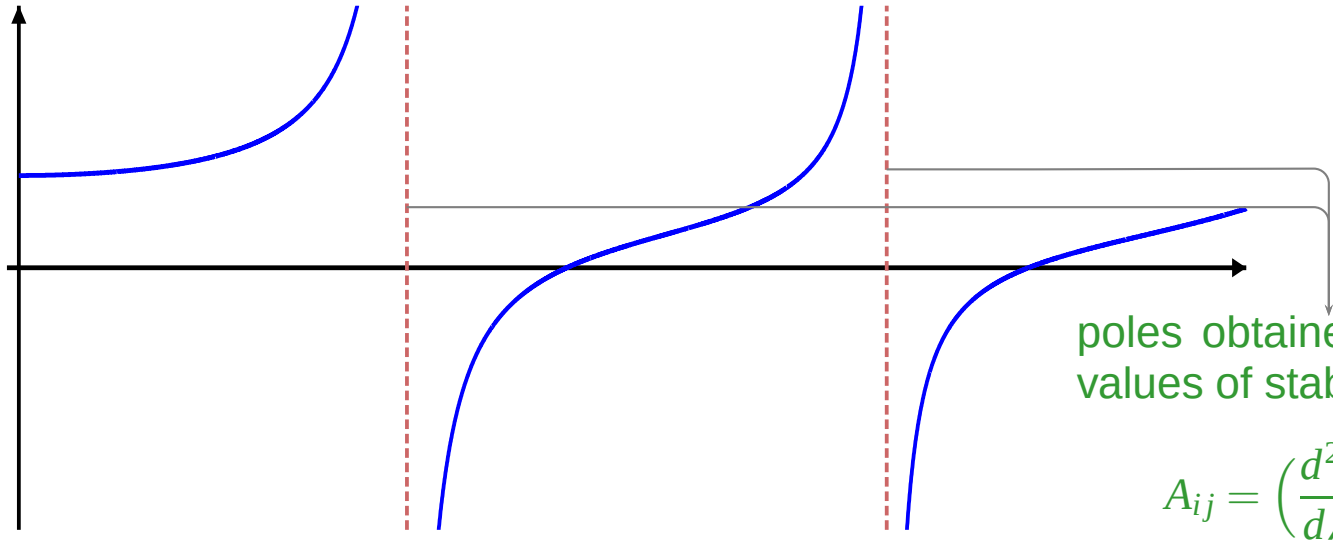
non-variational methods:

asymmetric electronic Jacoby matrix

$$A_{\mu\nu} = \left(\frac{d^2 L}{d\bar{t}_{\mu}\, dt_{\nu}}\right)_0$$

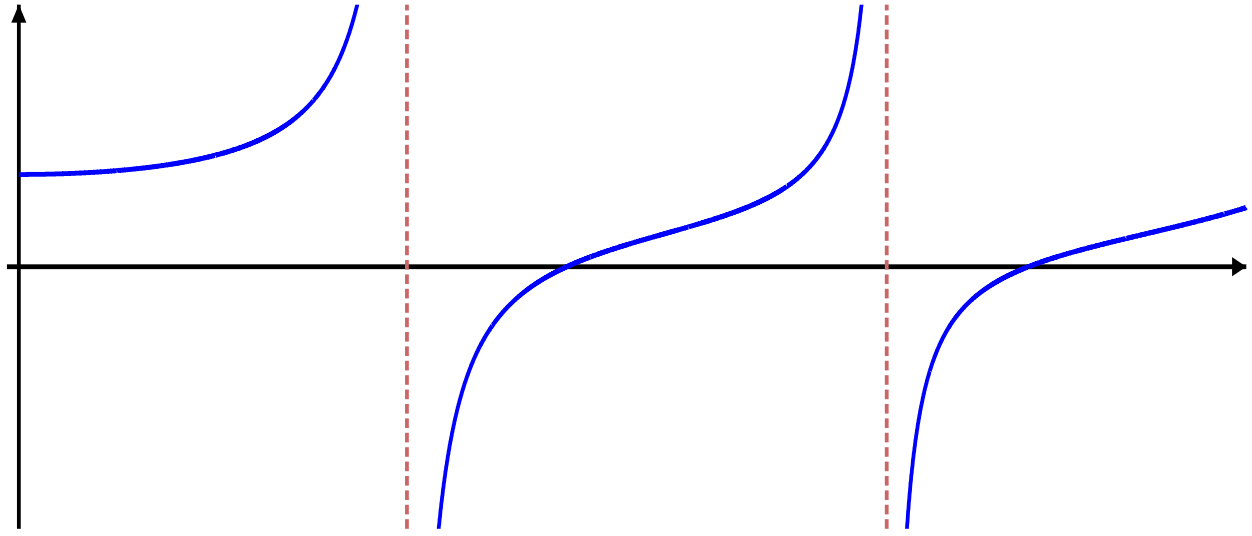
$$\left(\mathbf{A} - \omega_k \mathbf{S}\right)\vec{c}^{(k)} = 0$$

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

Requirements for Wavefunction Ansatz



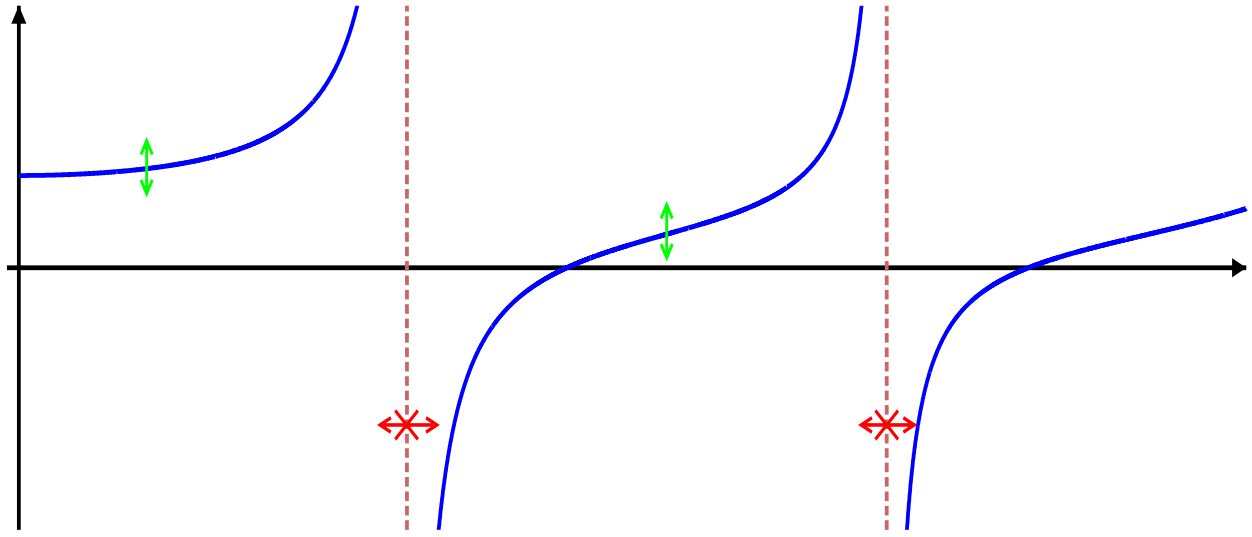
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  - CC response based on unperturbed Hartree-Fock determinant:

$$\left|\widetilde{\mathrm{CC}}(t)\right\rangle = \exp\left(\sum_{\mu} t_{\mu}(t)\hat{\tau}\right)\left|\mathrm{HF}\right\rangle$$

orbital-relaxed: ~~$\left|\widetilde{\mathrm{CC}}(t)\right\rangle = \exp\left(\sum_{\mu} t_{\mu}(t)\hat{\tau}\right)\left|\mathrm{HF}(t)\right\rangle$~~

$\rightsquigarrow$ ~~two sets of single excitation poles!~~

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
- 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

Requirements for Wavefunction Ansatz

- MP2 based approaches:
  - MBPT-2 dbl. pert. theory
  - PED-MP2
  - QED-MP2
  - TDMP2

↷ good results only far away from poles (e.g. for imaginary frequencies)

Requirements for Wavefunction Ansatz

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  - PED-MP2
  - QED-MP2
  - TDMP2

↷ good results only far away from poles (e.g. for imaginary frequencies)

- truncated CI methods:
  - $|\Psi^{(1)}\rangle = \sum_{f\neq 0} \frac{|f\rangle\langle f|}{E_f - E_0 - \omega} V|0\rangle$ cmp. $|\mathrm{CC}^{(1)}\rangle = T^{(1)}\exp(T)|\mathrm{HF}\rangle$

↷ requires triple excitations for dynamic correlation in $\Psi^{(1)}$,
i.e. polarizabilities and other second-order properties . . .

↷ CI ansatz inefficient for freq.-dep. properties

“Lego” Bricks for CC Response Theory

- **12 building blocks for all CC response functions/residues:**

$$A_{\mu\nu} = \left(\frac{\partial^2 L}{\partial \bar{t}_\mu \partial t_\nu}\right)_0 \qquad F_{\mu\nu} = \left(\frac{\partial^2 L}{\partial t_\mu \partial t_\nu}\right)_0$$

$$B_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial \bar{t}_\mu \partial t_\nu \partial t_\gamma}\right)_0 \qquad G_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial t_\mu \partial t_\nu \partial t_\gamma}\right)_0$$

$$C_{\mu\nu\gamma\eta} = \left(\frac{\partial^4 L}{\partial \bar{t}_\mu \partial t_\nu \partial t_\gamma \partial t_\eta}\right)_0 \qquad H_{\mu\nu\gamma\eta} = \left(\frac{\partial^4 L}{\partial t_\mu \partial t_\nu \partial t_\gamma \partial t_\eta}\right)_0$$

$$D_{\mu\nu\gamma\eta\delta} = \left(\frac{\partial^5 L}{\partial \bar{t}_\mu \partial t_\nu \partial t_\gamma \partial t_\eta \partial t_\delta}\right)_0 \qquad \xi^X_\mu = \left(\frac{\partial^2 L}{\partial f_X \partial \bar{t}_\nu}\right)_0$$

$$A^X_{\mu\nu} = \left(\frac{\partial^3 L}{\partial f_X \partial \bar{t}_\mu \partial t_\nu}\right)_0 \qquad \eta_\mu = \left(\frac{\partial^2 L}{\partial f_X \partial t_\mu}\right)_0$$

$$B^X_{\mu\nu\gamma} = \left(\frac{\partial^4 L}{\partial f_X \partial \bar{t}_\mu \partial t_\nu \partial t_\gamma}\right)_0 \qquad F^X_{\mu\nu} = \left(\frac{\partial^3 L}{\partial f_X \partial t_\mu \partial t_\nu}\right)_0$$

The Approximate Coupled-Cluster Models CC2 & CC3

- approximate equations for highest excitations in lowest order PT, assuming T_1 is of 0.th order as needed in unrelaxed response theory:

CC2: (Christiansen, *et al.*, *CPL* 243 (1995) 409) $\rightsquigarrow$ "iterative MP2"

$$
\begin{aligned}
0 &= \langle \mu_2 | \exp(-T_1 - T_2) H \exp(T_1 + T_2) | \mathrm{HF} \rangle \\
&\Downarrow \qquad\qquad\qquad \Downarrow \\
0 &= \langle \mu_2 | \exp(-T_1) \big([F, T_2] + H \big) \exp(T_1) | \mathrm{HF} \rangle
\end{aligned}
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\end{aligned}
$$

CC3: (Koch, *et al.*, *JCP* 106 (1997) 1808) $\rightsquigarrow$ "iterative CCSD(T)"

$$
\begin{aligned}
0 &= \langle \mu_2 | \exp(-T_1 - T_2 - T_3) H \exp(T_1 + T_2 + T_3) | \mathrm{HF} \rangle \\
&\Downarrow \qquad\qquad\qquad\quad \Downarrow \\
0 &= \langle \mu_2 | \exp(-T_1) \big([F, T_3] + [H, T_2] \big) \exp(T_1) | \mathrm{HF} \rangle
\end{aligned}
$$

Partitionend formulation of CC2/CC3

$$\left[\begin{pmatrix} \mathbf{A}_{\mu_S \nu_S} & \mathbf{A}_{\mu_S \nu_L} \\ \mathbf{A}_{\mu_L \nu_S} & \delta_{\mu_L \nu_L} \varepsilon_{\nu_L} \end{pmatrix} - \omega \mathbf{1} \right] \begin{pmatrix} R_{\nu_S} \\ R_{\nu_L} \end{pmatrix} = - \begin{pmatrix} \xi_{\mu_S} \\ \xi_{\mu_L} \end{pmatrix}$$

CC2: μ_S, ν_S singles; μ_L, ν_L doubles; CC3: μ_S, ν_S singles & doubles; μ_L, ν_L triples

$\varepsilon_{\nu_L} = \varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j + \ldots$ SCF orbital energy differences

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$\varepsilon_{\nu_L} = \varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j + \ldots$ SCF orbital energy differences

- Linear equations can be partitioned: $R_{\mu_L} = (\omega - \varepsilon_{\mu_L})^{-1} \left(\xi_{\nu_L} + \mathbf{A}_{\mu_L \nu_S} R_{\nu_S}\right)$

↷ iterative solution only in small space:

$$\left[\mathbf{A}_{\mu_S \nu_S} - \frac{\mathbf{A}_{\mu_S \mu_L} \mathbf{A}_{\mu_L \nu_S}}{\varepsilon_{\mu_L} - \omega} - \omega \mathbf{1}\right] R_{\nu_S} = - \left(\xi_{\mu_S} + \frac{\mathbf{A}_{\mu_S \nu_L} \xi_{\nu_L}}{(\varepsilon_{\mu_L} - \omega)}\right)$$

Partitionend formulation of CC2/CC3

$$\left[\begin{pmatrix} \mathbf{A}_{\mu_S \nu_S} & \mathbf{A}_{\mu_S \nu_L} \\ \mathbf{A}_{\mu_L \nu_S} & \delta_{\mu_L \nu_L} \varepsilon_{\nu_L} \end{pmatrix} - \omega \mathbf{1}\right] \begin{pmatrix} R_{\nu_S} \\ R_{\nu_L} \end{pmatrix} = - \begin{pmatrix} \xi_{\mu_S} \\ \xi_{\mu_L} \end{pmatrix}$$

CC2: μ_S, ν_S singles; μ_L, ν_L doubles; CC3: μ_S, ν_S singles & doubles; μ_L, ν_L triples

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- Linear equations can be partitioned: $R_{\mu_L} = (\omega - \varepsilon_{\mu_L})^{-1} \left(\xi_{\nu_L} + \mathbf{A}_{\mu_L \nu_S} R_{\nu_S}\right)$

  ↷ iterative solution only in small space:

$$\left[\mathbf{A}^{eff}_{\mu_S \mu_L}(\omega) - \omega \mathbf{1}\right] R_{\nu_S} = -\xi^{eff}_{\mu_S}(\omega)$$

- no storage of trial vectors/amplitudes for highest excitation class!

Partitionend formulation of CC2/CC3

- Problem: recursive dependence of right hand sides vectors on lower-order amplitudes:

$$\xi_{\mu}^{(n)} = \langle \mu | [V, R^{(n-1)}] + \ldots | \mathrm{HF} \rangle$$

↷ without having $R_{\mu_L}^{(n-1)}$ on file or increased scaling of operation count

the partitioned formulation is limited to

for CC2 to linear response (polarizabilities)

for CC3 to cubic response (second hyperpolarizabilities)

Single-Reference Response Methods

	Comput. Costs*	Disc Space	Ground State	Response Functions
SCF	N^4(iter.)	N^2	1	1
DFT	N^4(iter.)	N^2	√	√
CCS	N^4(iter.)	N^2	(SCF)	0
CCSD	n^2N^4(iter.)	n^2N^2	3	2
CCSDT	n^4N^4(iter.)	n^3N^3	4	4
⋮	⋮	⋮	⋮	⋮

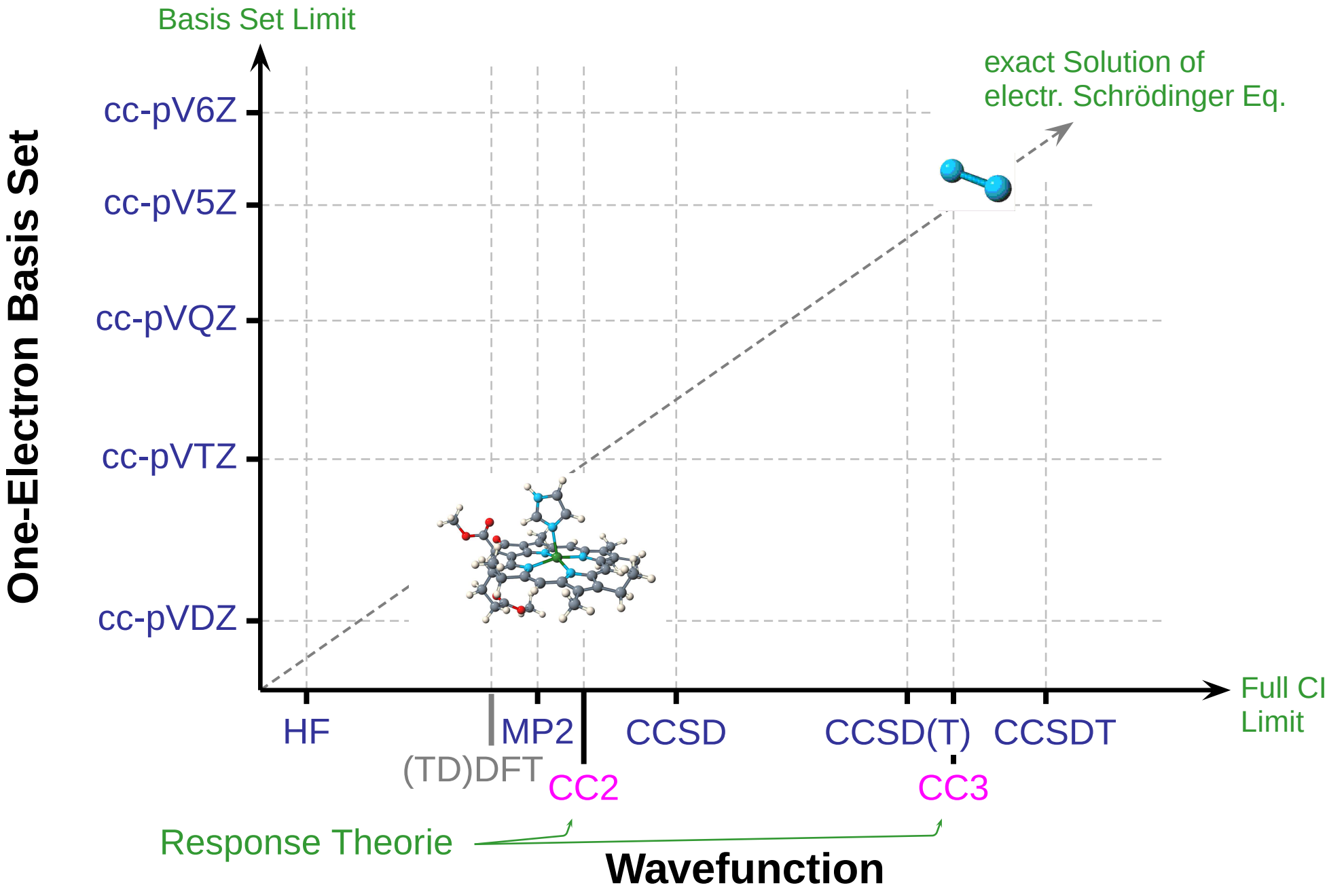
* prefactor depends strongly on type of application

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CCS	N^4(iter.)	N^2	(SCF)	0
CC2	nN^4(iter.)	n^2N^2	2	1
CCSD	n^2N^4(iter.)	n^2N^2	3	2
CC3	n^3N^4(iter.)	$nN^3 - n^2N^3$	4	3
CCSDT	n^4N^4(iter.)	n^3N^3	4	4
⋮	⋮	⋮	⋮	⋮

* prefactor depends strongly on type of application

Hierarchy of Wavefunctions and Basis Sets



Literature:

Response Theory:

P. W. Langhoff, S. T. Epstein, M. Karplus, Rev. Mod. Phys., 44 (1972) 602.
J. Olsen, P. Jørgensen, in “Modern Electronic Structure Theory”, pp. 857-990, Ed. D. Yarkony, World Scientifi c, Singapore, 1995.
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P. E. S. Wormer, H. Hettema, J. Chem. Phys. 97 (1992) 5592.
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CC2/CC3

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H. Koch, O. Christiansen, P. Jørgensen, A. Sánchez de Merás, T. U. Helgaker, J. Chem. Phys. 106 (1997) 1808.
O. Christiansen, H. Koch, P. Jørgensen, J. Chem. Phys. 103 (1995) 7429.

Part II

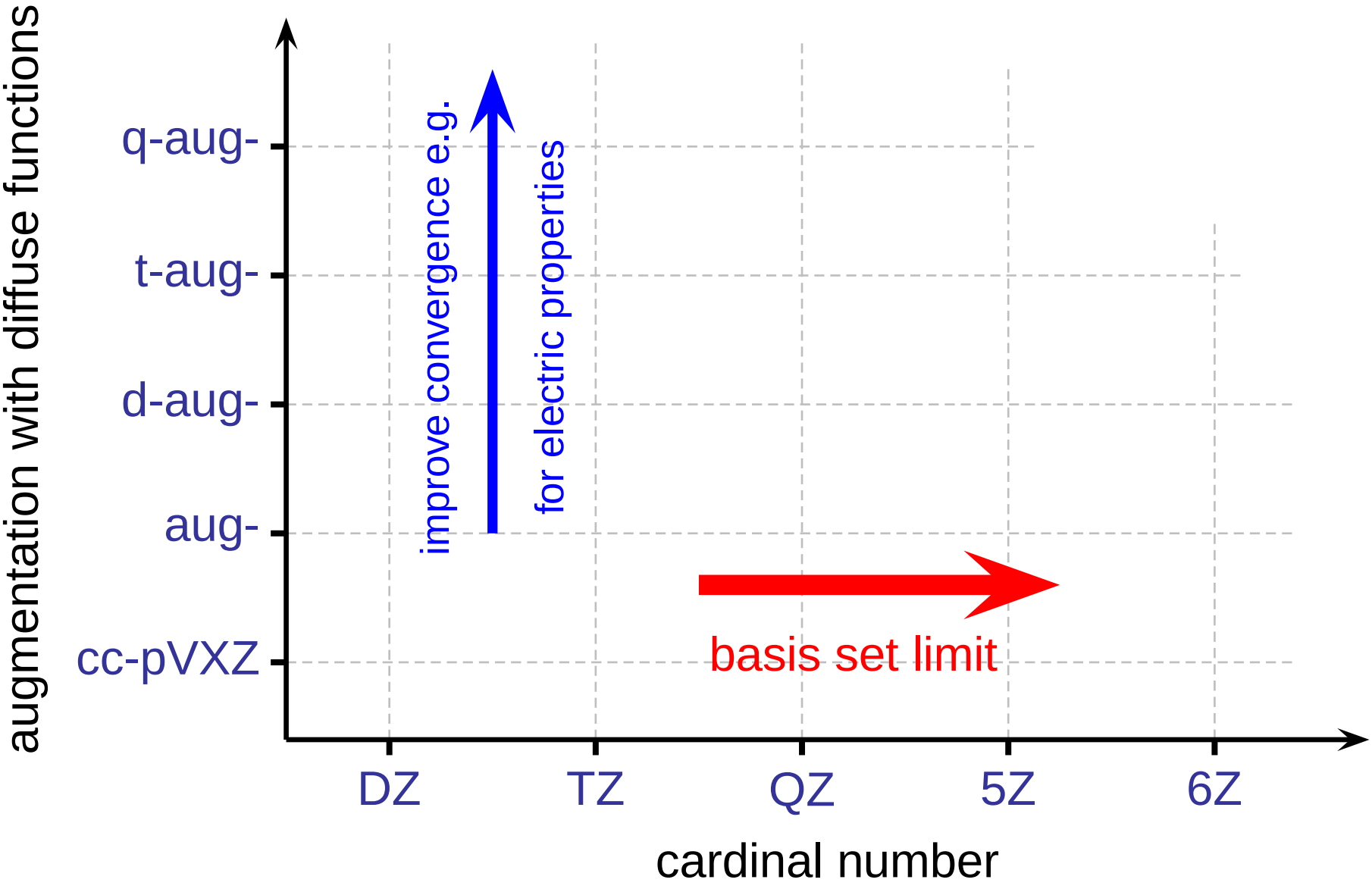
Accurate Frequency-dependent Hyperpolarizabilities of Small Systems

Part II

Accurate Frequency-dependent Hyperpolarizabilities of Small Systems

- Basis set convergence
- Convergence with wavefunction model
- Vibrational contributions

The basis set hierarchies n-aug-cc-pVXZ

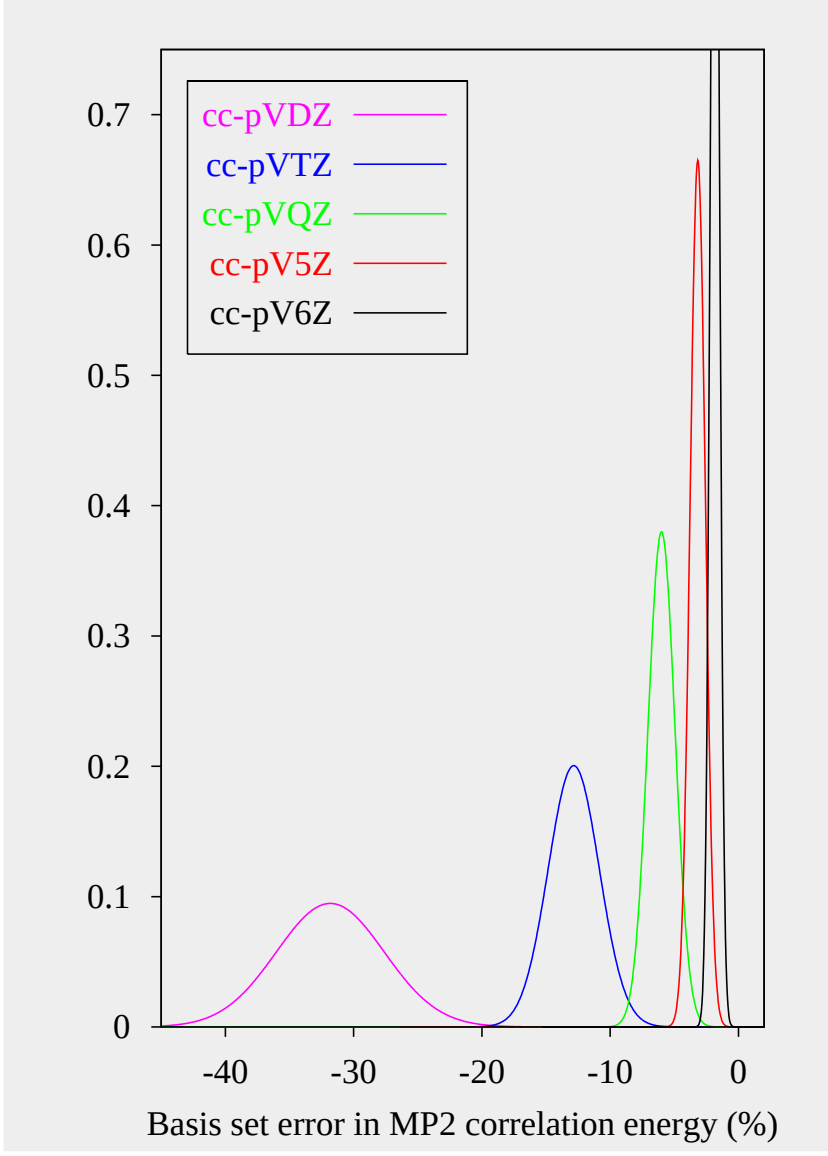


The basis set hierarchies n-aug-cc-pVXZ

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	$-1.8 \pm 0.4\%$

(converges as (empirical): $E_{lim} \approx E_X + a/X^3$)



Basis Set Convergence: Polarizabilities

SOS expression:

$$\alpha = \sum_{f \neq 0} \frac{2\langle 0|\vec{r}|f\rangle\langle f|\vec{r}|0\rangle}{E_f - E_0}$$

1. order wavefunction.:

$$|\Psi^{(1)}\rangle = \sum_{f \neq 0} |f\rangle \frac{\langle f|\vec{r}|0\rangle}{E_f - E_0}$$

- consider an atom:

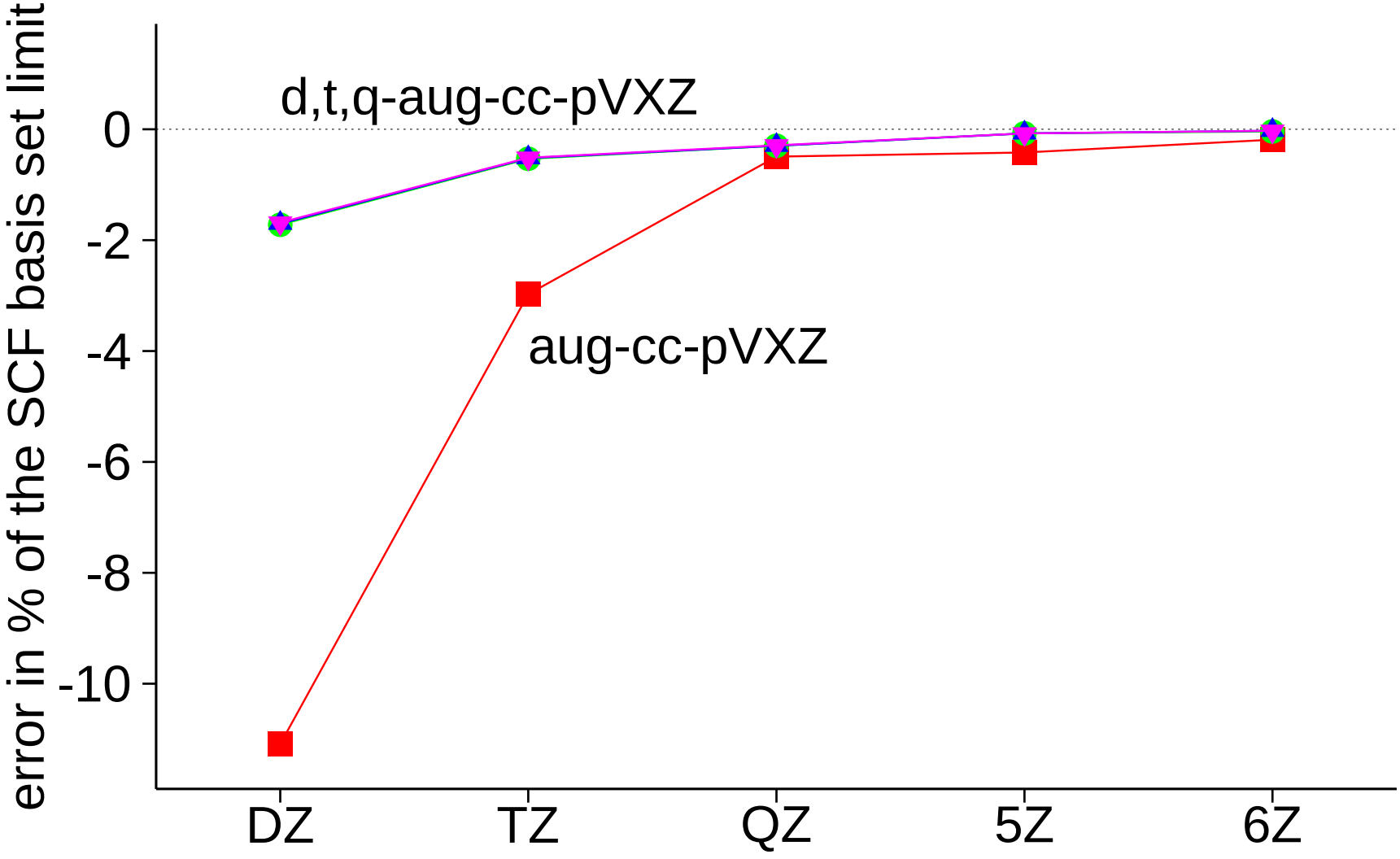
level	polarization functions required up to
SCF	$L+1$
correlated	$L+1$ ($\rightsquigarrow$ DZ, qualitative)
	$L+2$ ($\rightsquigarrow$ TZ, quantitative)
	$L+3$ ($\rightsquigarrow$ QZ, high accuracy)

(L highest occupied angular momentum in SCF wavefunction)

+ diffuse functions

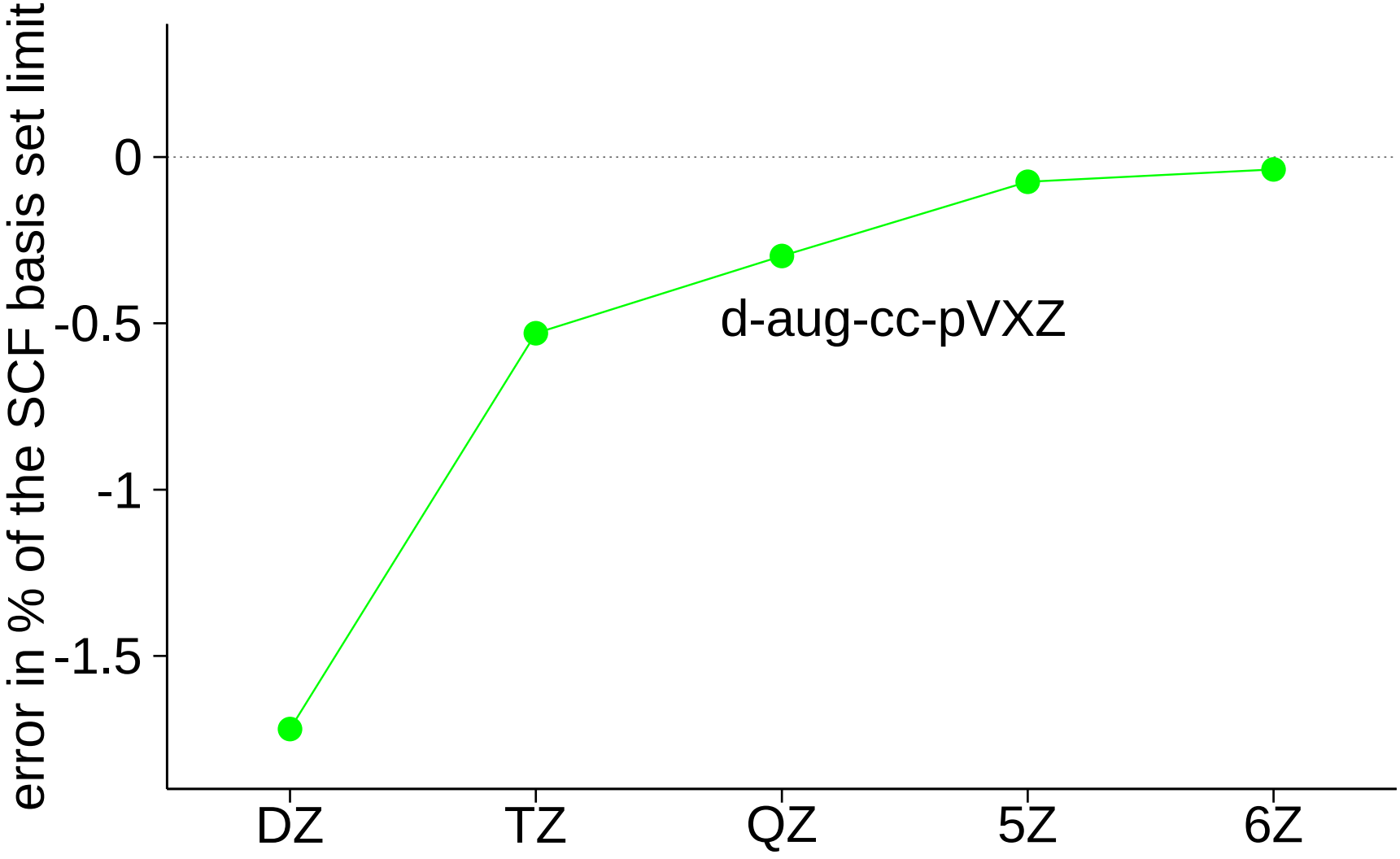
Basis Set Convergence: Polarizabilities

- Ar, static α, **SCF** results:



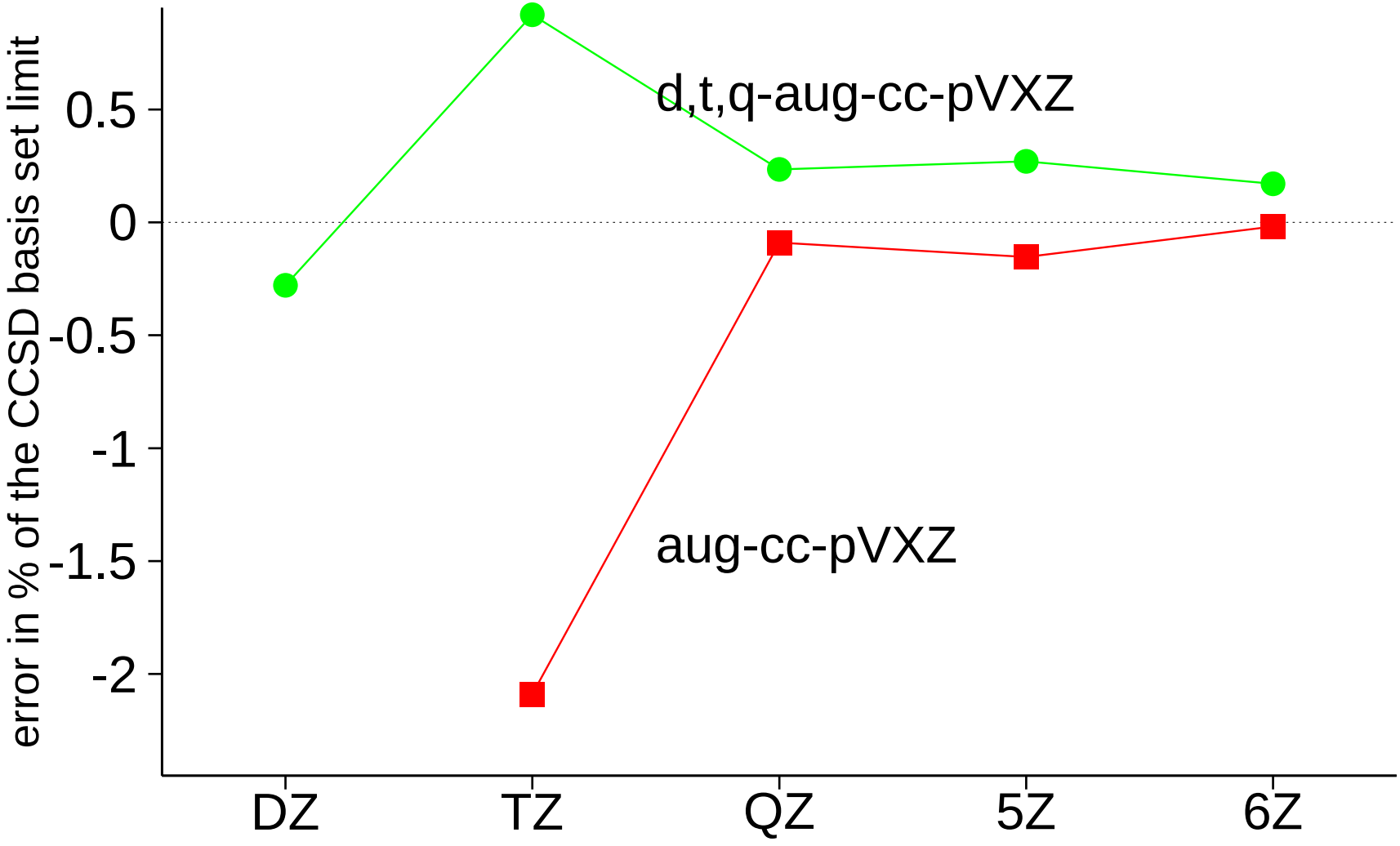
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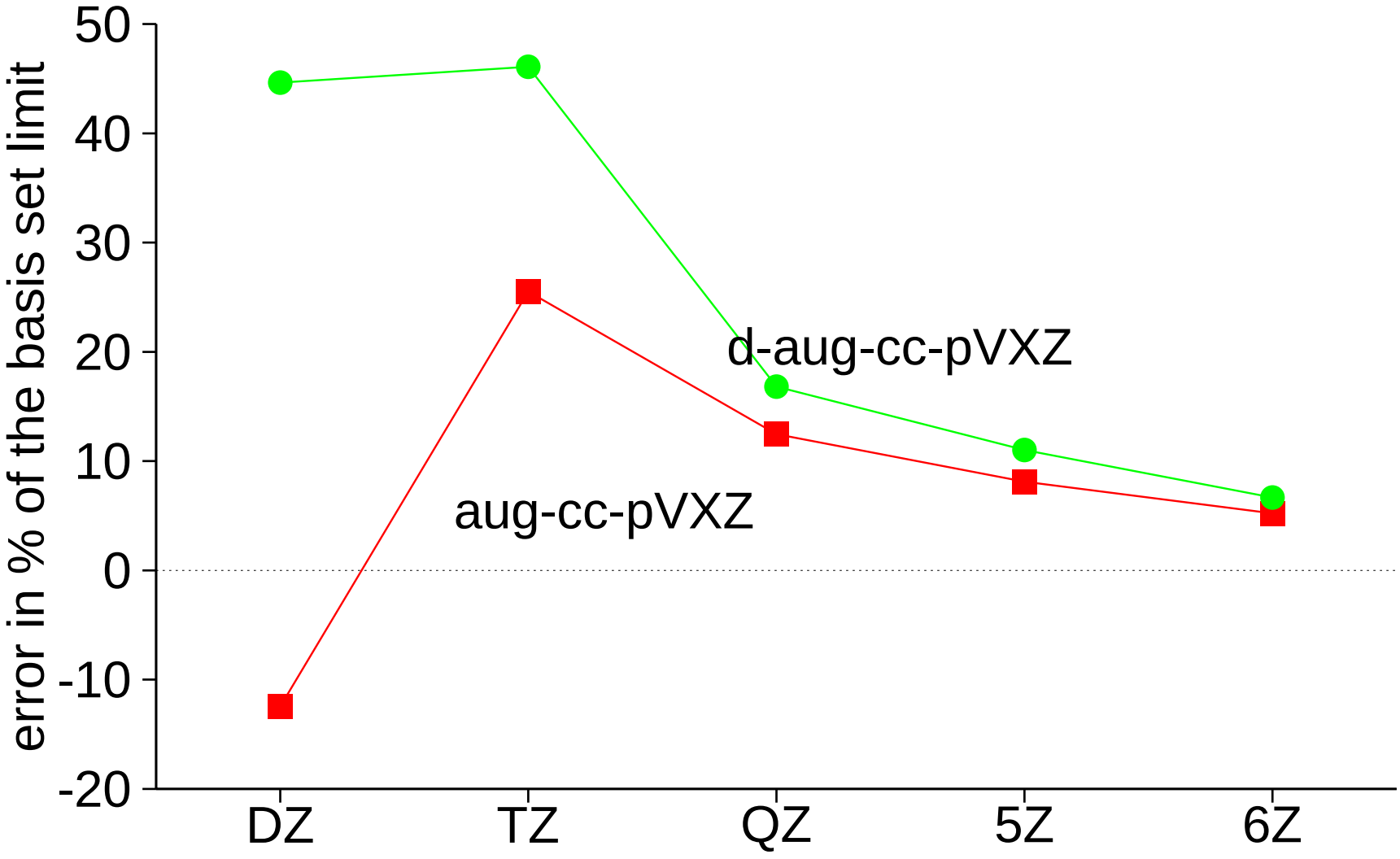
Basis Set Convergence: Polarizabilities

- Ar, static α, **CCSD** results:



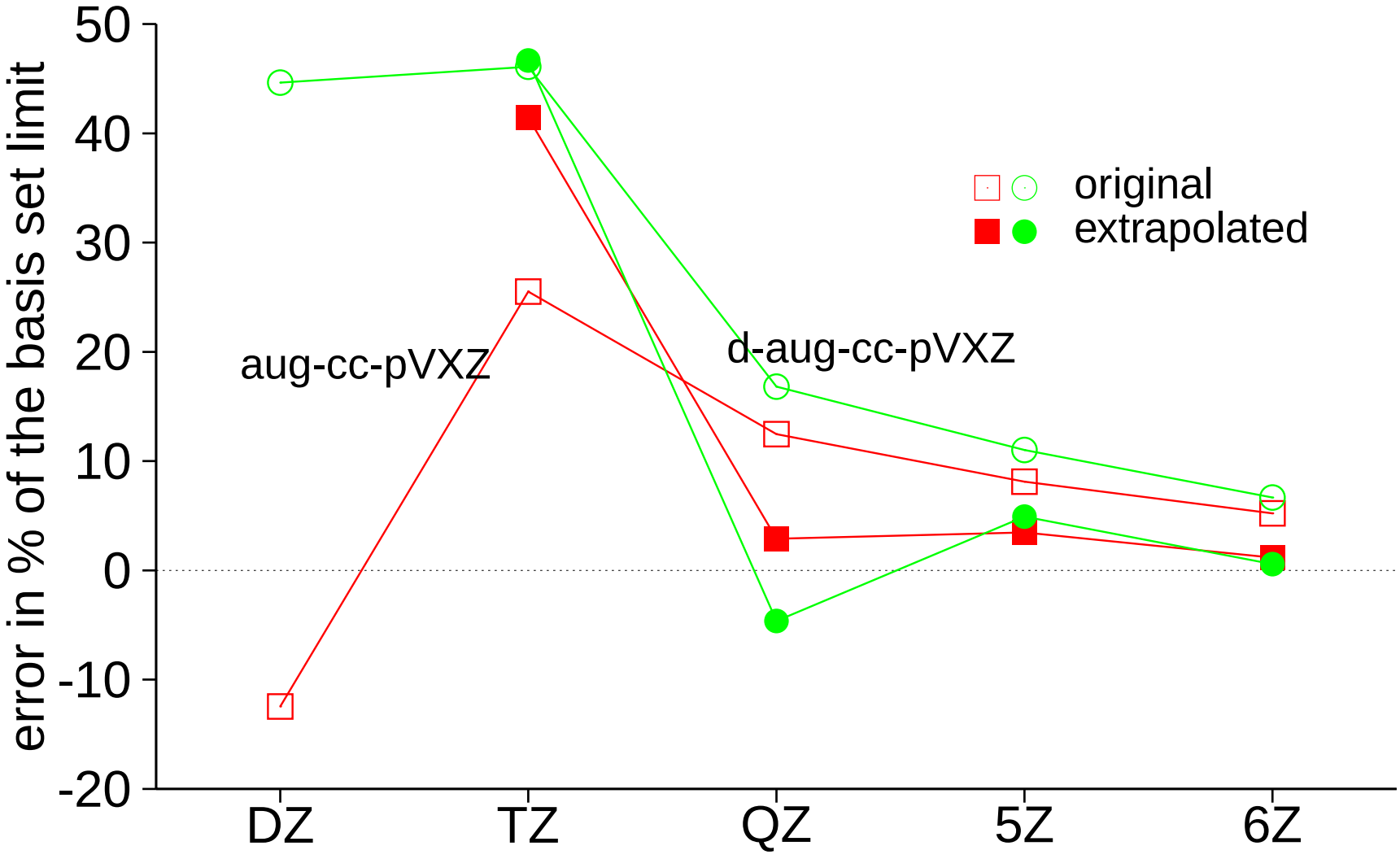
Basis Set Convergence: Polarizabilities

- Ar, static α, **correlation** contribution:



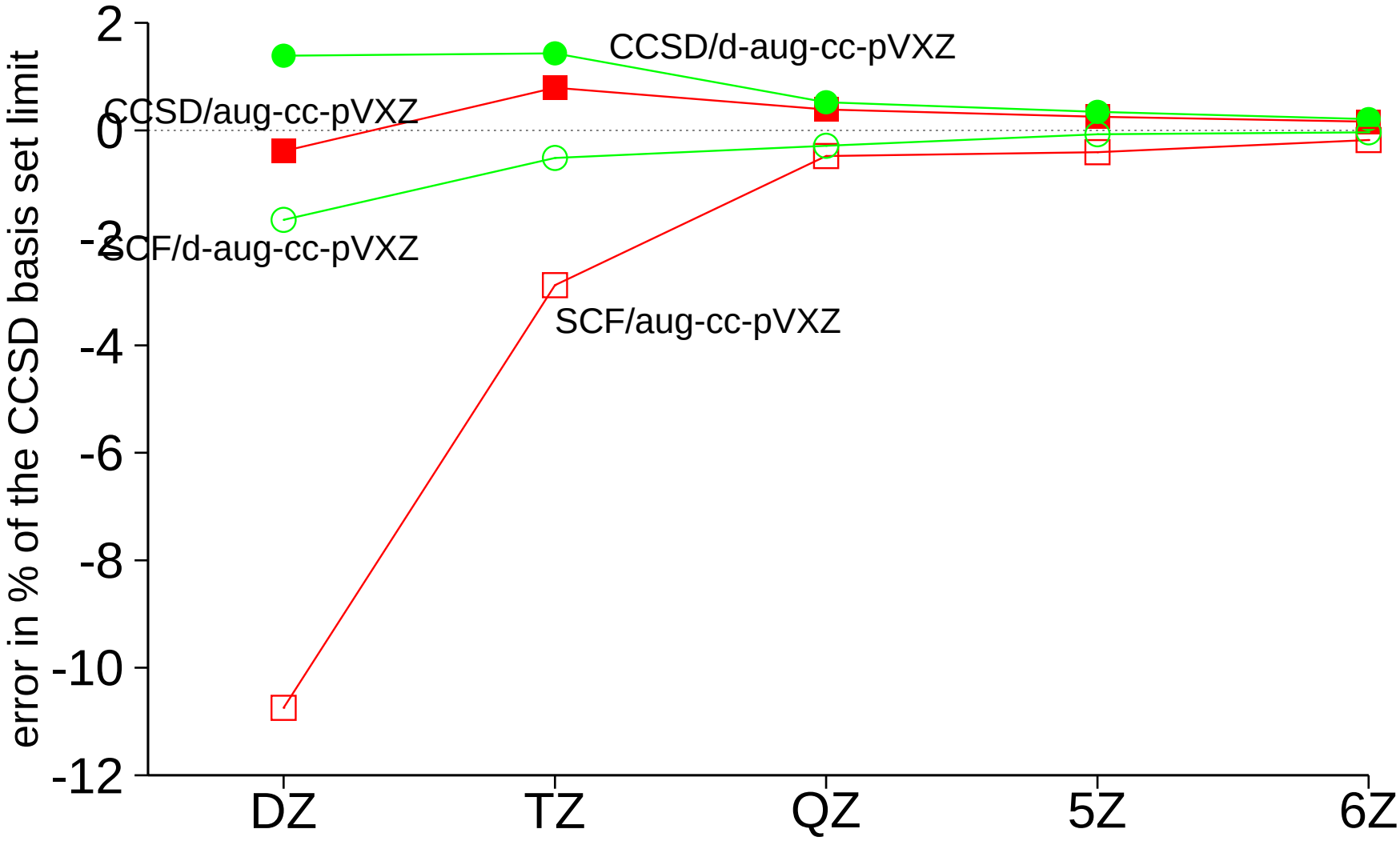
Basis Set Convergence: Polarizabilities

- Ar, static α, **correlation** contribution:



Basis Set Convergence: Polarizabilities

- Ar, static α, **SCF & correlation** contribution:



Basis Set Convergence: 2. Hyperpolarizabilities

SOS expression:

$$\gamma = \sum_{f_1 f_2 f_3} \frac{\langle 0|\vec{r}|f_3\rangle\langle f_3|\vec{r}|f_2\rangle\langle f_2|\vec{r}|f_1\rangle\langle f_1|\vec{r}|0\rangle}{(E_{f_3}-E_0)(E_{f_2}-E_0)(E_{f_1}-E_0)}$$

2. order wavefunction:

$$|\Psi^{(2)}\rangle = \sum_{f_2 f_1} |f_2\rangle \frac{\langle f_2|\vec{r}|f_1\rangle\langle f_1|\vec{r}|0\rangle}{(E_{f_2}-E_0)(E_{f_1}-E_0)}$$

- consider an atom:

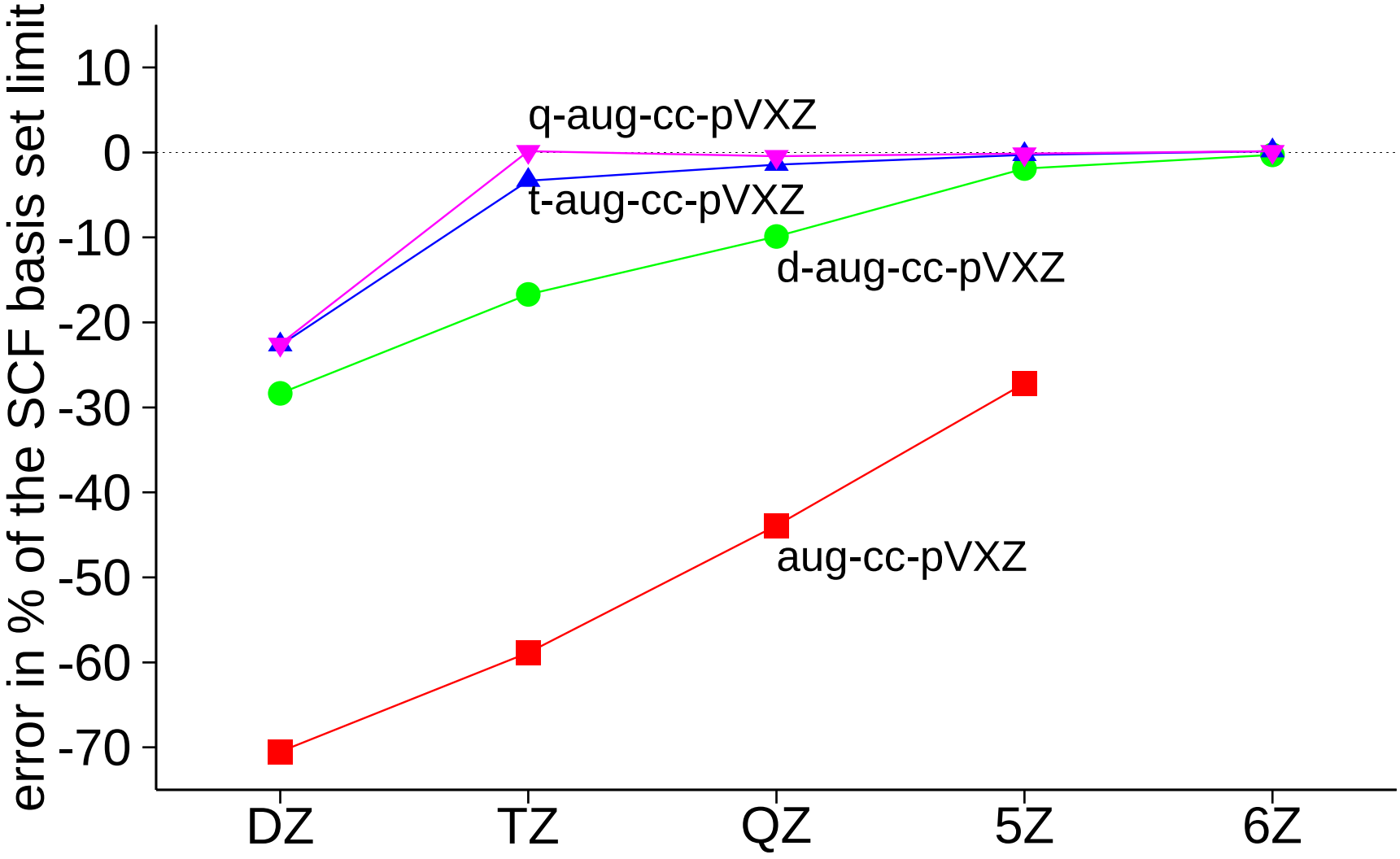
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correlated	$L+2$ ($\rightsquigarrow$ TZ, qualitative)
	$L+3$ ($\rightsquigarrow$ QZ, quantitative)
	$L+4$ ($\rightsquigarrow$ 5Z, high accuracy)

(L highest occupied angular momentum in SCF wavefunction)

+ several diffuse functions

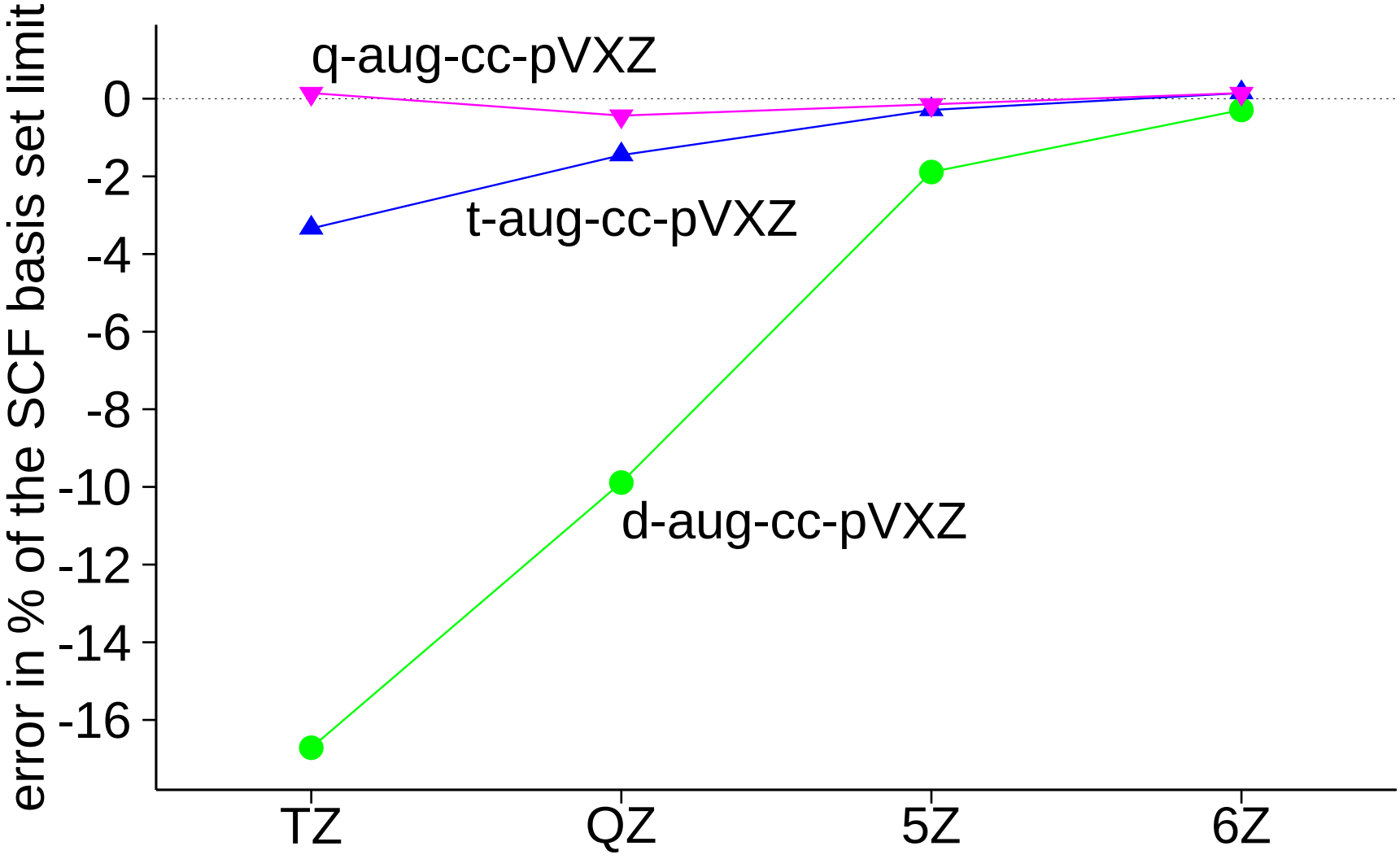
Basis Set Convergence: 2. Hyperpolarizabilities

- Ne, static $\gamma_{||}$, **SCF** results:



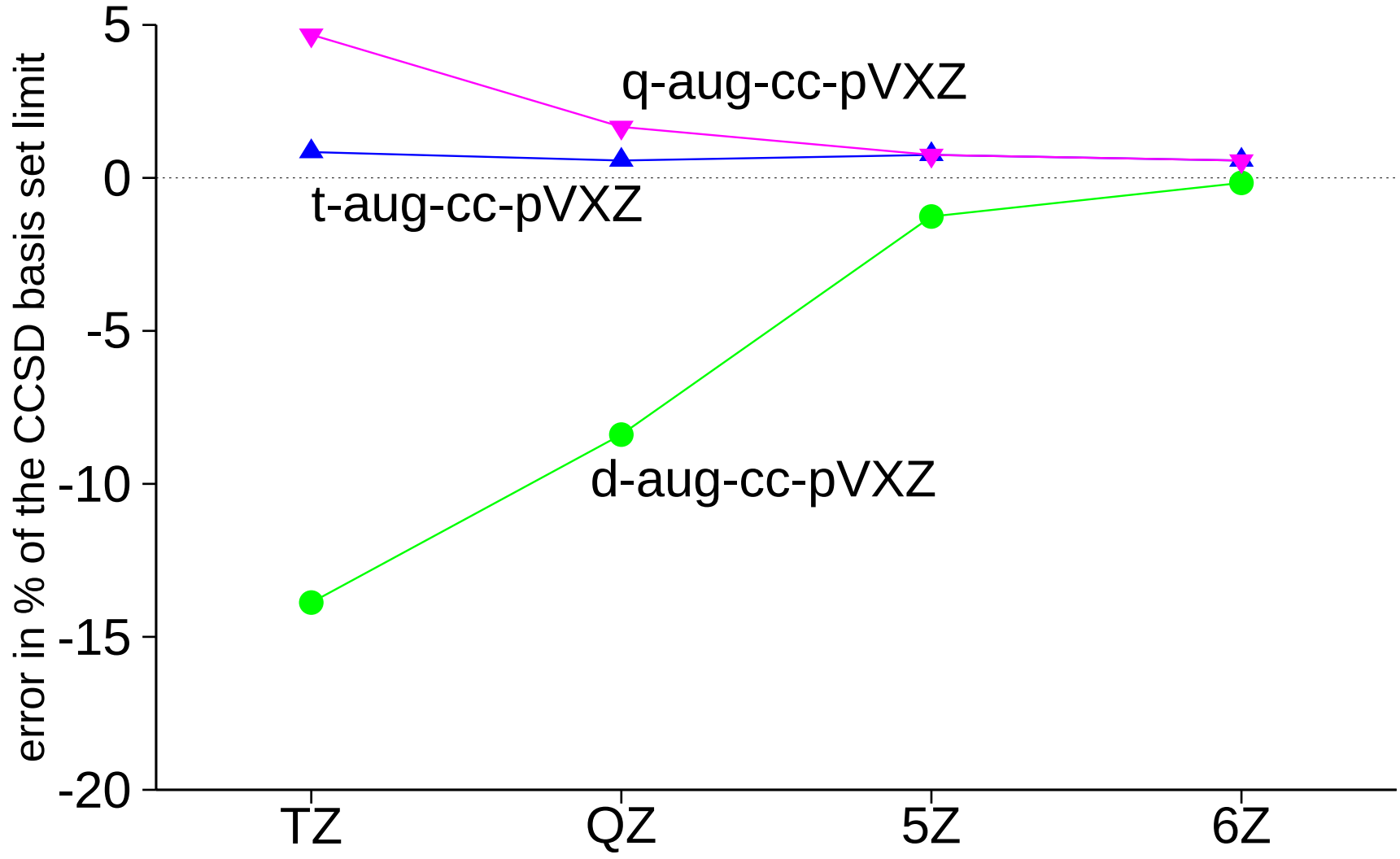
Basis Set Convergence: 2. Hyperpolarizabilities

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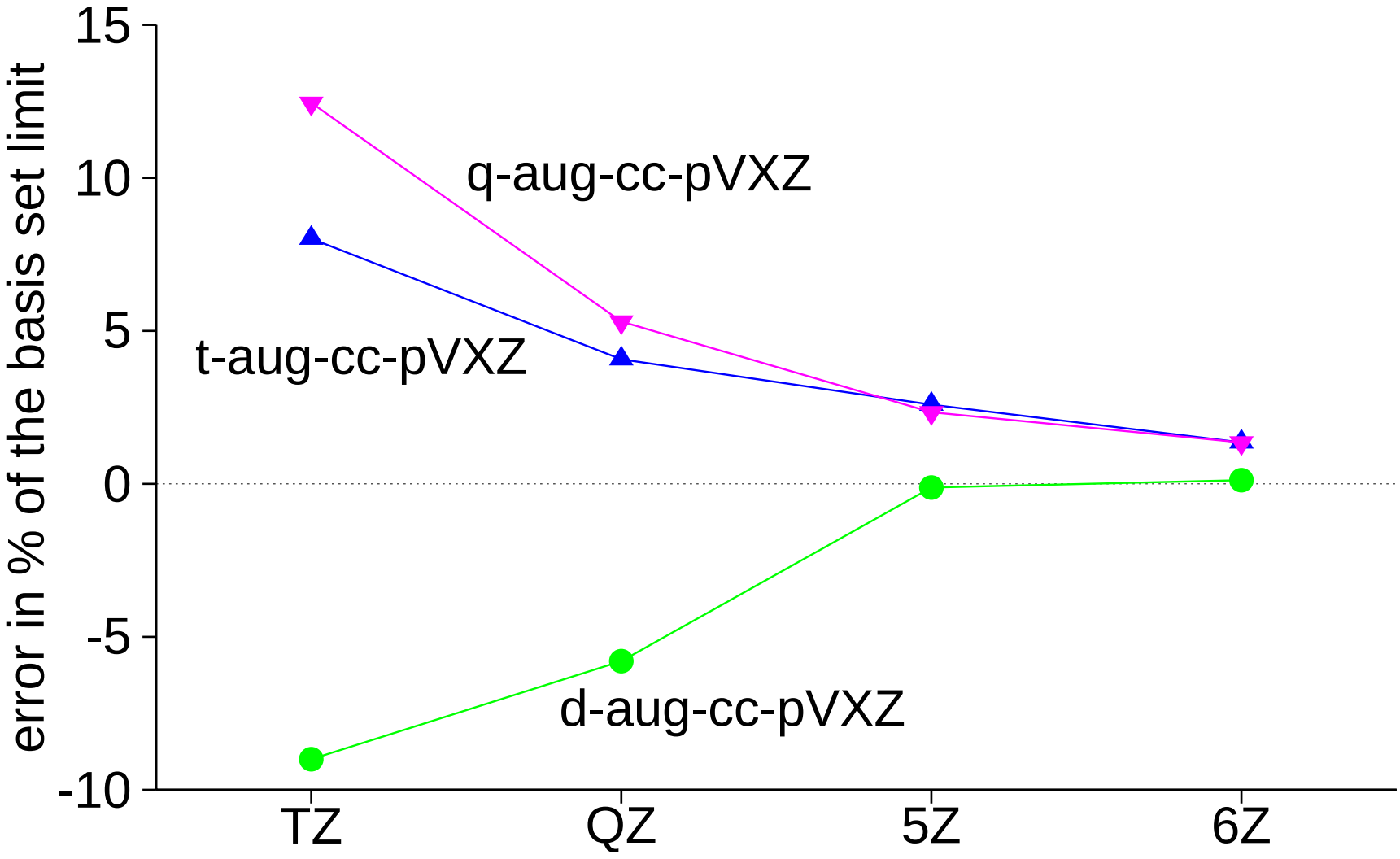
Basis Set Convergence: 2. Hyperpolarizabilities

- Ne, static $\gamma_{||}$, **CCSD** results:



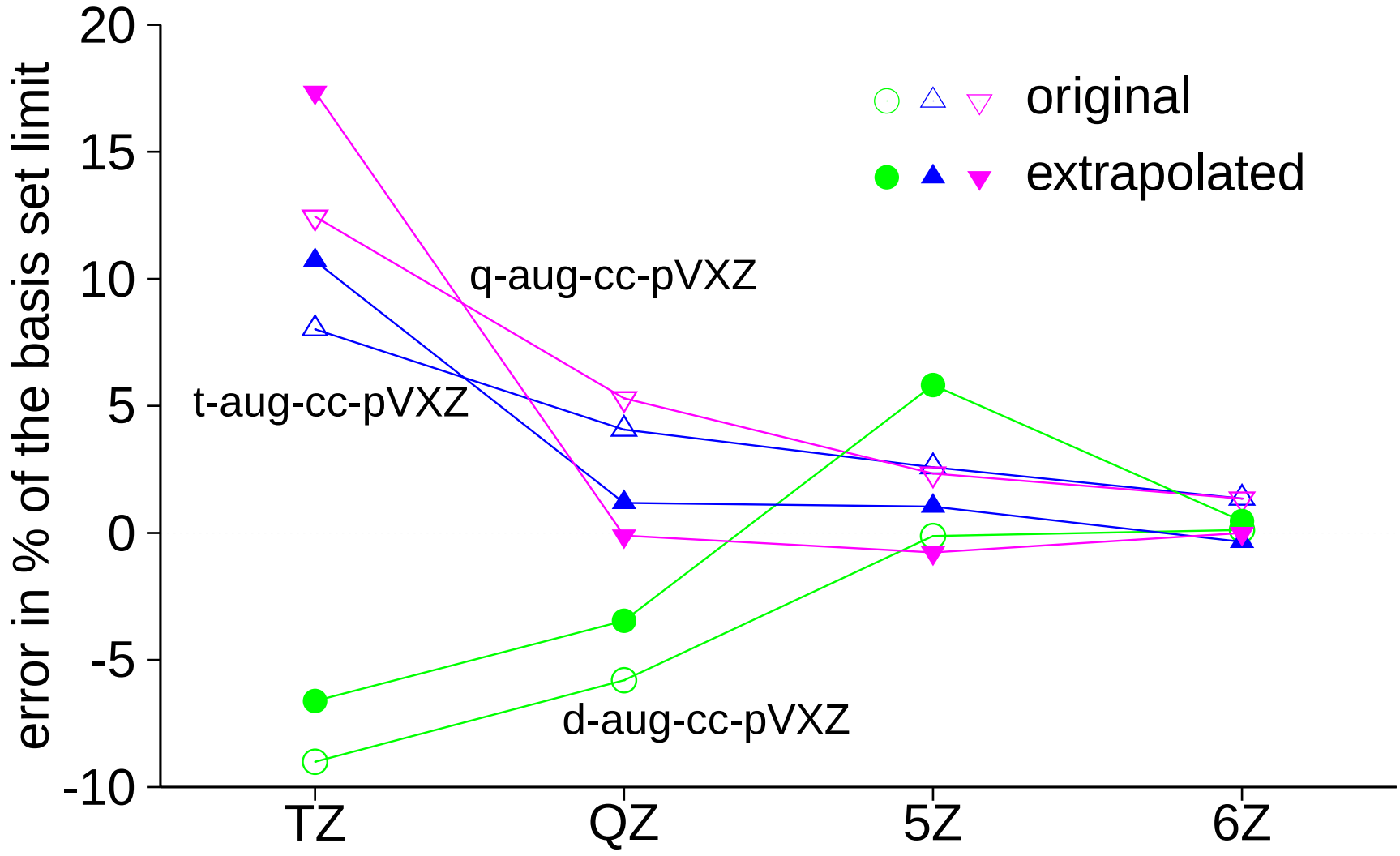
Basis Set Convergence: 2. Hyperpolarizabilities

- Ne, static $\gamma_{||}$, **correlation** contribution:



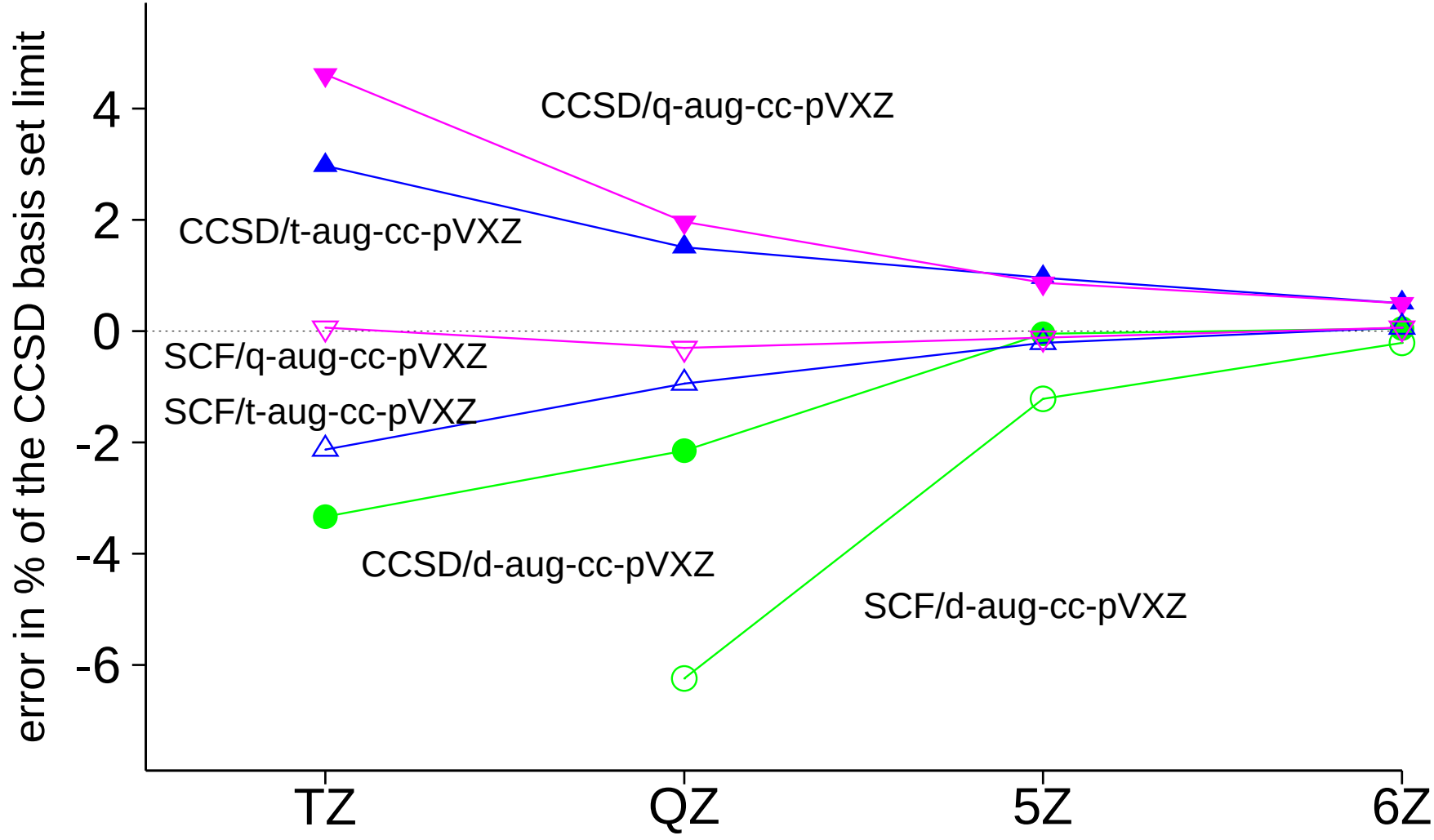
Basis Set Convergence: 2. Hyperpolarizabilities

- Ne, static $\gamma_{||}$, **correlation** contribution:



Basis Set Convergence: 2. Hyperpolarizabilities

- Ne, static $\gamma_{||}$, **SCF & correlation** contribution:



Basis Set Convergence: Summary

- **required number of diffuse functions depends strongly**
  - on size: the larger the less diffuse functions
  - on structure: 3-dim $<$ planar $<$ linear $<$ atoms

- **once $\bar{\alpha}$, $\bar{\gamma}$ described qualitatively correct**
  - SCF results converge with XZ fast from below/above/non-monotonic
  - correlation contribution should converge with XZ from above with

$$P_{lim}^{corr} \approx P_X^{corr} - a/X^3$$

(but: extrapolation fails in too small basis sets)

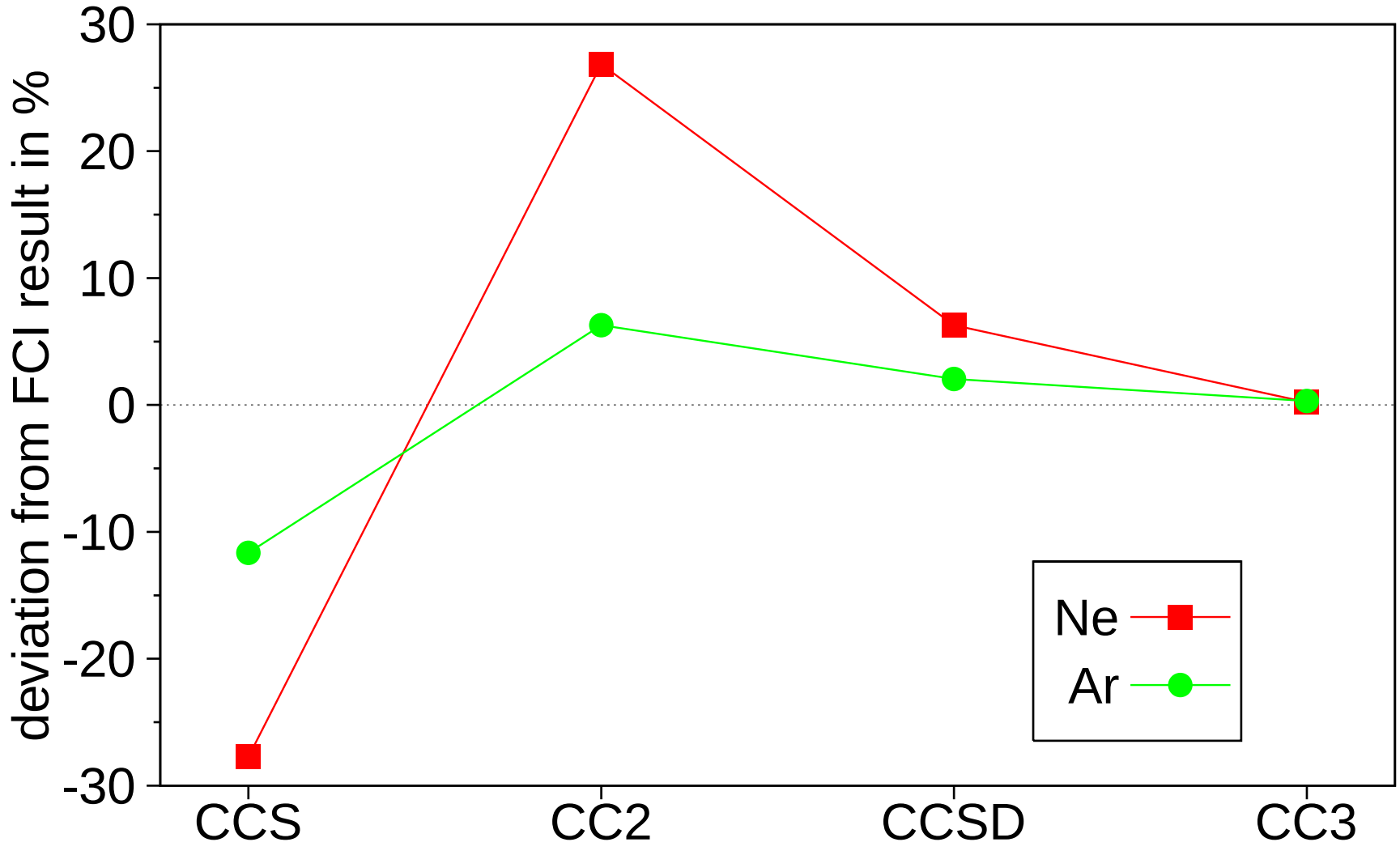
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CCS	N^4(iter.)	N^2	(SCF)	0
CC2	nN^4(iter.)	n^2N^2	2	1
CCSD	n^2N^4(iter.)	n^2N^2	3	2
CC3	n^3N^4(iter.)	$nN^3 - n^2N^3$	4	3
CCSDT	n^4N^4(iter.)	n^3N^3	4	4
⋮	⋮	⋮	⋮	⋮

* prefactor depends strongly on type of application

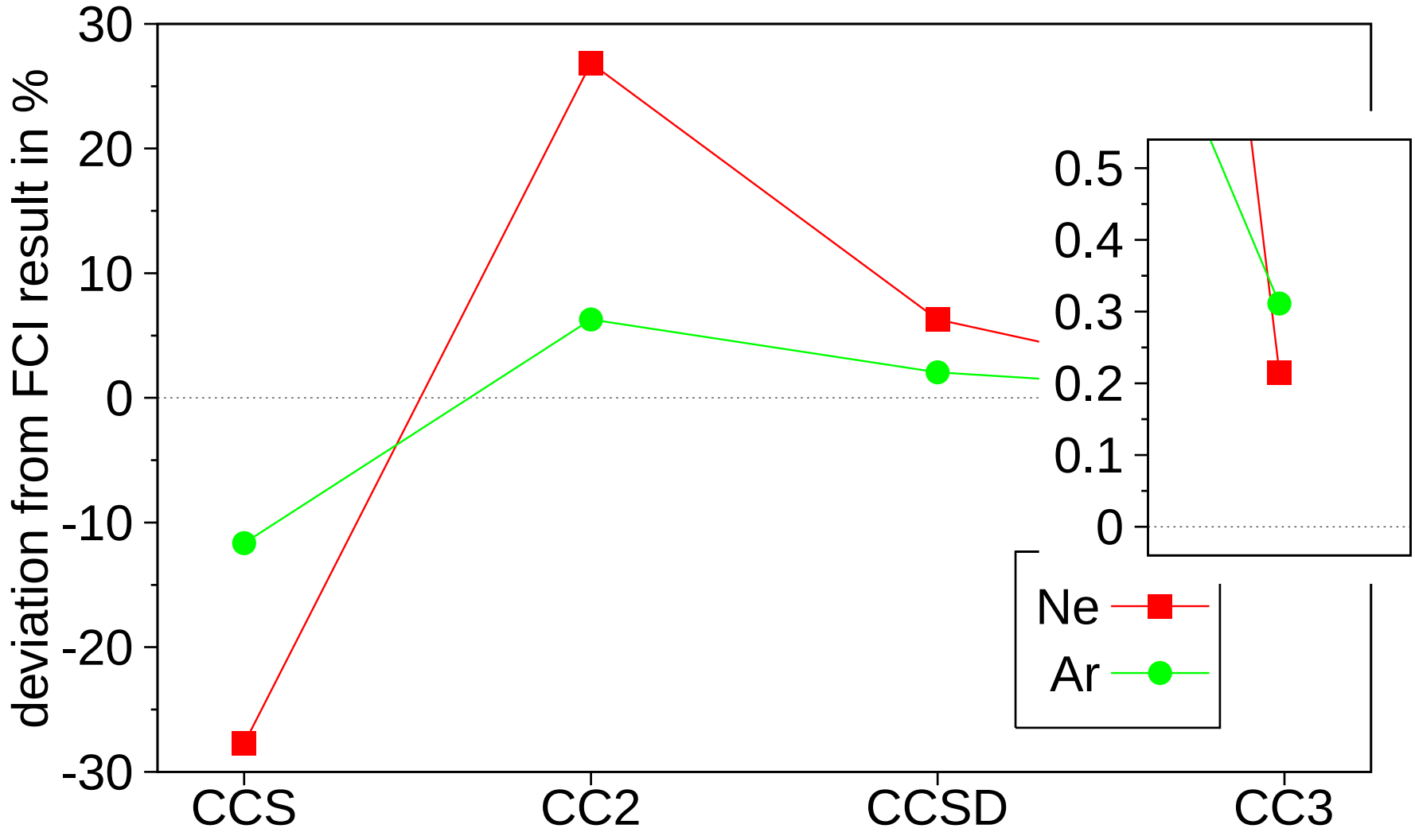
Convergence With Wavefunction Model

- Ne & Ar, static $\gamma_{||}$ (d-aug-cc-pVDZ basis):



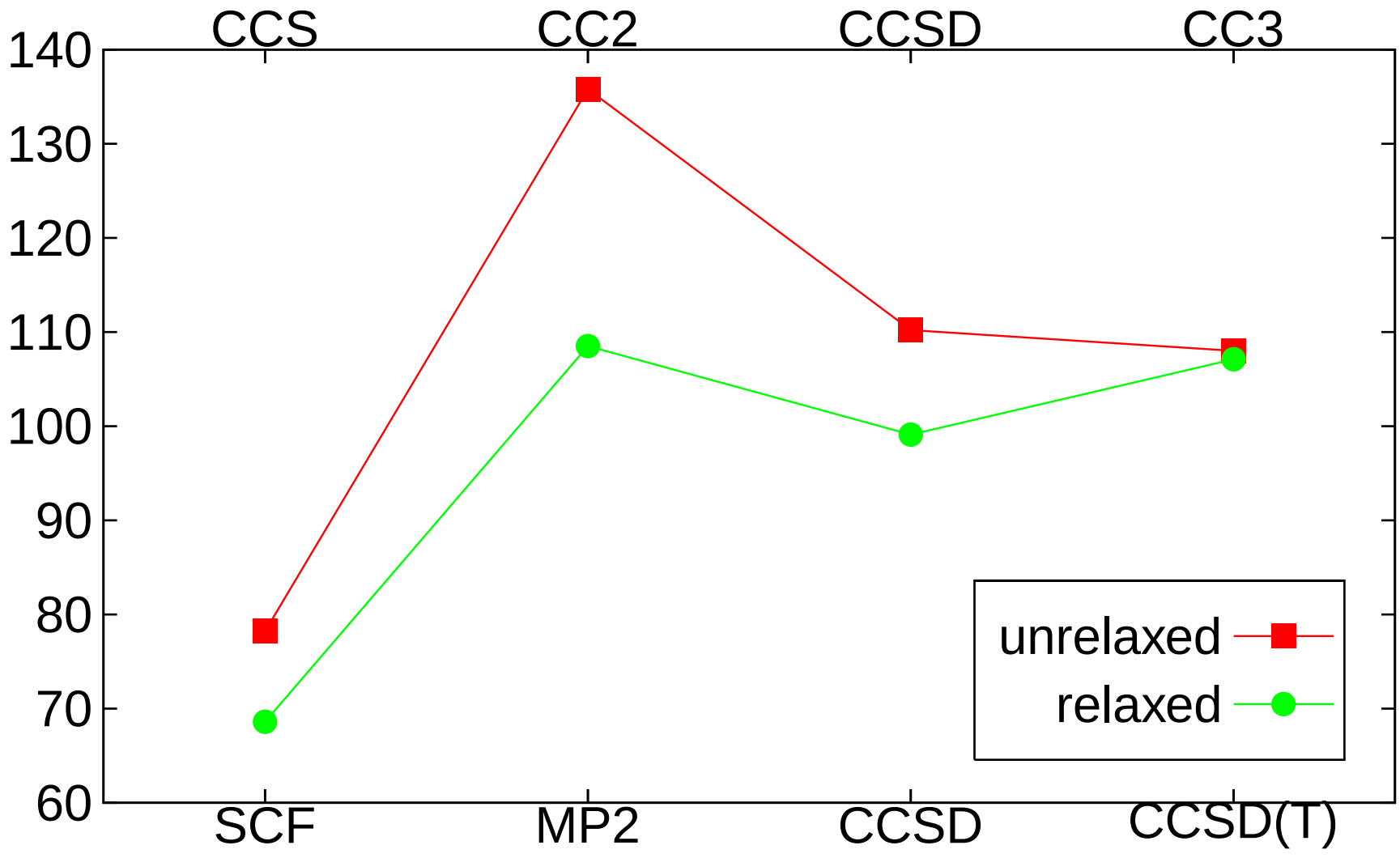
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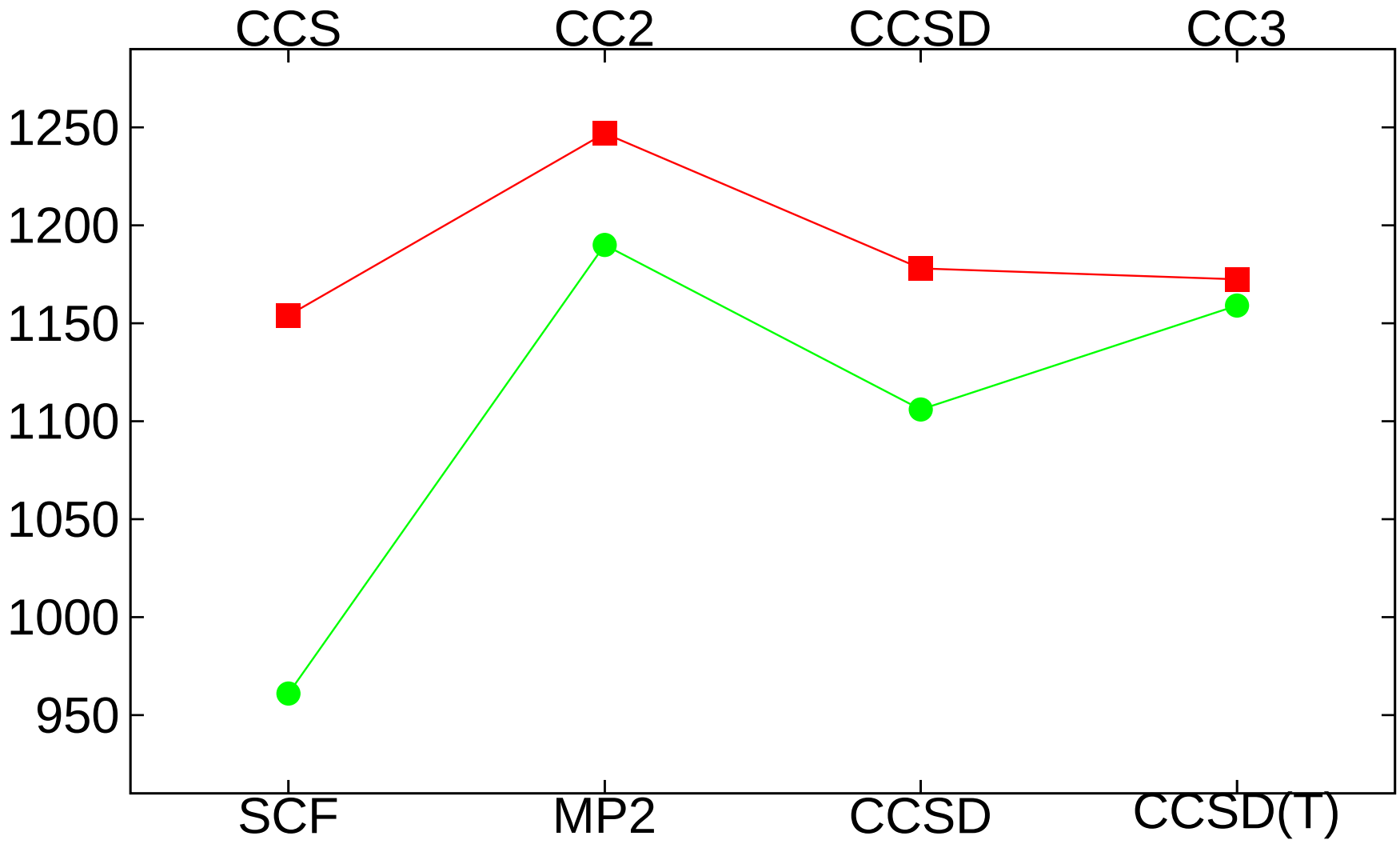
Convergence With Wavefunction Model

- Ne, static $\gamma_{||}$ (t-aug-cc-pV5Z basis):



Convergence With Wavefunction Model

- Ar, static $\gamma_{||}$ (t-aug-cc-pV5Z basis):



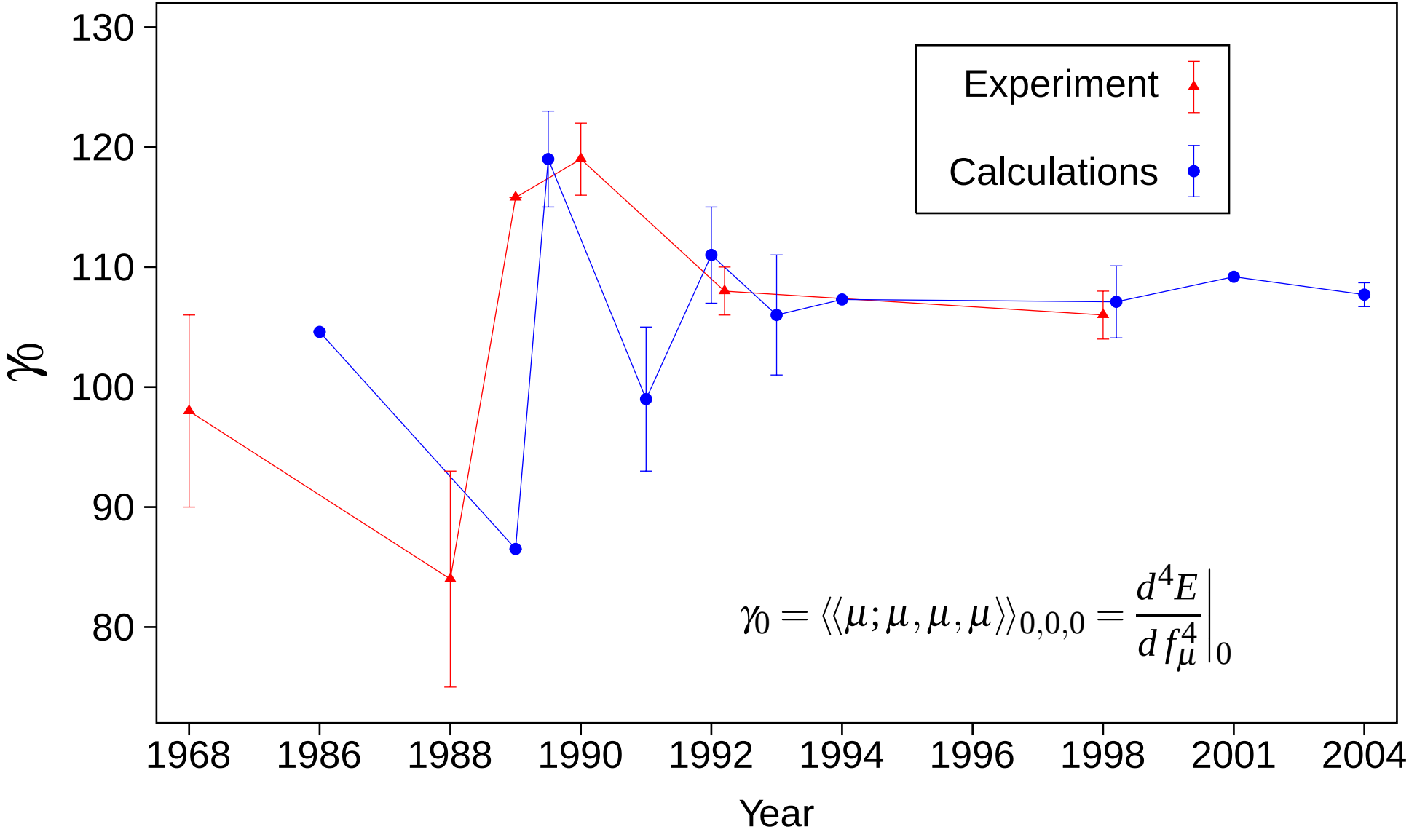
Convergence With Wavefunction Model

- **results converge as**

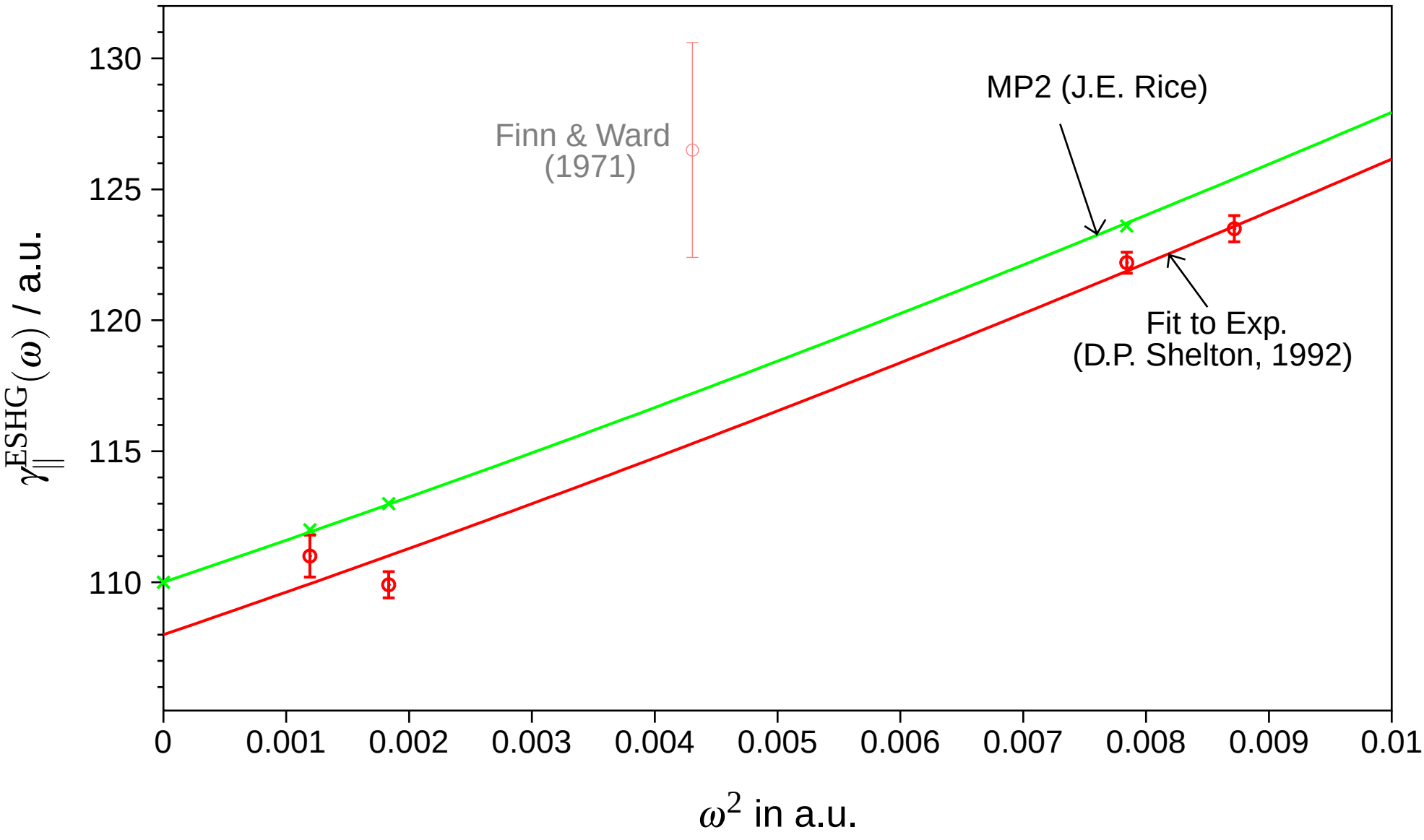
$$\mathrm{SCF}, \mathrm{CCS}, \mathrm{CC2} < \text{relax. CCSD} < \text{unrelax. CCSD} < \mathrm{CCSD(T)}, \mathrm{CC3} < \ldots$$

- CC2 gives no systematic improvement upon SCF, CCS
- triples effects usually smaller in unrelaxed CC (for γ a few %)
- contributions beyond CC3 are very small (for γ a few $^0/_{00}$)

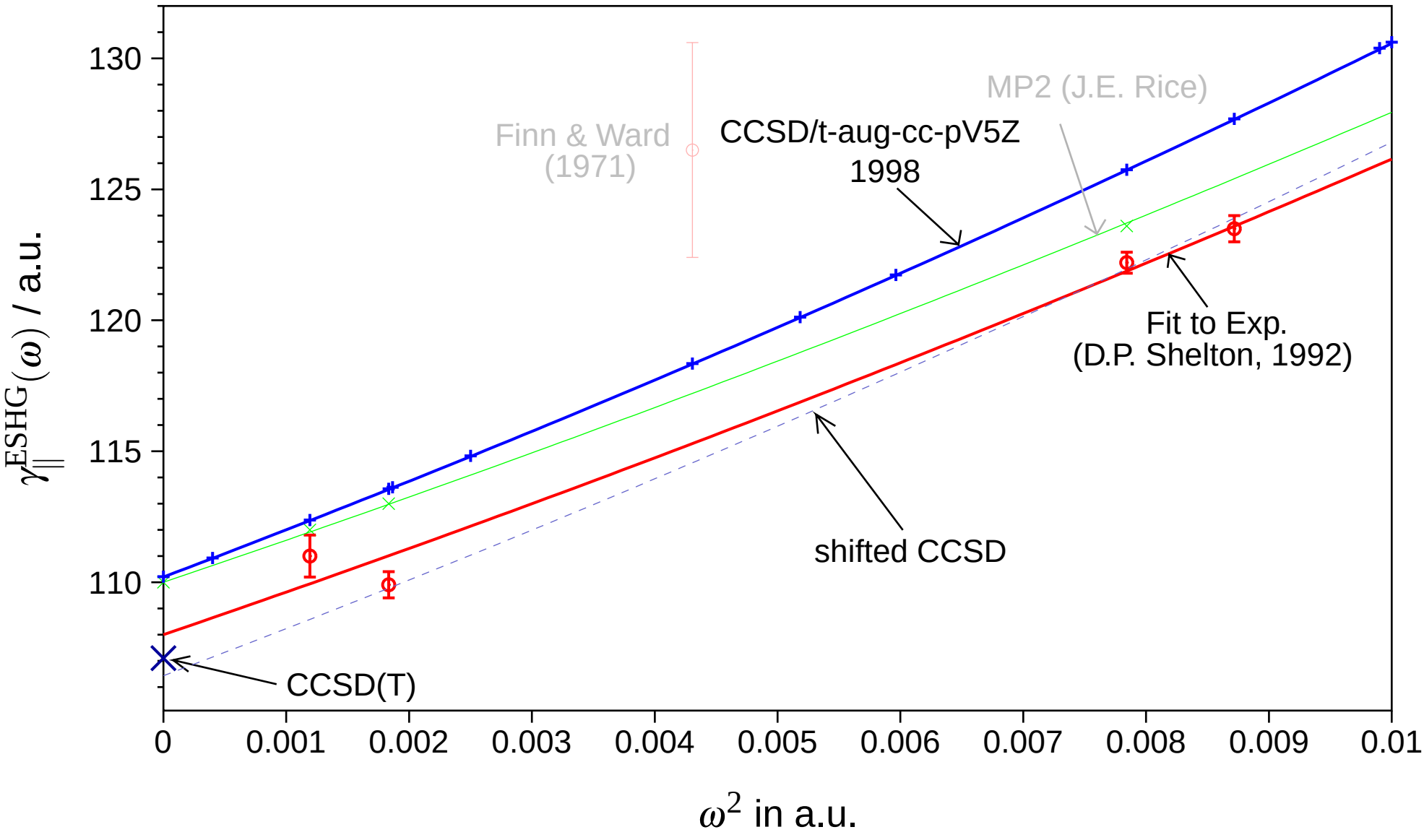
The Hyperpolarizability of Neon



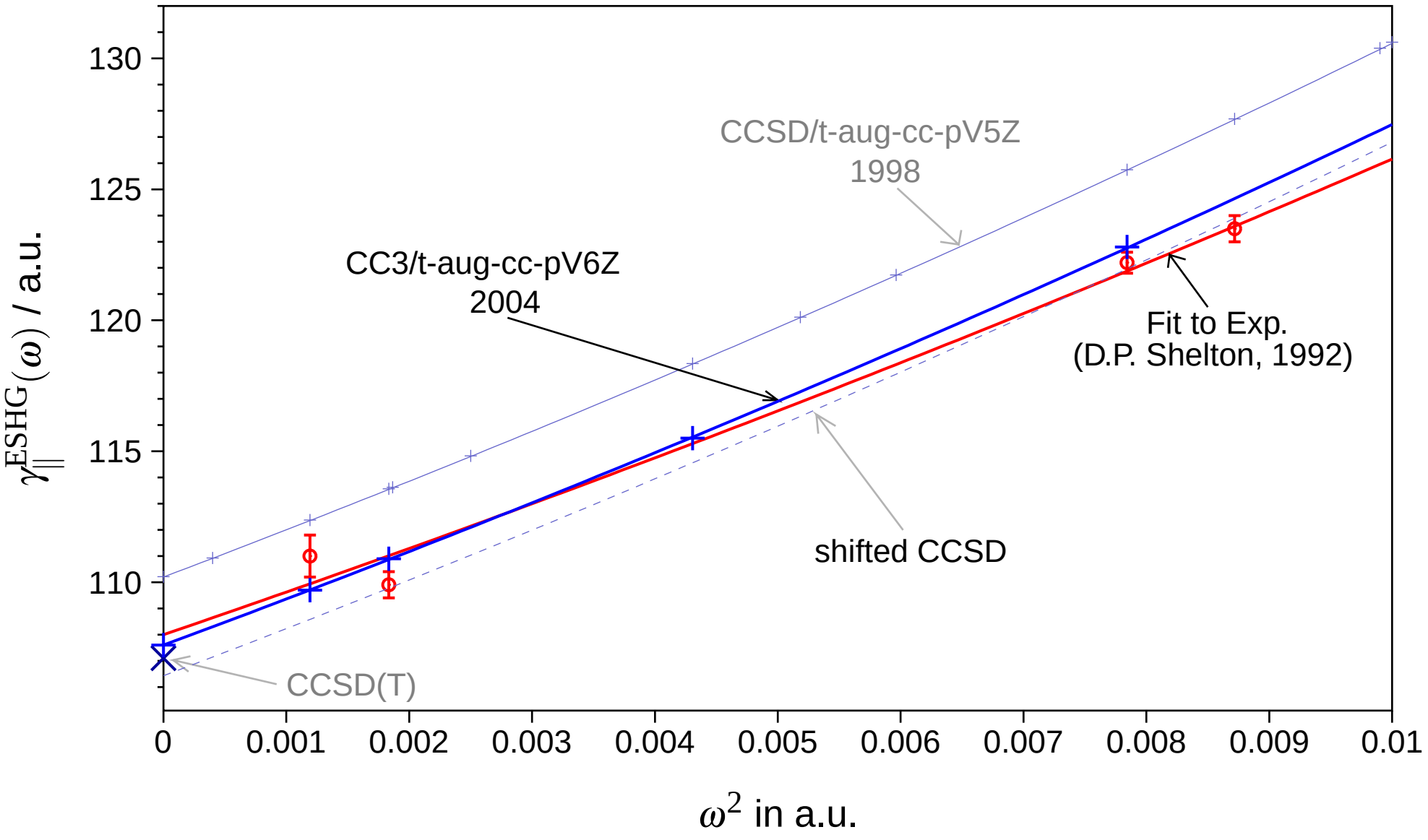
Electric Field Induced Second Harmonic Generation in Neon



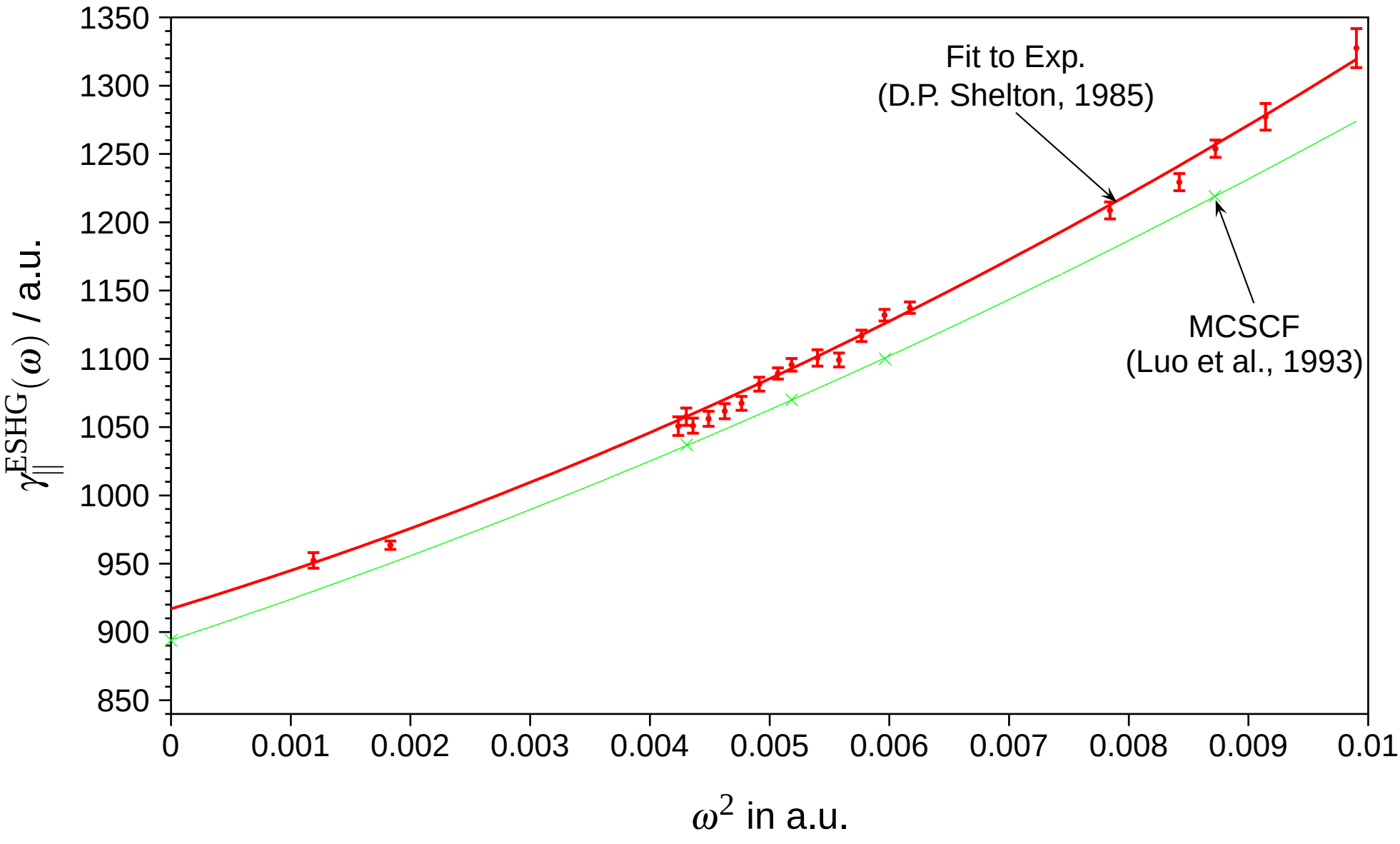
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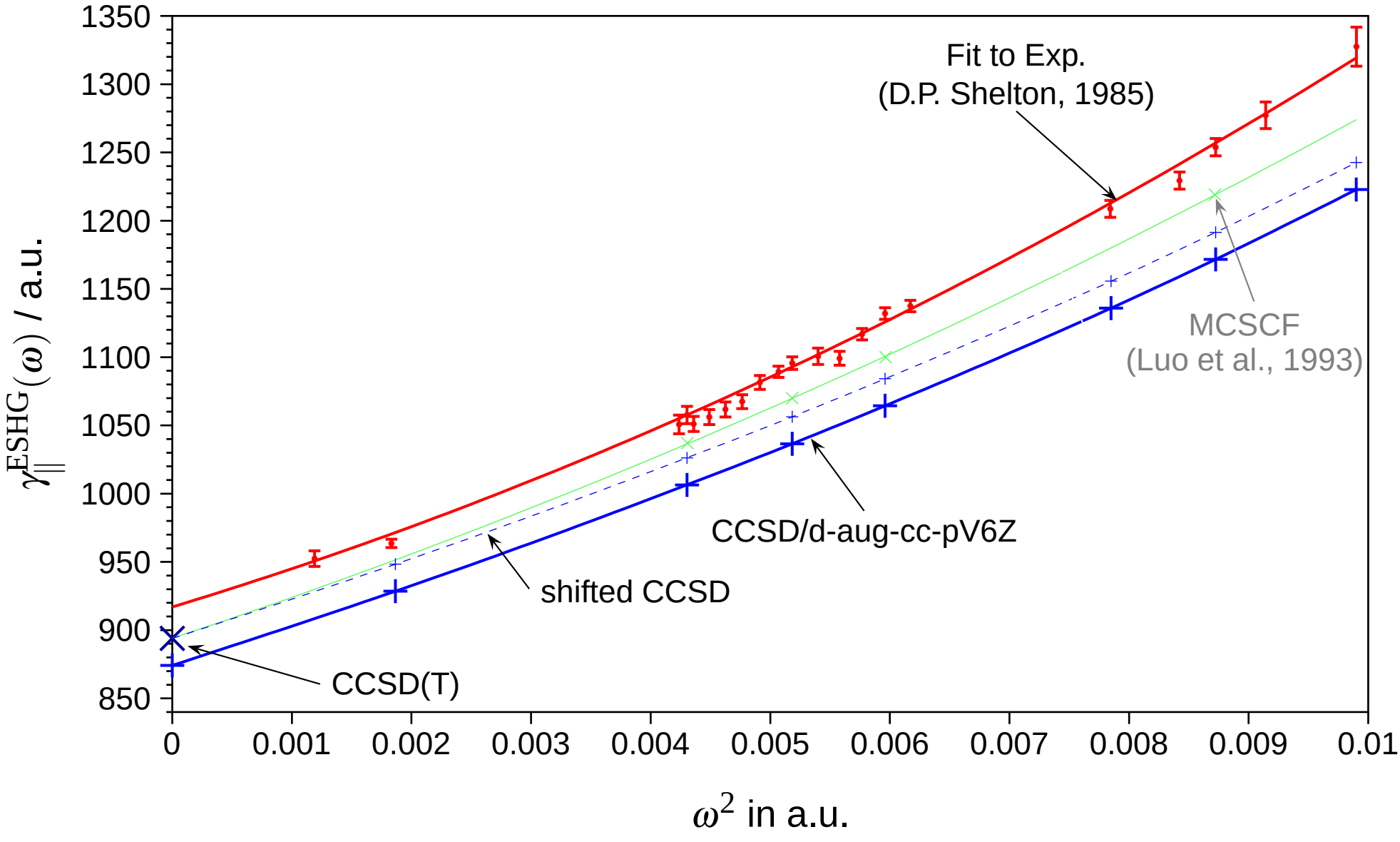
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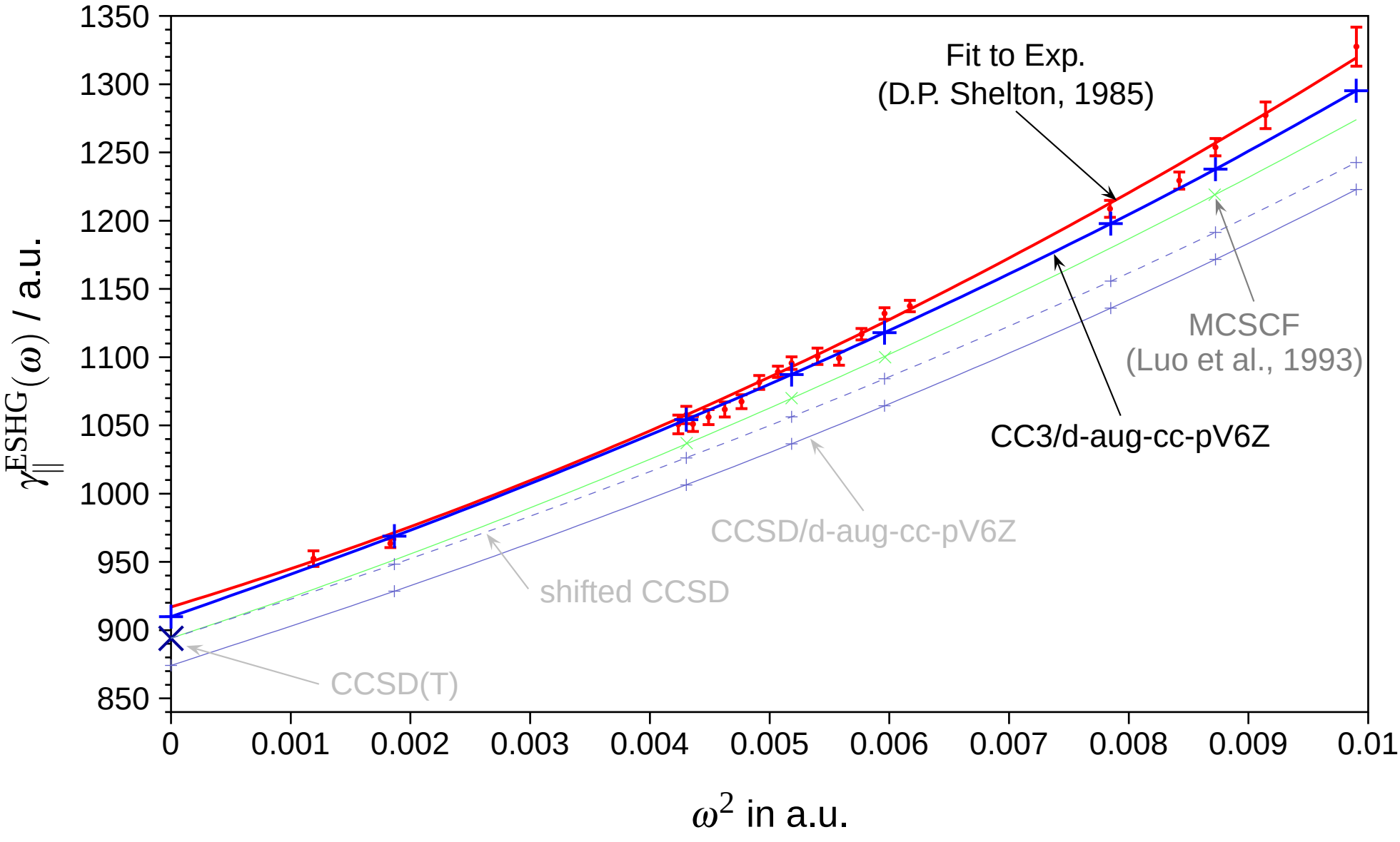
ESHG Hyperpolarizability of Nitrogen (N_2)



ESHG Hyperpolarizability of Nitrogen (N_2)



ESHG Hyperpolarizability of Nitrogen (N_2)



Vibrational Contributions

- zero point vibrational correction (ZPVC):

$$\alpha^{el}_{zpvc} = \alpha^{el}_0 - \alpha^{el}(\vec{R}_0) \qquad \text{with} \qquad \alpha^{el}_0 = \langle \Phi^{vib}_0 | \alpha^{el}(\vec{R}) | \Phi^{vib}_0 \rangle$$

- pure vibrational contribution:

$$\alpha^{vib}_0 = \sum_{n \neq 0} \left\{ \frac{\langle \Phi^{vib}_0 | \mu | \Phi^{vib}_n \rangle \langle \Phi^{vib}_n | \mu | \Phi^{vib}_0 \rangle}{E_n - E_0 - \omega} + \frac{\langle \Phi^{vib}_0 | \mu | \Phi^{vib}_n \rangle \langle \Phi^{vib}_n | \mu | \Phi^{vib}_0 \rangle}{E_n - E_0 + \omega} \right\}$$

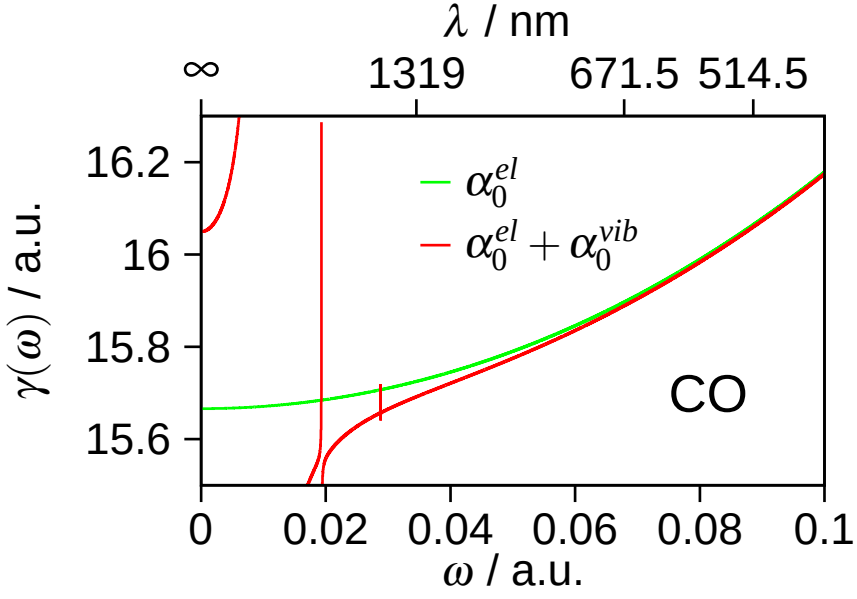
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Vibrational Contributions

- polyatomic molecules:
  - ↷ double harmonic approximation + anharmonic corrections
    - ⇝ geometric derivatives of (freq.-dep.) properties

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    - ⇝ geometric derivatives of (freq.-dep.) properties

- vibrational contribution for hyperpolarizabilities:
  - several terms (more lengthy expressions)
  - seperation into electronic and nuclear contrib. requires for freq.-dep. hyperpolarizabilities more severe approximations than for $\alpha(\omega)$
    ⇝ effect of these approximations not well known...
  - relative magnitude of vib. contrib. depends strongly on optical process:

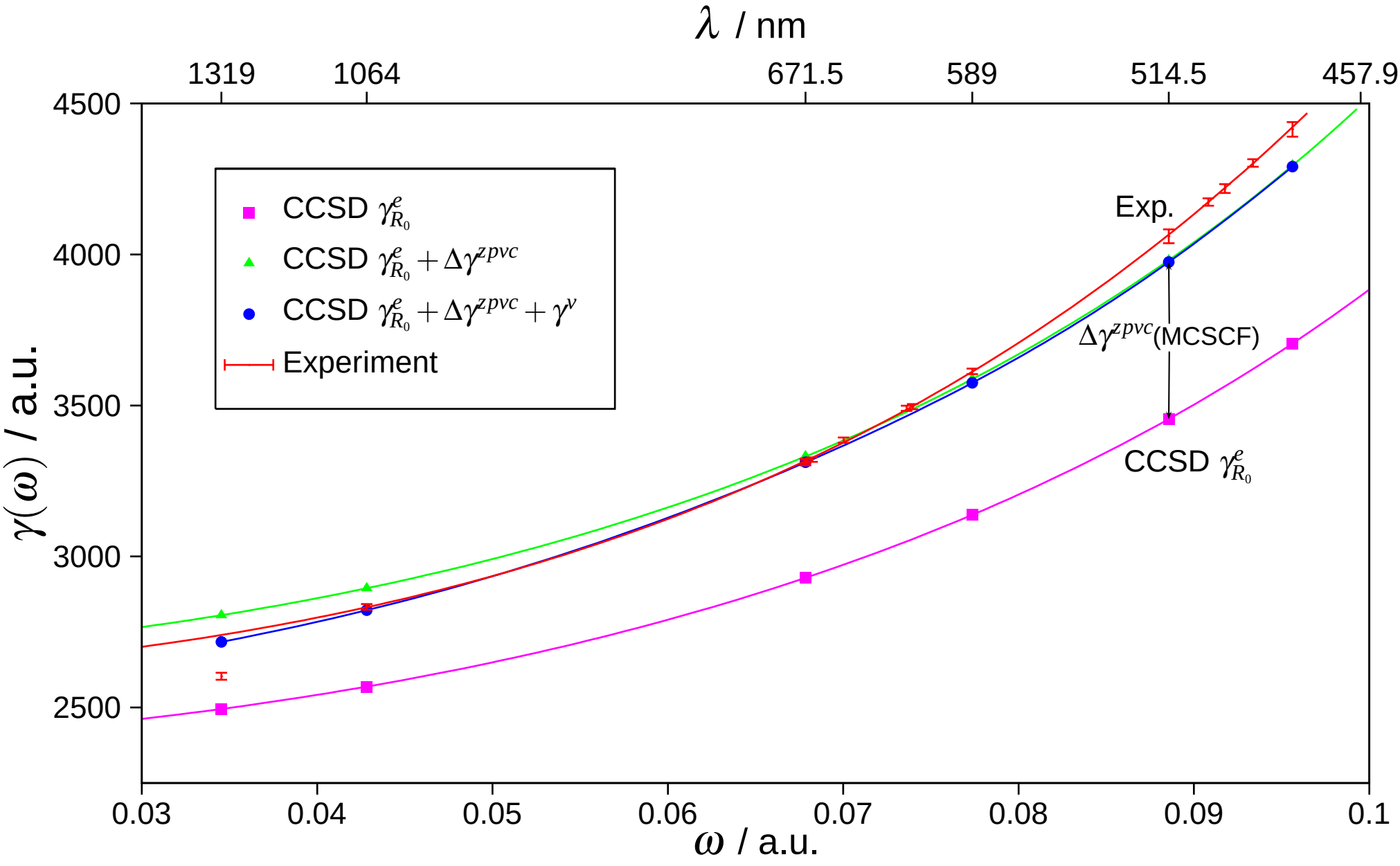
$$\gamma^{vib}_{THG}(-3\omega;\omega,\omega,\omega) \ll \gamma^{vib}_{ESHG}(-2\omega;\omega,\omega,0) \ll \gamma^{vib}_{Kerr}(-\omega;0,0,\omega) \ll \gamma^{vib}_{static}(0;0,0,0)$$

ESHG & Kerr Hyperpolarizabilities of Methane (CH_4)

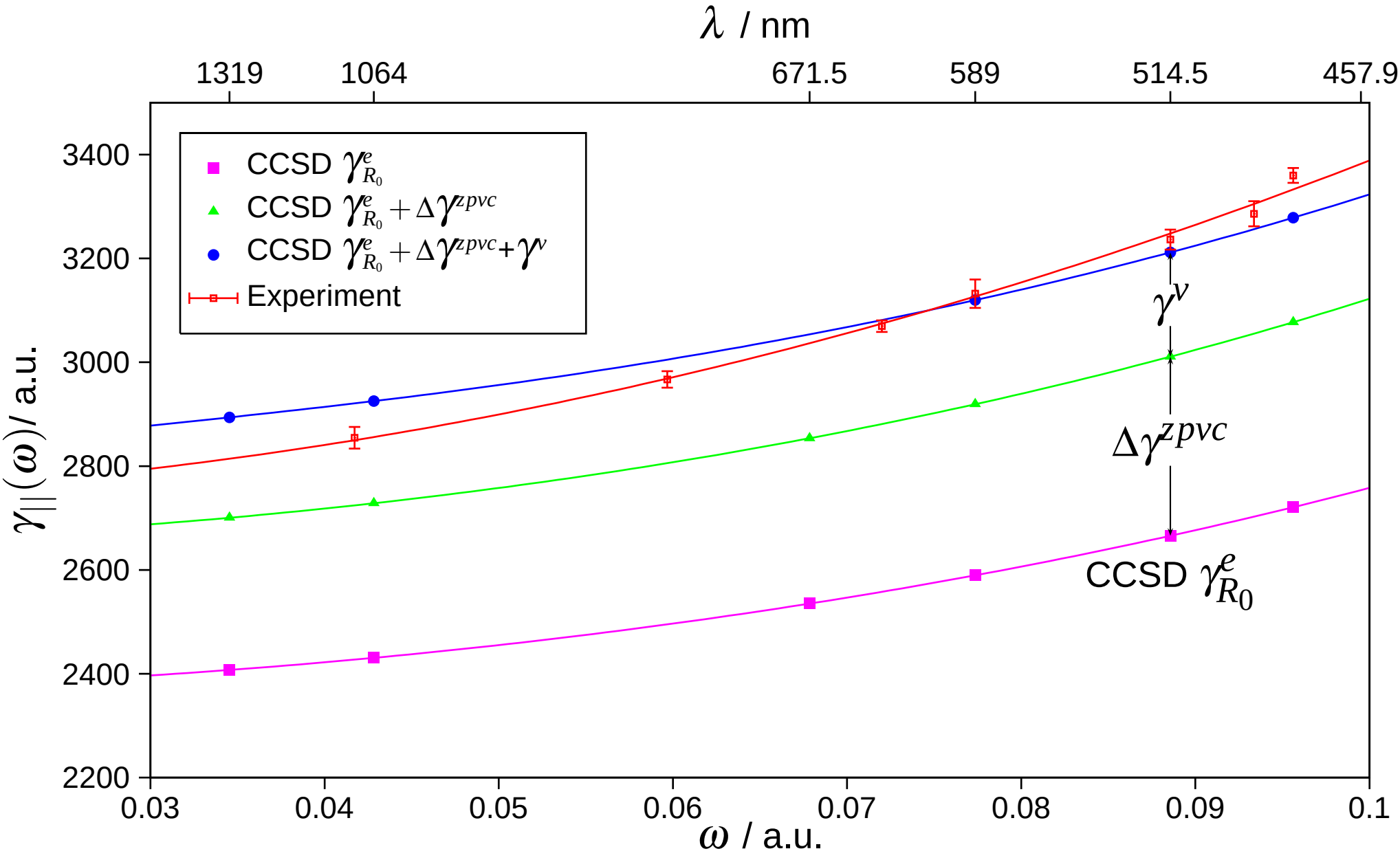
- Technical details:
  - CCSD calculations at R_0, t-aug-cc-pVTZ
  - zero point vibr. correct. from MCSCF
    Bishop, Sauer, JCP 108 (1997) 8502
  - purve vibr. contribution from SCF
    Bishop, Pipin, JCP 91 (1989) 3549

- Experimental data:
  - ESHG: Shelton, PRA 42 (1990) 2578
  - Kerr: Shelton, Palubinskas, JCP 104 (1996) 3549

ESHG Hyperpolarizability of Methane (CH_4)



Kerr Hyperpolarizability of Methane (CH_4)



Dispersion Coefficients vs. Freq.-dep. Calculations

$$\gamma_{\parallel}^{ESHG}(-2\omega;\omega,\omega,0) = \sum_{n=0}^{\infty} D_{\parallel}^{ESHG}(2n)\,\omega^{2n}$$

compare with

$$\alpha(\omega) = \sum_{n=0}^{\infty} S(-2n-n)\,\omega^{2n}$$

with $S(n)$ known as Cauchy moments

$\rightsquigarrow$ compute $D_{||}^{ESHG}(n)$ as analytic derivatives of $\gamma_{||}^{ESHG}(-2\omega;\omega,\omega,0)$

Dispersion Coefficients vs. Freq.-dep. Calculations

$$\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3) = \gamma_0(1 + A\omega_{L2}^2 + B\omega_{L2}^4 + B'\omega_{L4}^4 + C\omega_{L2}^6 + C'\omega_{L3}^6 + C''\omega_{L2}^2\omega_{L4}^4 + \ldots)$$

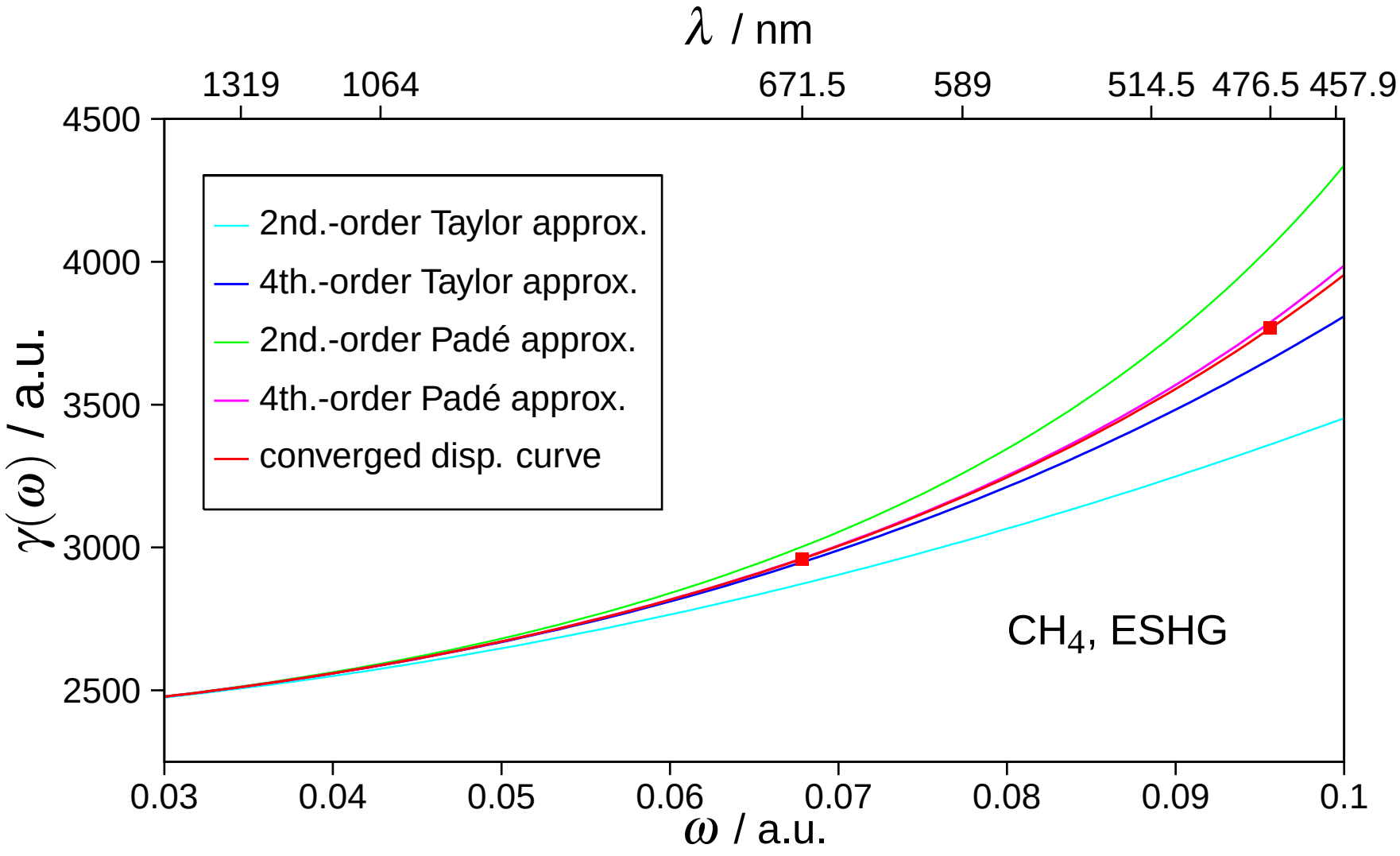
with: $\omega_{L2}^2 = \sum_i \omega_i^2$; $\omega_{L3}^3 = \sum_i \omega_i^3$; $\omega_{L4}^4 = \sum_i \omega_i^4 - \frac{1}{2}\omega_{L2}^4$

A, B, B', C, C', C'', etc. **independent** of NLO process!

$\rightsquigarrow$ can be calculated from $D_{||}$ coeffi cients

- costs for A and B coeffi cients comparable to 1 point for $\gamma_{||}^{ESHG}$

Dispersion Coefficients vs. Freq.-dep. Calculations



↷ fast convergence with rational function (Padé) approximations

Accurate Hyperpolarizabilities: Summary

- Electronic (hyper)polarizabilitites can with CC response methods be calculated with an accuracy comparable with experiment
  - hierarchy: SCF < DFT < CCSD < CC3
  - dispersion coefficients an economic alternative for dispersion curves

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Accurate Hyperpolarizabilities: Summary

- Electronic (hyper)polarizabilitites can with CC response methods be calculated with an accuracy comparable with experiment
  - hierarchy: SCF < DFT < CCSD < CC3
  - dispersion coefficients an economic alternative for dispersion curves
- vibrational contributions are more diffi cult to compute and accuracy of approximations not well known
- Comparison with experiments in condensed phase hindered by field effects, no reliable/accurate computat. approach available

Literature:

D. E. Woon, T. H. Dunning, J. Chem. Phys. 100 (1994) 2475.

O. Christiansen, C. Hättig, J. Gauss, J. Chem. Phys. 109 (1998) 4745.

C. Hättig, P. Jørgensen, J. Chem. Phys. 109 (1998) 2762.

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J. Gauss, O. Christiansen, J. F. Stanton, Chem. Phys. Lett. ???

F. Pawłowski, P. Jørgensen, C. Hättig, Chem. Phys. Lett. 391 (2004) 27.

S. Høst, P. Jørgesen, A. Köhn, F. Pawlowski, W. Klopper, C. Hättig, J. Chem. Phys. 123 (2005) 094303

F. Pawłowski, P. Jørgensen, C. Hättig, Chem. Phzsl. Lett. 413 (2005) 272

C. Hättig, Mol. Phys. 94 (1998) 455.

C. Hättig, P. Jørgensen, Adv. Quant. Chem. 35 (1999) 111.

O. Christiansen, S. Coriani, J. Gauss, C. Hättig, P. Jørgensen, F. Pawłowski, A. Rizzo,
in “Nonlinear optical properties: From molecules to condensed phases”,
Eds. M. G. Papadopoulos, J. Leszczynski, A. J. Sadlej, Kluwer Academic Publishers,
London, 2006, see also other chapters in this book

D. P. Shelton, J. E. Rice, Chem. Rev. 94 (1994) 3, as well as other articles in this issue.

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

- CC hierarchy for exc. energies & structures
- Implementation of CC2 with RI approximation
- Applications

Excitation Energies in Response Theory

The stability matrix for the quantum mechanical Lagrange functional:

$$L = \left\langle H - i\frac{\partial}{\partial t} \right\rangle + \underbrace{\sum_{\mu} \bar{t}_{\mu}\,\Omega_{\mu}}$$

constraints for
non-variational methods

variational methods:

symmetric electronic Hesse matrix

$$H_{\mu\nu} = \left(\frac{d^2 L}{dt_{\mu}\, dt_{\nu}}\right)_0$$

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

non-variational methods:

asymmetric electronic Jacoby matrix

$$A_{\mu\nu} = \left(\frac{d^2 L}{d\bar{t}_{\mu}\, dt_{\nu}}\right)_0$$

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

The Coupled-Cluster Jacobian & Excited States

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

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- $\mathbf{A}$ is a representation of $\hat{H} - E_0$ in the *similarity transformed* basis

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

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

- 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
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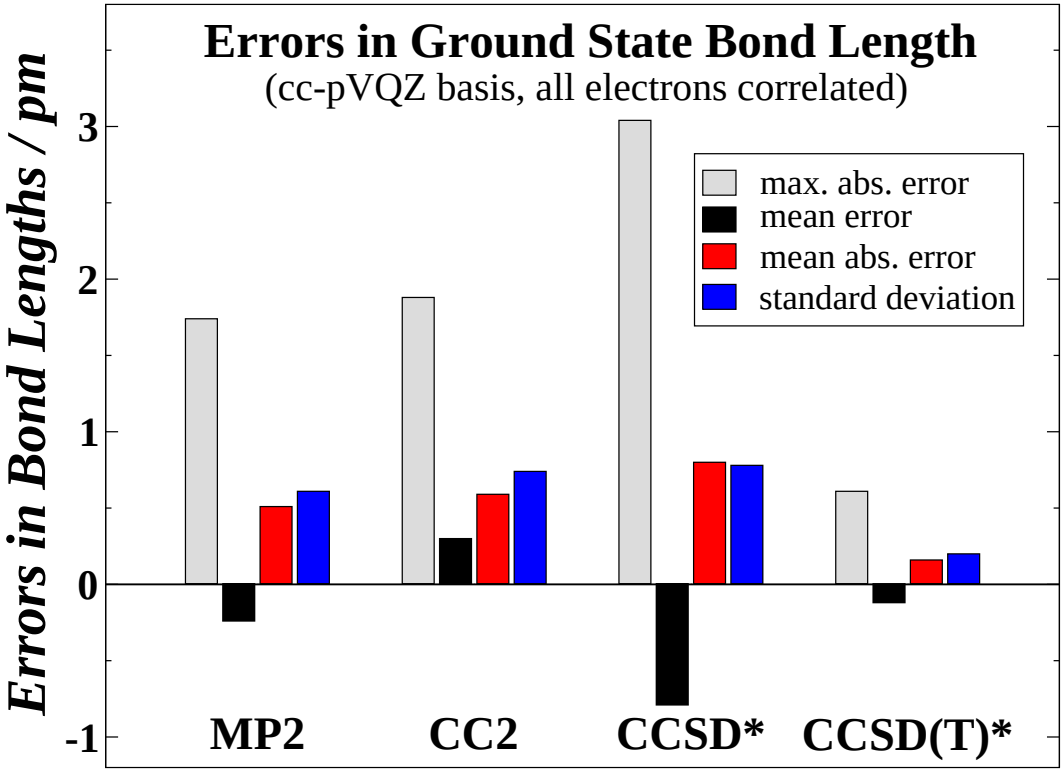
Disadvantages:

- 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.)	√	√ / √	—	√
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

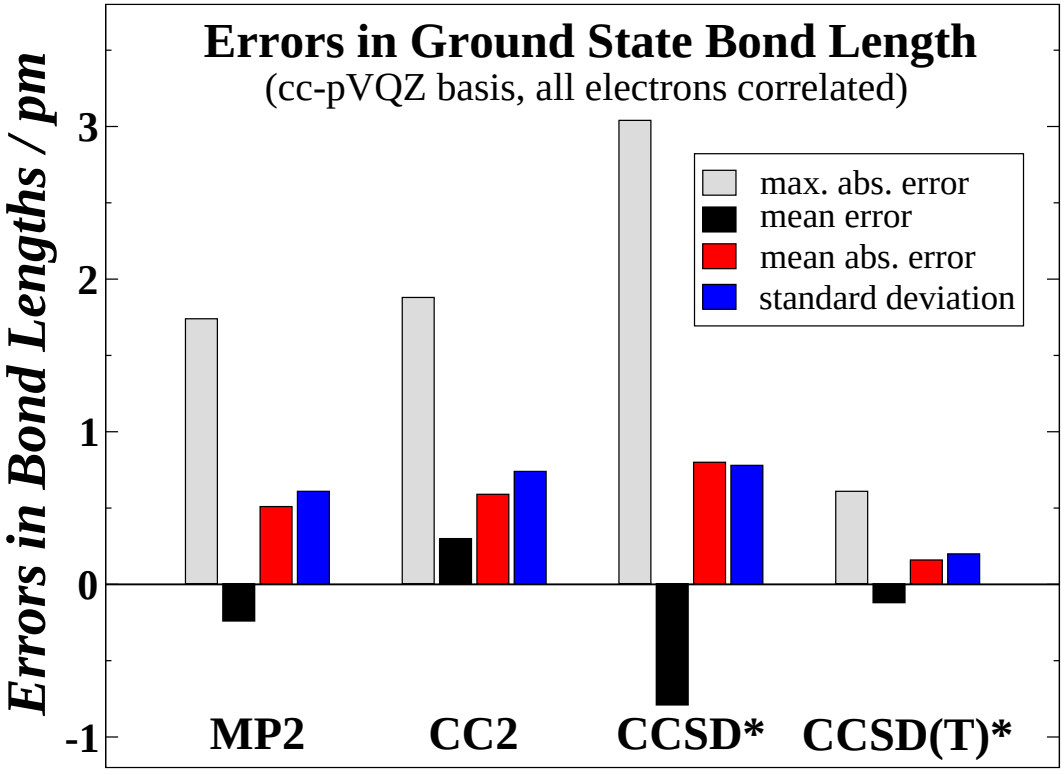


(*Test set for CCSD and CCSD(T) included in addition Ozon)

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

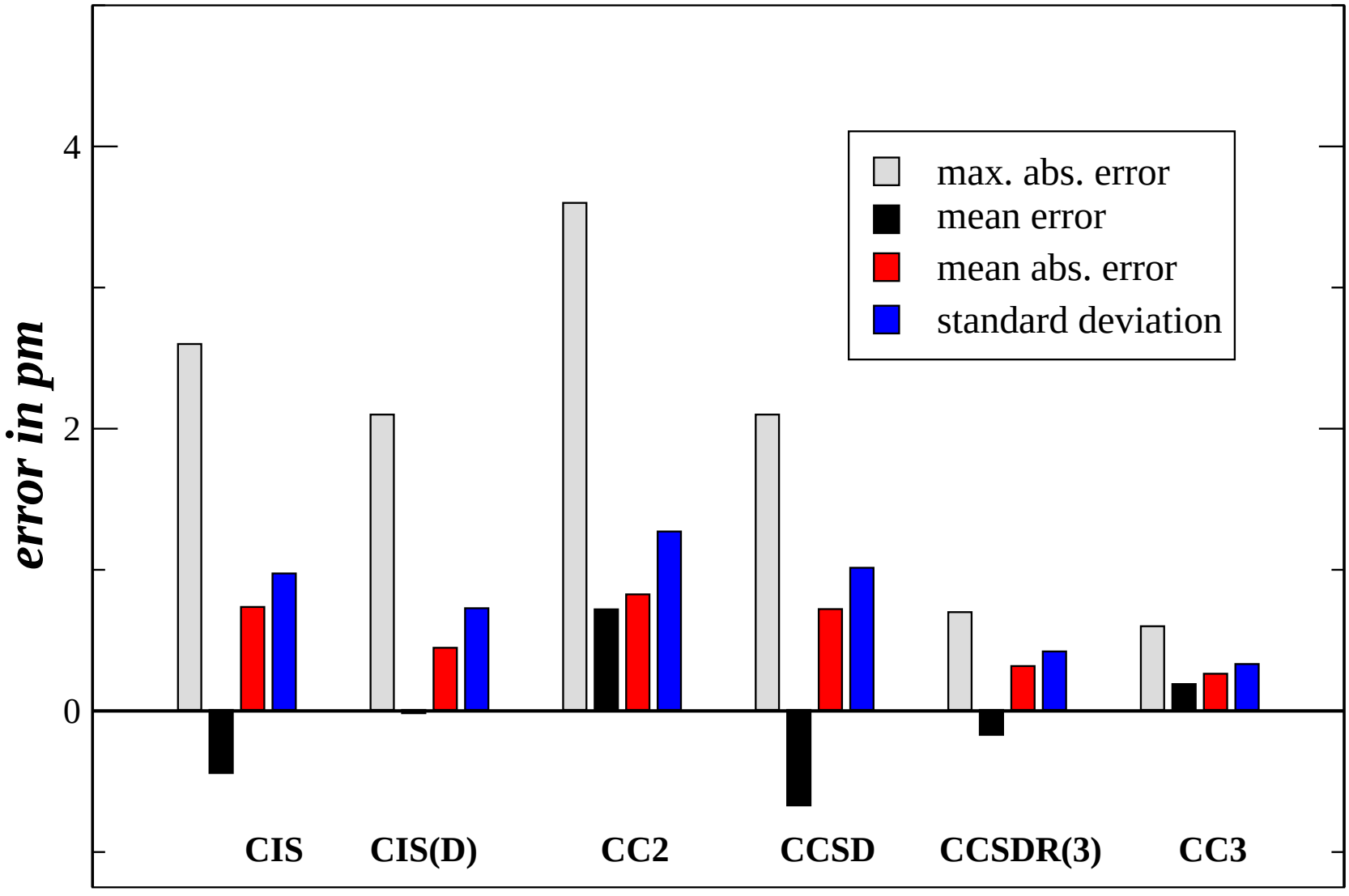
BF : $a\ ^3\Pi$, $A\ ^1\Pi$, $B\ ^1\Sigma^+$, $C\ ^1\Sigma^+$, $b\ ^3\Sigma^+$, $d\ ^3\Pi$

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

Technical details:

- aug-cc-pwCVQZ basis
- all electrons correlated

Change of Bond Lengths in Excited States



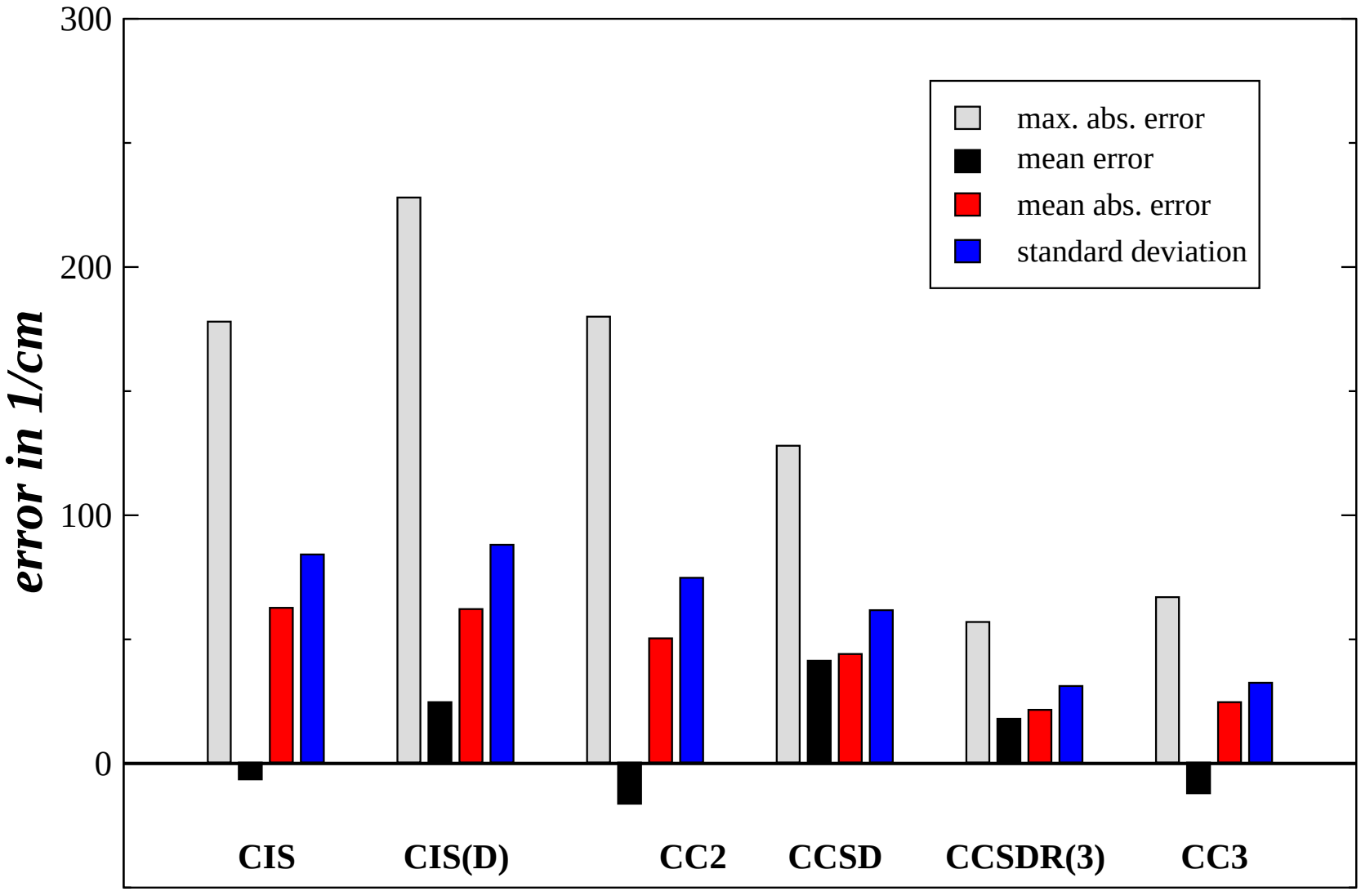
- bond lengths of excited states follow similar trends as in ground state

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

Change of Harmonic Frequencies in Excited States



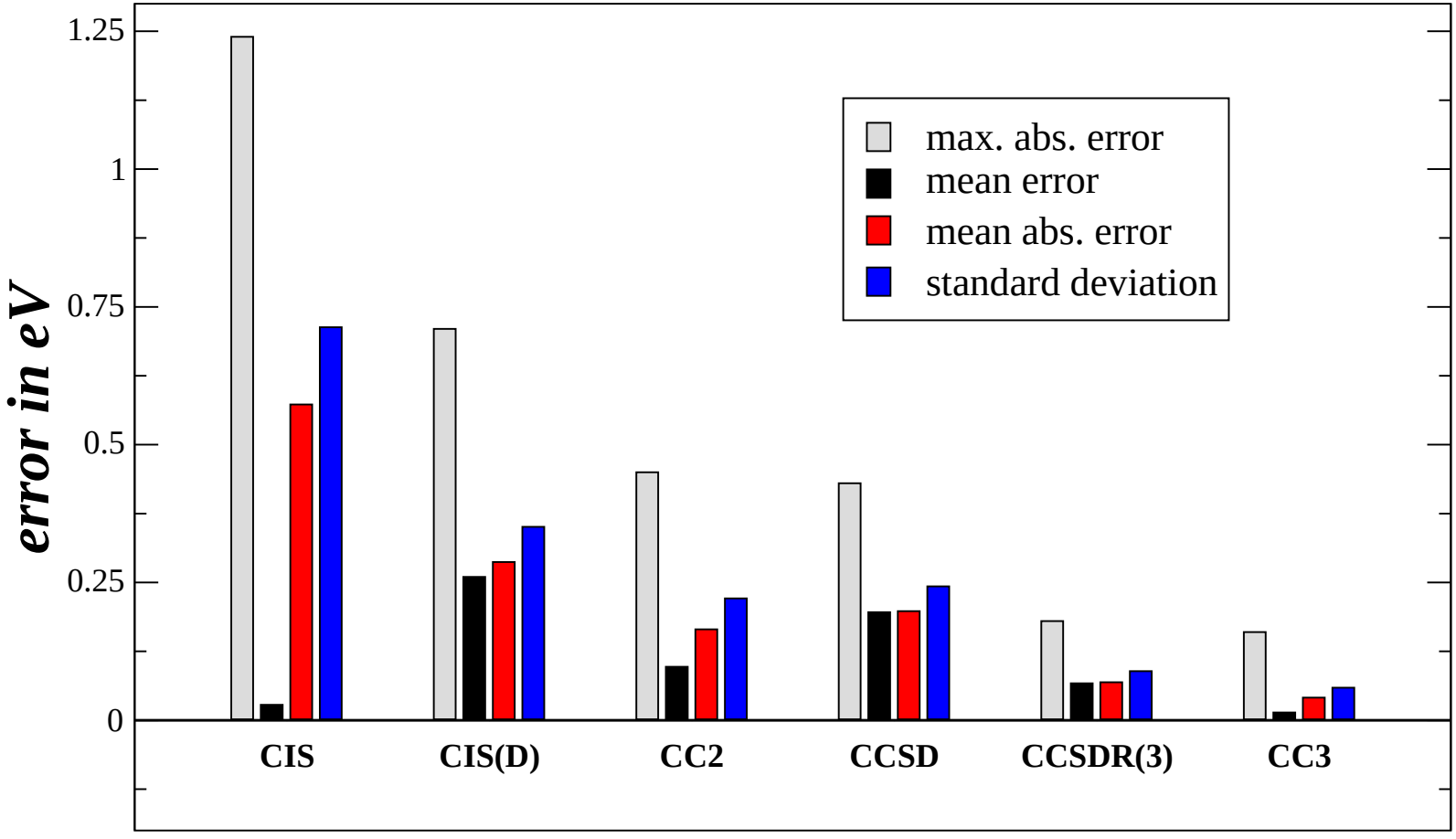
- harmonic frequencies follow the trends found for bond lengths

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

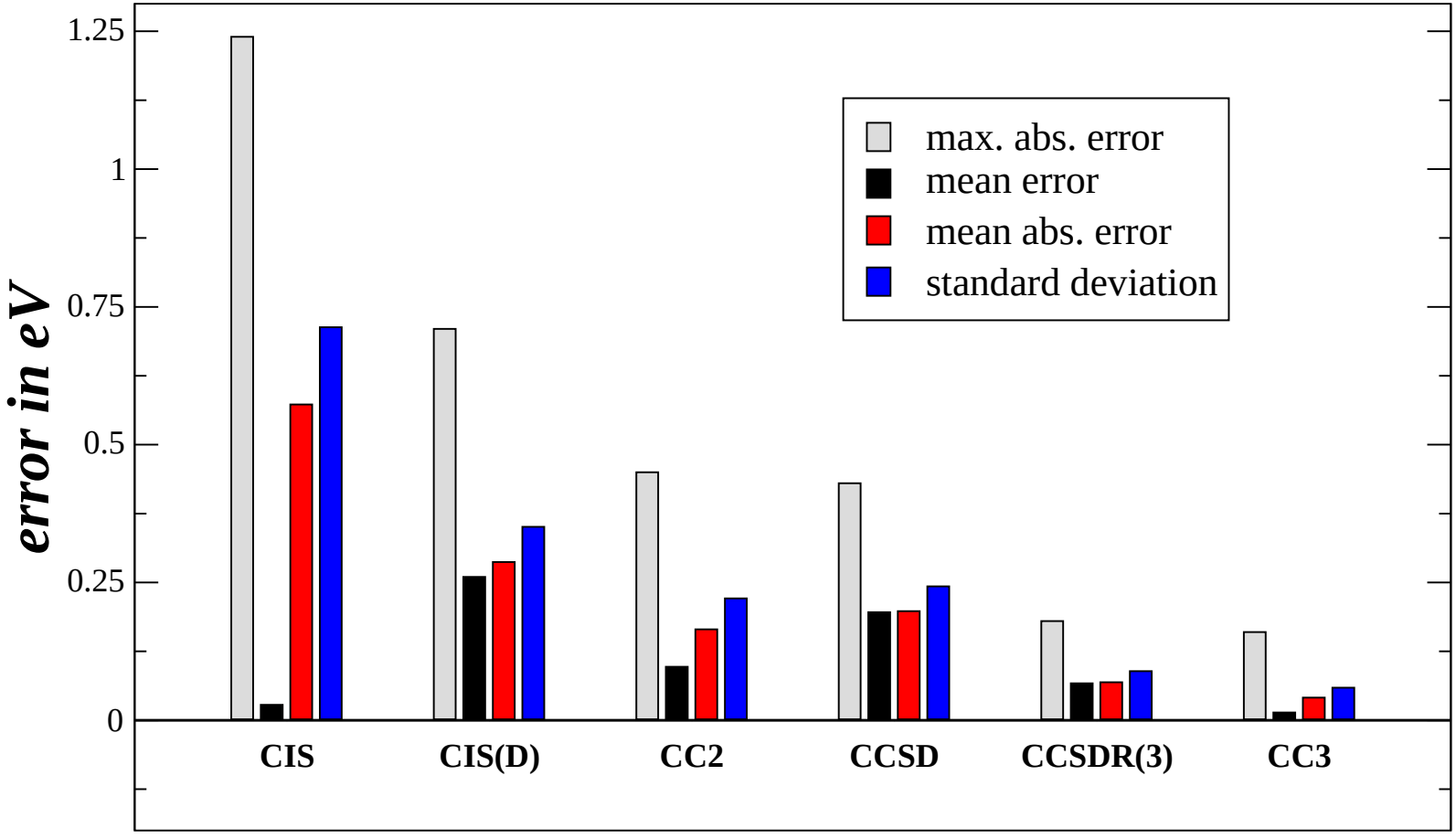
(calculated in the harmonic approximation; aug-cc-pVQZ basis; frozen core)

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



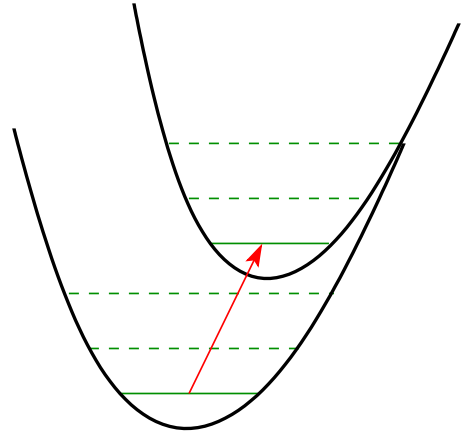
- **errors in adiabatic excitation energies decrease in the order:**

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



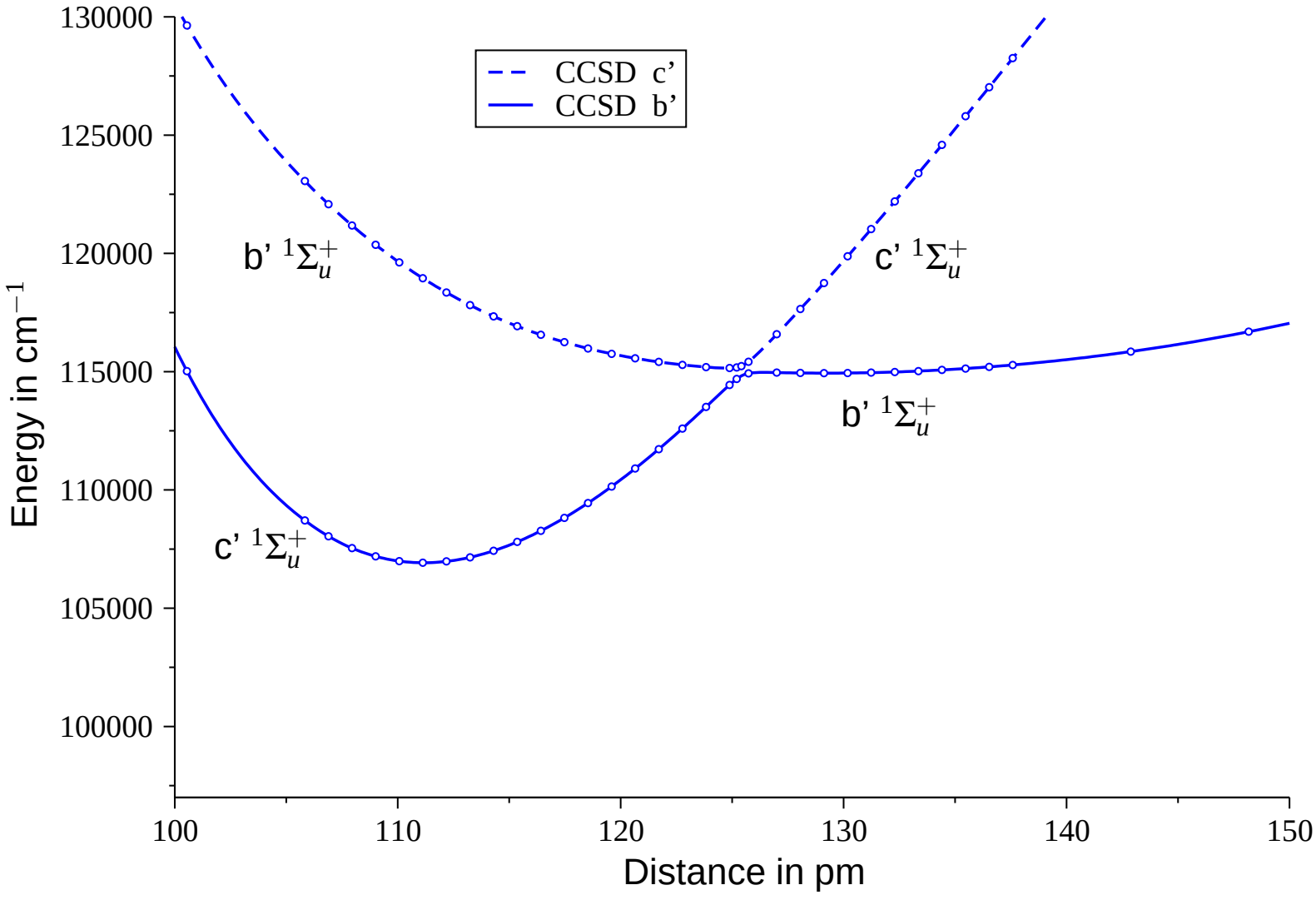
Breakdown of Perturbation Theory: (Avoided) Crossings

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)



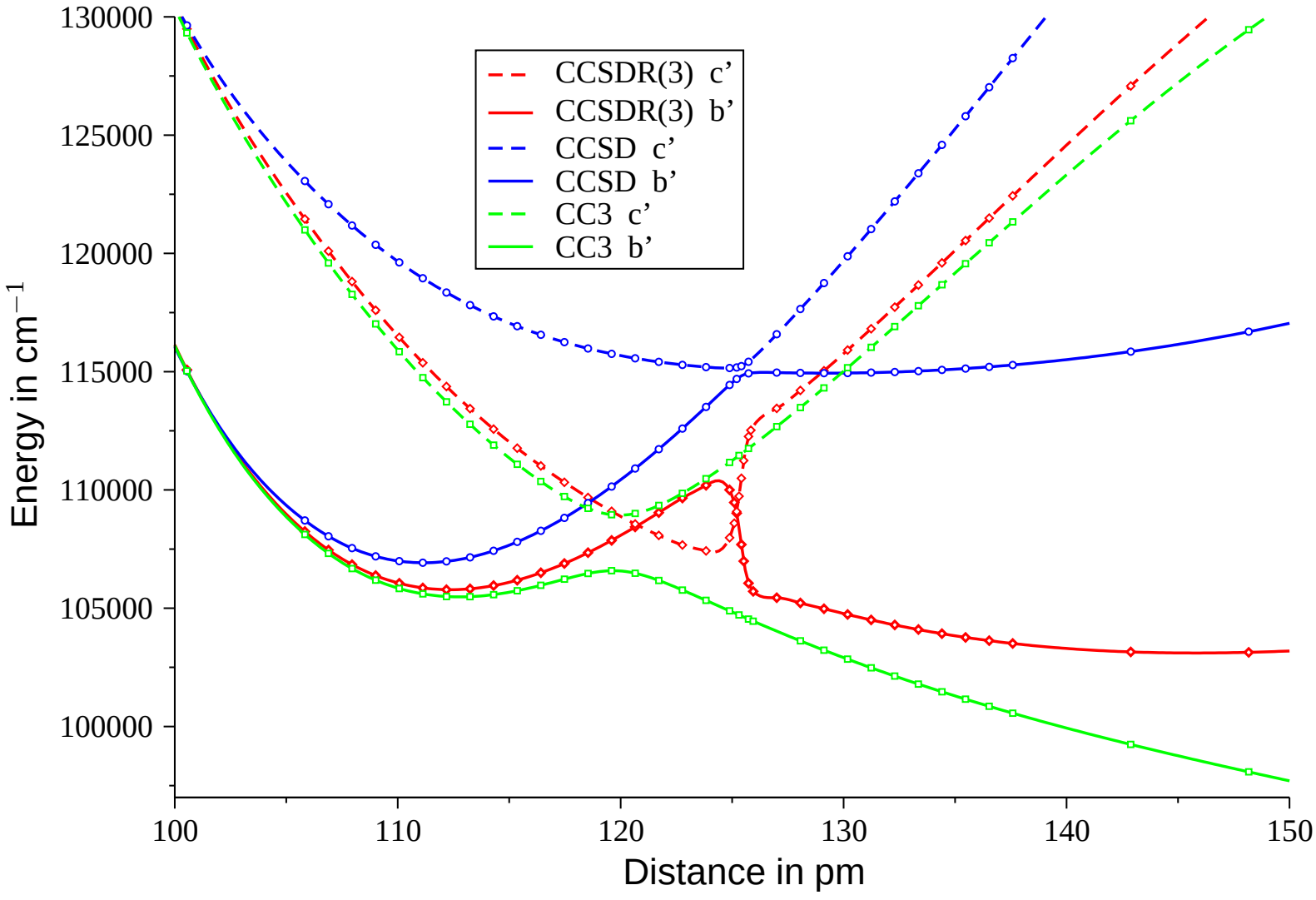
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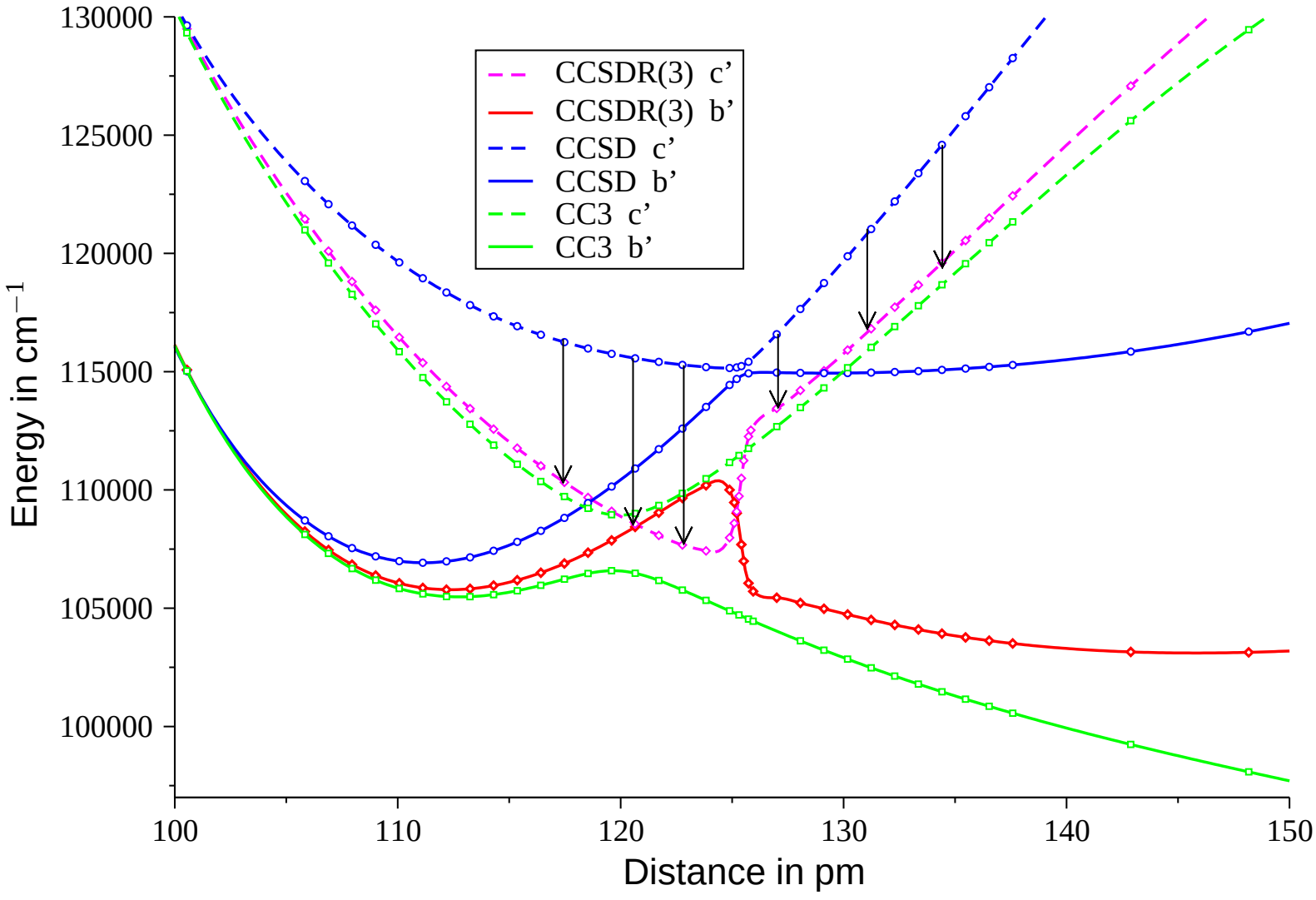
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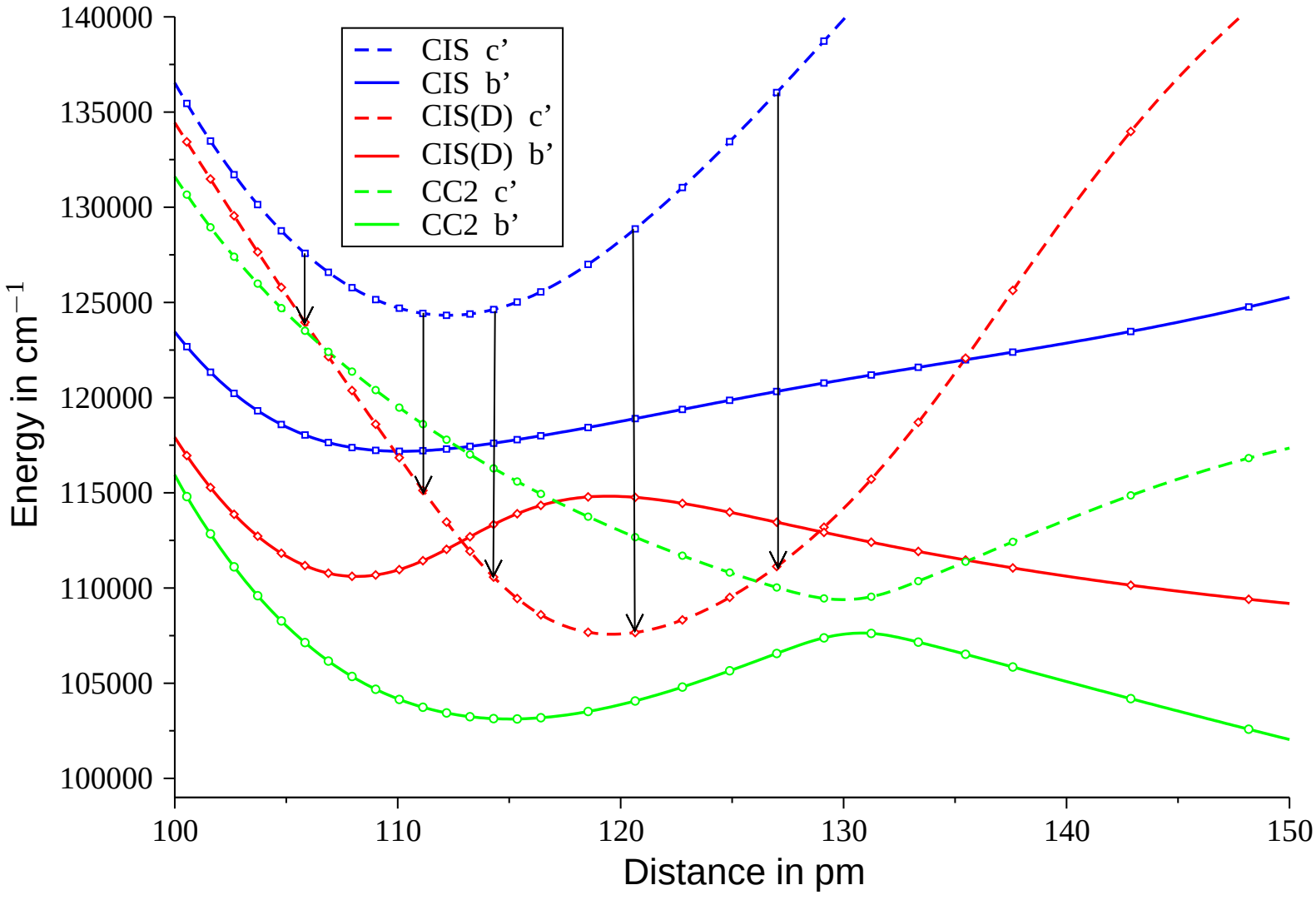
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The Eigenvalue Problem for Approximate Doubles Models

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

μ_1, ν_1 single replacements

μ_2, ν_2 double replacements

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

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

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

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

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

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

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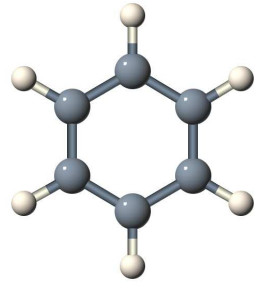
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Computational Savings of RI-MP2 ↔ MP2

Benzol:

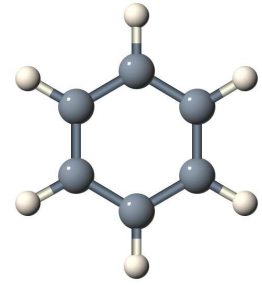
Basis	# Fkt.	MP2	RI-MP2
QZVPP	522	28 min	24 sec
aug-cc-pVQZ	756	3.8 h	1.2 min



Computational Savings of RI-MP2 ↔ MP2

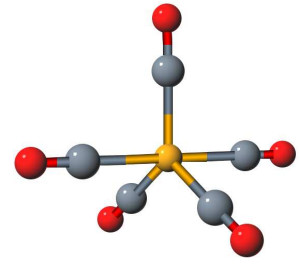
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$Fe(CO)_5$:

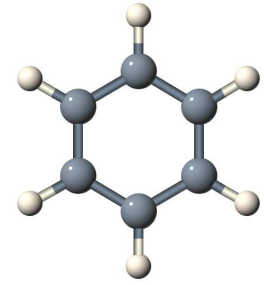
Basis	# Fkt.	MP2	RI-MP2
QZVPP	670	11.3 h	8.7 min



Computational Savings of RI-MP2 ↔ MP2

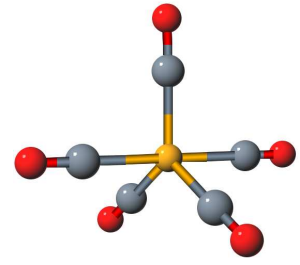
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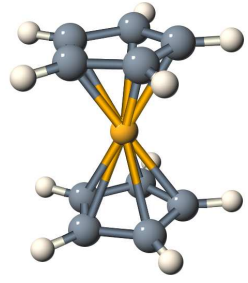
$Fe(CO)_5$:

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



Ferrocen:

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



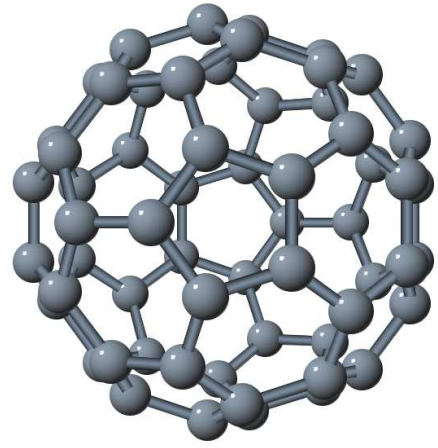
Parallel Implementation of RI-MP2: Fullerenes

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



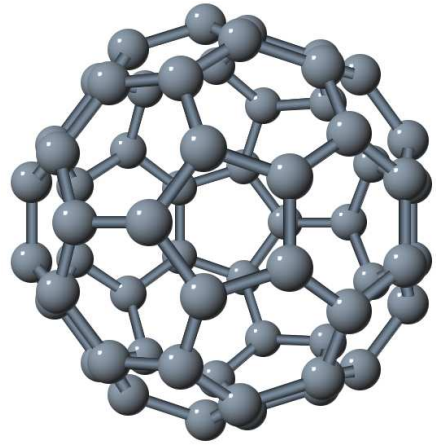
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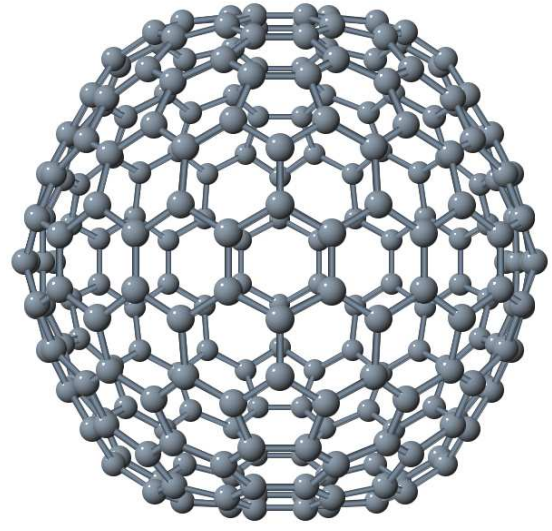
cc-pVQZ, 3300 Bf.

RI-MP2:	7 CPUs	59 min



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

RI-MP2:	19 CPUs	16 h 6 min



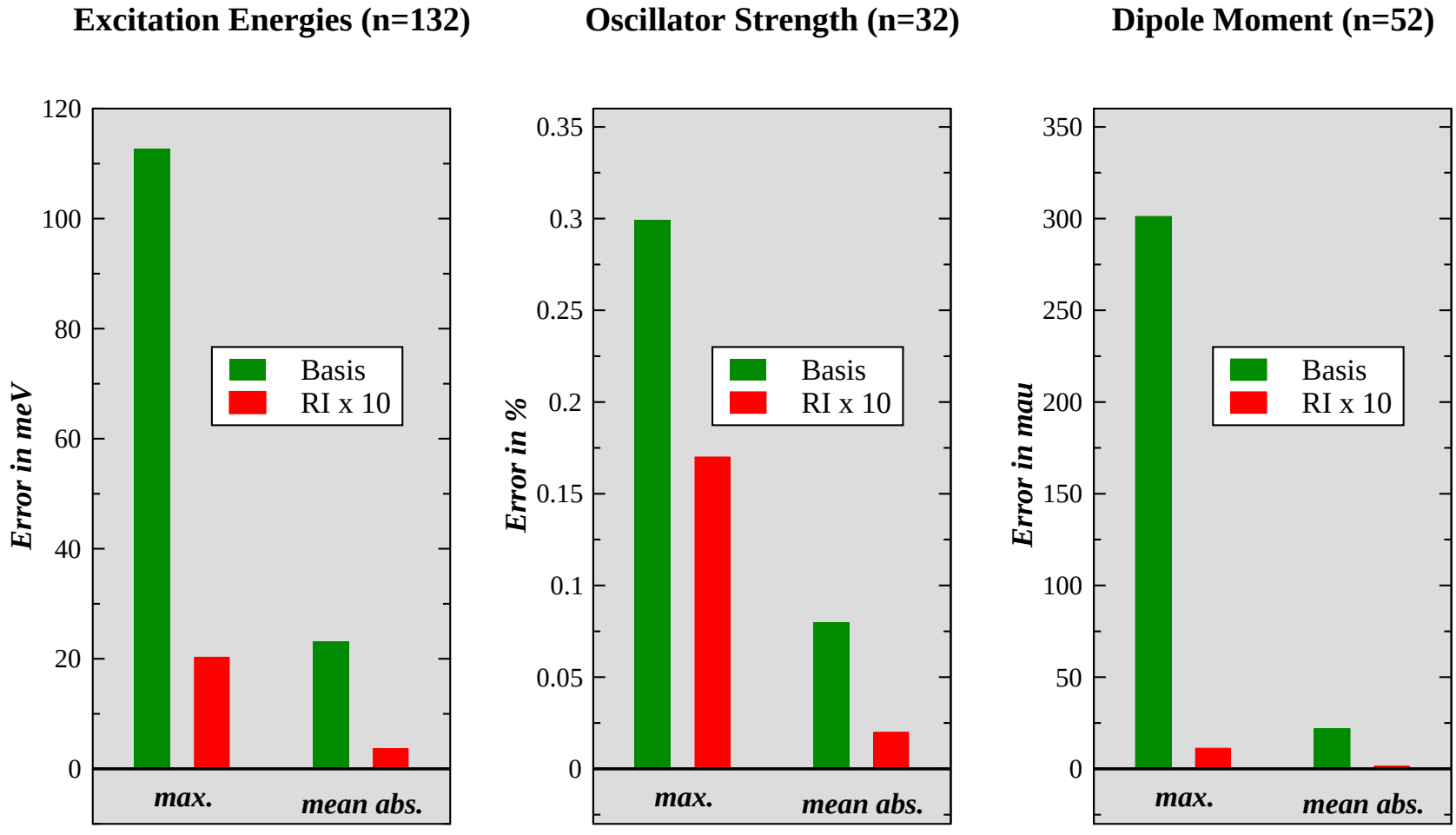
Advantages of the Resolution-of-the-Identity Approximation

- CPU time reduced typically by a factor of 10–100 or more
- allows efficient doubles amplitude-direct implementation
  $\Rightarrow$ no storage of $\mathcal{N}^4$ intermediates in memory or on disk!
- independent of localization and/or prescreening schemes
  $\Rightarrow$ applicable to excitation energy calculations

Comparison of Basis Set and RI Errors

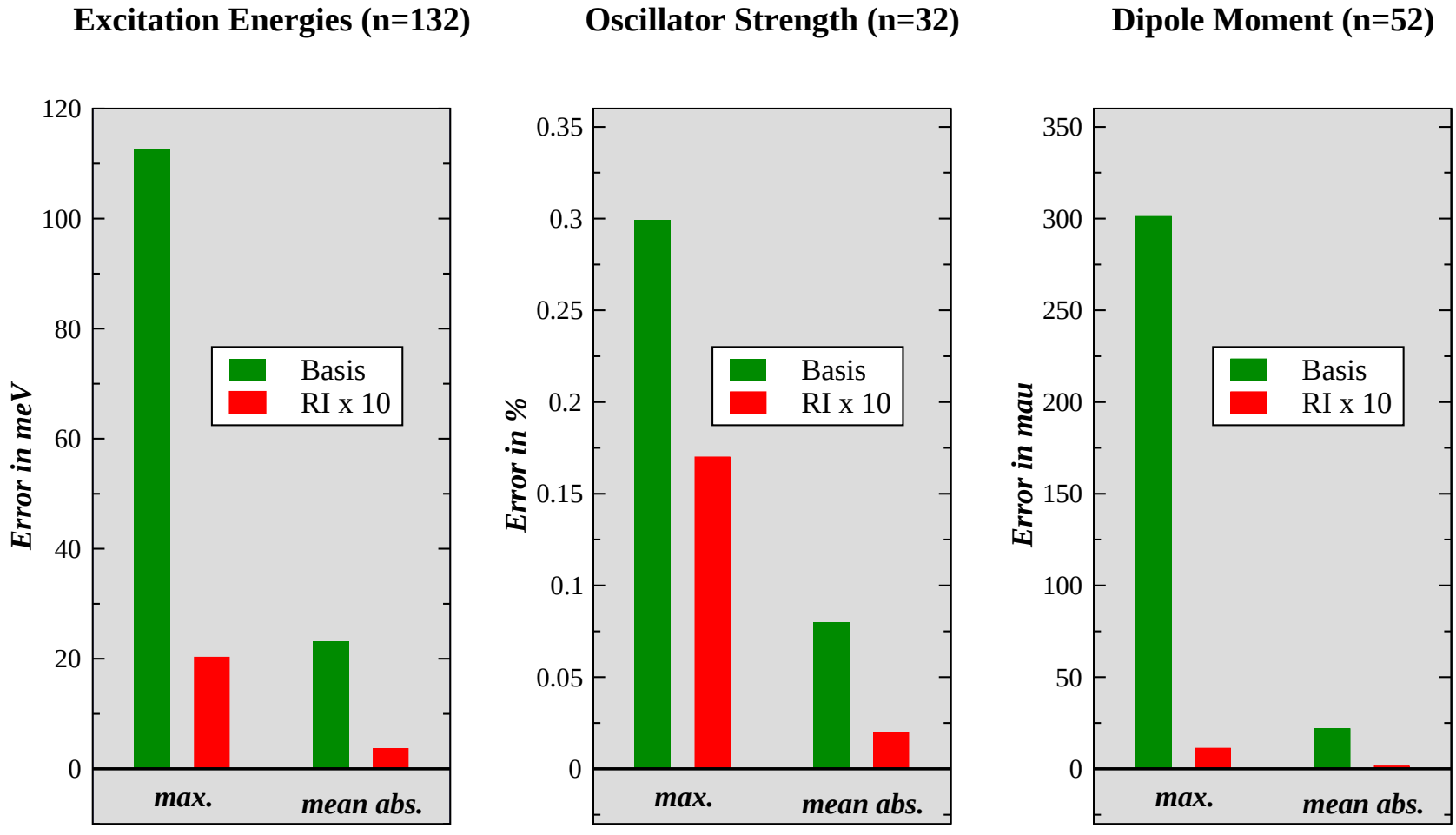
orbital basis: aug-cc-pVTZ

auxiliary basis: aug-cc-pVTZ



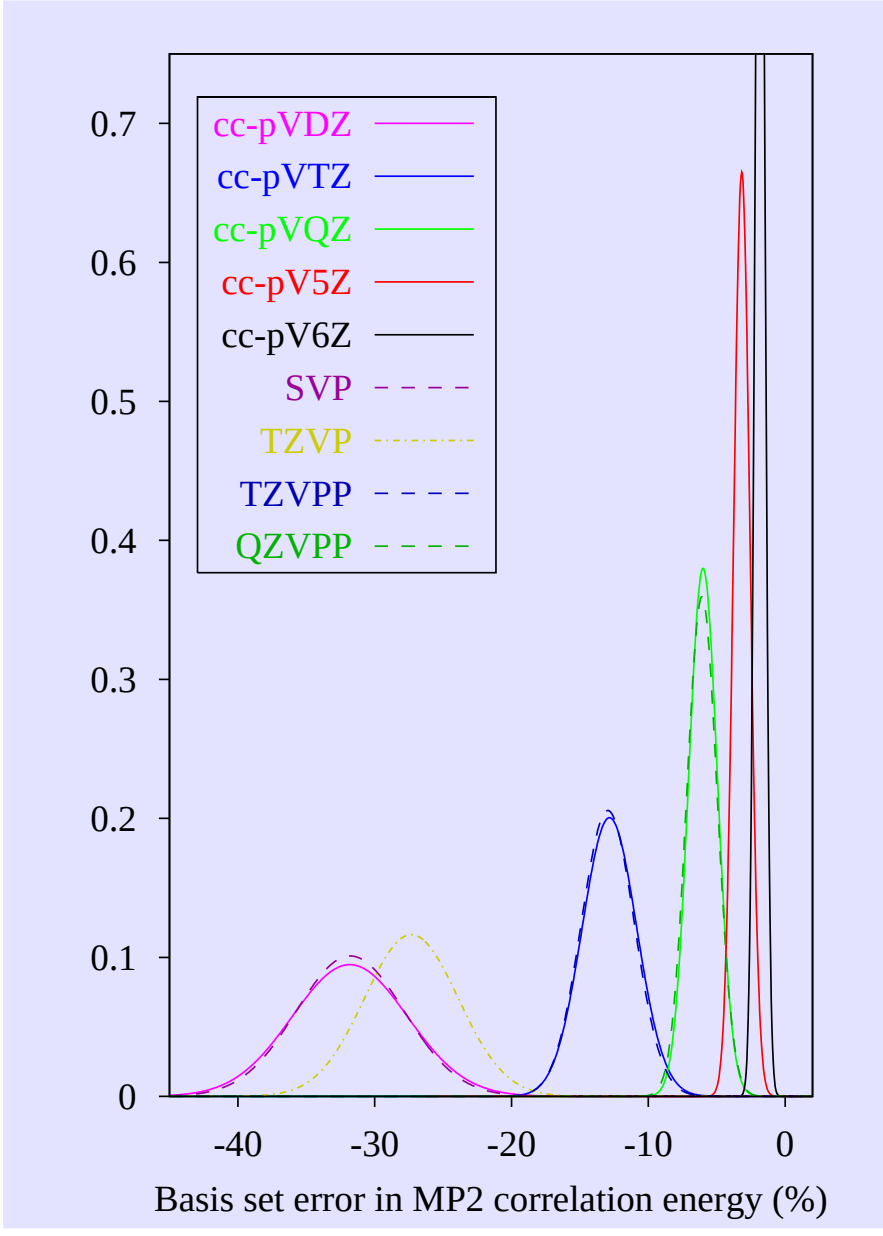
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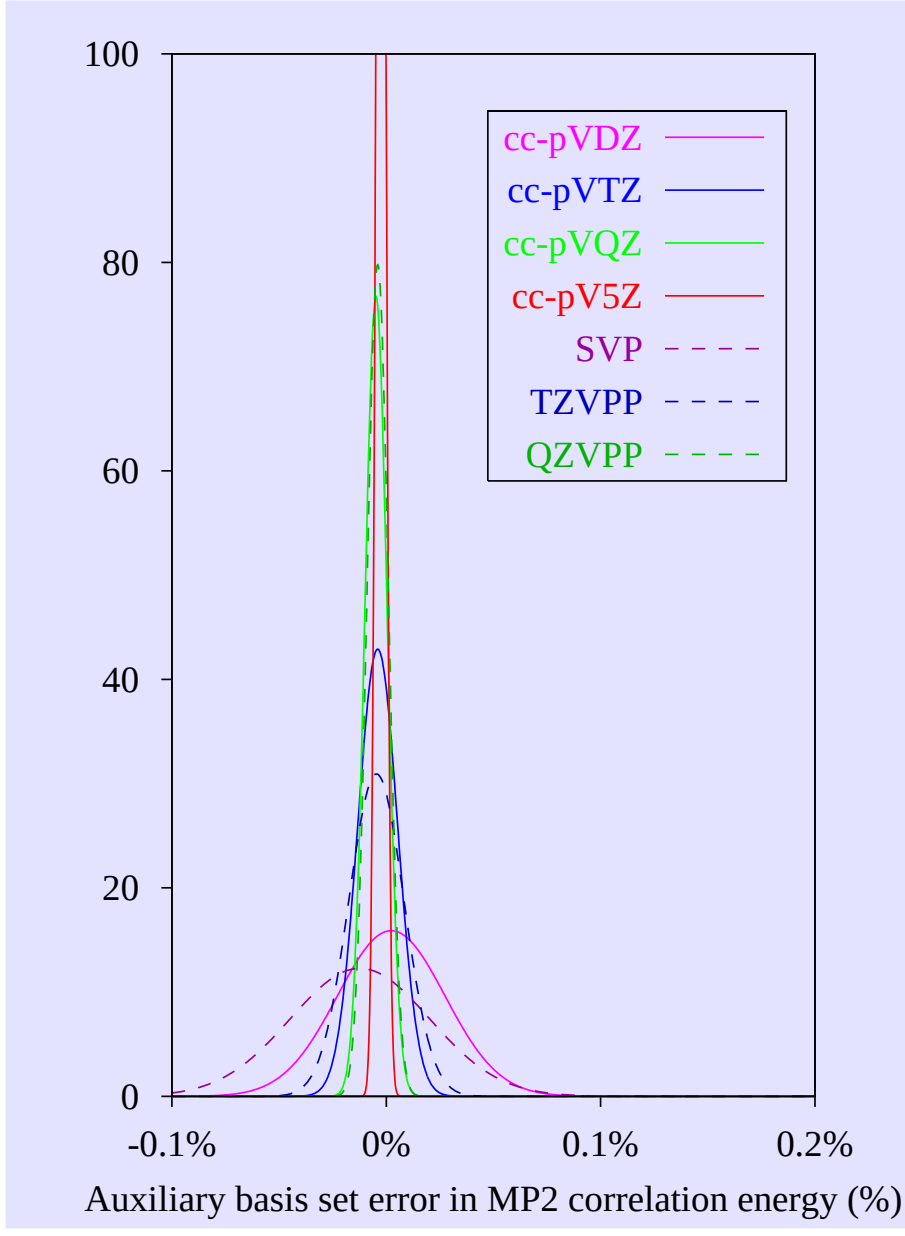
orbital basis: aug-cc-pVTZ auxiliary basis: aug-cc-pVTZ



- Error caused by RI approximation is 10–1000 times smaller than basis set error.

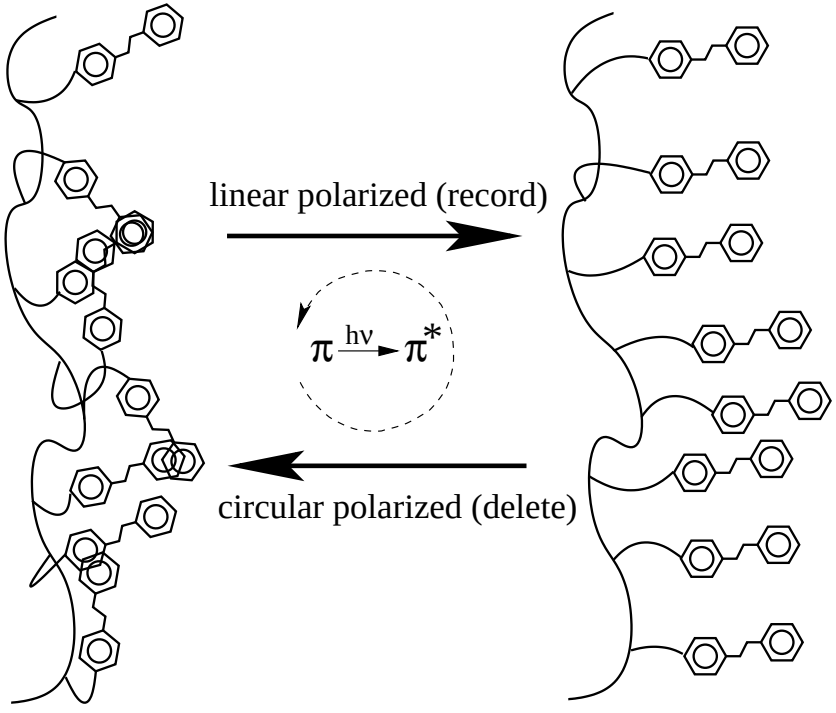
Auxiliary basis sets for the hierarchy cc-pVXZ





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

Optical data storage in polymers containing azobenzene dyes:

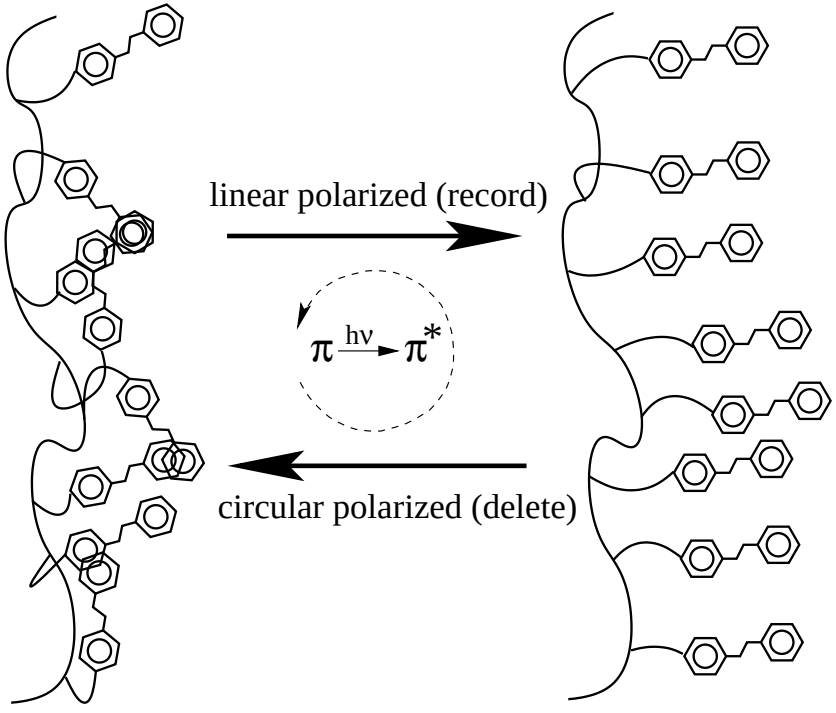


$\Rightarrow$ motivated a SOPPA study:

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

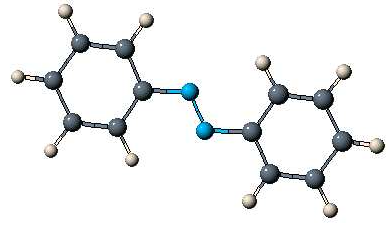
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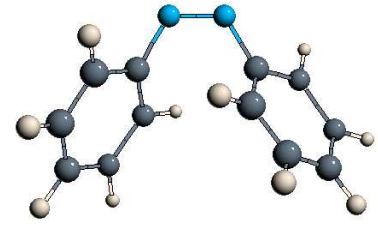


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P.-O. Åstrand et al., JACS 2000, 122, 3482



trans



cis

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

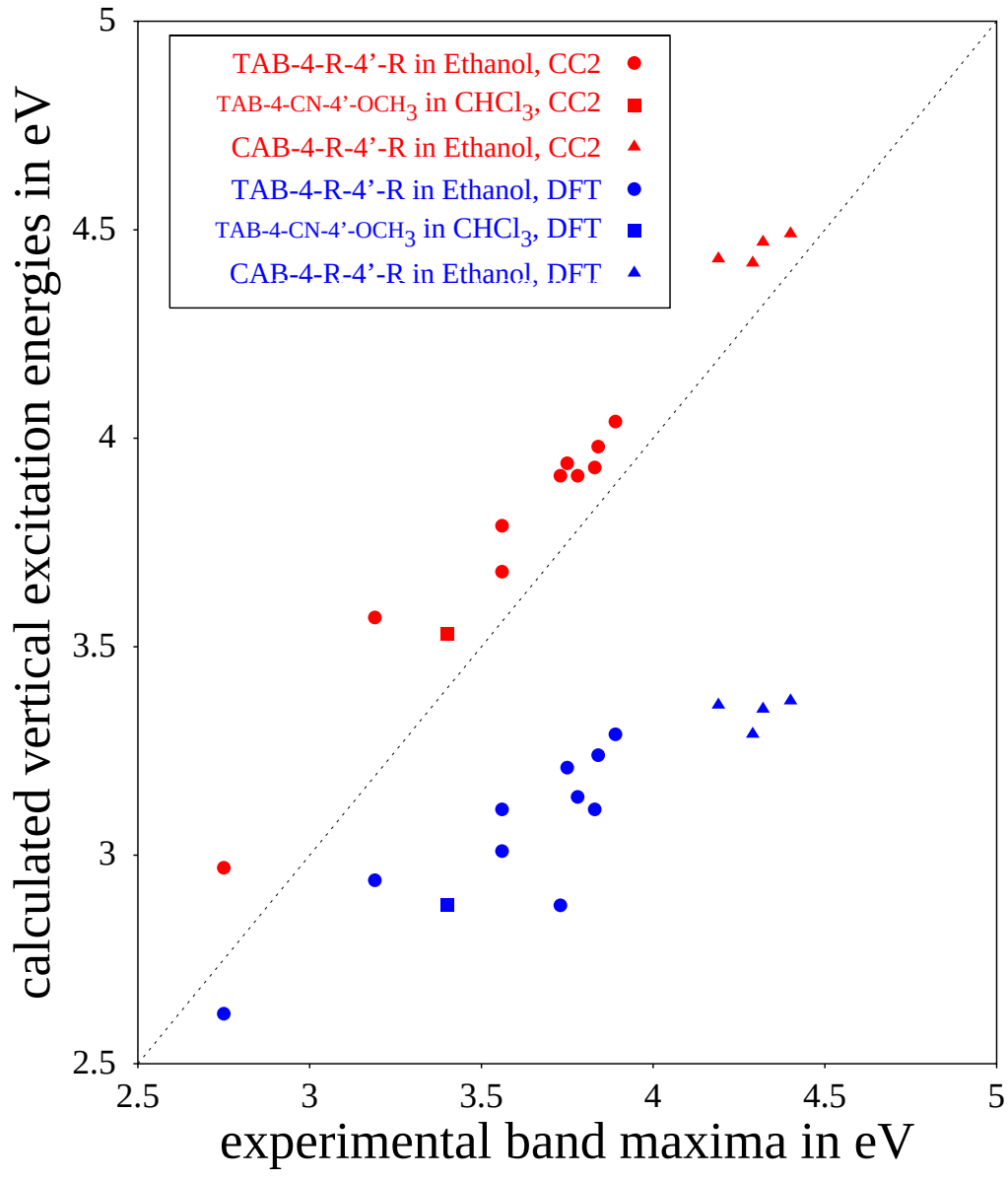
config.	State	SOPPA*	CC2	Exp.
trans	$1\ ^1B_g$	2.49	2.84	2.82
trans	$1\ ^1B_u$	3.90	4.04	4.12
trans	$3\ ^1B_u$	5.82	5.79	(5.64)
cis	$1\ ^1B$	2.52	3.00	2.92
cis	$1\ ^3B$		4.79	(4.68)

*[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

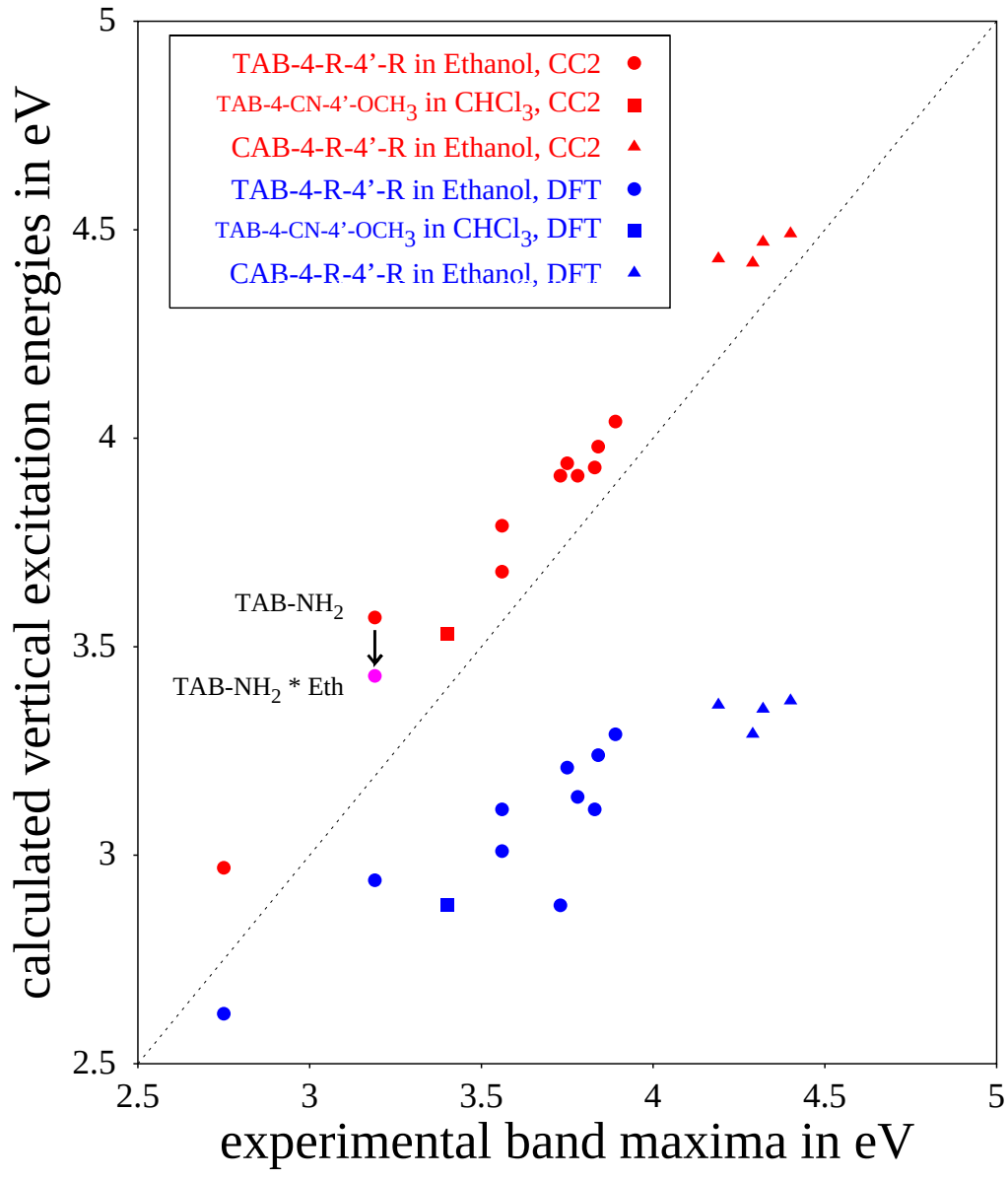
Substitution	*trans*-AB		*cis*-AB	
	CC2	Exp.	CC2	Exp.
-4-CN	3.93	3.83	4.41	
-4-CH_3	3.94	3.75	4.43	4.19
-4-NH_2	3.57	3.19	4.09	
-4-OH	3.79	3.56	4.29	3.94
-4-OCH_3	3.68	3.56	4.23	
-4-NO_2	3.91	3.73	4.34	
-4-F	3.98	3.84	4.47	4.32
-4-Cl	3.91	3.73	4.42	4.29
-4-CHO	3.91		3.77	
-4-COOH	3.94		4.40	
-4-CN-4'-OCH_3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



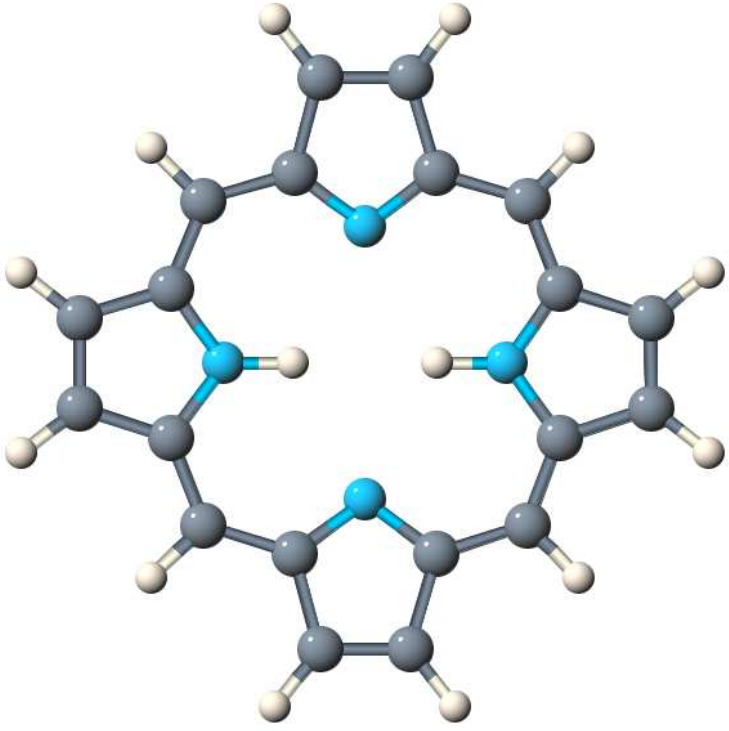
$\pi - \pi^*$-Transitions in Azobenzenes

- 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.
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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



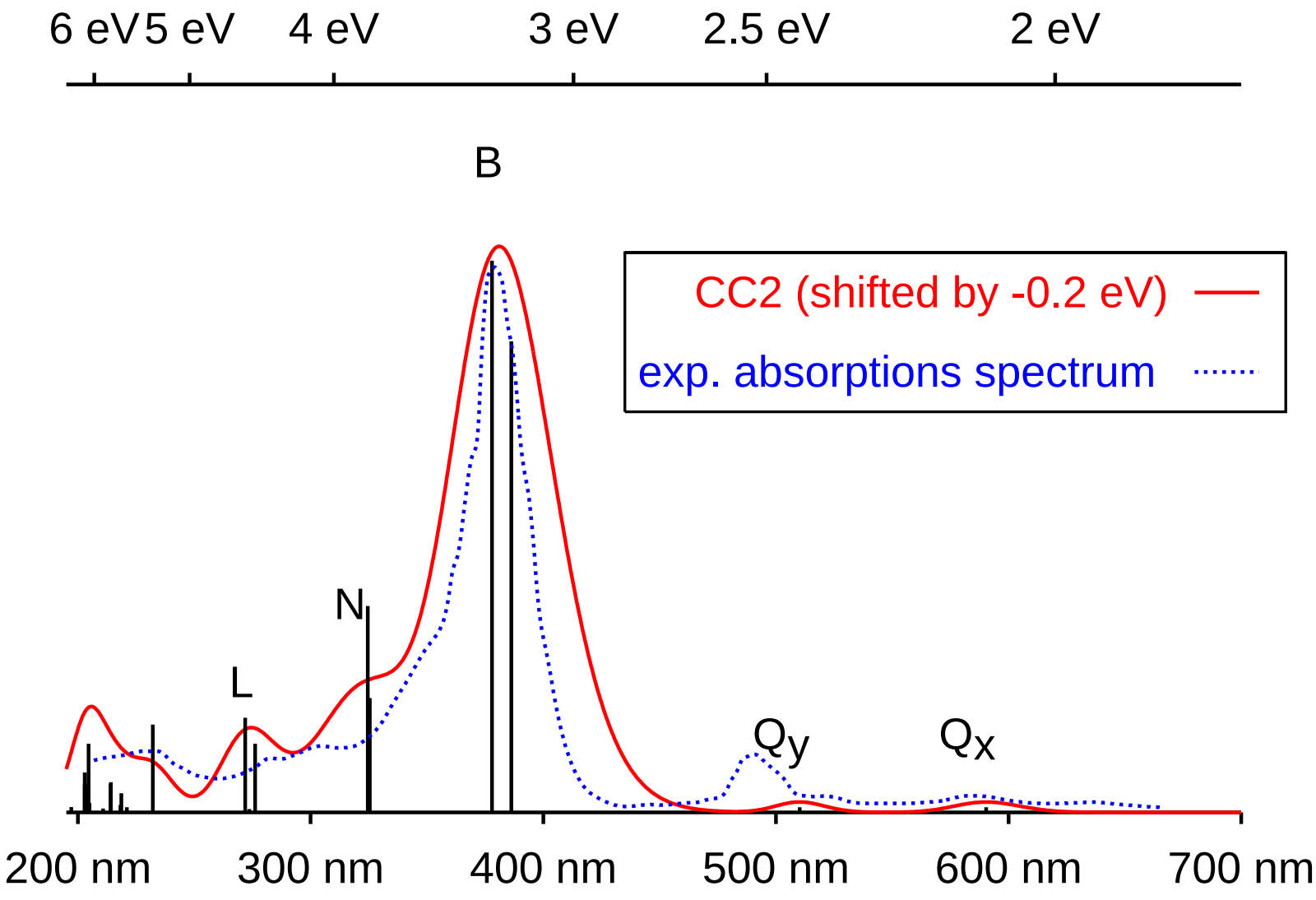
(almost D_{4h} symmetry)

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:

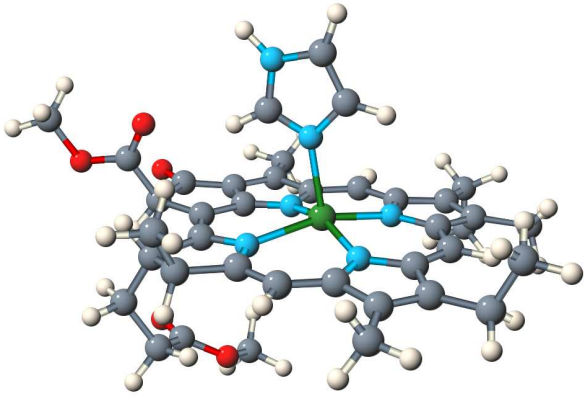
- CC2/cc-pVTZ optimized geometry
- aug-cc-pVTZ basis for the vertical excitation energies

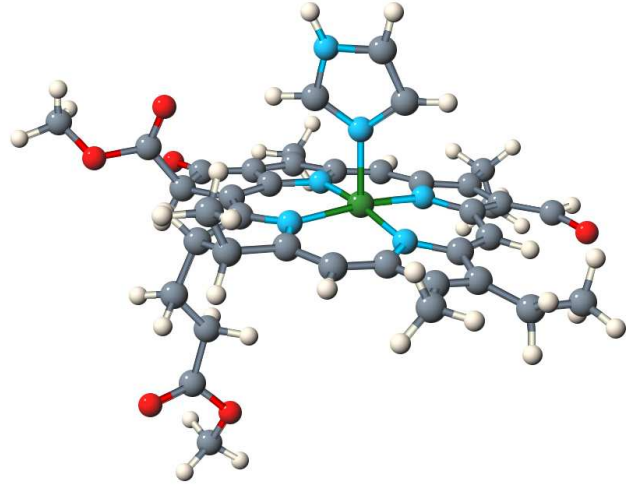
The UV/VIS Spectrum of Free-Base Porphyrin



UV/VIS Spectra of Chlorophylls

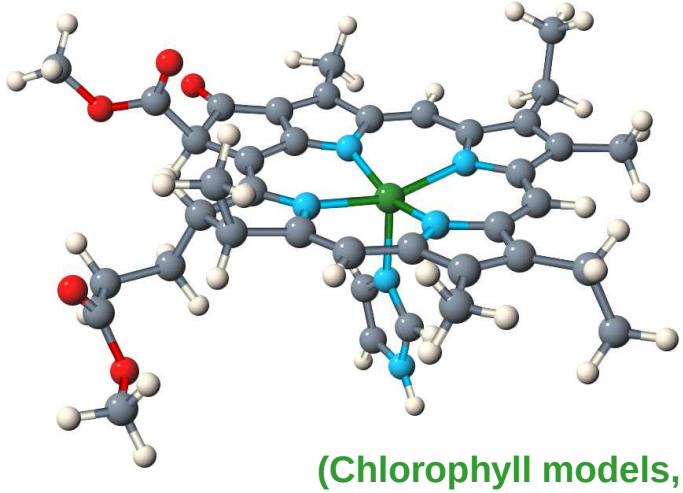
Chlorophyll a anti

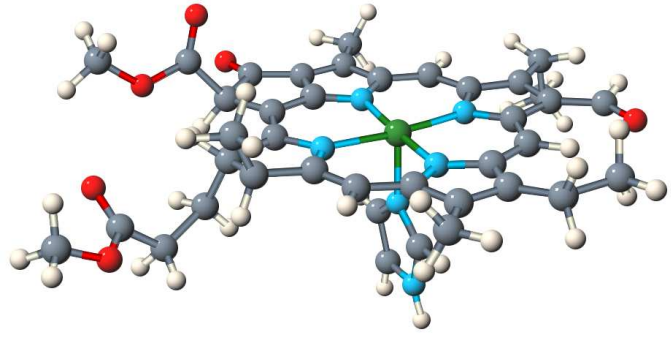




Chlorophyll b anti

Chlorophyll a syn





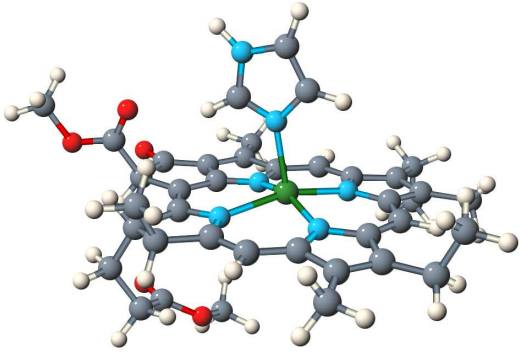
Chlorophyll b syn

(Chlorophyll models, Silviu Balaban, INT)

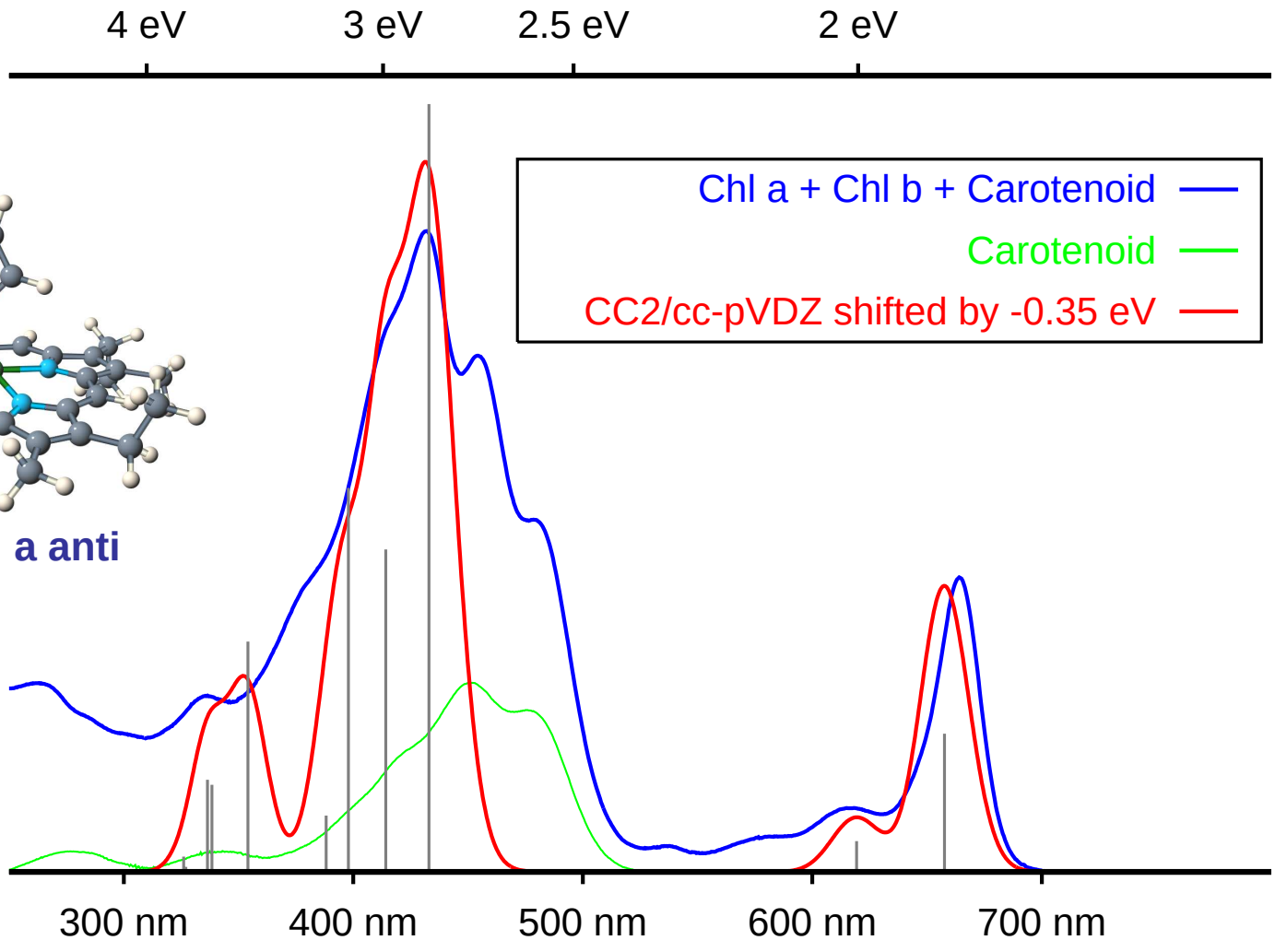
Computational Details:

- 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

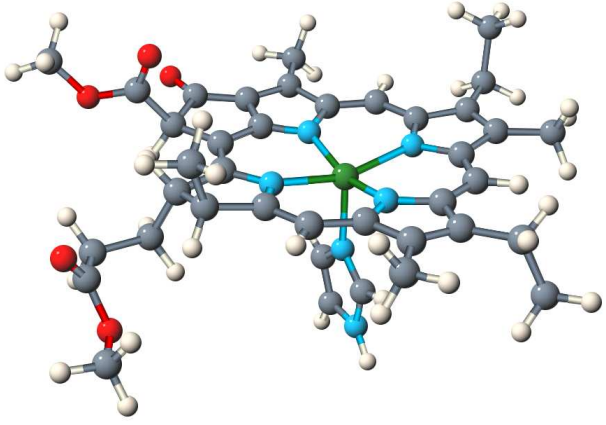
UV/VIS Spectra of Chlorophylls



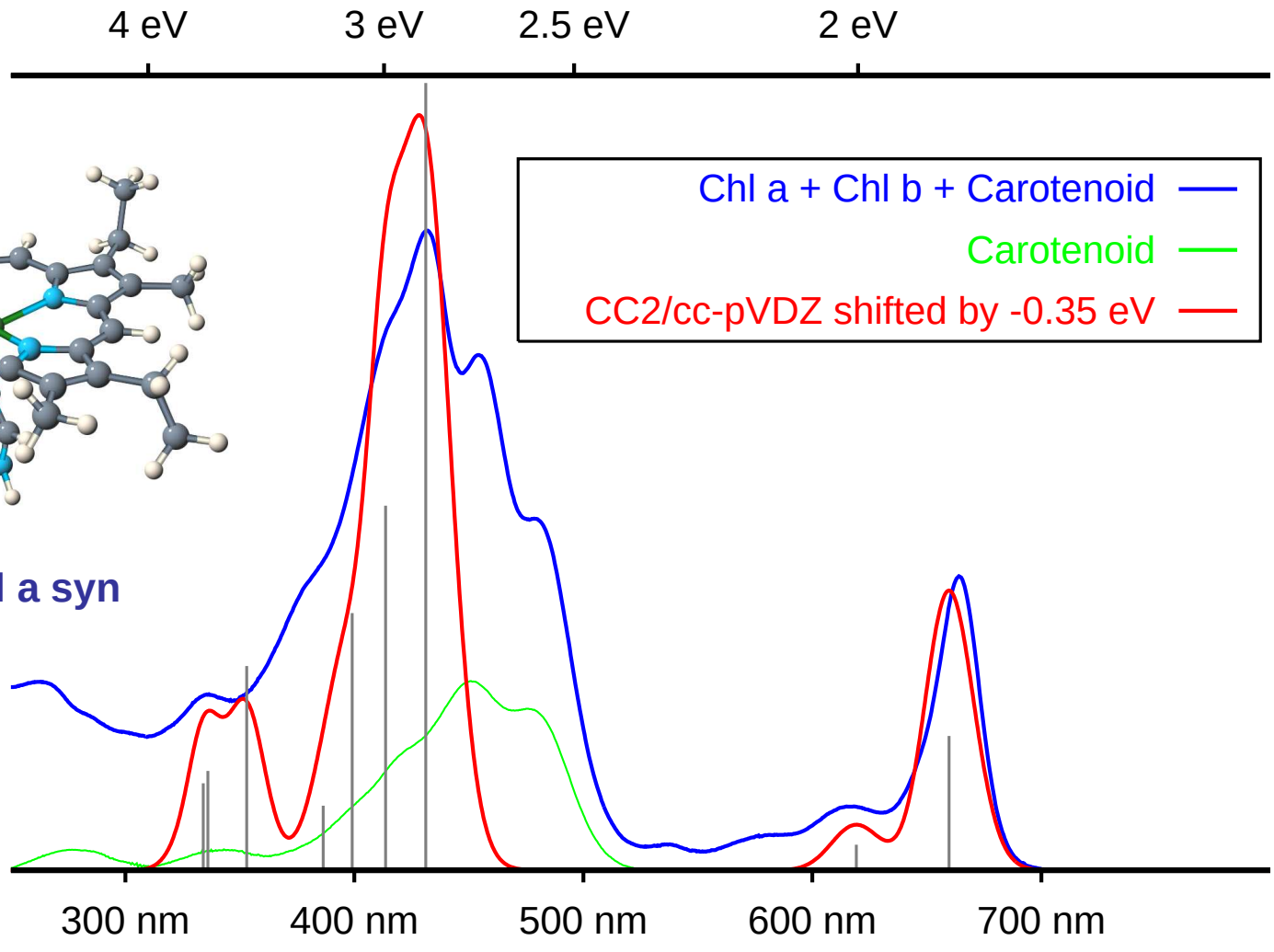
Chlorophyll a anti



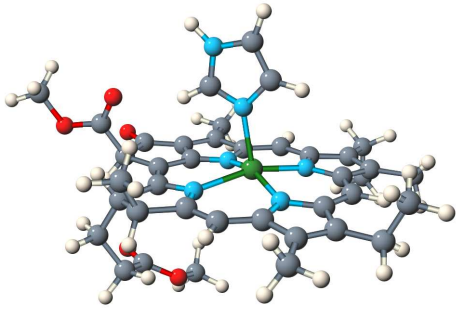
UV/VIS Spectra of Chlorophylls



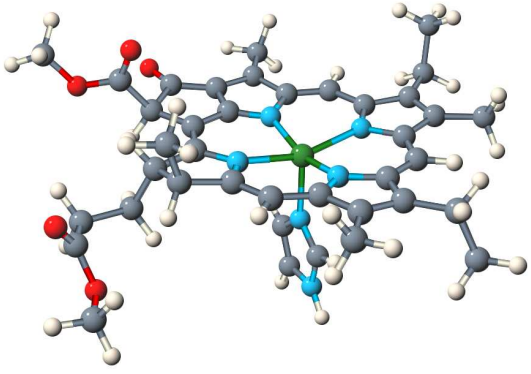
Chlorophyll a syn



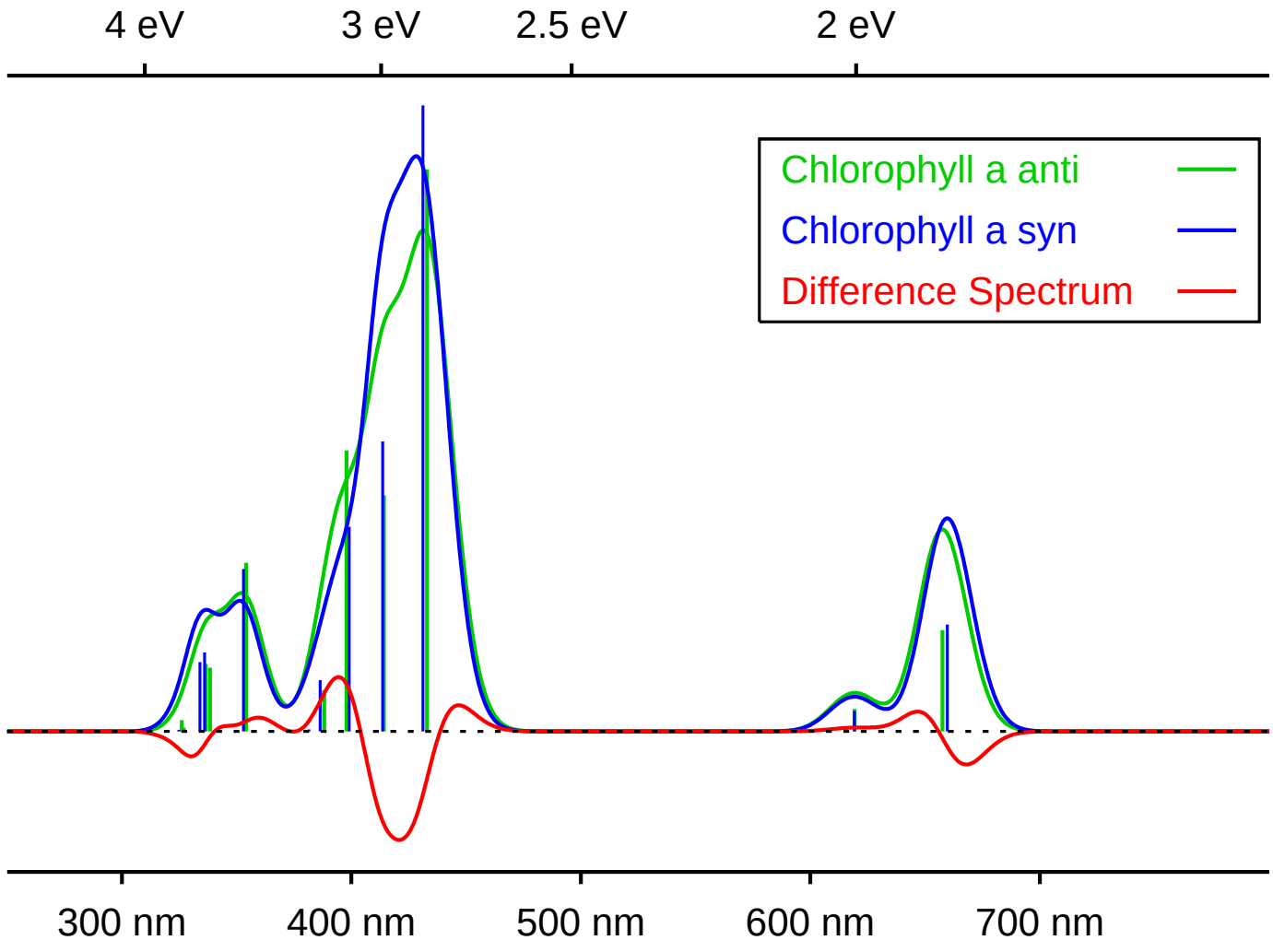
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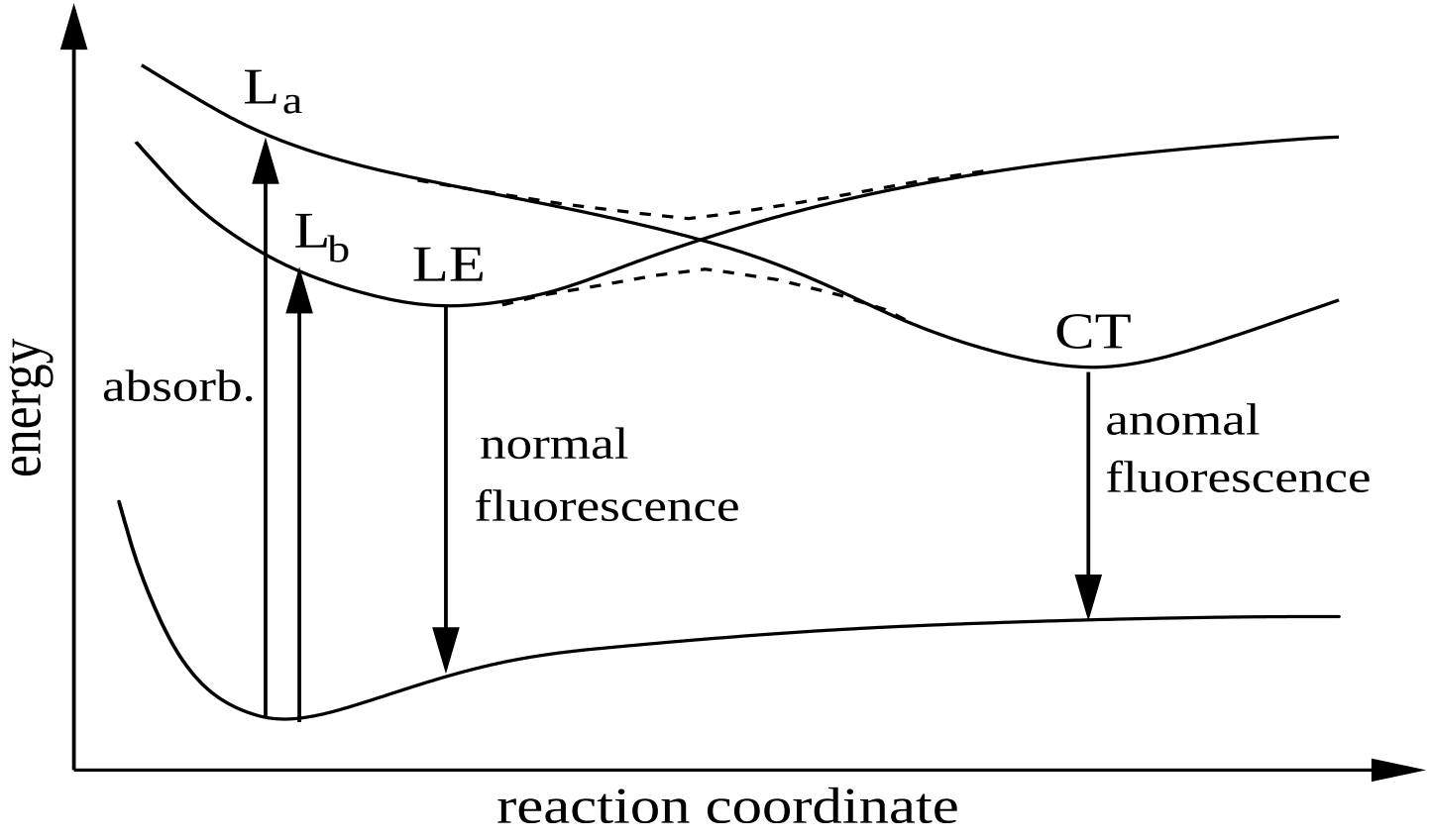
Chlorophyll a anti

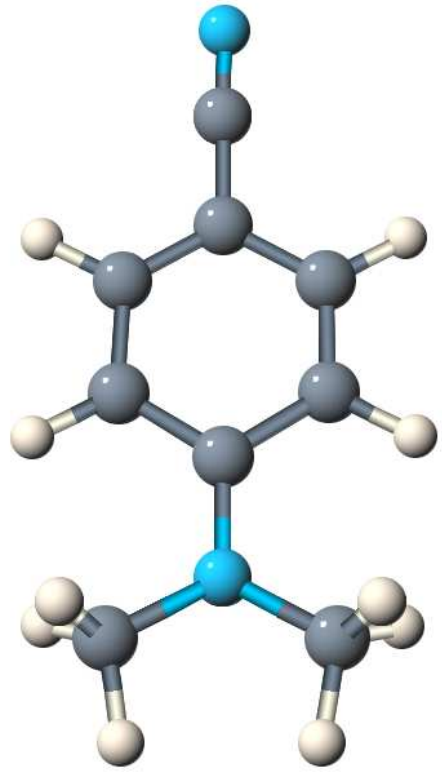


Chlorophyll a syn



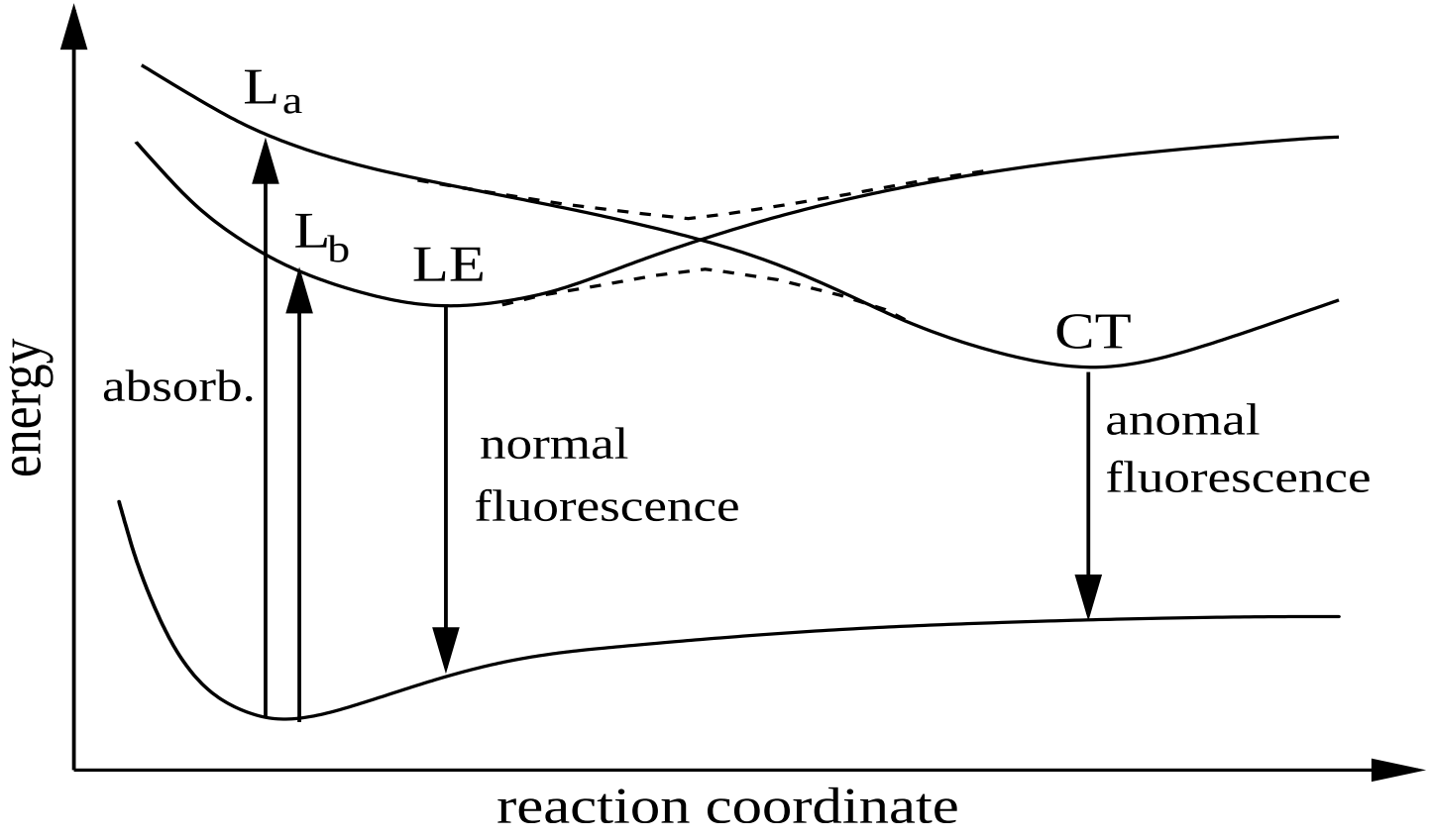
Dual Fluorescence in Dimethylaminobenzonitril (DMABN)

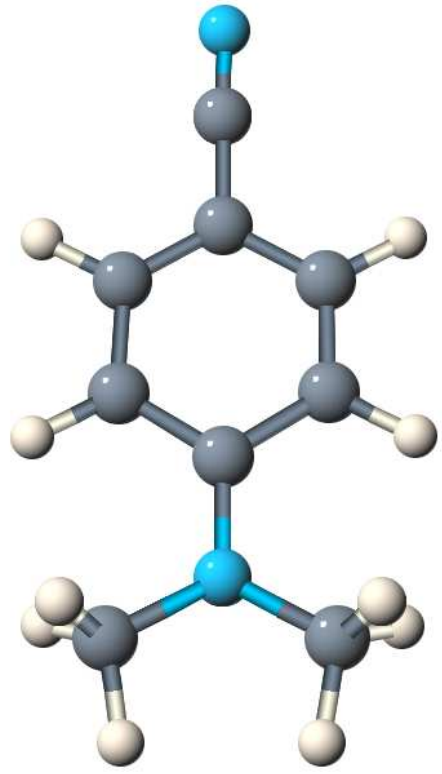




C_S symmetry

Dual Fluorescence in Dimethylaminobenzonitril (DMABN)





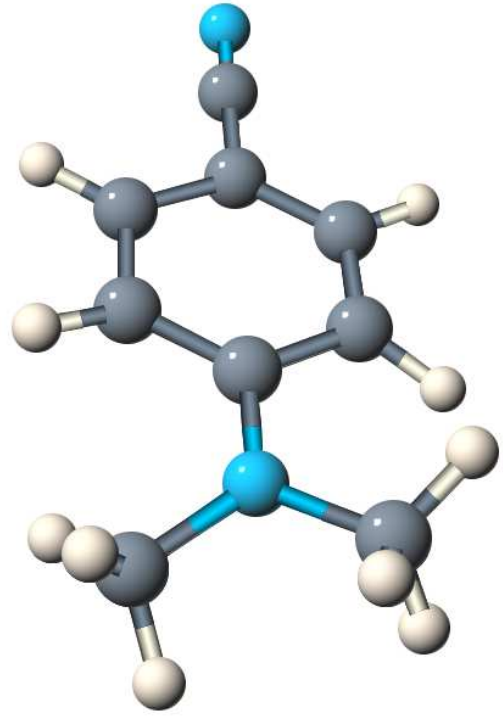
C_S symmetry

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)

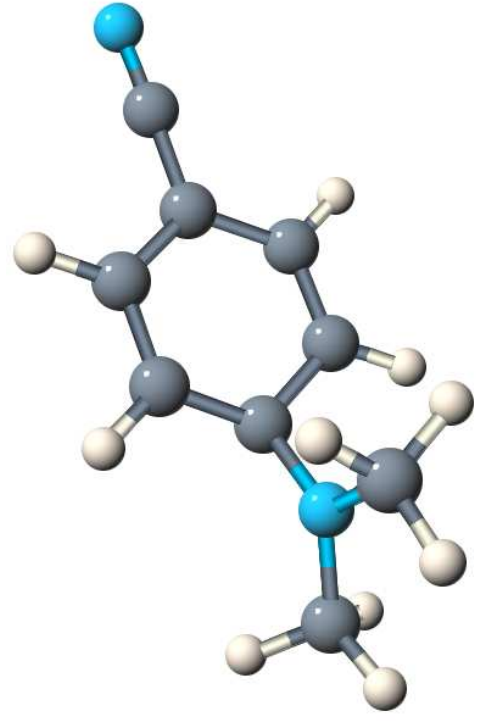
	CC2/TZVPP	Exp.
μ	10.1 D	9.7 D
ΔE	3.78 eV	
ν_{00}	3.96 eV	3.998 eV
torsion	19°	0–30° (?)
$\nu(\mathrm{Ph-NMe_2})$	1353 (-37) cm^{-1}	1423 cm^{-1} (?)
$\nu(\mathrm{Ph-CN})$	1181 (-55) cm^{-1}	
$\nu(\mathrm{C{\equiv}N})$	2074 (-30) cm^{-1}	2181 (-38) cm^{-1}



C_2 symmetry

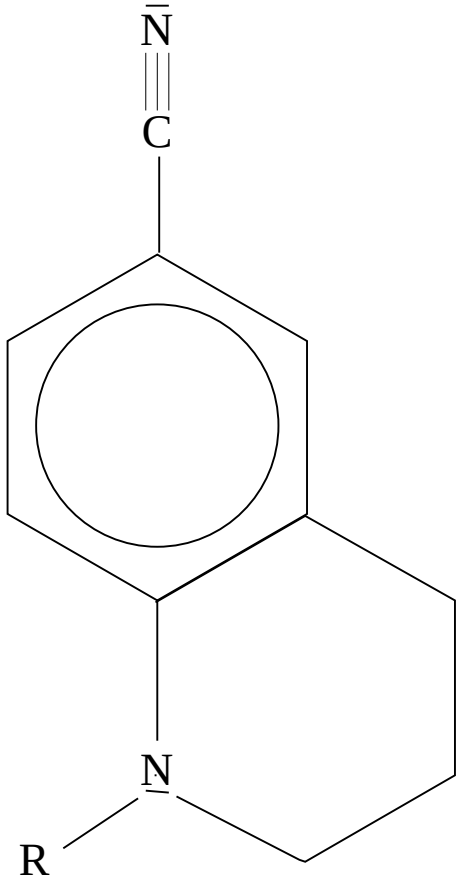
The Charge Transfer State in Dimethylaminobenzonitril (DMABN)

	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

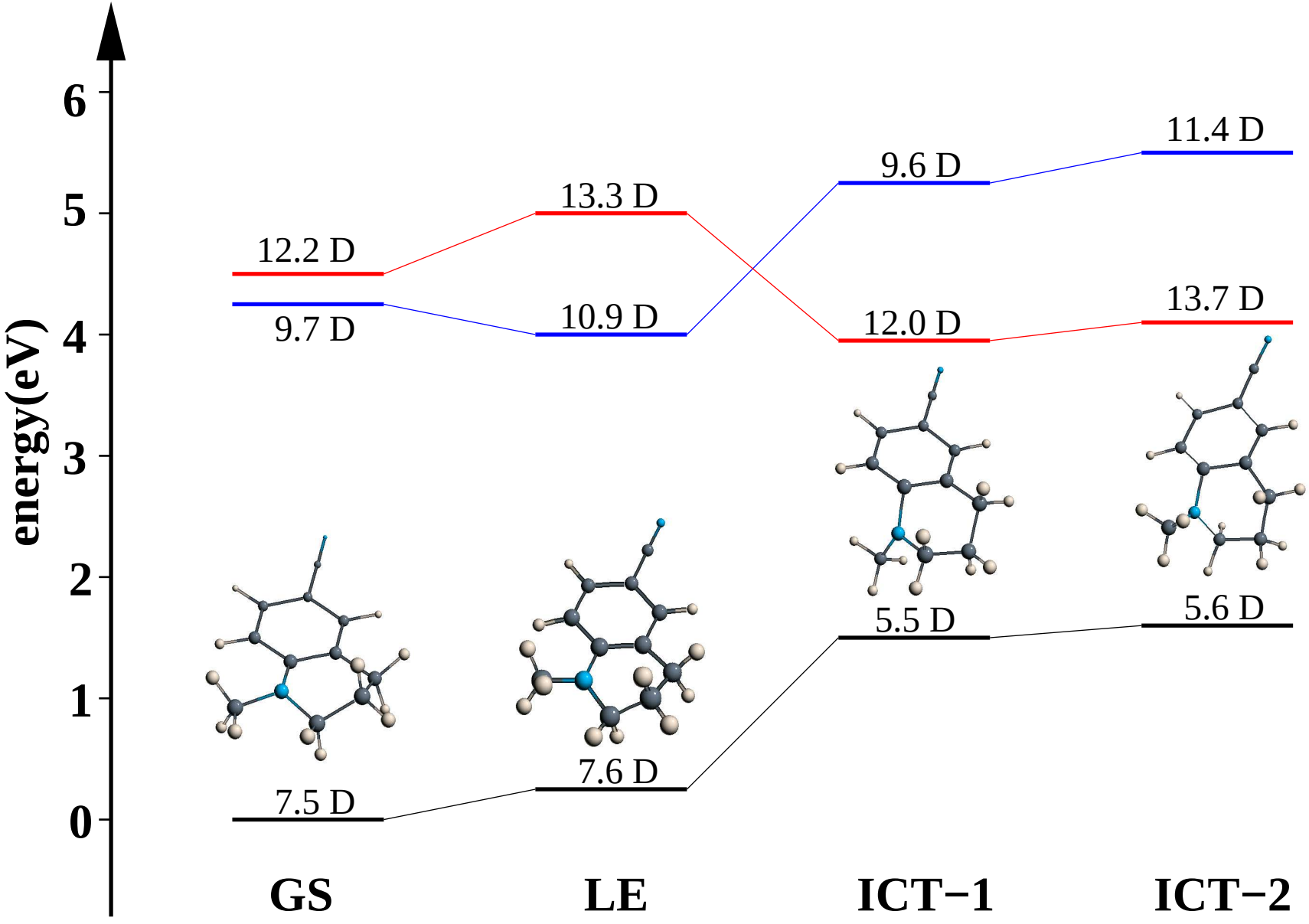
    (1-Methyl-6-cyano-1,2,3,4-tetrahydroquinoline)
  - R = ethyl, $-CH_2-CH_3$: NEC6

    (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)

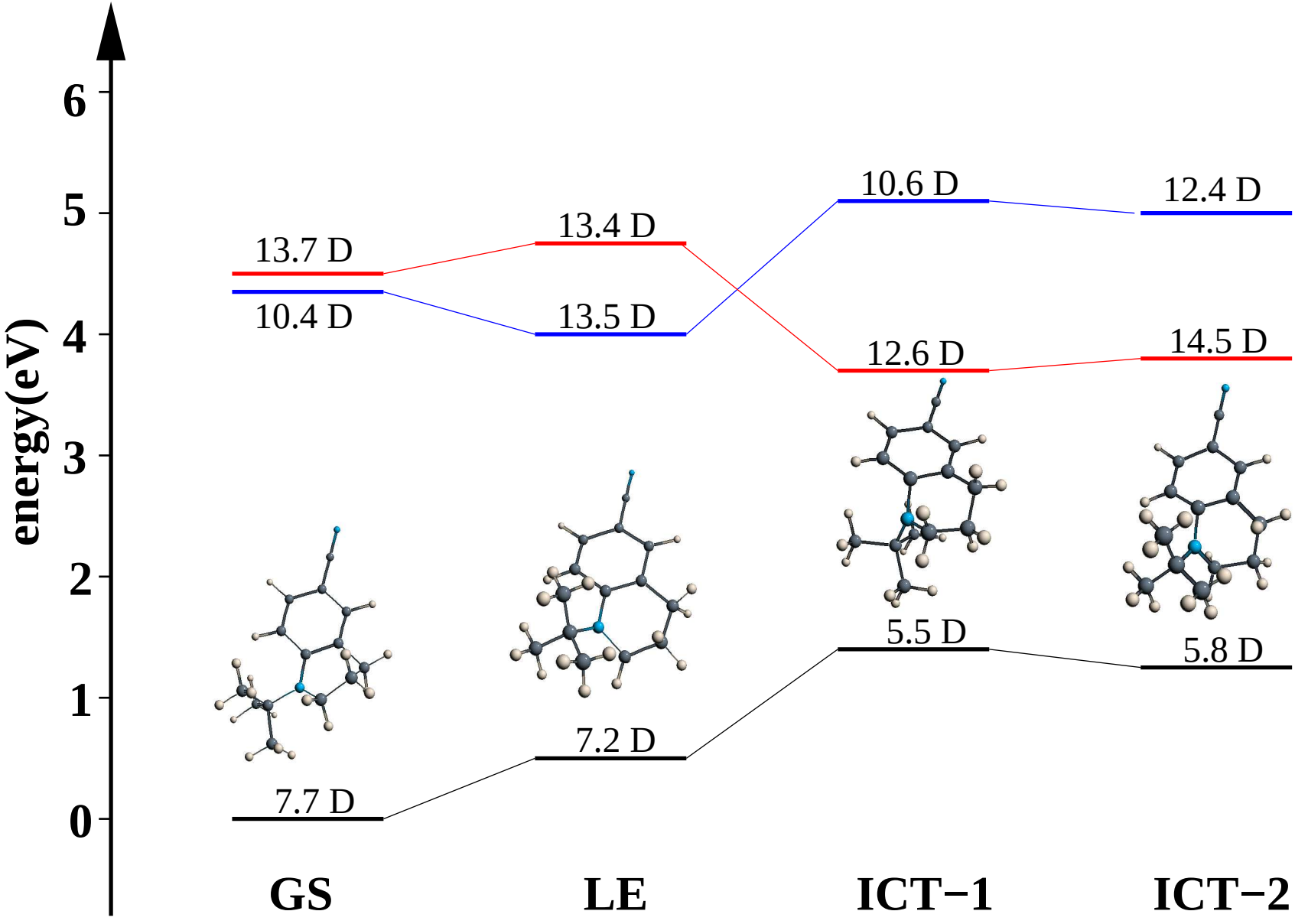
Lowest Excited States of NMC6

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

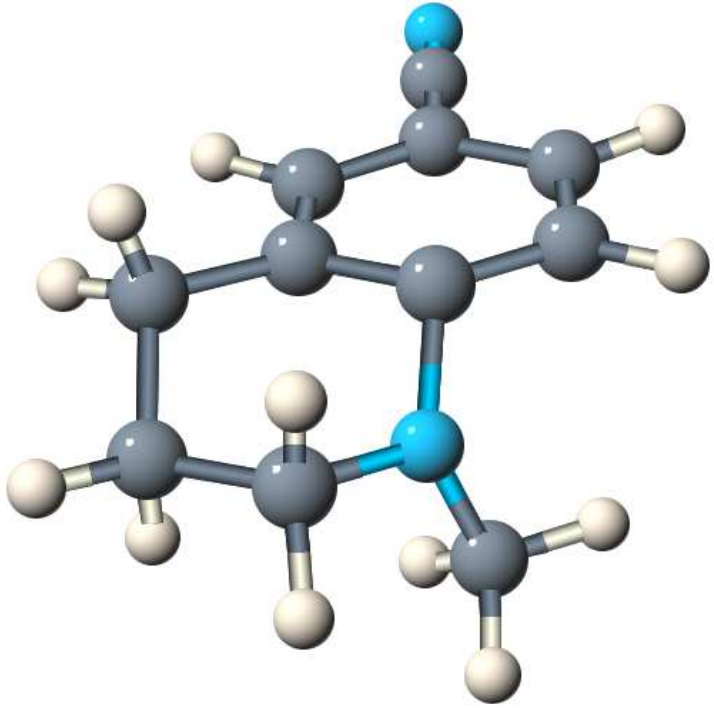


Lowest Excited States of NTC6

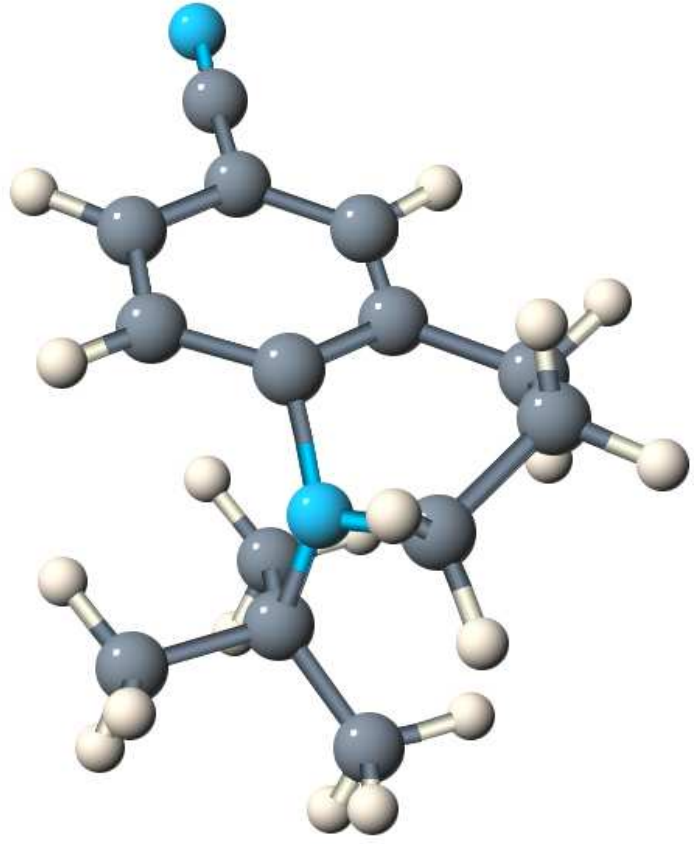
(1-*tert*-Butyl-6-cyano-1,2,3,4-tetrahydroquinoline)



TICT States in Sterically Hindered Aminobenzonitrils

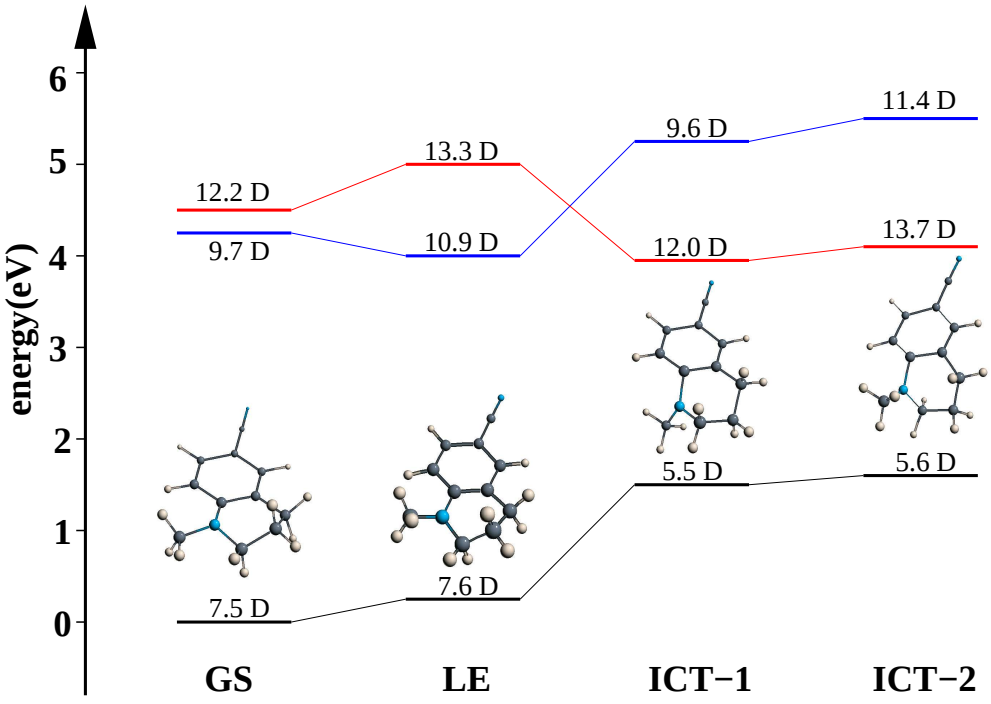


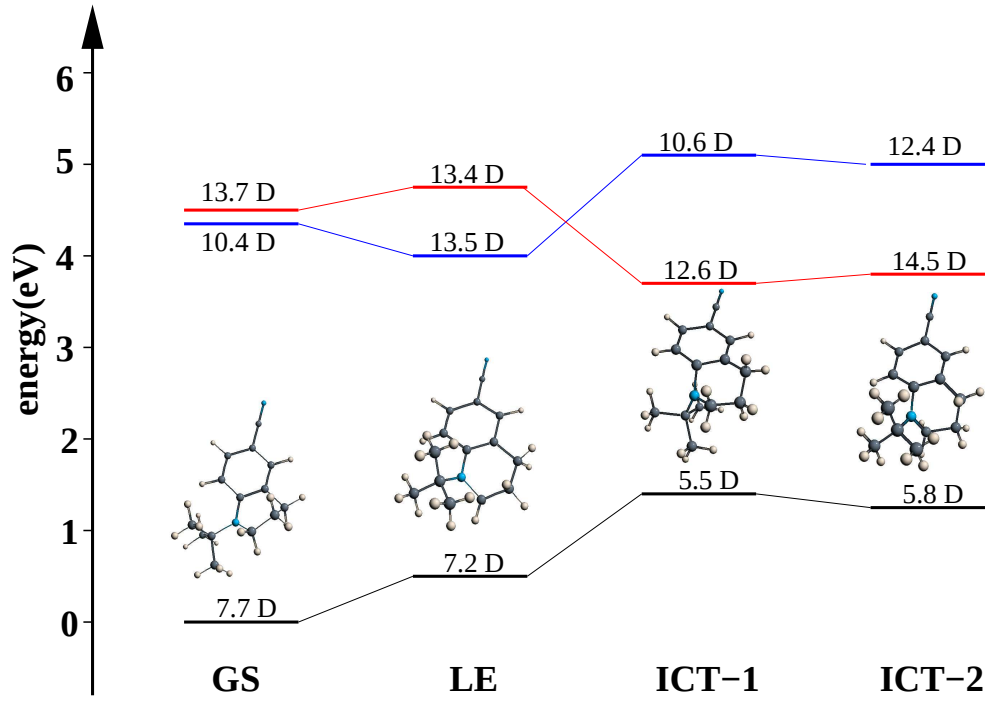
1-Methyl-6-cyano-
1,2,3,4-tetrahydroquinoline



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!

RI-CC2 — 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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- **Alternative to TDDFT calculations**
  - for: charge-transfer, valence-Rydberg mixing, anions
  - if: single excited states out of single-reference ground state

Literature:

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