A General Model Order Reduction Scheme for the Evaluation of Spectroscopic Properties and Excited States

wavefunction91.github.io

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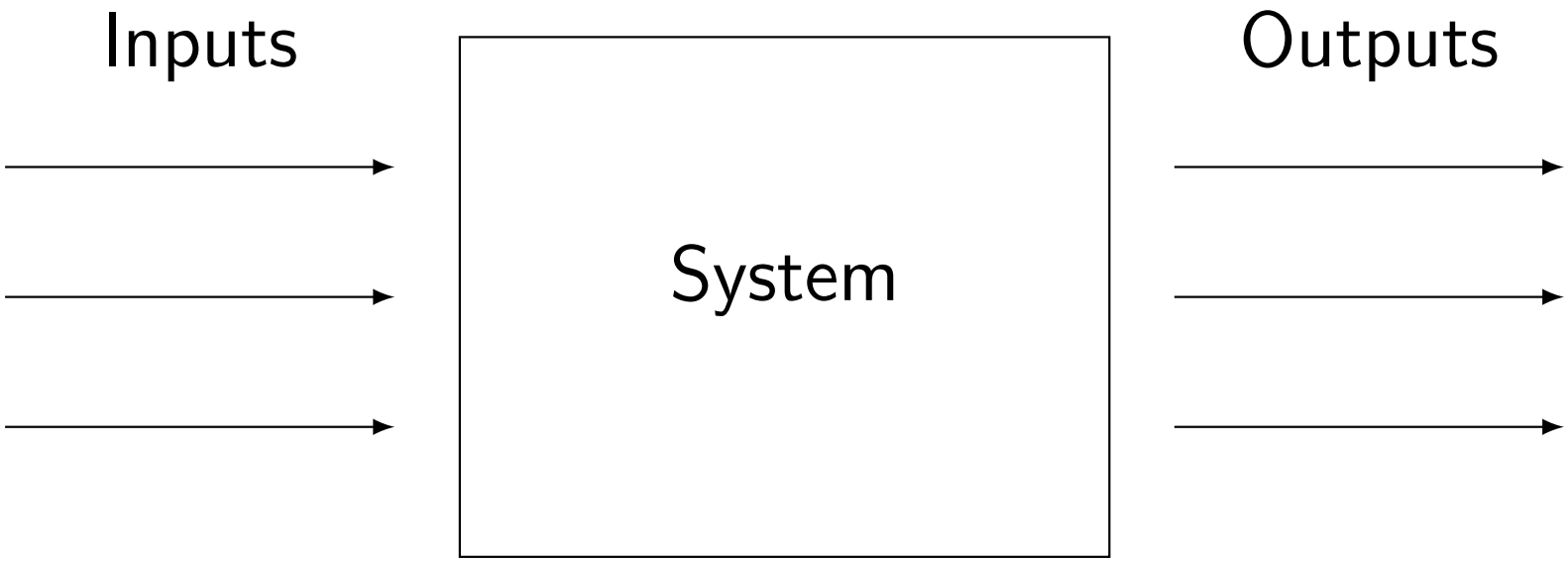
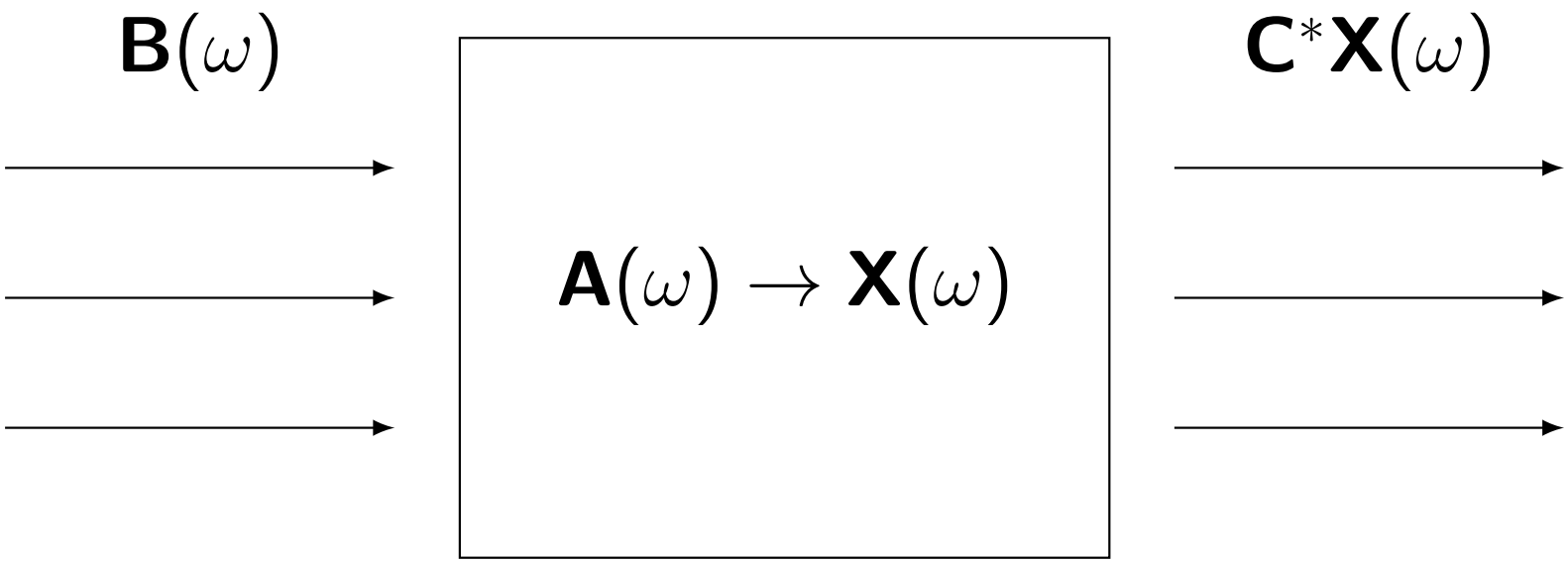
General Dynamical System



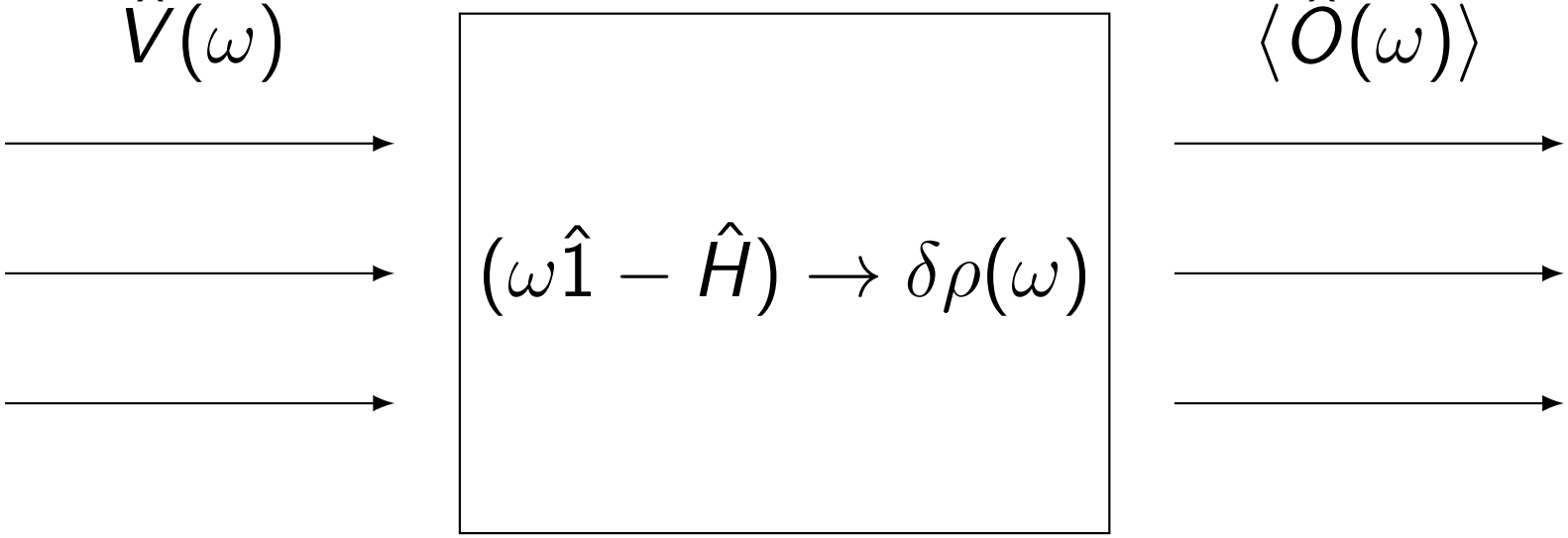
Transfer Function: Inputs $\rightarrow$ Outputs

Linear Dynamical System: $\mathbf{A}(\omega)\mathbf{X}(\omega) = \mathbf{B}(\omega)$



Transfer Function: $\gamma(\omega) = \mathbf{C}^*\mathbf{A}^{-1}(\omega)\mathbf{B}(\omega)$

Linear Response (Kubo Formalism)



Two-Time Retarded Green's Function:

$$\langle\langle \hat{V}; \hat{O} \rangle\rangle_{\omega}^{\eta} = \mathbf{O}^{*} \left((\omega + i\eta)\mathbf{I} - \mathbf{H} \right)^{-1} \mathbf{V}(\omega)$$

Current Methods (in Electronic Structure)

Two primary solution methods:

- Diagonalization: $\mathbf{H} = \sum_k \lambda_k \mathbf{Z}_k^R \mathbf{Z}_k^{L*}$

$$\langle\langle \hat{V}; \hat{O} \rangle\rangle_\omega^\eta = \sum_k \frac{\left(\mathbf{O}^* \mathbf{Z}_k^R\right)\left(\mathbf{Z}_k^{L*} \mathbf{V}\right)}{\omega - \lambda_k + i\eta}$$

✓ Rapid evaluation
✓ Direct access to "excited states"
✗ Requires a full diagonalization (in principle)
  ✗ Partial diagonalization in spectral interior is difficult

Current Methods (in Electronic Structure)

Two primary solution methods:

- Linear System

$$\langle\langle \hat{V}; \hat{O} \rangle\rangle_{\omega}^{\eta} = \mathbf{O}^{*} \left((\omega + i\eta)\mathbf{I} - \mathbf{H} \right)^{-1} \mathbf{V}$$

  - ✓ Direct evaluation for a particular ω
    - ✓ Direct access to spectral interior
  - ✗ Requires a linear system solution for *each* ω
  - ✗ No *direct* access to "excited states"

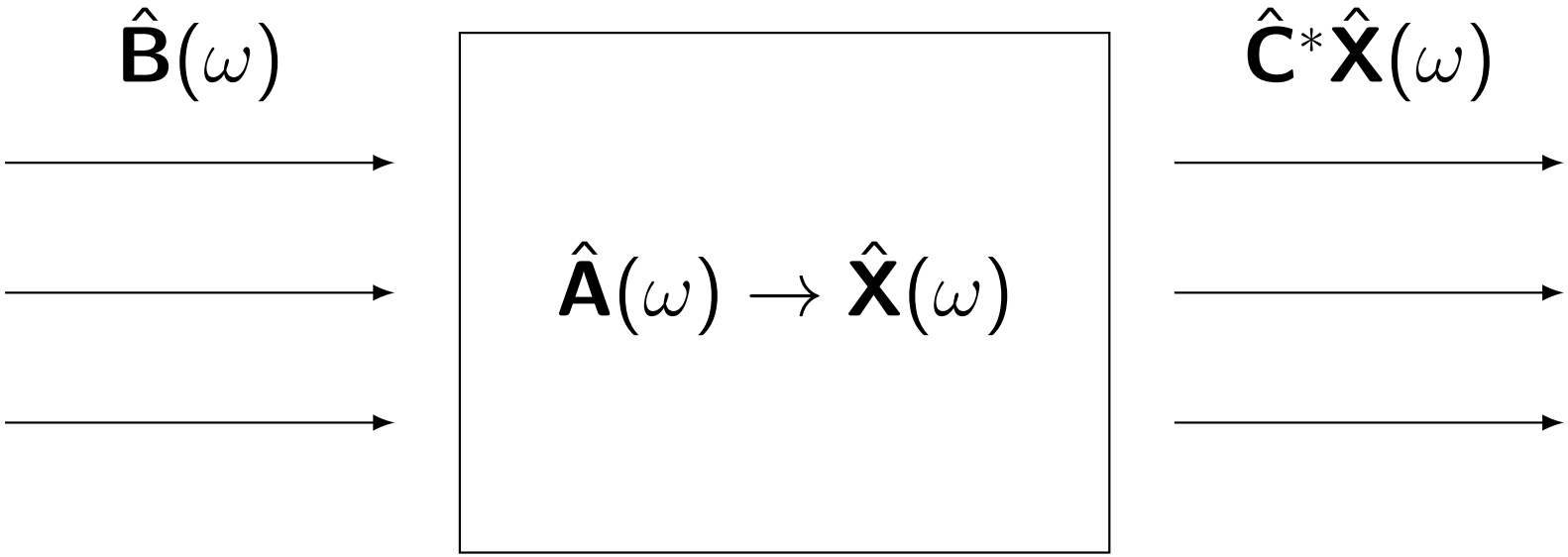
Problem Statement

Can we develop a method which exhibits the best characteristics of both methods without their respective deficiencies?

- Able to be rapidly evaluated
- Direct evaluation of RF for any ω (including interior)
- Avoid full (or partial) diagonalization
- Able to obtain "excited states" directly

Model Order Reduction

Reduced Order System: $\hat{\mathbf{A}}(\omega)\hat{\mathbf{X}}(\omega) = \hat{\mathbf{B}}(\omega)$

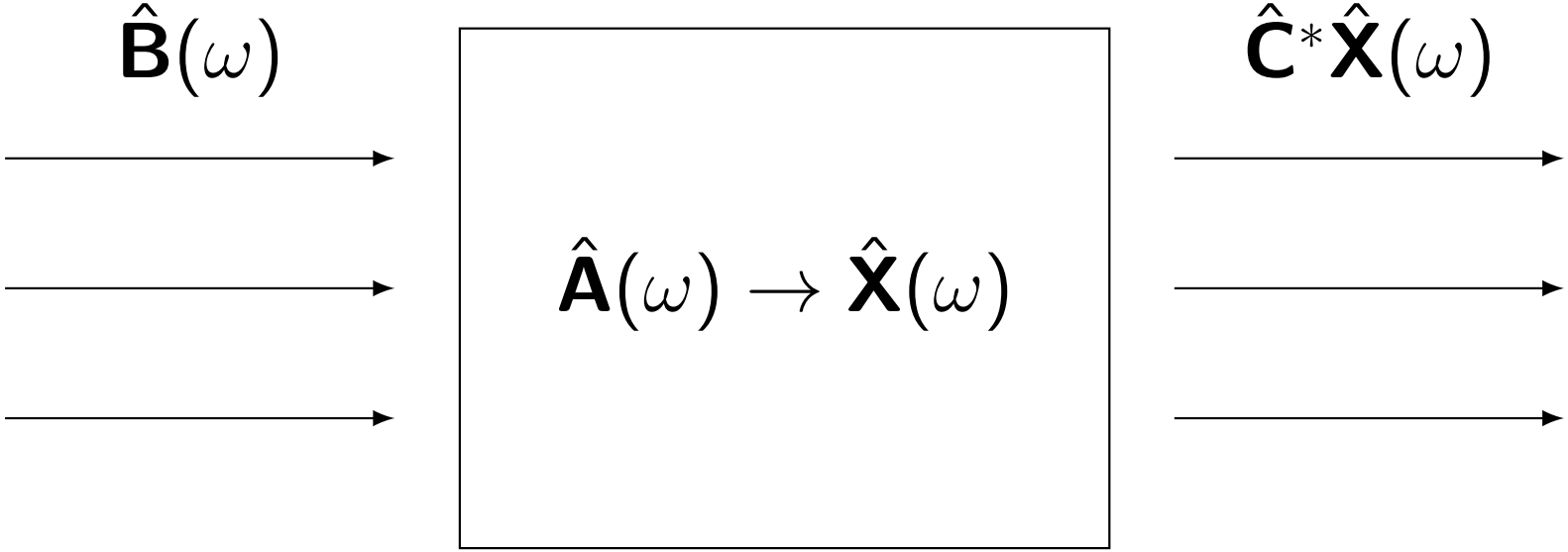


Galerkin Projection (under $\mathcal{V}$):

$$\hat{\mathbf{A}} = \mathcal{V}^*\mathbf{A}\mathcal{V} \qquad \hat{\mathbf{B}} = \mathcal{V}^*\mathbf{B} \qquad \hat{\mathbf{C}}^* = \mathbf{C}^*\mathcal{V}$$

Model Order Reduction

Reduced Order System: $\hat{\mathbf{A}}(\omega)\hat{\mathbf{X}}(\omega) = \hat{\mathbf{B}}(\omega)$



Transfer Function: $\hat{\gamma}(\omega) = \hat{\mathbf{C}}^*\hat{\mathbf{A}}^{-1}(\omega)\hat{\mathbf{B}}(\omega)$

Model Order Reduction

Desired Properties of $\mathcal{V}$:

- $\dim \mathcal{V} \lll \dim \mathbf{A}$ s.t. evaluation of $\hat{\gamma}$ is much more efficient than γ
- Choosing $\mathcal{V}$ s.t. $\gamma(\omega) \approx \hat{\gamma}(\omega)$ for some interval of interest.

Solution: **Rational Interpolation via Moment Matching**

- Choose interpolation set $\{\tau_i\}_{i=1}^{n}$ and construct $\mathcal{V}$ to enforce

$$\frac{\mathrm{d}^j \gamma(\tau_i)}{\mathrm{d}\omega^j} = \frac{\mathrm{d}^j \hat{\gamma}(\tau_i)}{\mathrm{d}\omega^j}, \quad \forall \tau_i, j \in [0, k]$$

Model Order Reduction via Moment Matching

A rational Krylov subspace of order k takes the general form

$$\begin{aligned}\mathcal{RK}^k_{\mathbf{b}}(\mathbf{A}, \{\tau_i\}) = \mathrm{span}(&\\ &\mathbf{b},\\ &(\mathbf{A}-\tau_1\mathbf{I})^{-1}\mathbf{b}, \cdots, (\mathbf{A}-\tau_1\mathbf{I})^{-k}\mathbf{b},\\ &\cdots,\\ &(\mathbf{A}-\tau_n\mathbf{I})^{-1}\mathbf{b}, \cdots, (\mathbf{A}-\tau_n\mathbf{I})^{-k}\mathbf{b}\\ )&\end{aligned}$$

Choosing $\mathcal{V}$ as an orthonormal basis for $\mathcal{RK}^k_{\mathbf{b}}(\mathbf{A}, \{\tau_i\})$ is sufficient to match k moments of the the transfer function. Given $\{\tau_i\}$, $\mathcal{V}$ may be constructed for $k = 1$ as

1. Solve $(\tau_i\mathbf{I} - \mathbf{A})\mathbf{X}_i = \mathbf{B}$ for each τ_i
2. $\mathcal{V} \leftarrow \mathrm{QR}(\mathbf{X}_1, \mathbf{X}_2, \cdots, \mathbf{X}_n)$

Adaptive Selection of Interpolation Frequencies

arXiv:1704.05923
doi:10.1021/acs.jctc.7b00402

Application: TD-HF X-Ray Absorption Spectroscopy

Casida expression for the Polarization Propagator:

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\bar{\mathbf{B}} & -\bar{\mathbf{A}} \end{bmatrix}$$

$$A_{ai,bj} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \langle aj||ib\rangle$$
$$B_{ai,bj} = \langle ab||ij\rangle$$

We aim to approximate the (linear) photoabsorption cross section

$$\sigma(\omega) = \frac{4\omega}{3}\Im \mathrm{Tr}\boldsymbol{\alpha}(\omega)$$
$$\alpha_{ij}(\omega) = \langle\langle r_i; r_j\rangle\rangle_\omega^\eta$$

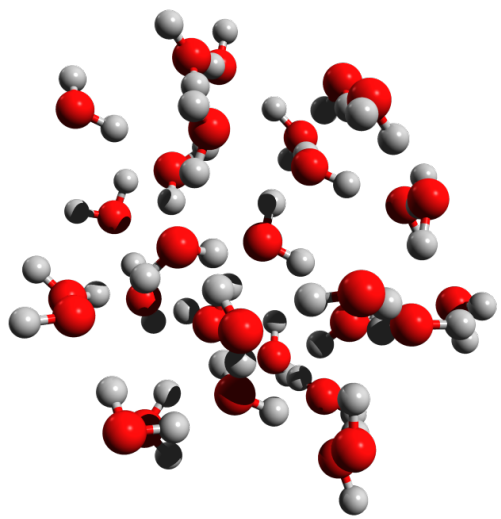
Application: TD-HF X-Ray Absorption Spectroscopy

Treat $\boldsymbol{\alpha}(\omega)$ as the transfer function of a LDS,

$$\boldsymbol{\alpha}(\omega) = \mathbf{D}^*((\omega + i\eta)\mathbf{I} - \mathbf{H})^{-1}\mathbf{D} \in \mathbb{C}^{3\times 3}$$

Oxygen K-edge for water clusters:

- $\omega \in [540, 600]$ eV
- TD-HF/6-31G(d)
- Chosen for dense clustering of eigenvalues in energy window (impractical by e.g. energy specific Davidson)



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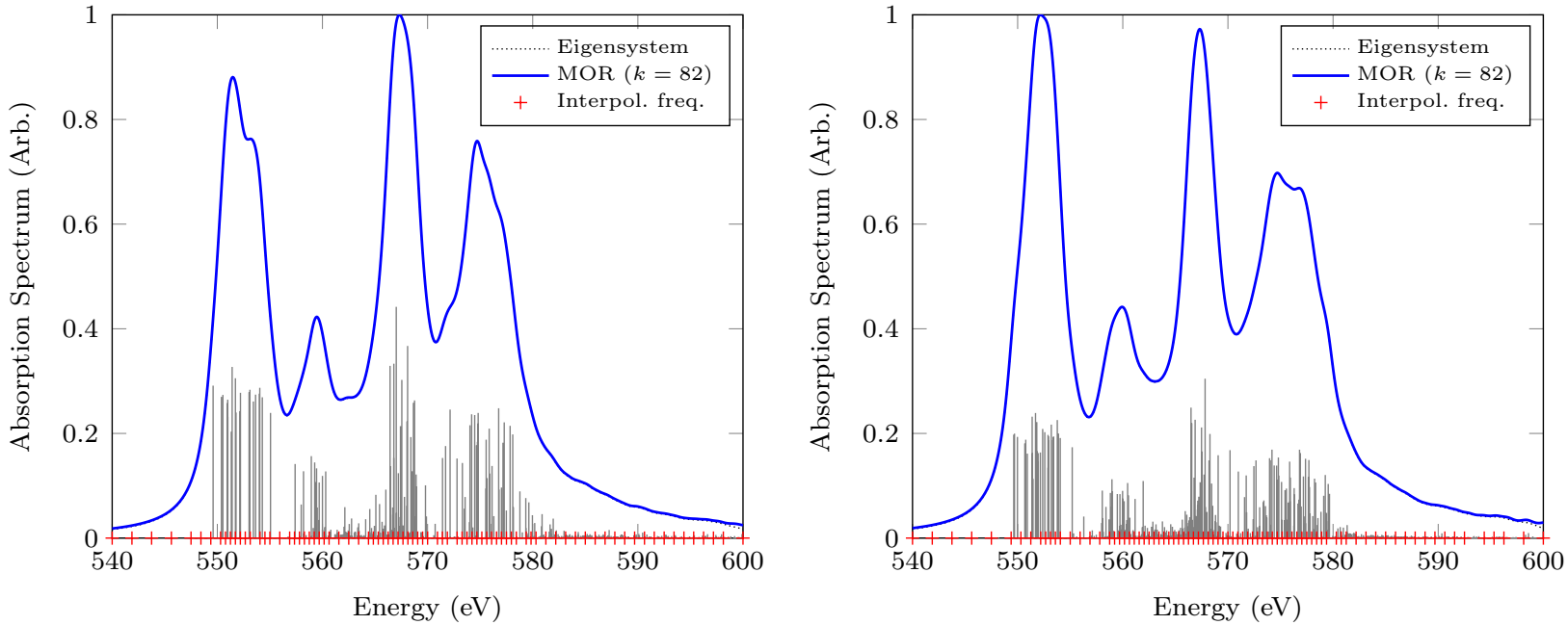


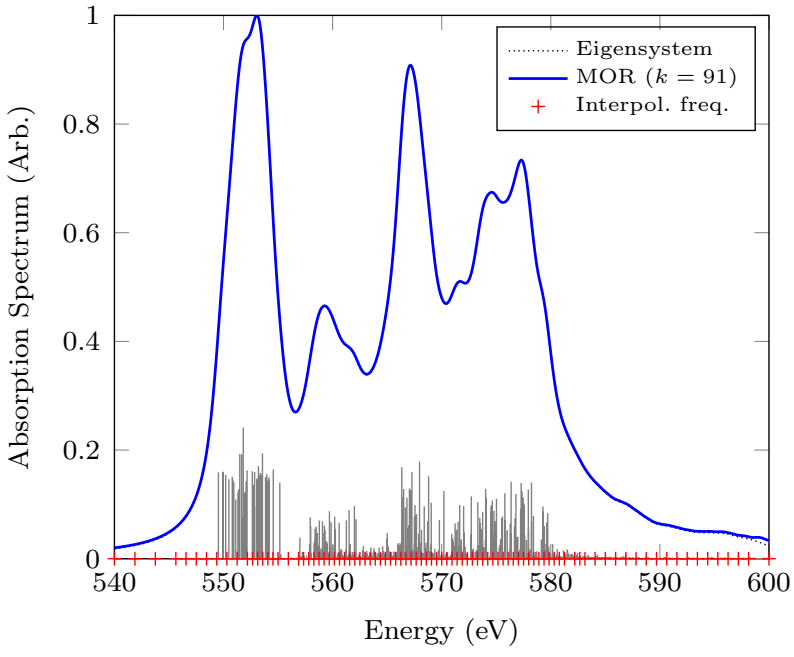
(a) 10 H2O

(b) 15 H2O

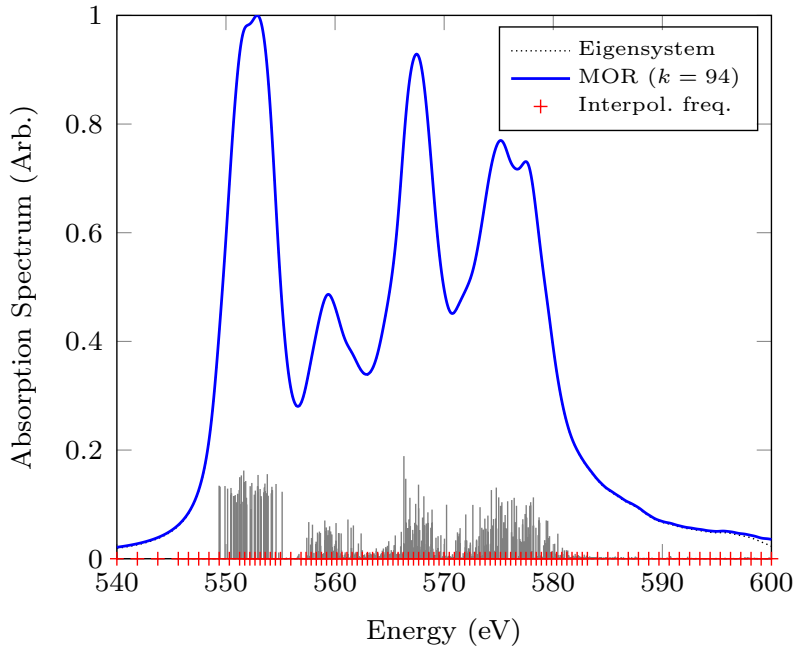
Figure: Demonstration of the MOR method for various sizes of water clusters.

arXiv:1704.05923
J. Chem. Theory Comput. 2017, 13, 10, 4950-4961. doi:10.1021/acs.jctc.7b00402

Application: TD-HF X-Ray Absorption Spectroscopy



(a) 20 H2O



(b) 25 H2O

Figure: Demonstration of the MOR method for various sizes of water clusters.

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Current Work

- Extraction of eigenvectors from MOR basis (in prep)

$$\text{Rayleigh-Ritz:} \quad (\mathcal{V}^* \mathbf{H} \mathcal{V}) \mathbf{Y} = \mathbf{Y} \mathbf{\Lambda} \quad \Longrightarrow \mathbf{H}(\mathcal{V}\mathbf{Y}) \approx (\mathcal{V}\mathbf{Y}) \mathbf{\Lambda}$$

- Application to Green's Function Coupled Cluster (GFCC)
  - arXiv:1902.06016 (Submitted JCTC 2019)
- Application to Linear Response Coupled Cluster (in prep)

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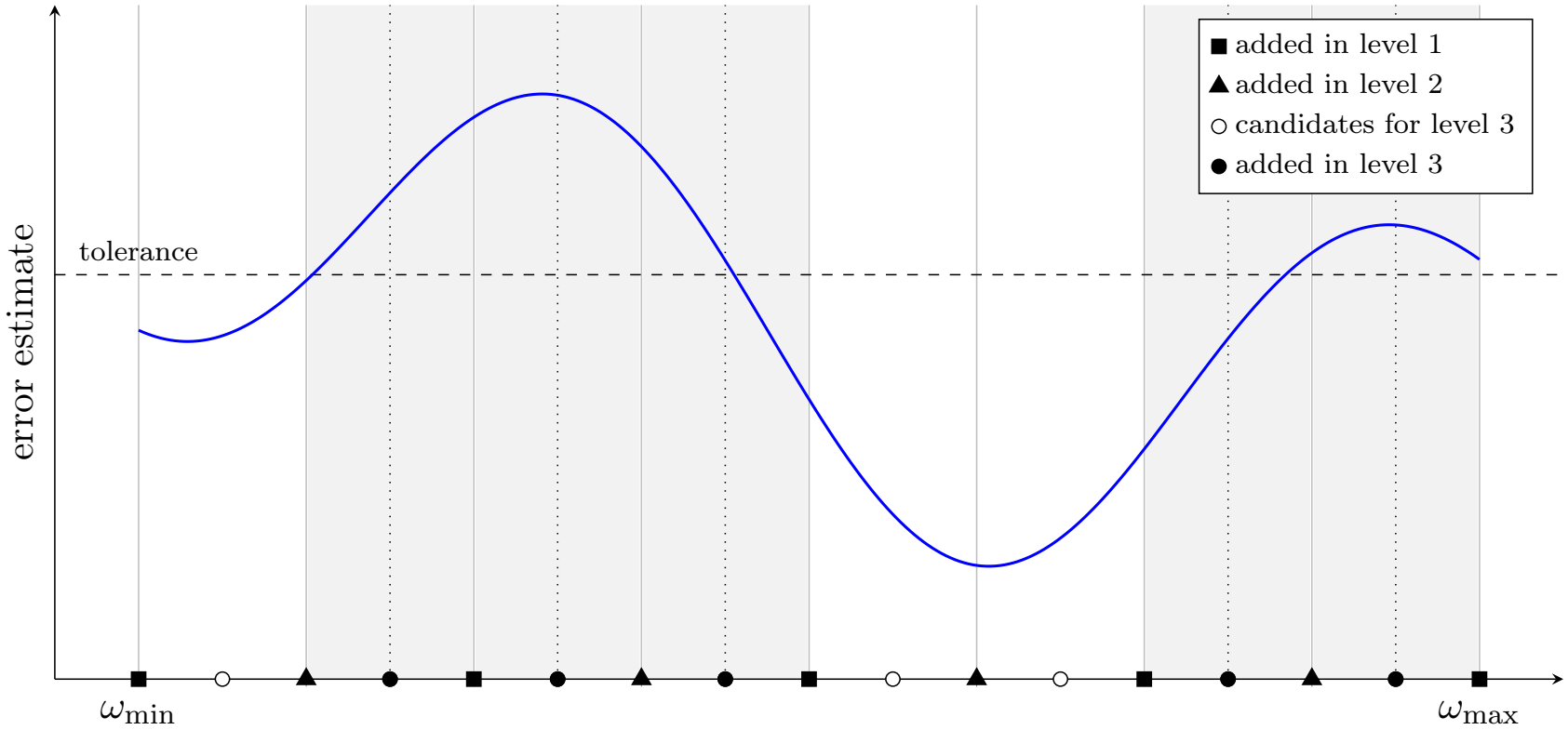
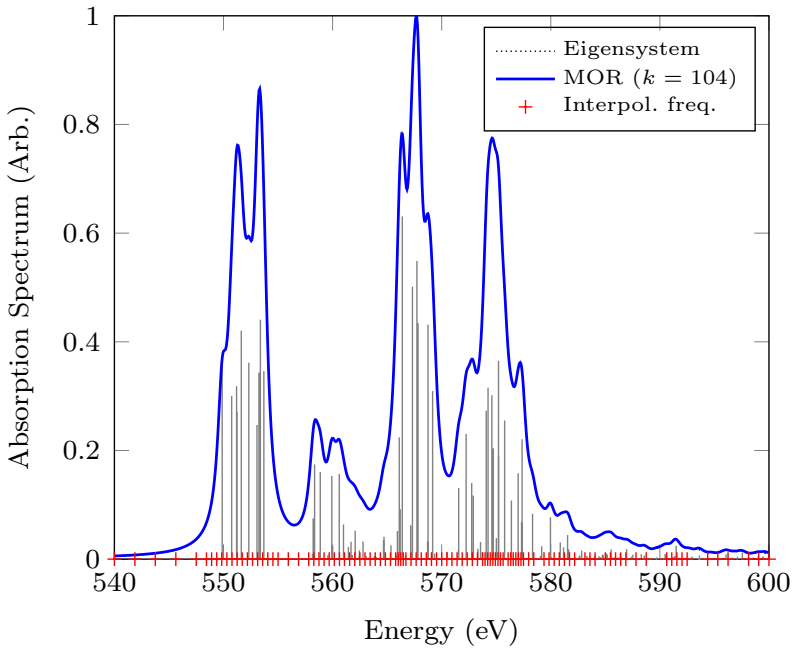
- $$$ CHE-1565520 (NSF)
- $$$ DOE-BES
- Organizers
- Audience

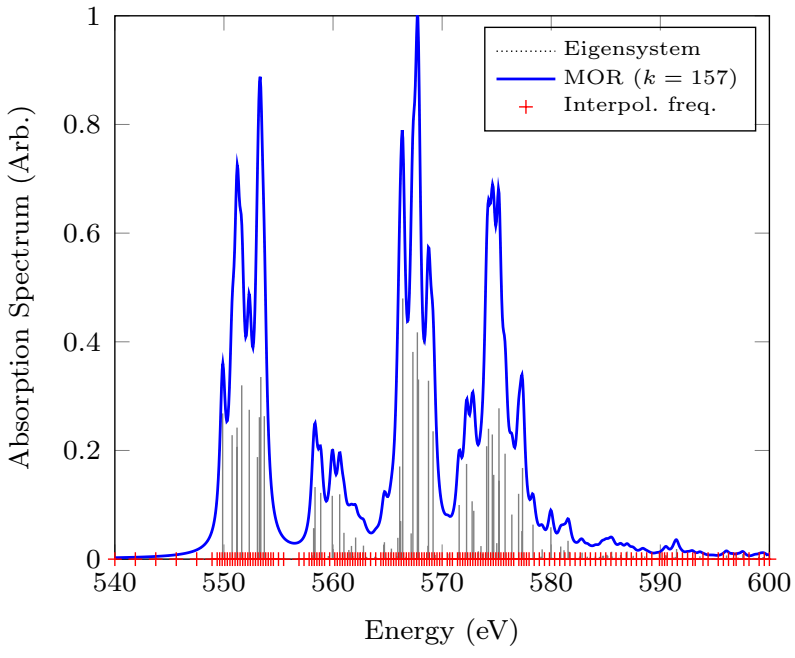
Adaptive Selection of Interpolation Frequencies



Application: TD-HF X-Ray Absorption Spectroscopy

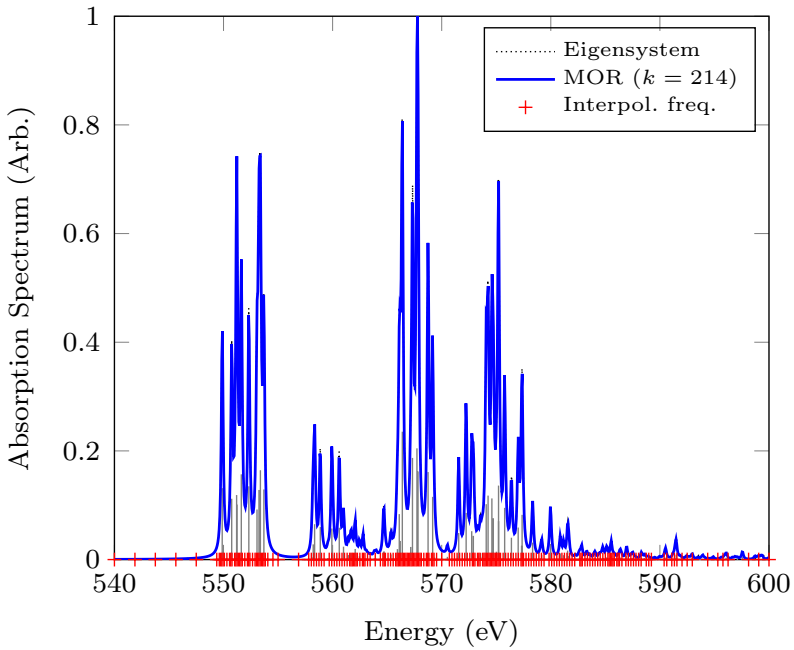


(a) $\eta = 0.5$eV

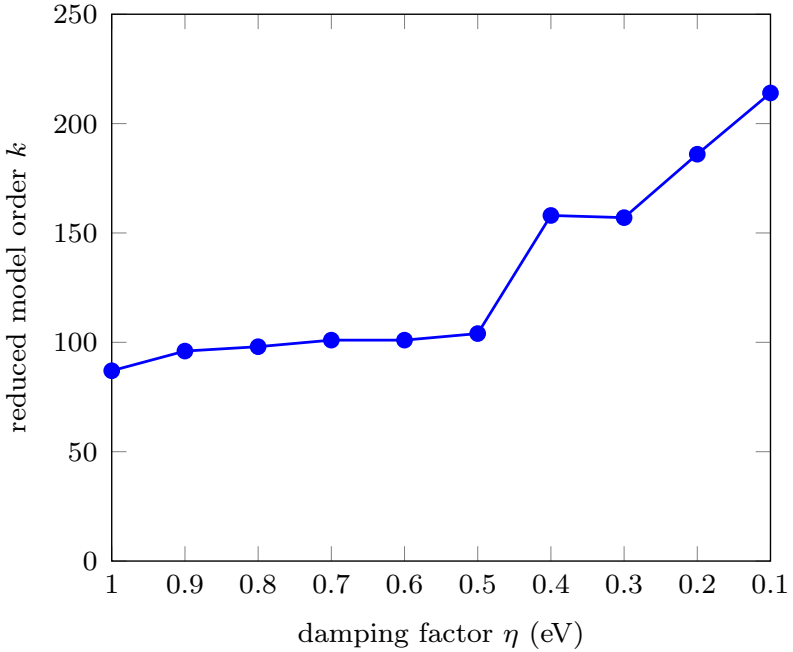


(b) $\eta = 0.3$eV

Application: TD-HF X-Ray Absorption Spectroscopy

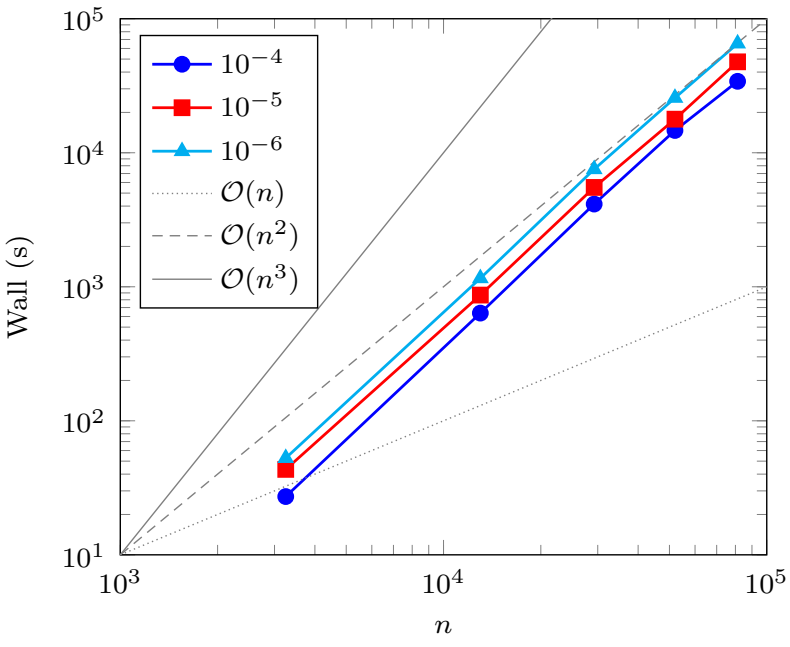


(a) $\eta = 0.1$eV

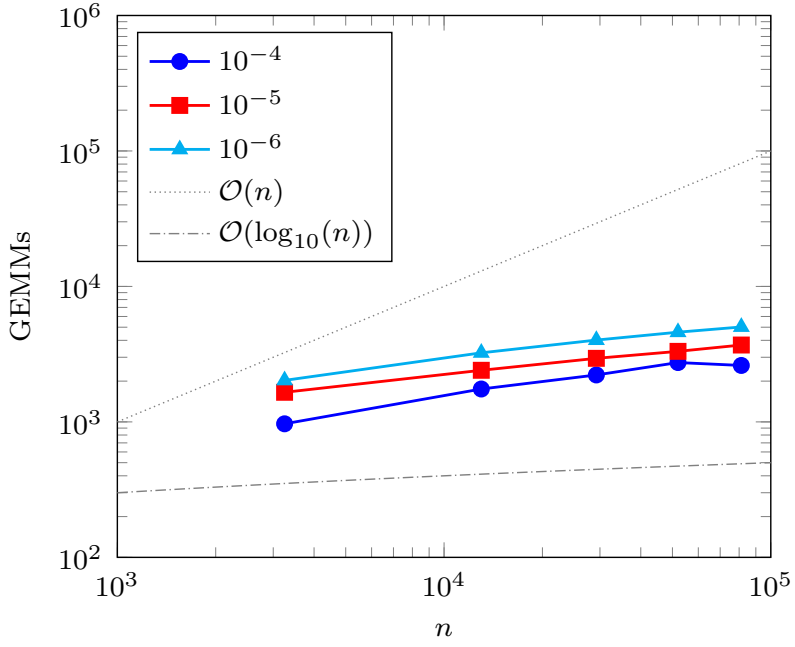


(b) Effects of damping factor

Application: TD-HF X-Ray Absorption Spectroscopy



(a) Wall Time



(b) GEMM calls

Figure: Strong scaling for the MOR procedure