Day 2: Excited-State Electronic Structure & Spectroscopic Properties

CyberTraining: Modeling Quantum Dynamics of Excited States in Materials in the Era of Machine Learning

July 7, 2026

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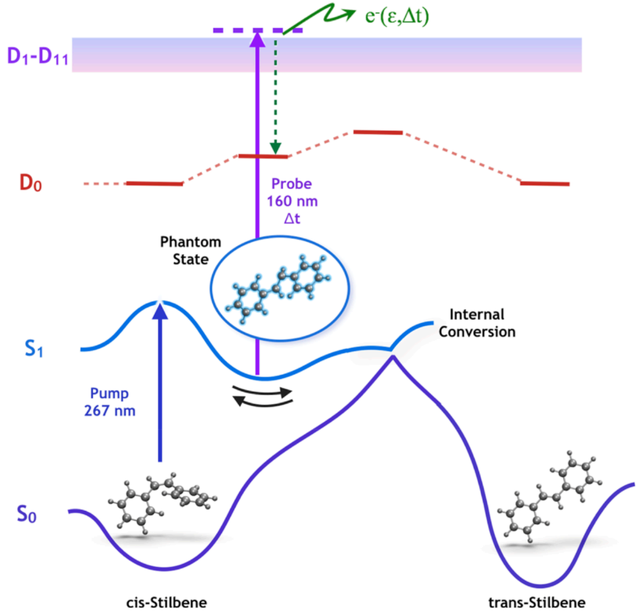
Motivation

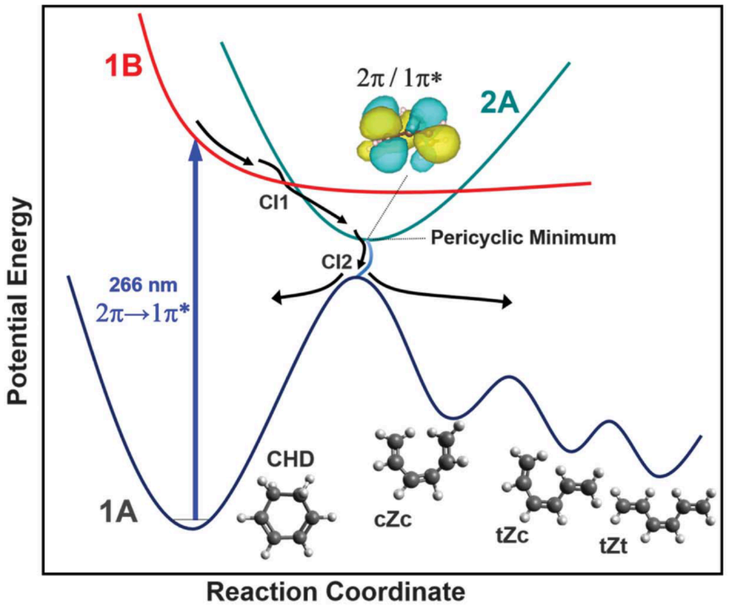
Fundamental understanding of light-matter interactions

Excited-state electronic structure



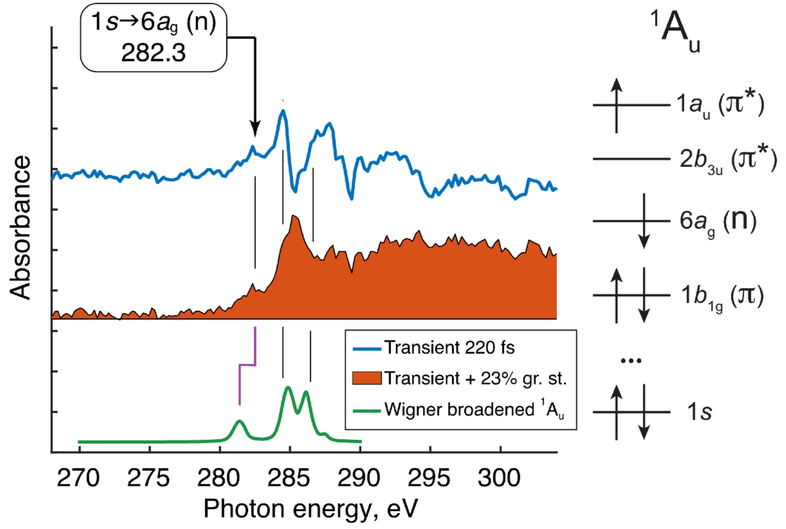
Williams et al., *JPCL*, 6363, **12** (2021)

Ultrafast electron and nuclear dynamics



Attar et al., *Science,* 356, ***54*** (2017)

Spectroscopic properties

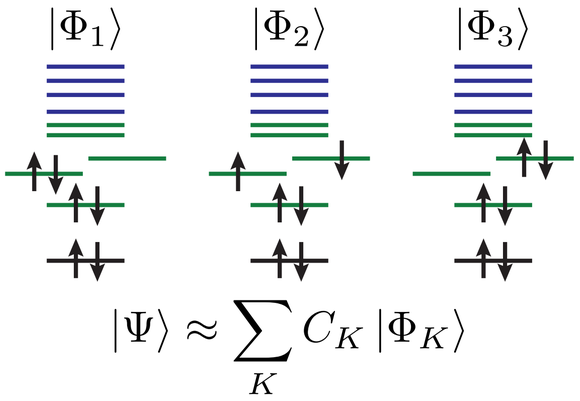


Scutelnic et al., *Nat. Comm.* 5003, ***12*** (2021)

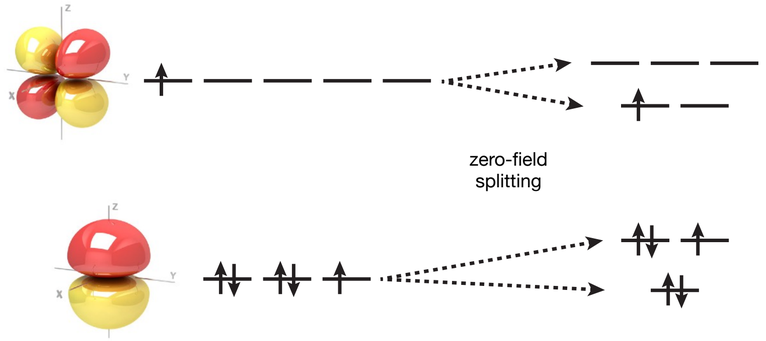
Crucial for advancing photochemistry, solar energy conversion, etc...

Requirements for Accurate Theory

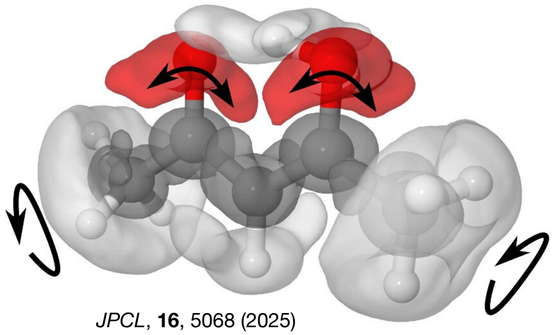
Describe static and dynamic correlation



Capture relativistic effects



Incorporate nonadiabatic nuclear dynamics



JPCL, **16**, 5068 (2025)

Provide access to spectroscopic observables

Accurately describe valence-excited states

Accurately describe core-excited states

Compute many states and broad spectral regions

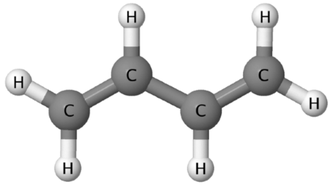
Computationally efficient

Numerically stable

Challenging for most computational methods!

Single- vs Multireference Methods

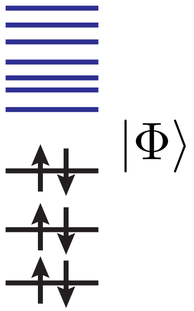
Butadiene:



HOMO – LUMO gap is large

Weak electron correlation:

Important electronic configurations:



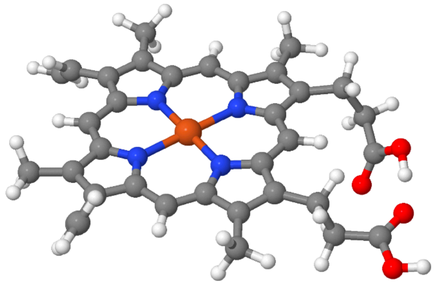
Wavefunction:

$$|\Psi\rangle \approx |\Phi\rangle$$

single configuration

appropriate methods: single-reference

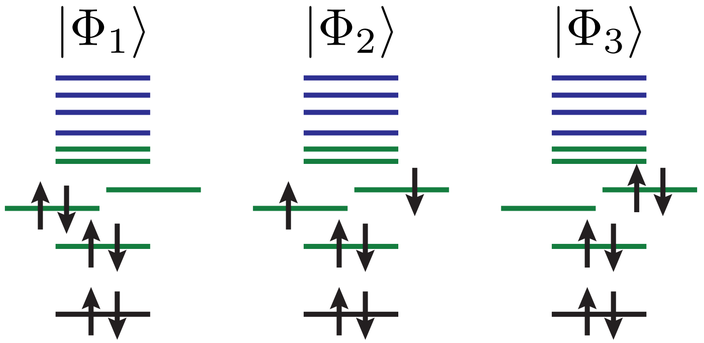
Heme B complex:



HOMO – LUMO gap is small

Strong electron correlation:

Important electronic configurations:



Wavefunction:

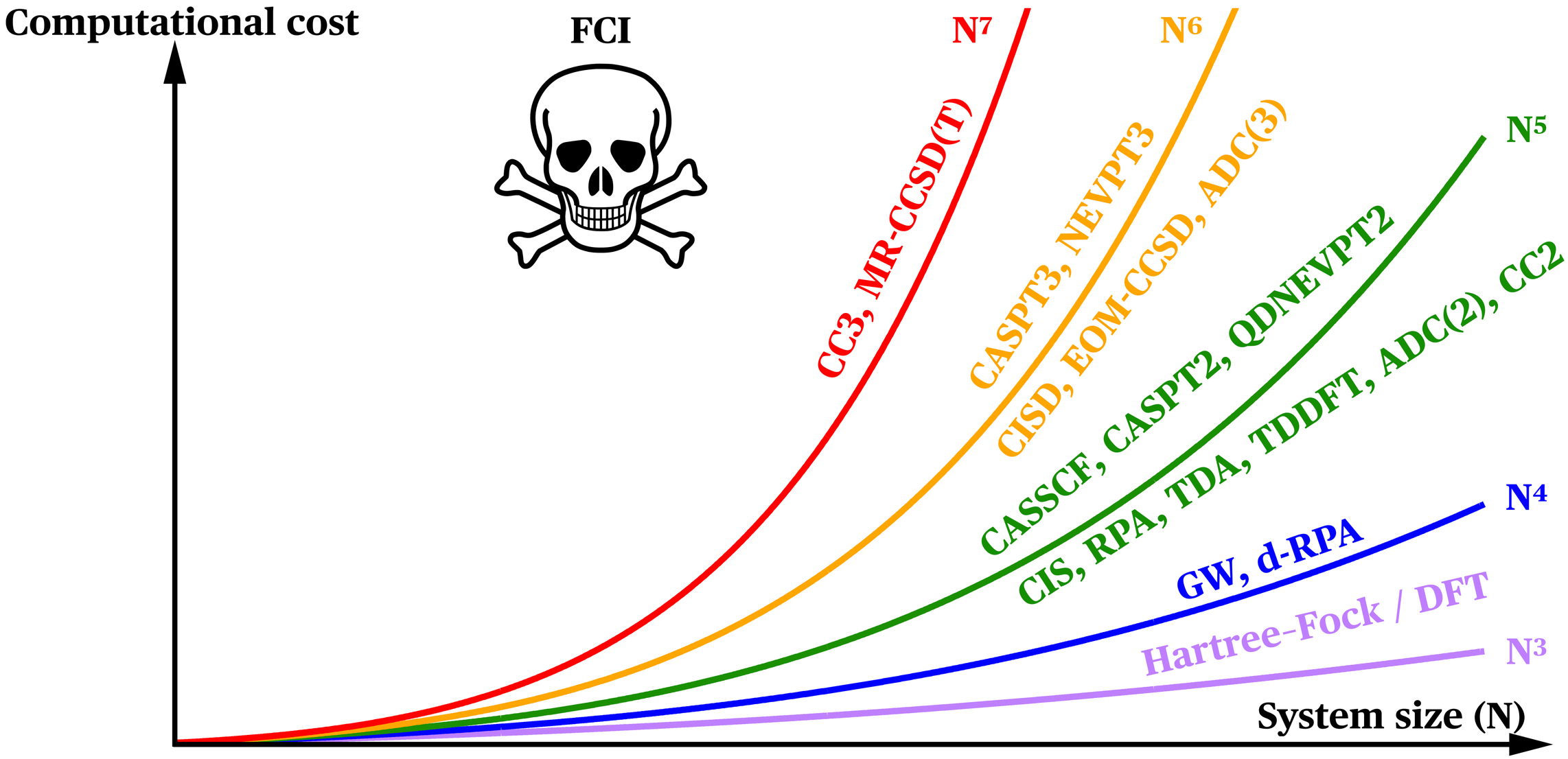
$$|\Psi\rangle \approx \sum_K C_K |\Phi_K\rangle$$

many configurations

appropriate methods: multireference

Very important in excited states and non-equilibrium geometries

Computational Cost



Incorporating electron correlation is computationally very costly!

Day 2 Software Infrastructure

PySCF v.2.13

https://github.com/pyscf/pyscf

Prism v.0.9

https://github.com/sokolov-group/prism

Available excited-state methods:

- ⋆ CIS, TDA, RPA, TD-DFT
- ⋆ GW, AGF2
- ⋆ ADC(2), (2)-X, and (3) for EE, IP, EA
- ⋆ CISD, EOM-CCSD for EE, IP, EA
- ⋆ CASSCF, NEVPT2 (SC), MCPDFT
- ⋆ Molecules and materials
- ⋆ NEVPT2 and QDNEVPT2 (FIC)
- ⋆ MR-ADC(1), (2) and (2)-X for core ionization (CVS-IP)
- ⋆ State-interaction spin-orbit coupling
- ⋆ Magnetic properties

Day 2 Software Infrastructure

PySCF v.2.13

https://github.com/pyscf/pyscf

Prism v.0.9

https://github.com/sokolov-group/prism

Installation requirements:

- ★ Python 3 environment (e.g., conda)
- ★ Modules: numpy, scipy, h5py
- ★ Compiled version: C & C++ compiler, BLAS library (e,g., Intel MKL), CMake
- ★ Optional: matplotlib, mkl, opt_einsum, pytblis

- ★ PySCF and its dependencies
- ★ Modules: psutils
- ★ Optional: sympy (SOC), socutils (SOC)

Day 2 Tentative Plan

Morning (9 am – 12 pm):

- 9:00 – 9:25: Motivation and day overview
- 9:25 – 9:30: Testing software environment
- 9:30 – 10:15: Single-reference methods: theory, practical guidelines, live demos
- 10:15 – 12:00: Single-reference methods breakout session

Afternoon (1:30 – 5:00 pm):

- 1:30 – 2:15: Multireference methods: theory, practical guidelines, live demos
- 2:15 – 3:45: Multireference methods breakout session
- 3:45 – 5:00: Reports from each group

Exercise #1: Testing Software Environment

Follow these steps if you are using UB CCR:

1. Log in to UB CCR
2. Create an interactive session (optional if just testing)
3. Enable PySCF/Prism conda environment:
   - source /projects/academic/cyberwksp21/SOFTWARE_2026/pyscf_prism_environment.sh
4. Copy the folder with PySCF/Prism examples to your home area:
   - cp -r /projects/academic/cyberwksp21/SOFTWARE_2026/pyscf_prism_examples ~
5. Run a test calculation to check if the environment is set up correctly:
   - cd ~/pyscf_prism_examples/01_test_environment
   - python 01_test_environment.py

Day 2 Useful Links

- **More detailed day 2 overview on the website:**
  - https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2026/_episodes/03-electronic-structure
- **GitHub repos with examples:**
  - https://github.com/compchem-cybertraining/Tutorials_PySCF
  - https://github.com/compchem-cybertraining/Tutorials_Prism_SQA
- **PySCF manual:**
  - https://pyscf.org/user/index.html
- **PySCF examples:**
  - https://github.com/pyscf/pyscf/tree/master/examples
- **Prism examples:**
  - https://github.com/sokolov-group/prism/tree/main/examples

General Considerations: Basis Sets

Excited-state calculations require using proper basis sets!

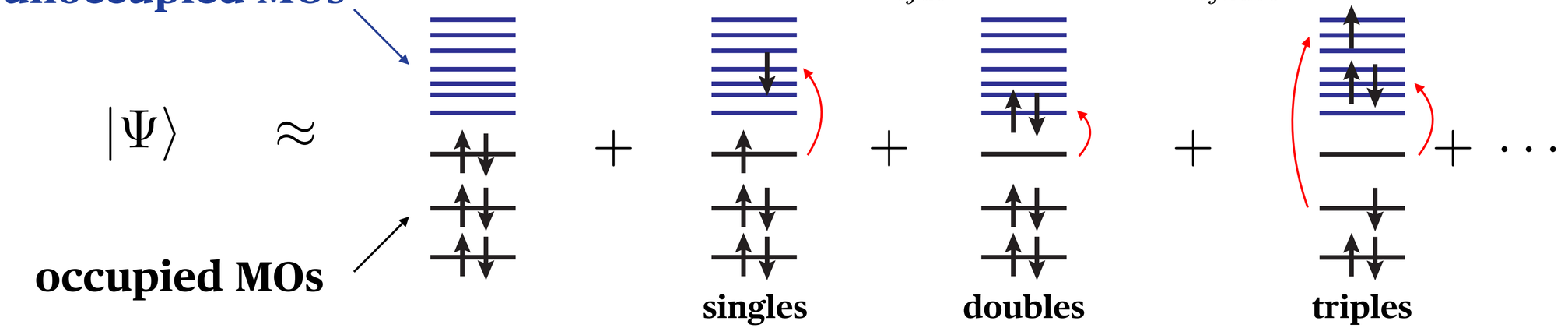
- Most excited-state calculations require **at least a diffuse double-zeta basis set** to produce qualitatively correct results (e.g., aug-cc-pVDZ)
- Triple- or higher-zeta basis sets are required for quantitive accuracy using correlated methods
- Core-level calculations need core-polarized or uncontracted basis sets (e.g., cc-pCVXZ)
- Accurate treatment of relativistic effects requires special basis sets (e.g., ANO-RCC, Sapporo-XZP, etc.)
- In the interest of time, we will mainly use aug-cc-pVDZ in this workshop

Single-Reference Methods

Initial approximation: single Slater determinant

Corrections: excited determinants

$$|\Psi\rangle \approx |\Phi\rangle + \sum_{ia} C_i^a |\Phi_i^a\rangle + \frac{1}{4}\sum_{ijab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \frac{1}{36}\sum_{ijkabc} C_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots$$



Popular methods:

Single-state: HF, DFT, MP2, CISD, CCSD, CCSD(T)

Multi-state: CIS, RPA, TD-DFT, ADC(2), CC2, EOM-CCSD

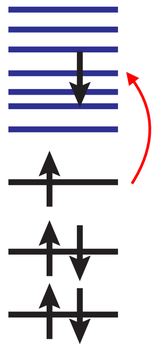
Efficient at describing weak (dynamic) electron correlation

RPA/CIS and TDDFT/TDA

Linear response of a single determinant:

excited-state wavefunction:

$$|\Psi_I\rangle \approx \sum_{ia} X^a_{i,I} |\Phi^a_i\rangle$$



singles

RPA/TDDFT eigenvalue equation:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \omega_I \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}$$

Hierarchy of methods:

- ⋆ **TDA-HF (CIS):** HF orbitals, **B** = **0** (single excitations only)
- ⋆ **TD-HF (RPA):** HF orbitals, **B** ≠ **0** (single exc. and de-exc.)
- ⋆ **TDA-DFT:** DFT orbitals, **B** = **0** (single excitations only)
- ⋆ **TD-DFT:** DFT orbitals, **B** ≠ **0** (single exc. and de-exc.)

⋆ **Computational scaling: O(N^5) with basis set (N) but only O(N_{occ}*N_{vir}) in memory**

Workhorses of excited-state quantum chemistry

RPA/CIS and TDDFT/TDA

Strengths:

- ✓ Computationally efficient
- ✓ Can compute many transitions
- ✓ Conceptually simple, textbook picture of excitations
- ✓ Efficient nuclear gradients and properties

Weaknesses:

- ➡ Doesn't capture double and higher excitations, multireference effects
- ➡ TDDFT depends strongly on the functional of choice
- ➡ TD-HF and TDDFT are non-Hermitian, can exhibit instabilities
- ➡ Problems with charge transfer, conical intersections, charge localization (TDDFT)

Accuracy should be verified with higher-level approaches

Algebraic Diagrammatic Construction (ADC)

Linear-response (propagator) perturbation theory

Frequency-dependent propagator

$$G(\omega) = \sum_m \frac{\langle \Psi_0 | \hat{O} | \Psi_m \rangle \langle \Psi_m | \hat{V} | \Psi_0 \rangle}{\omega - (E_m - E_0)}$$

transition probability

transition energy

Contains information about spectroscopic properties (UV/Vis, photoelectron, two-photon, etc)

ADC(n): $G(\omega) \approx G^{(0)}(\omega) + G^{(1)}(\omega) + \ldots + G^{(n)}(\omega)$

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

ADC capabilities:

- **Systematically improvable hierarchy of methods: ADC(0), ADC(1), ADC(2), ...**
- **Access to a wide range of excitations (IP, EA, EE, etc)**
- **Computational scaling:**
  - **ADC(2): O(N^5);**
  - **ADC(3): O(N^6);**
  - **ADC(4): O(N^7);**
  - **...**

Powerful approach for excited states and spectroscopic properties

Algebraic Diagrammatic Construction (ADC)

ADC propagator in a matrix form:

$$\mathbf{G}(\omega) = \mathbf{T}(\omega\mathbf{S} - \mathbf{M})^{-1}\mathbf{T}^{\dagger}$$

Transition moments

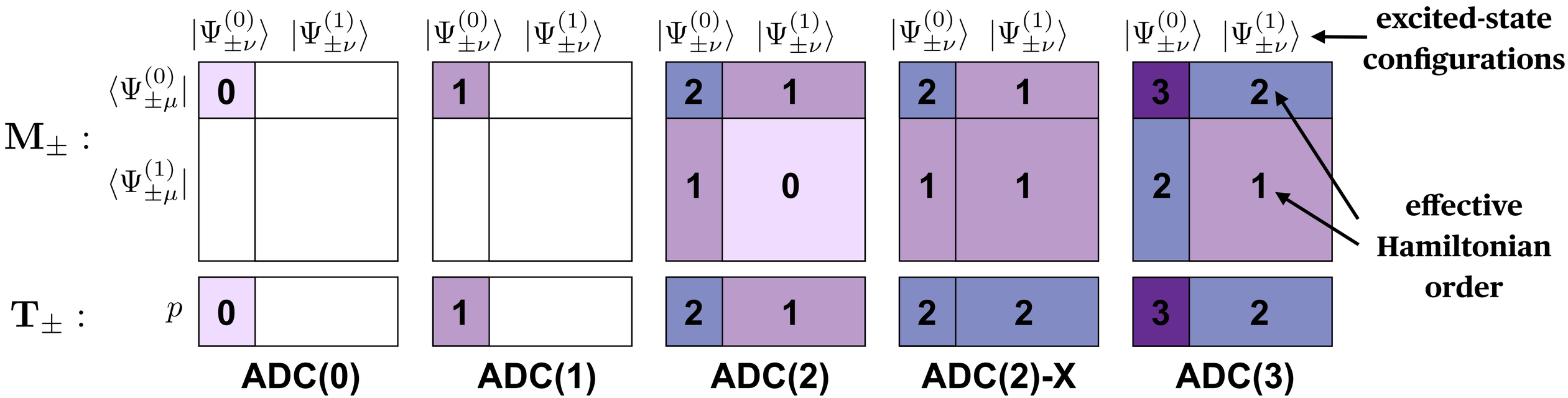
$$\mathbf{T} \approx \mathbf{T}^{(0)} + \mathbf{T}^{(1)} + \ldots + \mathbf{T}^{(n)}$$

Overlap matrix

Effective Hamiltonian

$$\mathbf{M} \approx \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \ldots + \mathbf{M}^{(n)}$$

Increasing level of ADC approximation:



Banerjee, **AYS**, *J. Chem. Theory Comput.* **19**, 3037 (2023)

Algebraic Diagrammatic Construction (ADC)

Algebraic Diagrammatic Construction Theory for Simulating Charged Excited States and Photoelectron Spectra

Samragni Banerjee and Alexander Yu. Sokolov*

Cite This: *J. Chem. Theory Comput.* 2023, 19, 3037–3053

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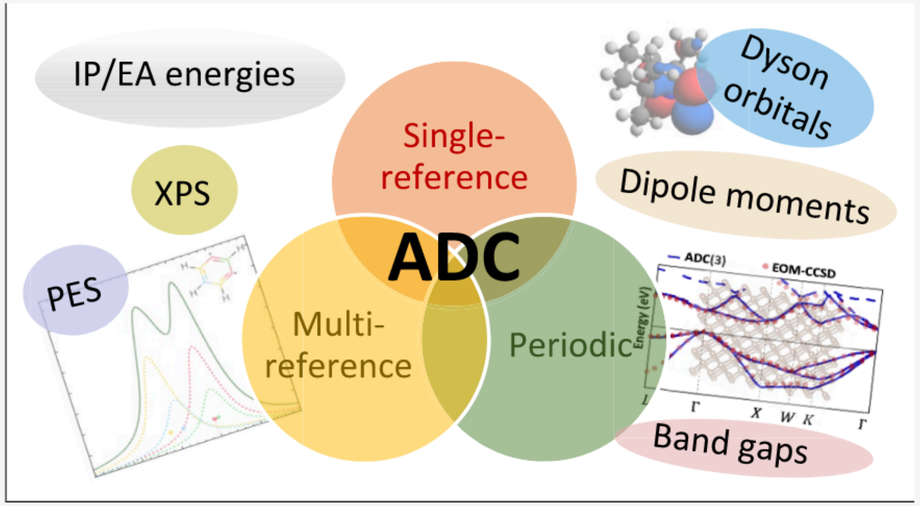
ABSTRACT: Charged excitations are electronic transitions that involve a change in the total charge of a molecule or material. Understanding the properties and reactivity of charged species requires insights from theoretical calculations that can accurately describe orbital relaxation and electron correlation effects in open-shell electronic states. In this Review, we describe the current state of algebraic diagrammatic construction (ADC) theory for simulating charged excitations and its recent developments. We start with a short overview of ADC formalism for the one-particle Green's function, including its single- and multireference formulations and extension to periodic systems. Next, we focus on the capabilities of ADC methods and discuss recent findings about their accuracy for calculating a wide range of excited-state properties. We conclude our Review by outlining possible directions for future developments of this theoretical approach.



Banerjee, **AYS**, *J. Chem. Theory Comput.* **19**, 3037 (2023)

Algebraic Diagrammatic Construction (ADC)

Strengths:

- ✓ Provides access to a wide range of excitations (IP, EA, EE, DIP, etc)
- ✓ Straightforward evaluation of spectroscopic properties
- ✓ Can compute many states and broad spectral regions
- ✓ Size-consistent
- ✓ Hermitian

Weaknesses:

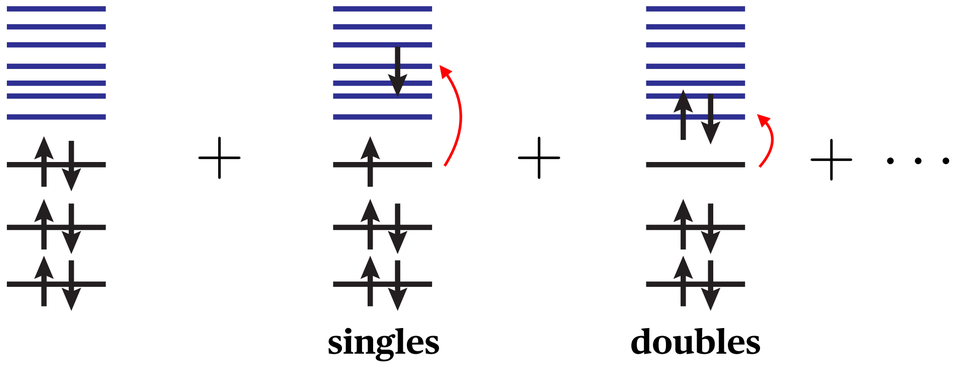
- ➡ Single-reference ADC doesn't capture multireference effects
- ➡ Requires SR-ADC(4) or MR-ADC to accurately treat double excitations
- ➡ SR-ADC suffers from spin contamination for open-shell molecules
- ➡ Problems with charge transfer, conical intersections

Excited-state methods with intermediate cost and accuracy

Equation-of-Motion Coupled Cluster (EOM-CC)

Excited-state CC wavefunction:

$$|\Psi_K\rangle = \hat{R}_K e^{\hat{T}} |\Phi_0\rangle \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$$

$|\Psi\rangle \approx$  $+ \cdots$

EOM-CC eigenvalue equation:

$$\bar{H}\hat{R}_K|\Phi_0\rangle = \omega_K \hat{R}_K|\Phi_0\rangle$$

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$$

EOM-CC capabilities:

- ⋆ **Systematically improvable hierarchy of methods: EOM-CCSD, CCSDT, ...**
- ⋆ **Access to a wide range of excitations (IP, EA, EE, etc)**

⋆ **Computational scaling: O(N⁶) for EOM-CCSD, O(N⁸) for EOM-CCSDT, ...**

Highly accurate framework for weakly correlated electronic states

Equation-of-Motion Coupled Cluster (EOM-CC)

Strengths:

- ✓ High accuracy for states dominated by single excitations
- ✓ Relatively insensitive to the quality of reference orbitals
- ✓ Systematically improvable hierarchy of methods that converge fast for weakly correlated systems
- ✓ Can describe wide range of excitations (IP, EA, EE, SF, DIP, etc)

Weaknesses:

- ➡ Computationally expensive
- ➡ Requires high levels (e.g., MRCC or EOM-CCSDTQ) to capture MR effects and double excitations
- ➡ Non-Hermitian, can yield complex excitation energies
- ➡ Excited-state properties and gradients are not straightforward
- ➡ Problems with conical intersections

Benchmark quality for small molecules and singly excited states

Single-Reference Methods Breakout Session

1. Split into 8 groups (6 in-person, 2 virtual)
2. Find your assigned molecule: https://docs.google.com/spreadsheets/d/1jClch129Uzuj4JSznpDHZQ4nTcph4YF2wLHmXrfHmrA/edit?usp=sharing
3. Molecular geometries can be found on GitHub or CCR (/projects/academic/cyberwksp21/SOFTWARE_2026/pyscf_prism_examples/geometries)
4. Use PySCF and Prism to compute excited states of your molecule, feel free to start with provided examples
5. Tabulate the data, analyze the character of excitation, visualize densities and orbitals, assign excited states where possible
6. Compare results to the QUEST database data (https://github.com/compchem-cybertraining/Tutorials_PySCF/blob/main/QUEST/QUEST-All.xlsx) and assess the performance of each method

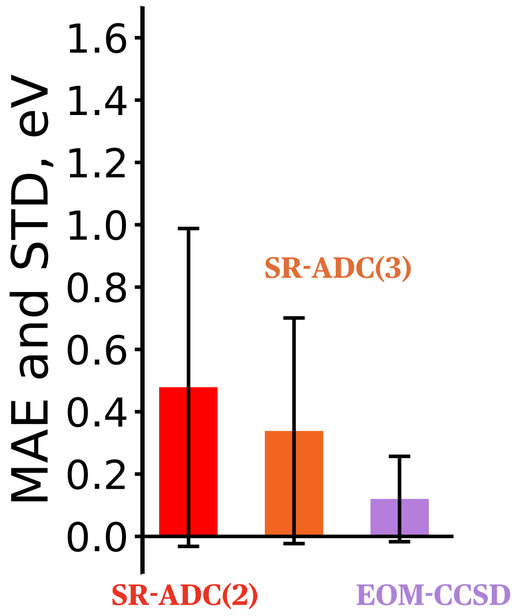
Single-Reference Methods Breakout Session

7. Prepare short summary for the group reports in the afternoon:
   - ⋆ State character:
     - ➡ What is the dominant character of each state?
     - ➡ Do NTOs and density differences give the same interpretation?
   - ⋆ Method comparison:
     - ➡ Do all methods predict the same state ordering?
     - ➡ Which method is the most accurate and where do they fail?
   - ⋆ Report conclusions:
     - ⋆ What is the main spectroscopic assignment for your molecule?
     - ⋆ Which method would you trust most, and why?
     - ⋆ Which calculations became expensive or difficult to converge?
     - ⋆ What would you test next if you had more time?

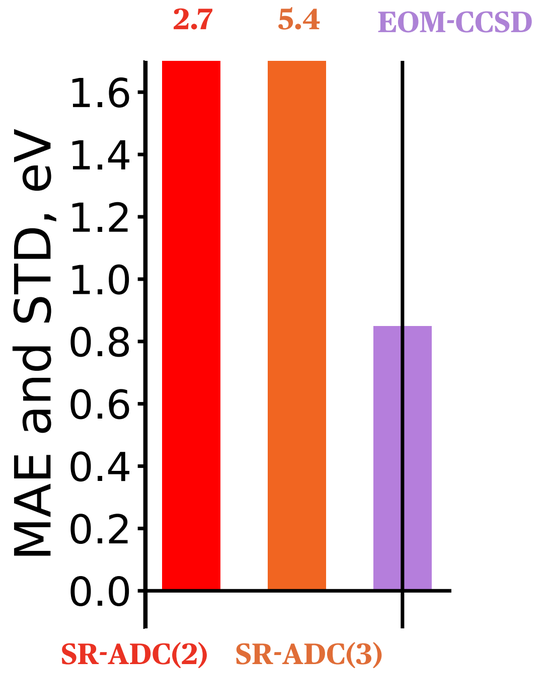
Multireference Methods: Motivation

Errors in excitation energies (eV) relative to benchmark:

Equilibrium geometries:



Stretched geometries:



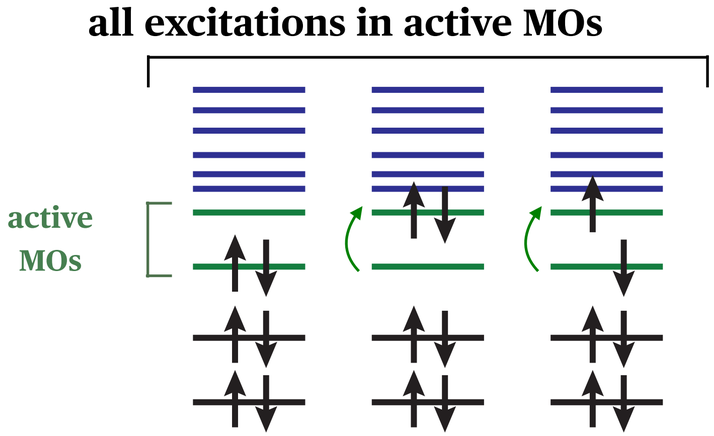
Molecules: HF, F_2, CO, N_2, H_2O (40 electronic states)
aug-cc-pVDZ basis set

Single-reference electronic structure methods are not reliable when electron correlation is strong

Complete Active Space Self-Consistent Field (CASSCF)

CASSCF wavefunctions:

$$|\Psi\rangle \quad \approx \quad |\Psi^{(0)}\rangle = \sum_K |\Phi_K\rangle$$



incorporate strong ("static") correlation in the active space

Capabilities:

- ⋆ Captures static correlation and all electronic excitations in the active space
- ⋆ Neglects excitations and dynamical correlation outside active space
- ⋆ Multiple states of same symmetry can be computed with state averaging
- ⋆ Conventional CAS limit: ~18 active orbitals (N_{act})
- ⋆ Efficient implementations using selected CI, quantum Monte Carlo or DMRG can treat $\lesssim$ 100 active orbitals

⋆ **Computational scaling:** $O(N^5)$ with basis set (N), factorial scaling with N_{act}

Most commonly used multireference method

Complete Active Space Self-Consistent Field (CASSCF)

Strengths:

- ✓ Captures static correlation in the active space
- ✓ Can describe double (and higher) excitations in active space
- ✓ Correct description of conical intersections, charge transfer, bond breaking
- ✓ Efficient for small active spaces and large basis sets

Weaknesses:

- ➡ Requires careful active space choice (often non-intuitive)
- ➡ Results are very sensitive to the quality of optimized orbitals
- ➡ Neglects most of dynamical correlation
- ➡ Doesn't describe excitations outside active space
- ➡ Very expensive for $N_{act} > 15$

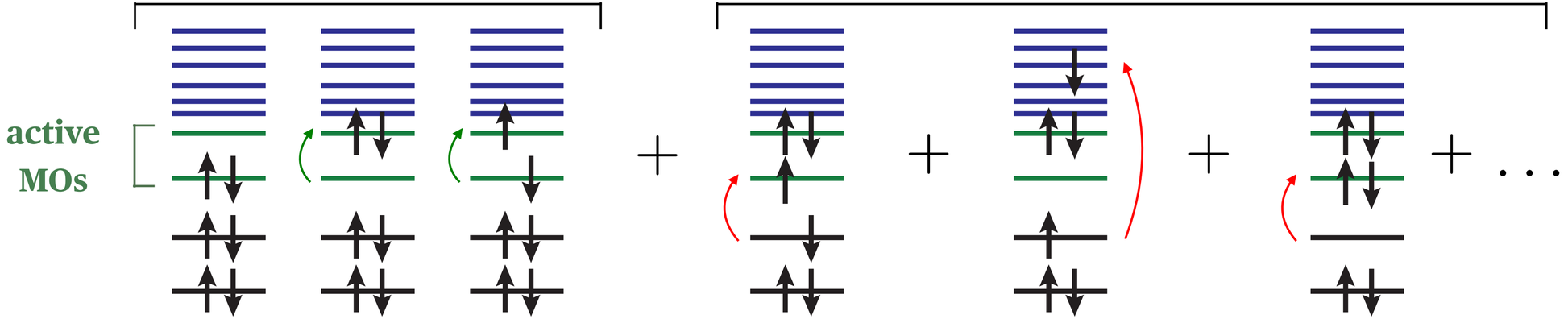
Starting point of most multireference calculations

Multireference Perturbation Theories

Treat both static and dynamic correlation for many electronic states

$$|\Psi\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle + |\Psi^{(2)}\rangle + \dots$$

reference: (all) excitations in active MOs | **corrections: excitations outside active space**



incorporate strong ("static") correlation (CASSCF)

capture the remaining dynamic correlation using perturbation theory

- ✓ **Correctly describe excited states and nonequilibrium geometries**
- ✓ **Accurate if active space includes all strongly correlated orbitals**
- ✓ **Computationally efficient for large basis sets and active spaces at low order**

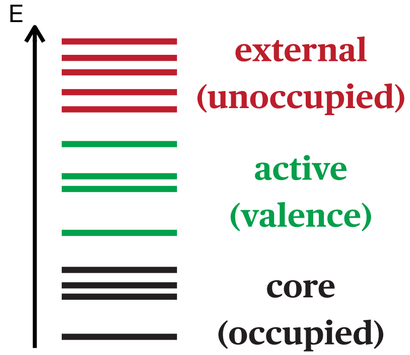
Powerful approach for multiply excited states and non-equilibrium geometries

N-Electron Valence Perturbation Theory

Intruder-resilient* multireference perturbation theory[1]

$$|\Psi_I\rangle \approx |\Psi_I^{(0)}\rangle + |\Psi_I^{(1)}\rangle + \ldots + |\Psi_I^{(n)}\rangle$$

1. Reference wavefunctions are obtained from CASCI or CASSCF:



$$|\Psi_m^{(0)}\rangle = \sum_I C_{mI} |\Phi_I\rangle$$

Linear combination of all determinants in the active space

[1] Angeli, Cimiraglia, Evangelisti, Leininger, and Malrieu, *J. Chem. Phys.* **114**, 10252 (2001)

[2] K.G. Dyall, *J. Chem. Phys.* **102**, 4909 (1995)

2. Zeroth-order Hamiltonian is bielectronic in the active space:

Dyall Hamiltonian[2]: $\hat{H}^{(0)} = C + \underbrace{\sum_i^{\text{core}} \varepsilon_i a_i^\dagger a_i}_{\text{core}} + \underbrace{\sum_a^{\text{ext}} \varepsilon_a a_a^\dagger a_a}_{\text{external}} + \underbrace{\hat{H}_{act}}_{\text{active}}$

Contains all terms of the full Hamiltonian in the active space

*** Intruder problems may still arise for higher-lying states close to ionization continuum[3,4]**

[3] M. Hayashi, M. Saitow, K. Uemura, T. Yanai, *J. Chem. Phys.*, **160**, 194105 (2024)

[4] N.Y. Chiang, R. Majumder, **AYS**. *J. Chem. Phys.* **164**, 174117 (2026)

⋆ **Computational scaling (NEVPT2): O(N^5) with basis set (N), factorial scaling with N$_{act}$**

CHAPTER FOUR

Multireference perturbation theories based on the Dyall Hamiltonian

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AYS, *Adv. Quant. Chem.* **90,** 121 (2024) https://arxiv.org/pdf/2401.11262

Prism v.0.9: Multireference Methods for Spectroscopy

Method	Reference
SS-NEVPT2	CASCI, CASSCF, SA-CASSCF
QD-NEVPT2	CASCI, CASSCF, SA-CASSCF
CVS-IP-MR-ADC(1)	CASCI, CASSCF
CVS-IP-MR-ADC(2)	CASCI, CASSCF
CVS-IP-MR-ADC(2)-X	CASCI, CASSCF

Implementation features:

- ✓ Native PySCF interface
- ✓ Full internal contraction (a.k.a. pc-NEVPT2)
- ✓ In-core and out-of-core integrals
- ✓ Density fitting (highly recommended!)
- ✓ Frozen core approximation
- ✓ Dyson, natural transition orbitals
- ✓ Correlated one-particle densities and properties
- ✓ State-interaction spin–orbit coupling using Breit–Pauli and X2C-DKH1 Hamiltonians
- ✓ Magnetic g-tensors
- ✓ Helper functions to plot spectra

PRISM

https://github.com/sokolov-group/prism/

Prism v.0.9: Multireference Methods for Spectroscopy

Method	Reference	Properties
SS-NEVPT2	CASCI, CASSCF, SA-CASSCF	Energies, osc. strengths, correlated 1-RDMs, natural transition orbitals, zero-field splitting, *g*-tensors
QD-NEVPT2	CASCI, CASSCF, SA-CASSCF	Energies, osc. strengths, correlated 1-RDMs, natural transition orbitals, zero-field splitting, *g*-tensors
CVS-IP-MR-ADC(1)	CASCI, CASSCF	Core IPs, spec. factors, Dyson orb, transition 1-RDMs
CVS-IP-MR-ADC(2)	CASCI, CASSCF	Core IPs, spec. factors, Dyson orb, transition 1-RDMs
CVS-IP-MR-ADC(2)-X	CASCI, CASSCF	Core IPs, spec. factors, Dyson orb, transition 1-RDMs

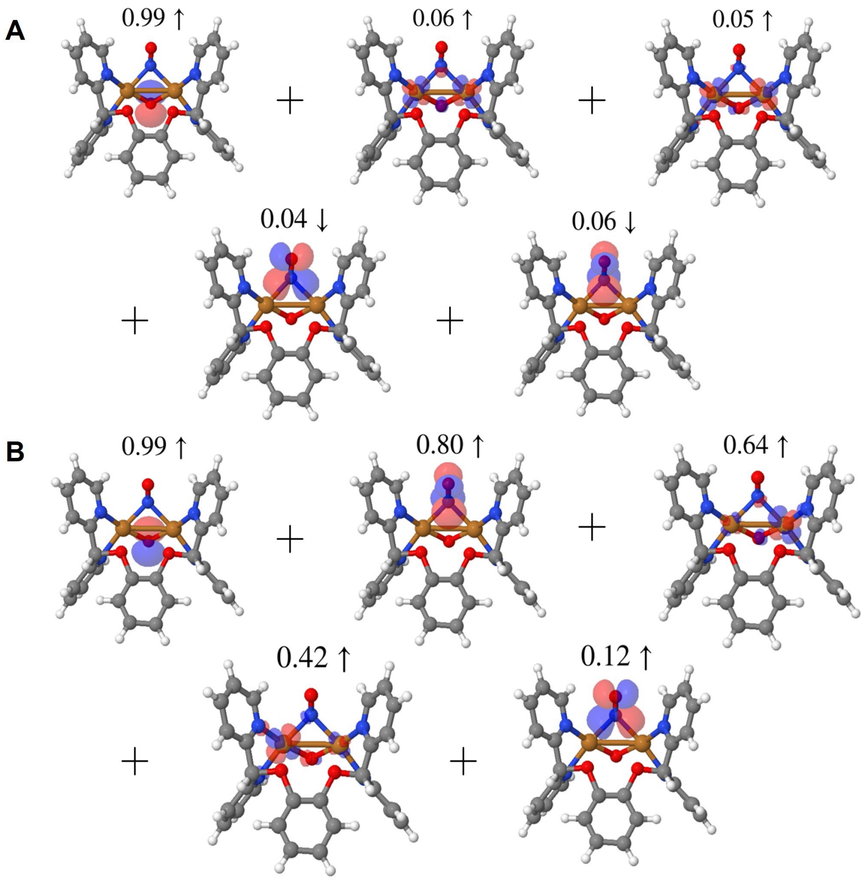
PRISM

https://github.com/sokolov-group/prism/

Prism Capabilities: SI-SOC and *g*-Tensors

Spin-switching $[Cu_2(O)(NO)]^{2+}$ complex:

Spin density analysis:



S. Carter, W. Tao, R. Majumder, **AYS**, and S. Zhang,
J. Am. Chem. Soc. **145**, 17779 (2023)

Ground- and excited *g*-tensors:

S = 1/2:

S = 3/2:

```
Magnetic g-tensor principal axes:
[[ 0.617852  0.100298  0.779871]
 [-0.409216 -0.805909  0.427847]
 [ 0.671417 -0.583482 -0.456889]]
[[ 0.552544 -0.559406  0.617867]
 [ 0.833483  0.371268 -0.409226]
 [-0.000471  0.741097  0.671398]]

Magnetic g-factors (ge = 2.002319):
      2.002319,       2.003636,       2.003636
      0.000000,       0.001317,       0.001317 (g-shift)
         0.000,          1.317,          1.317 (g-shift, ppt)
      2.001661,       2.001661,       2.002319
     -0.000658,      -0.000658,       0.000000 (g-shift)
        -0.658,         -0.658,          0.000 (g-shift, ppt)
```

S = 1/2:

S = 3/2:

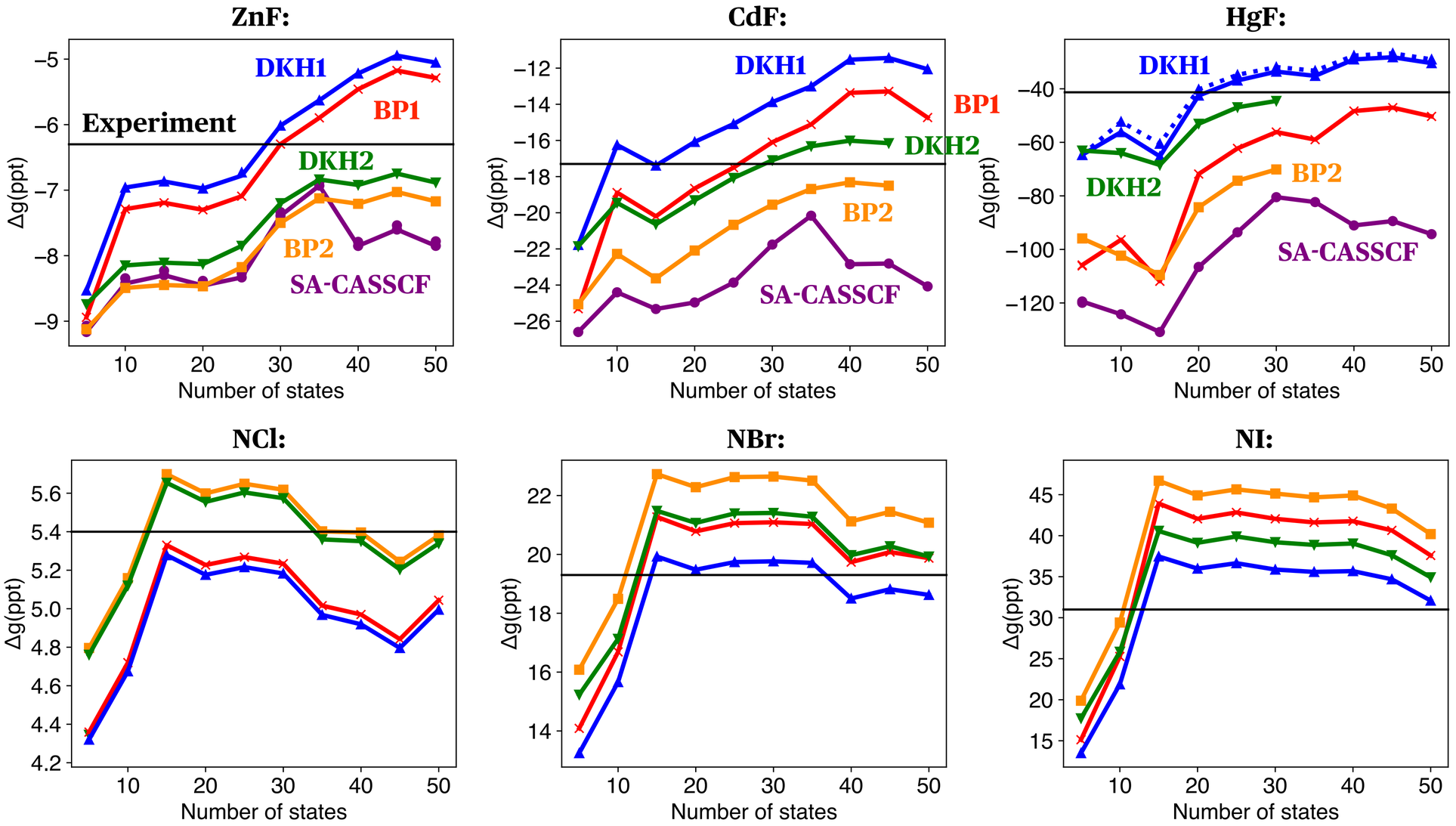
def2-SVP (690 MO's), (13e, 15o) active space, DKH1 Hamiltonian, 32 hours @ Intel Xeon CPU Max 9470 (20 cores, 2.0 GHz)

Doublet–quartet gap is less than 200 cm^{-1}!

Spin state changes with increasing temperature!

Upcoming: 2nd-Order SOC in QDNEVPT2

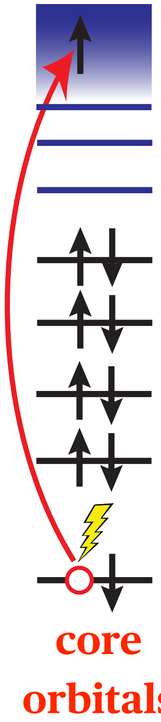
Molecular *g*-shifts computed using first- and second-order spin–orbit QDNEVPT2:



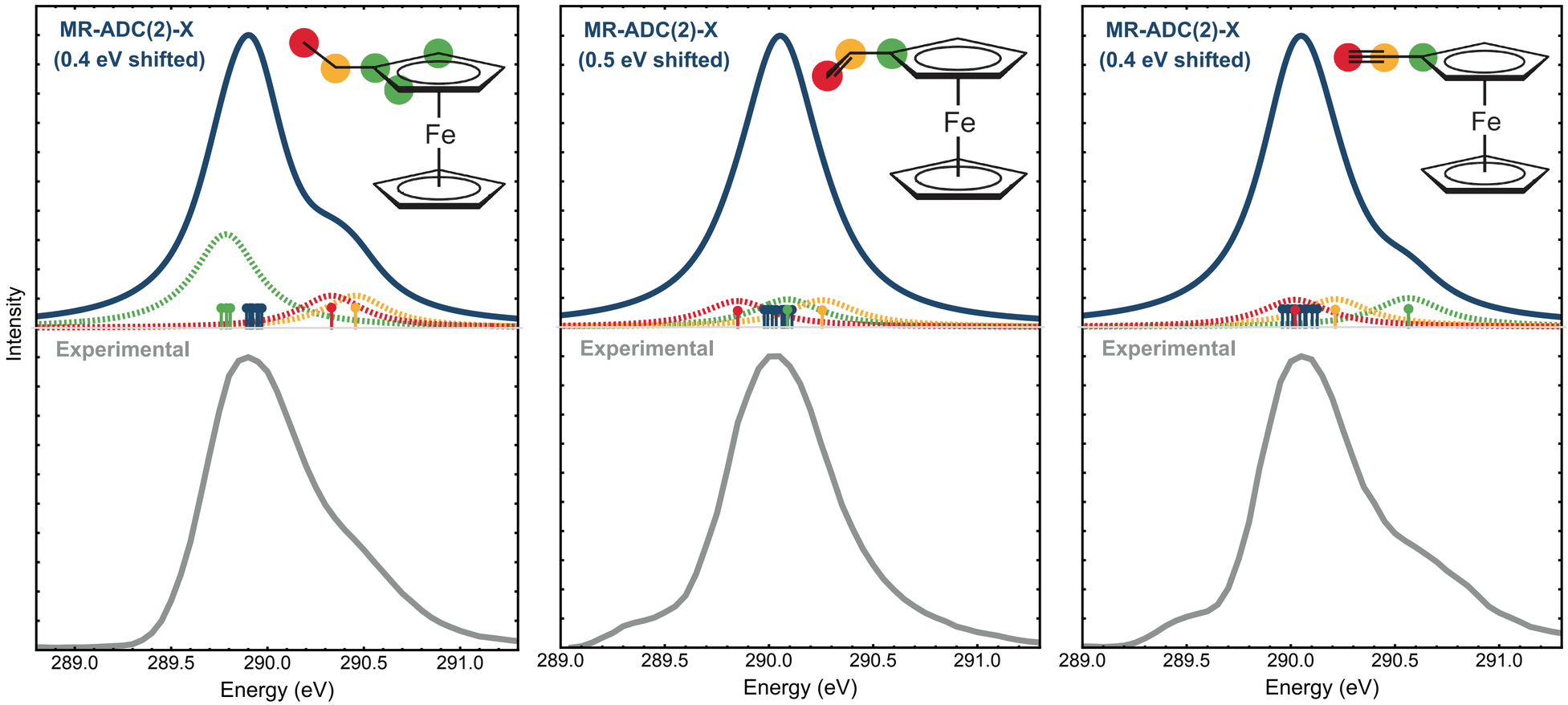
N.Y. Chiang, R. Majumder, **AYS**. *J. Chem. Phys.* **164**, 174117 (2026)

Prism Capabilities: CVS-IP-MR-ADC

X-ray photoelectron spectroscopy:



Substituted ferrocene C K-edge X-ray photoelectron spectra:



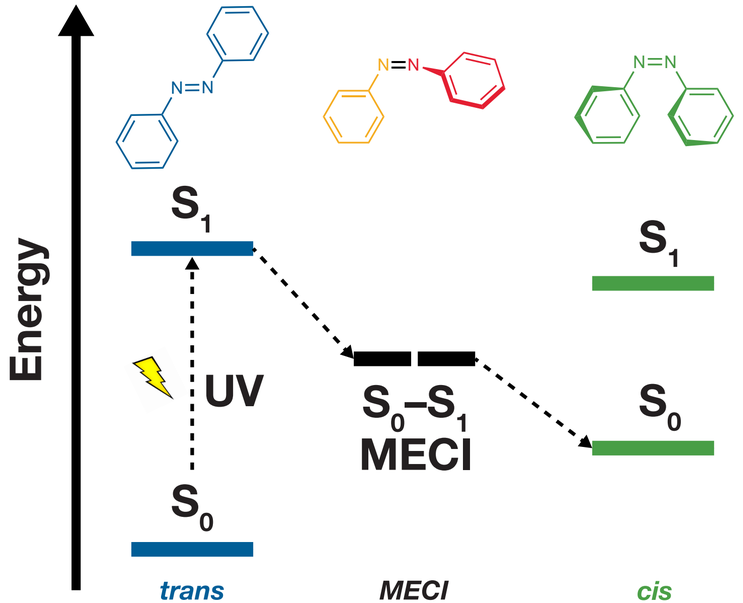
cc-pwCVQZ basis set (~1500 MO's),
X2C scalar relativistic effects, active space: (ne, no) with n = 8, 10, 12

C. E. V. de Moura, **AYS**, *J. Phys. Chem. A*, **128**, 5816 (2024)

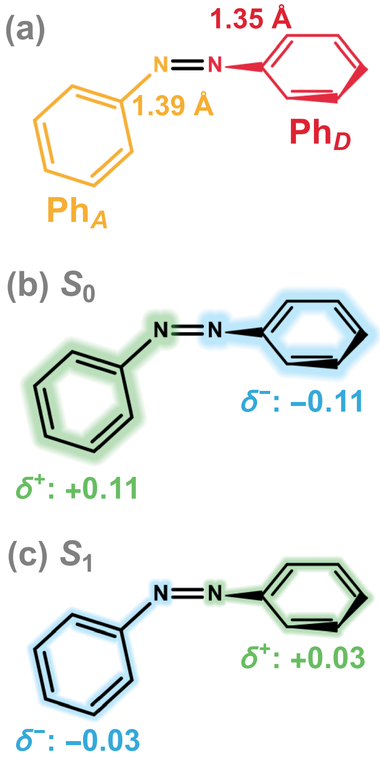
Experiment: A. Boccia, et al. *J. Chem. Phys.*, **136**, 134308 (2012)

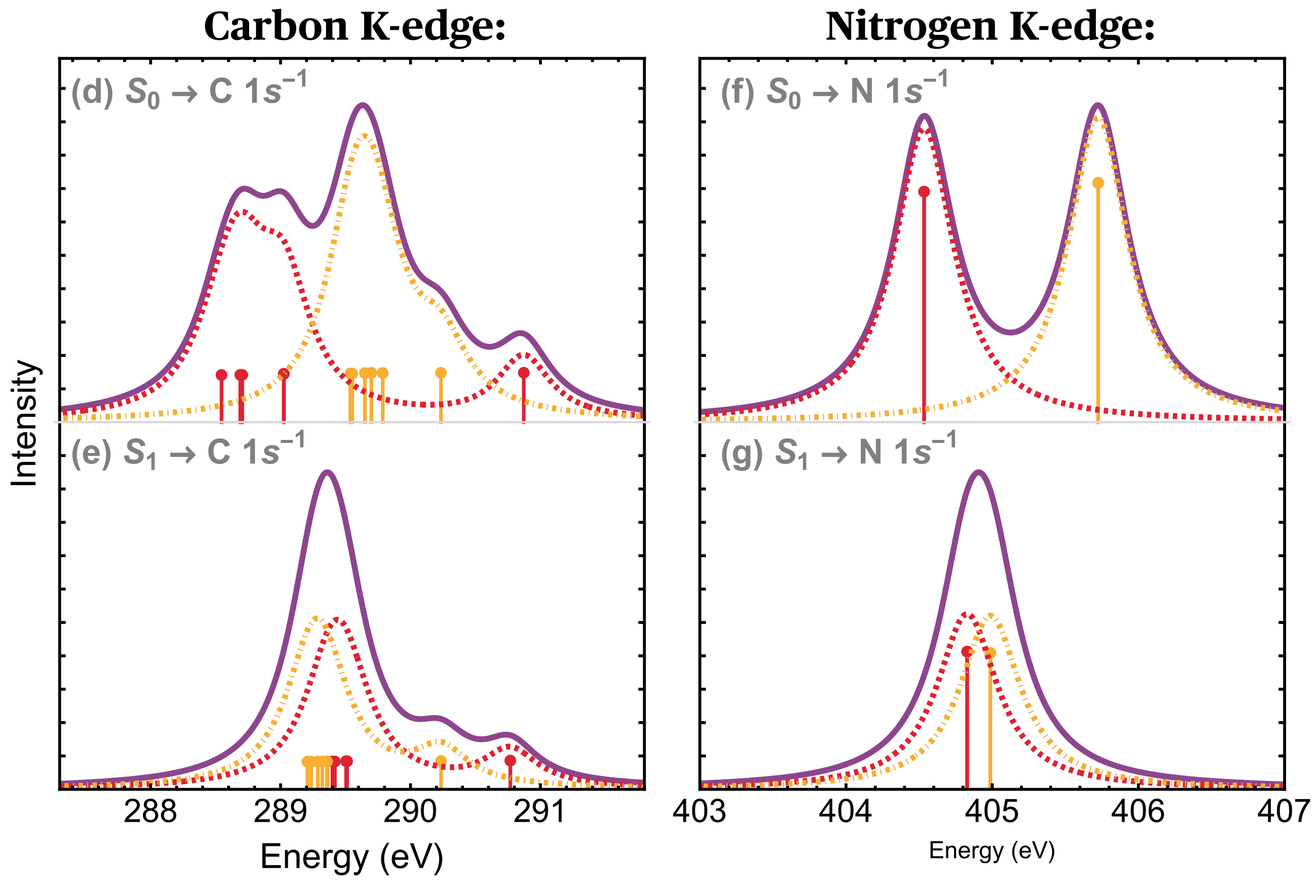
Prism Capabilities: CVS-IP-MR-ADC

Photorelaxation mechanism:



XPS Spectra of S_0–S_1 minimum energy conical intersection:





CVS-IP-MR-ADC(2)-X, cc-pwCVQZ basis set (1476 MO's), X2C scalar relativistic effects, active space: (16e, 15o)

C. E. V. de Moura, **AYS**, *J. Phys. Chem. A*, **128**, 5816 (2024)

Upcoming: Prism v.1.0 features (Summer 2026)

New methods	Reference
CVS-EE-MR-ADC(2)	RHF, ROHF, CASCI, CASSCF
CVS-EE-MR-ADC(2)-X	RHF, ROHF, CASCI, CASSCF
IP-MR-ADC(2)	RHF, ROHF, CASCI, CASSCF
IP-MR-ADC(2)-X	RHF, ROHF, CASCI, CASSCF
EA-MR-ADC(2)	RHF, ROHF, CASCI, CASSCF
EA-MR-ADC(2)-X	RHF, ROHF, CASCI, CASSCF

Upcoming features:

- Enhanced integration of PySCF modules with Prism capabilities
- Second-order spin–orbit coupling in SS-NEVPT2 and QD-NEVPT2
- State-interaction spin–orbit coupling with MR-ADC
- Expanded magnetic property capabilities
- QM/MM calculations with polarizable embedding
- Helper functions for wavefunction and transition intensity analysis

https://github.com/sokolov-group/prism/

Summary

- ✓ Molecular CIS/RPA, TDA/TDDFT, IP/EA/EE-SR-ADC, EOM-CCSD, CASSCF
- ✓ Extensions to periodic methods for crystalline systems
- ✓ Density fitting
- ✓ Frozen core approximation
- ✓ Excited-state wavefunction (“eigenvector”) analysis
- ✓ Transition intensity analysis
- ✓ Dyson and natural transition orbitals
- ✓ Correlated one-particle densities and properties

- ✓ Native PySCF interface
- ✓ Fully internally contracted SS- and QD-NEVPT2, CVS-IP-MR-ADC
- ✓ Density fitting
- ✓ Frozen core approximation
- ✓ Dyson and natural transition orbitals
- ✓ Correlated one-particle densities and properties
- ✓ State-interaction spin–orbit coupling using BP and X2C-DKH1 Hamiltonians
- ✓ Magnetic g-tensors

Multireference Methods Breakout Session

1. For your group's molecule, perform calculations using multireference methods available in PySCF and Prism
2. Investigate the dependence of results on active-space size, initial guess, number of state-averaged states
3. Tabulate the data, analyze the character of excitation, visualize densities and orbitals, assign excited states where possible
4. If possible, locate doubly excited states and analyze their electronic structure
5. Compare the performance of multireference and single-reference methods
6. Discuss pros and cons of multireference methods

Multireference Methods Breakout Session

7. Prepare short summary for the group reports in the afternoon:
   - ⋆ Active space and state averaging:
     - ➡ What active spaces did you use and why?
     - ➡ How many states were included in the SA-CASSCF calculation?
   - ⋆ Dynamic correlation:
     - ➡ Does dynamic correlation change the state ordering?
     - ➡ Which states receive the largest perturbative corrections, and why?
   - ⋆ Report conclusions:
     - ⋆ Is multireference character important for your system?
     - ⋆ Which active space and method would you trust most, and why?
     - ⋆ Which calculations became expensive or difficult to converge?
     - ⋆ What would you test next if you had more time?