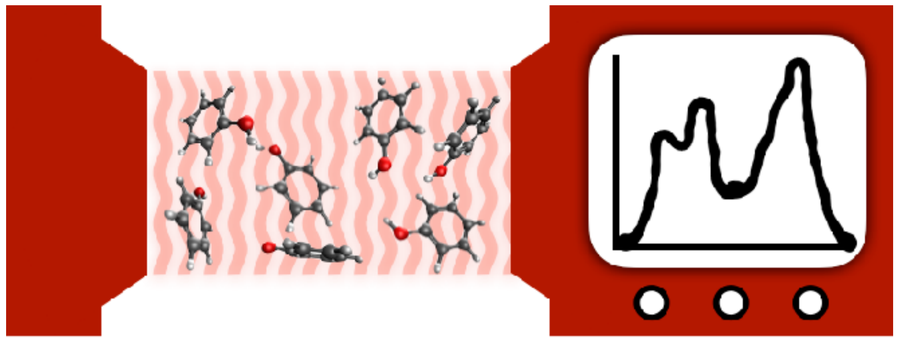
From energies and wave-functions to spectroscopic observables: Challenges and solutions



$$\Psi = \mathrm{Re}^{T}\,\Phi_0$$
$$\overline{H} = \exp(-T)H\exp(T)$$
$$\overline{H}R\Phi_0 = ER\Phi_0$$

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A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

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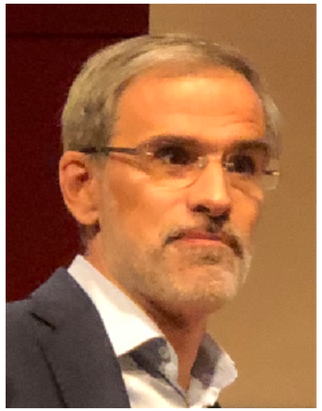
Acknowledgments



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Software: Q-Chem

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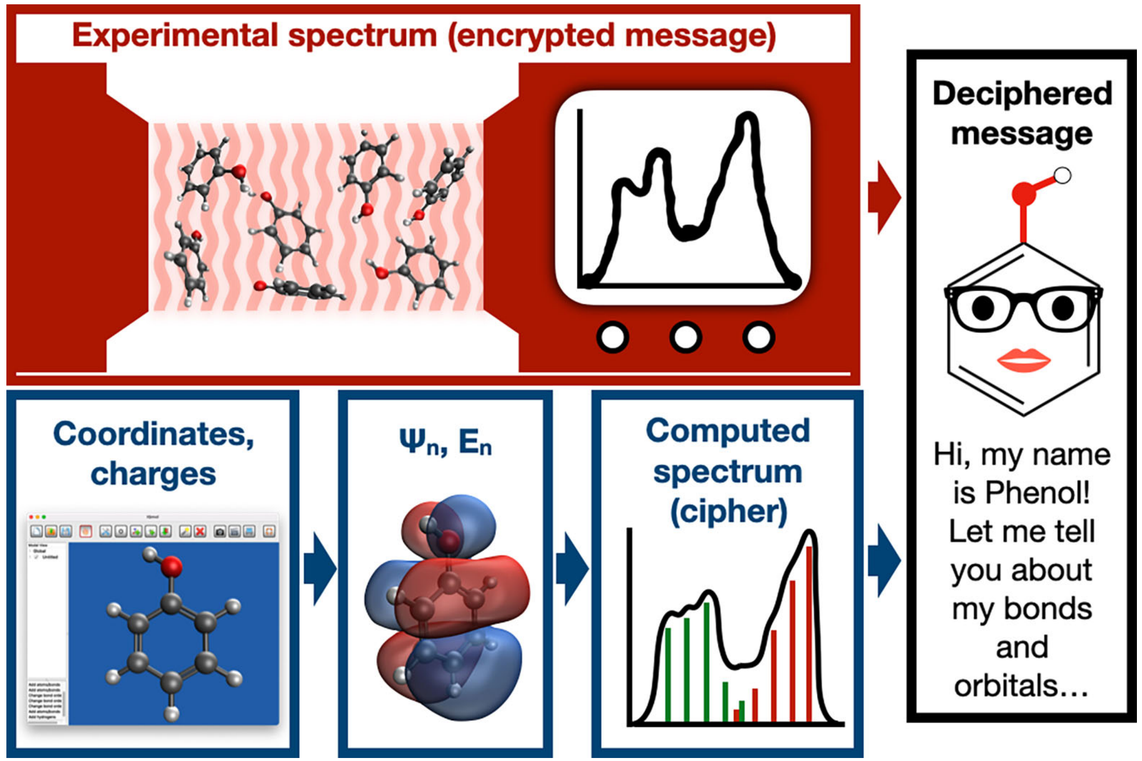
Spectroscopy: Light + matter

Light + molecule = spectrum

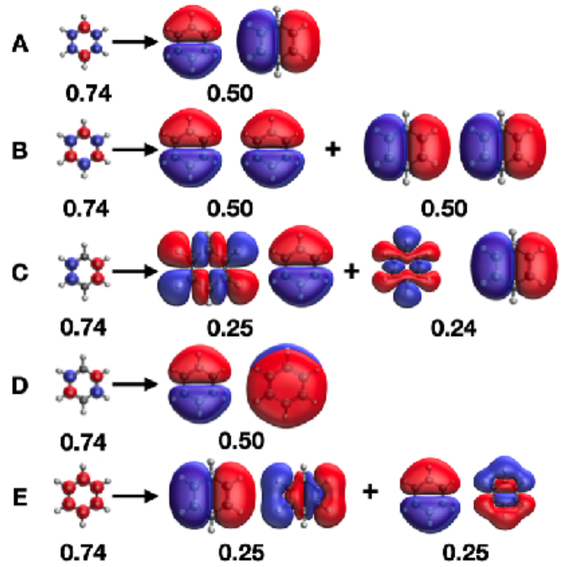
The spectrum is the message from the molecule

The theory is a key for deciphering the message



Outline

1. Spectroscopy in chemistry
2. Electronic spectroscopy
3. Challenges
4. Equation-of-motion coupled-cluster methods: Theory and examples
5. From wave functions to properties
   - linear and non-linear response
   - from bound states to the continuum
6. Conclusion



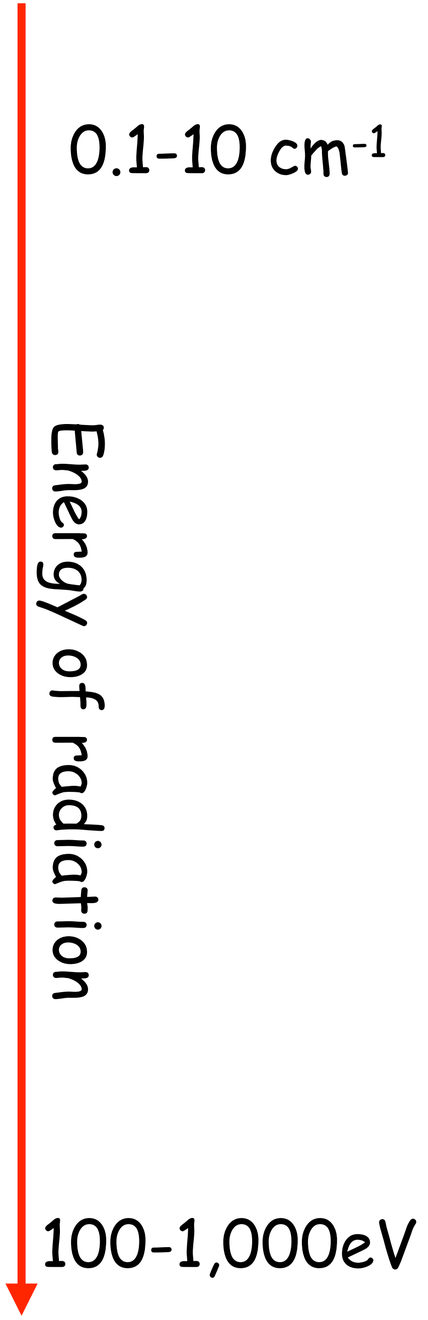
Spectroscopy in chemistry

1. Rotational spectroscopy
2. Spin and magnetic fields: Electronic paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), magnetazability
3. Vibrational spectroscopies: Infra-red (IR), Raman, vibrational circular dichroism (VCD)
4. Electronic spectroscopies in UV-Vis:

- Absorption, emission, electronic circular dichroism
- Nonlinear regimes: two-photon absorption, etc
- Photoelectron spectroscopies

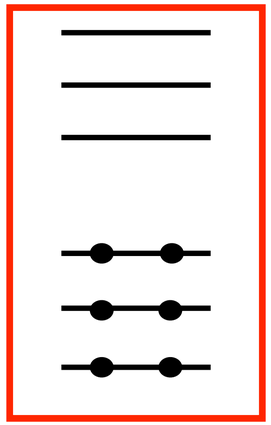
4. Electronic spectroscopies in X-ray domain:

XAS, XPS, XES, RIXS, XCD, Auger, ICD, etc…

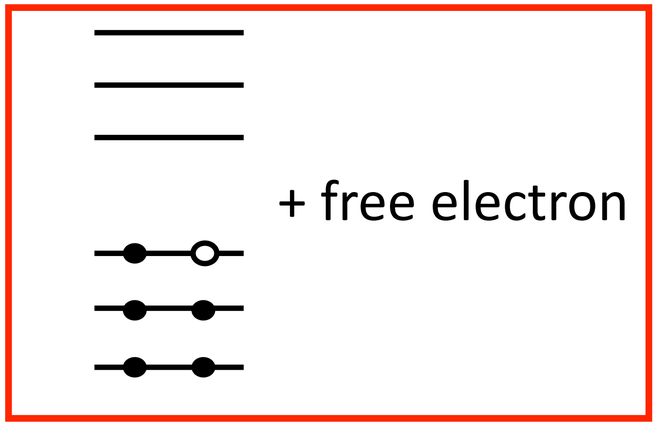


Electronic spectroscopies in the valence domain

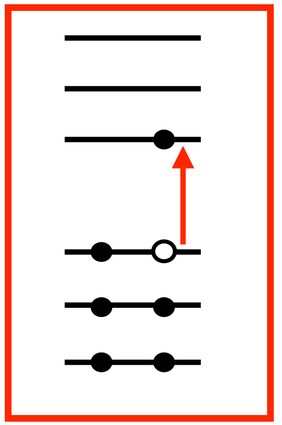
Initial state



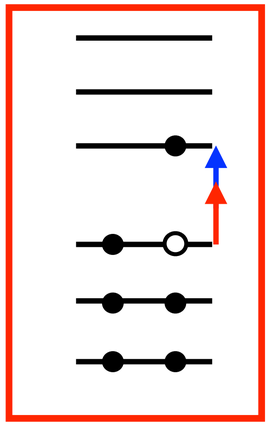
Final states



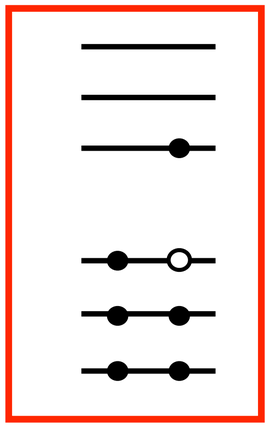
UV ionization (UPS)

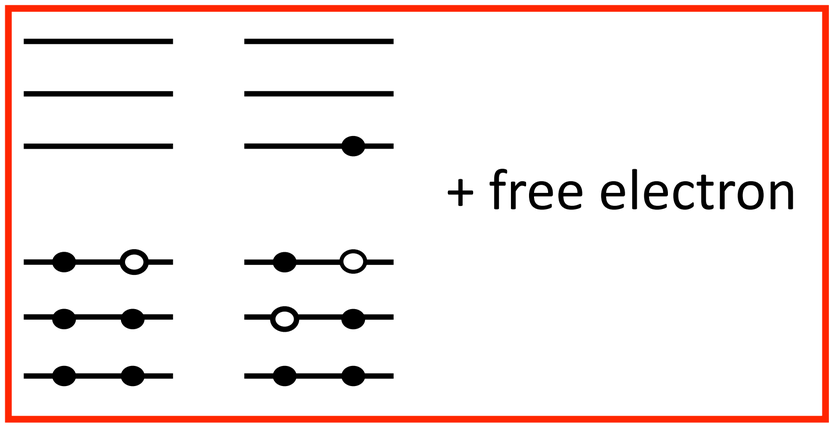


UV/Vis absorption

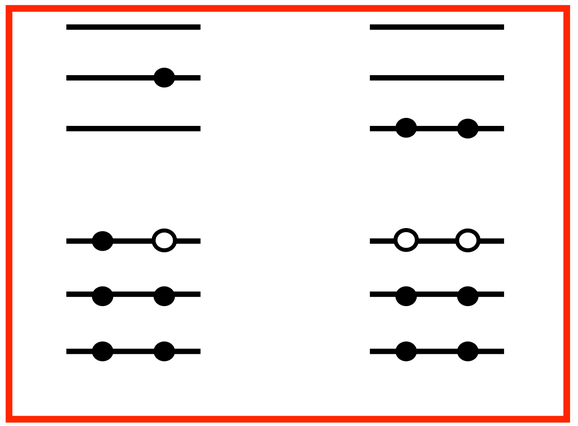


Two-photon absorption (2PA)



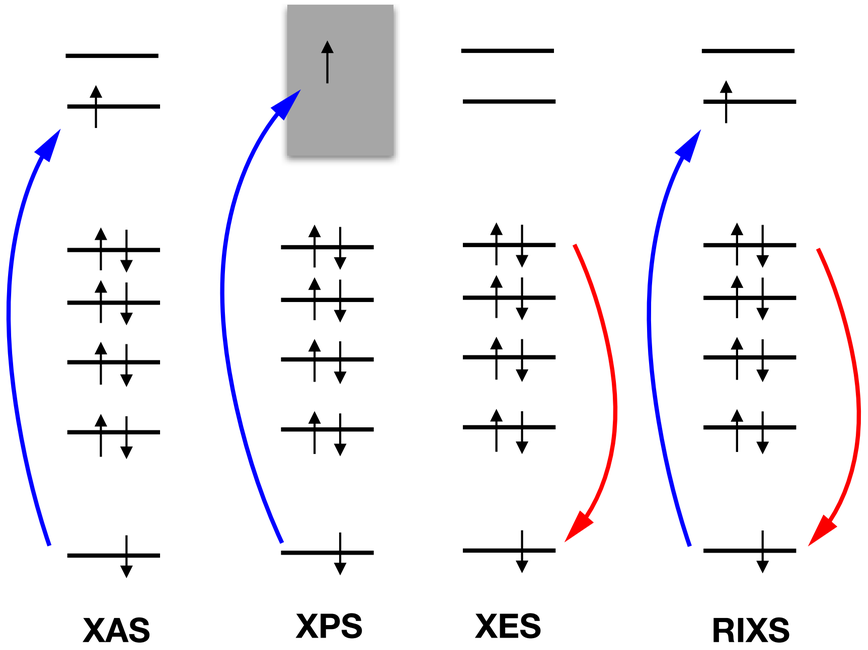


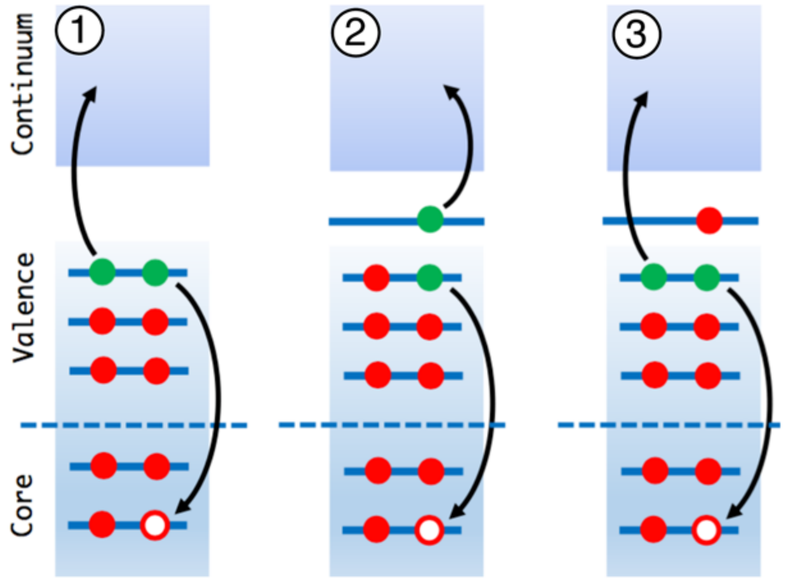
Time-resolved PES



Transient absorption

Electronic spectroscopies in the X-ray domains





Auger and Interatomic Coulomb Decay

X-ray spectroscopies exploit transitions involving core electrons

Electronic spectroscopies in the X-ray domains

1. Need to compute different electronic states (initial and final)
2. In some cases, need to describe states in the continuum (free-electron states, decaying states)
3. Need to compute transition probability (transition moment, intensity, cross-section)
4. Need to compute optimized geometries of initial and final states
5. Often need to compute vibrational structure (FCFs, Franck-Condon Factors, vibronic effects)

Which method to use?

- Multistate methods versus state-specific (Delta-SCF) approaches
- DFT, TDDFT, …
- CCSD, EOM-CCSD, ADC
- RASCI, CASSCF, …

My choice: Equation-of-motion coupled-cluster framework

EOM-CC for bound states and resonances

EOM-CC ansatz: $\Psi = \mathrm{R}e^{T}\,\Phi_0$

$$\overline{H}R\Phi_0 = ER\Phi_0 \qquad \overline{H} = \exp(-T)H\exp(T)$$

Foundational papers:

Rowe, Equations-of-motion method and the extended shell model, Rev. Mod. Phys. **40** 153 (1968)

Nakatsuji, Hirao, Cluster expansion of the wavefunction. Symmetry-adapted-cluster expansion, its variational determinantion, and extension to open-shell orbital theory, J. Chem. Phys. **68** 2053 (1978)

Sekino, Bartlett, A linear response, coupled-cluster theory for excitation energy. Int. J. Quant. Chem. Symp. **18** 255 (1984)

Koch, Jensen, Jørgensen, Helgaker, Excitation energies from the coupled clusters singles and doubles linear response functions (CCSDLR): applications to Be, CH^+, CO, and H_2O. J. Chem. Phys. **93** 3345 (1990)

Stanton, Bartlett, The equation of motion coupled-cluster method: a systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. J. Chem. Phys. **98** 7029 (1993)

Stanton and Gauss, Analytic Energy Gradients for the Equation-of-Motion Coupled-Cluster Method: Implementation and Application to the HCN/HNC System, J. Chem. Phys. **100** 4695 (1994)

Reviews:

Krylov, Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker's guide to Fock space, Krylov, Ann. Rev. Phys. Chem. **59** 433 (2008); Krylov, The quantum chemistry of open-shell species, Reviews in Comp. Chem. **30** 151 (2017); Jagau, Bravaya, Krylov, Extending quantum chemistry of bound states to electronic resonances, Ann. Rev. Phys. Chem. **68** 525 (2017).

Equation of motion coupled-cluster methods

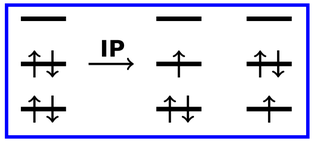
EOM-CC ansatz: $\Psi = \mathrm{Re}^{T}\,\Phi_0$

EOM-CC bi-variational principle: $\delta\left[\dfrac{<\Phi_0 L|\bar{H}|R\Phi_0>}{<\Phi_0 L|R\Phi_0>}\right] = 0$

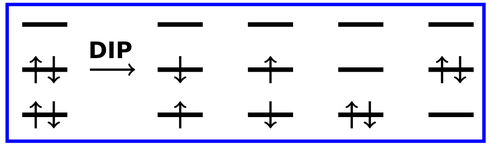
EOM-CC eigenproblem: $\overline{H}R\Phi_0 = ER\Phi_0 \qquad \overline{H} = \exp(-T)H\exp(T)$

Choice of reference and operator R opens access to different target states:

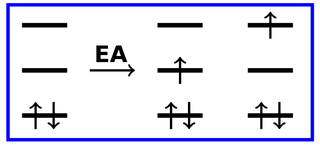
$$R^{IP} = \sum_i r_i i + \ldots$$



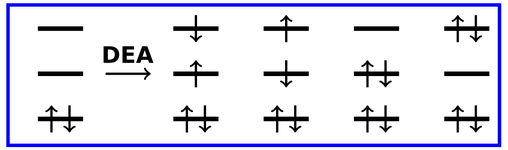
$$R^{DIP} = \frac{1}{2}\sum_{ij} r_{ij} ij + \ldots$$



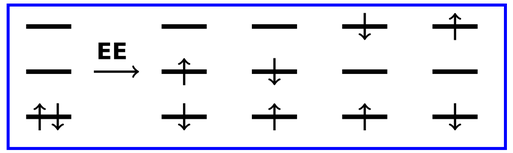
$$R^{EA} = \sum_a r^a a^\dagger + \ldots$$

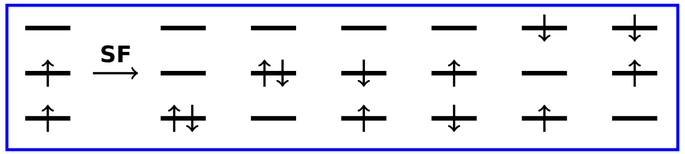


$$R^{DEA} = \frac{1}{2}\sum_{ab} r^{ab} a^\dagger b^\dagger + \ldots$$



$$R^{EE} = r_0 + \sum_{ia} r_i^a a^\dagger i + \ldots$$





$$\overline{H} =$$

Φ_0	Φ_1	Φ_2	
E_0	X	X	Φ_0
0	X	X	Φ_1
0	X	X	Φ_2

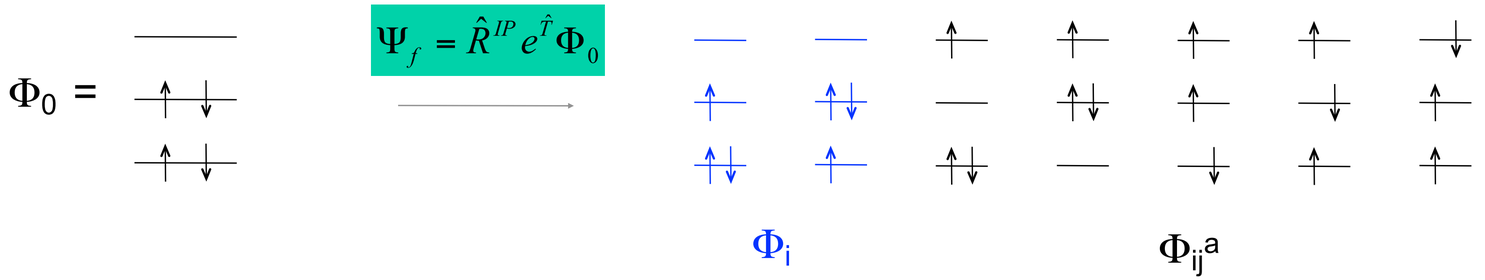
Equation-of-motion coupled-cluster methods for electronically excited and open-shell species: The Hitchhikers guide to Fock space, Krylov, Ann. Rev. Phys. Chem. **59** 433 (2008)

EOM-CC methods:

- Size-intensive
- Bi-variational
- Systematically improvable
- Include dynamic and non-dynamic correlation in the same framework
- Treat open-shell states without spin-contamination
- Describe multi-configurational wfns in a single-reference formalism
- Multi-state
- Correctly treat many types of electronic degeneracies
- Treat different states on the same footing (balance, transition properties)
- Elegant formalism facilitates calculation of properties

- Scaling: N^6 for EOM-CCSD, N^8 for EOM-CCSDT…
- Medium-sized molecules (~1000 b.f.) are doable
- Cost-saving techniques are being actively developed

EOM-IP-CC (EOM-CC for ionization potentials)

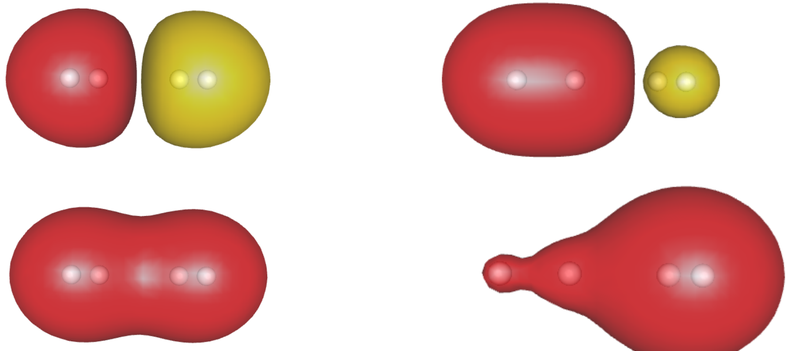


N-electron reference

N-1 electron target states

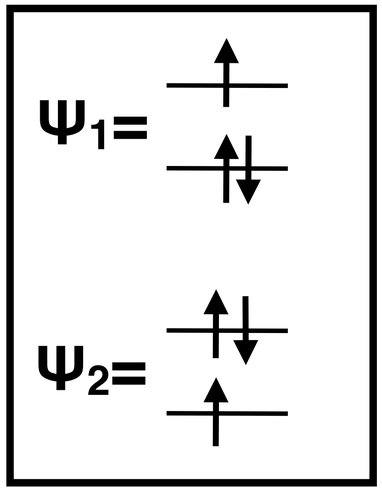
- Naturally spin-adapted
- Does not suffer from artificial symmetry breaking
- Correctly describes charge localization patterns in ionized systems
- Describes both the ground and excited states
- Correctly describes degenerate states (e.g., Jahn-Teller problem)

Charge-localization and symmetry breaking in molecular aggregates



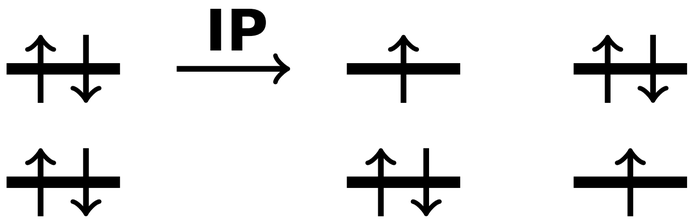
$(H\text{-}H\ldots.H\text{-}H)^+$

$H—H^+\ldots.H\text{-}H$

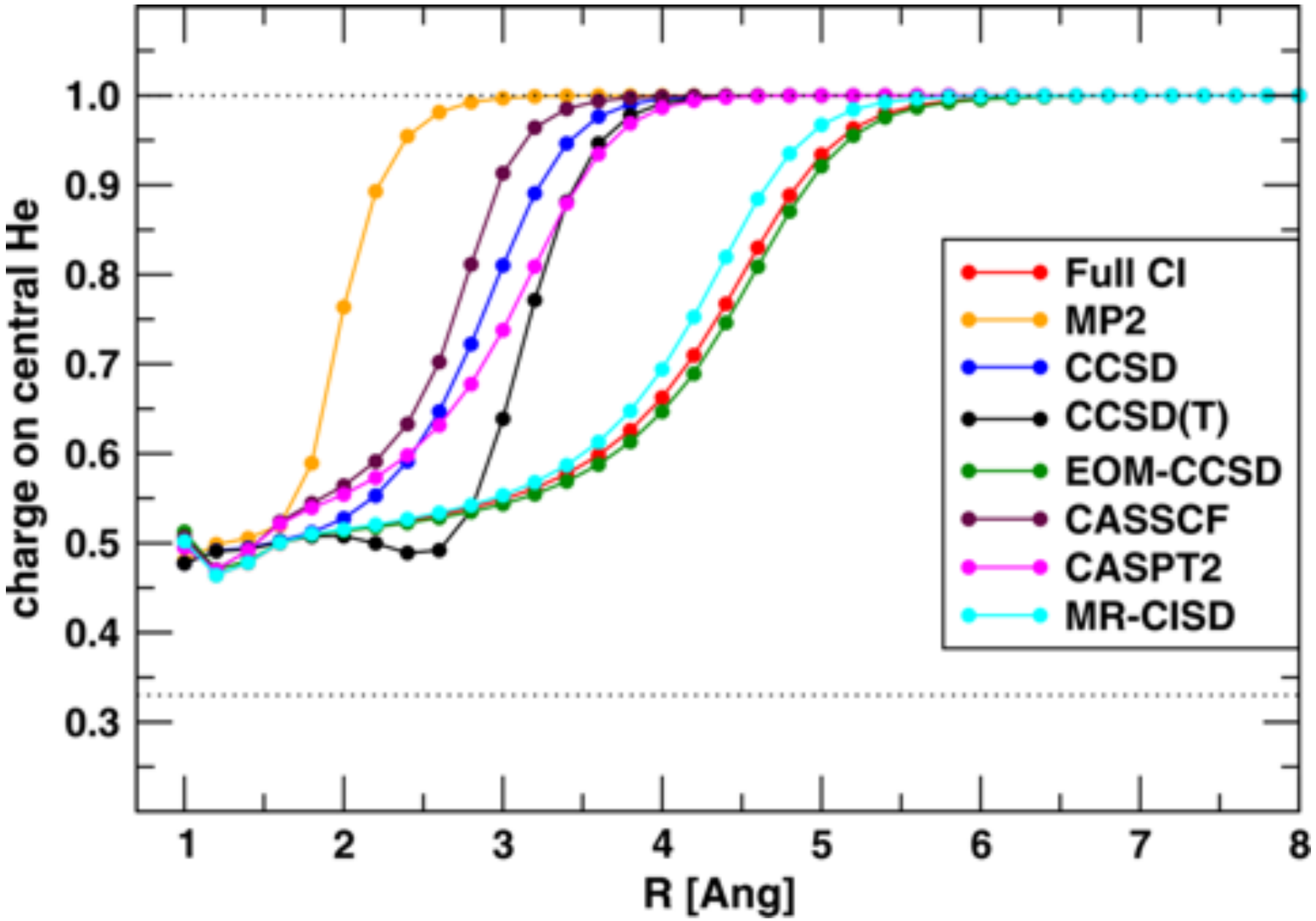


EOM-IP treats both configurations on equal footing:

$$R^{IP} = \sum_i r_i i + \ldots$$



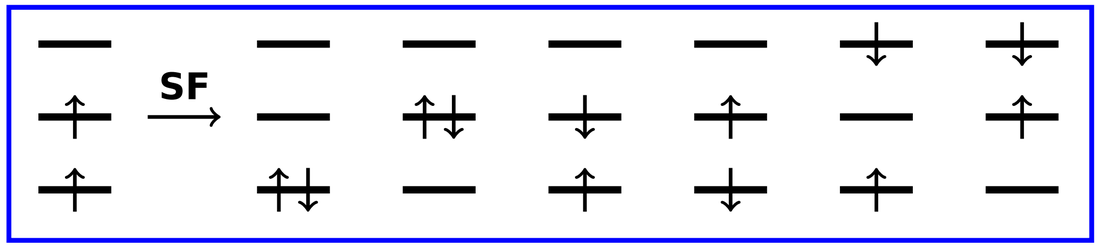
Charge localization: $(He_3)^+$ example

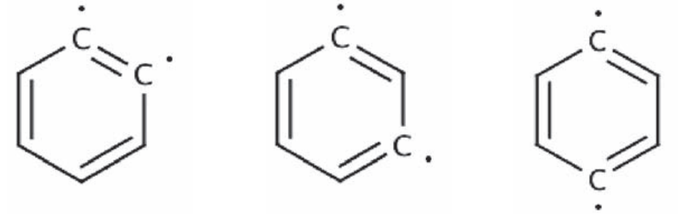


Courtesy of Thomas Koerzdoerfer, Potsdam University

EOM-CC for multi-configurational wave-functions: Examples from chemistry

EOM with spin-flip



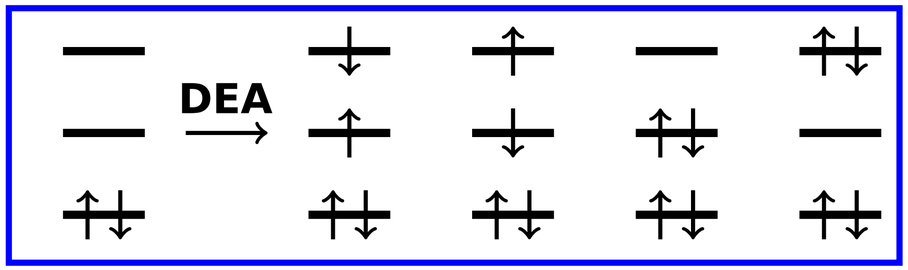


o-benzyne m-benzyne p-benzyne

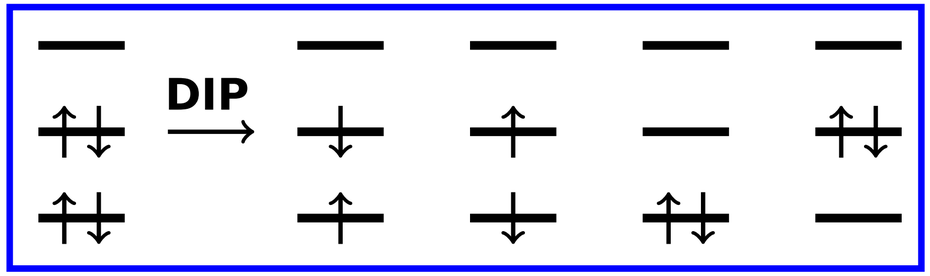
Singlet-triplet gaps, eV; Basis: cc-pVTZ

Method	o-C_6H_4	m-C_6H_4	p-C_6H_4
SF-CCSD	1.58	0.78	0.164
SF-CCSD(dT)	1.62	0.89	0.17
Exp-t.	1.66	0.87	0.14

EOM with double attachment (2 particle)



EOM with double ionization (2 hole)

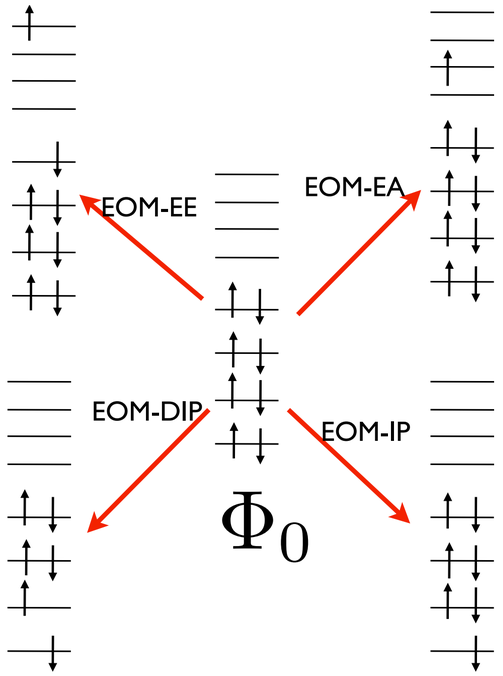


EOM-CC for bound states and resonances

EOM-CC ansatz: $\Psi = \mathrm{Re}^{T}\,\Phi_0$

$\overline{H}R\Phi_0 = ER\Phi_0 \qquad \overline{H} = \exp(-T)H\exp(T)$

Excited and highly excited states



Electron-attached states, transient anions

Doubly ionized states

Ionized and core-ionized states

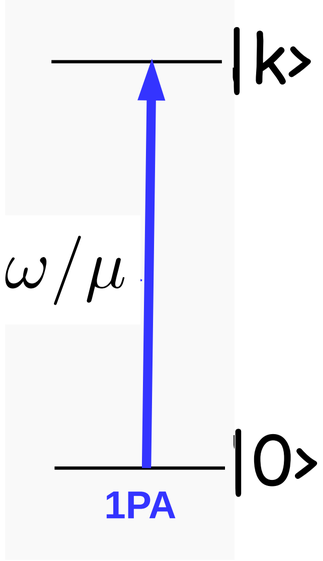
Extension of EOM-CC for resonances via non-Hermitian quantum mechanics

- Complex absorbing potential;
- Complex basis functions;
- Feshbach-Fano formalism.

Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker's guide to Fock space, Krylov, Ann. Rev. Phys. Chem. **59** 433 (2008); Extending quantum chemistry of bound states to electronic resonances, Jagau, Bravaya, Krylov, Ann. Rev. Phys. Chem. **68** 525 (2017).

Calculation of properties within EOM-CC

Key equations can be derived by time-dependent PT using EM field as perturbation



First order: Linear response (e.g., UV-vis absorption)

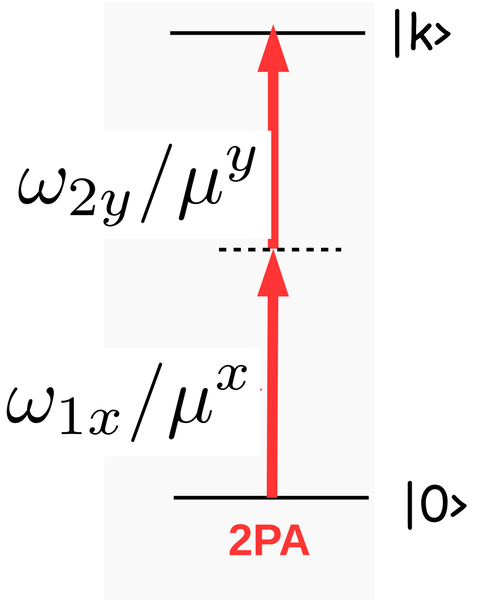
Transitions occur when occur when $\omega = E_k - E_0$ (resonance) and $\sigma \sim |\langle 0|\mu|k\rangle|^2$

Higher orders: Non-linear optical properties (e.g., two-photon absorption or RIXS)

Resonance condition: $\omega_{1x} + \omega_{2y} = E_k - E_0 = \Omega_{k0}$

2PA moments: $M_{xy}^{k\leftarrow 0}(\omega_{1x}, \omega_{2y}) = -\sum_n \left(\frac{\langle k|\mu^y|n\rangle\langle n|\mu^x|0\rangle}{\Omega_{n0} - \omega_{1x}} + \frac{\langle k|\mu^x|n\rangle\langle n|\mu^y|0\rangle}{\Omega_{n0} - \omega_{2y}} \right)$

2PA cross section: $S_{ab,cd} = M_{ab}^{0\leftarrow k} M_{cd}^{k\leftarrow 0}$



How to compute these effectively?

Linear properties: Easy

Need to compute transition density matrices

For one-electron properties such as dipole moment only one-particle TDM is needed

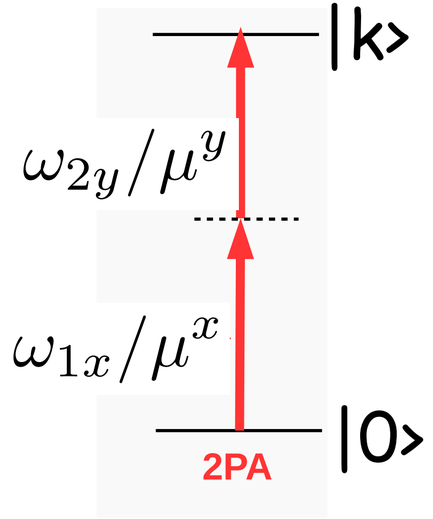
$$\langle k|\mu|0\rangle = Tr[\gamma^{k0}\mu]$$

$$\gamma_{pq}^{k0} = \langle k|p^{\dagger}q|0\rangle$$

For two-electron properties such as SOC, two-particle TDM is needed (but in some cases its separable part may suffice (mean-field approximation or normal-ordering)

Beyond linear response

$$M_{xy}^{k\leftarrow 0}(\omega_{1x},\omega_{2y}) = -\sum_n \left(\frac{\langle k|\mu^y|n\rangle\langle n|\mu^x|0\rangle}{\Omega_{n0}-\omega_{1x}} + \frac{\langle k|\mu^x|n\rangle\langle n|\mu^y|0\rangle}{\Omega_{n0}-\omega_{2y}} \right)$$



Because of sum-over-states, one cannot compute 2PA moments as simple matrix element between the initial and final state

Strategy: Convert SOS into a tractable form by using resolvent

$$\sum_n \frac{|n\rangle\langle n|}{E_n - E_0 - \omega} = [H-\omega]^{-1}$$

$$M_{xy} = \langle k|\mu^y[H-\omega_{1x}]^{-1}\mu^x|0\rangle + \ldots = \langle k|\mu^y|Z^x\rangle + \ldots$$

$$|Z^x\rangle = [H-\omega_{1x}]^{-1}\mu^x|0\rangle$$

Response vectors Z can be computed with the same effort as the states |k> and |0>

$$[H-\omega_{1x}]|Z^x\rangle = \mu^x|0\rangle$$

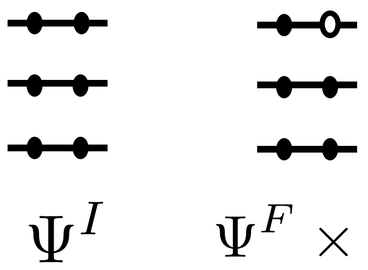
One- and two-electron transition involving continuum (free electrons)

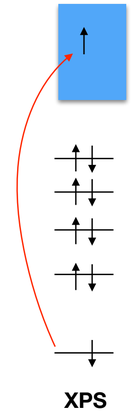
Photoionization:

Probability of photoionization

$$D_k^{IF} = \mathbf{u}\left\langle \Psi_I^N | \mathbf{r} | \Psi_F^{N-1} \cdot \Psi_k^{el} \right\rangle = \mathbf{u}\left\langle \phi^d | \mathbf{r} | \Psi_k^{el} \right\rangle$$

Dyson orbital: $\gamma_p = \left\langle \Psi_F^{N-1} | p | \Psi_I^N \right\rangle$





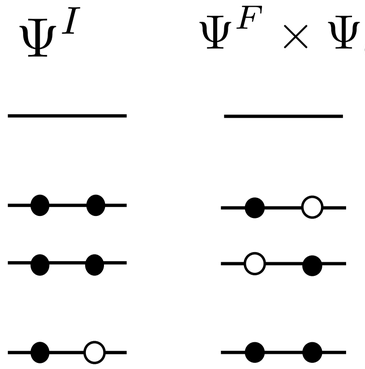
$$\Psi_{el} = \sqrt{\frac{k}{(2\pi)^3}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

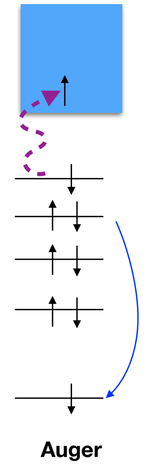
Auger decay:

Decay width:

$$\tilde{\Gamma} = 2\pi \left\langle \Psi^I | H | \Psi^F \times \Psi_{el} \right\rangle \left\langle \Psi^F \times \Psi_{el} | H | \Psi^I \right\rangle$$

$$\tilde{\Gamma} = \frac{\pi}{2} \int d\Omega_{\mathbf{k}} \left(\sum_{pqr} \langle pq || \mathbf{k}r \rangle \Gamma_r^{pq} \right) \left(\sum_{pqr} \langle \mathbf{k}r || pq \rangle \Gamma_{pq}^r \right)$$

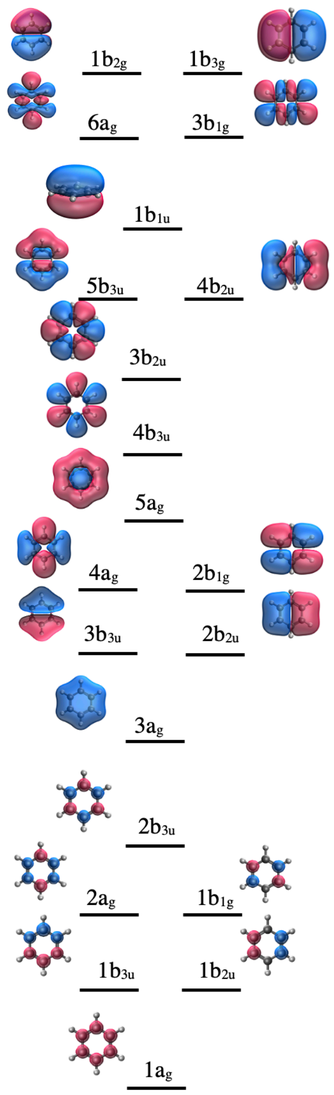




Two-body Dyson orbital: $\Gamma_r^{pq} = \left\langle \Psi^I | p^\dagger q^\dagger r | \Psi^F \right\rangle$

Krylov, From orbitals to observables and back, JCP **153** 080901 (2020); Skomorowski, Krylov, JCP **154** 084124 (2021); Jayadev, Skomorowski, Krylov, JPCL **14** 8612 (2023)

Example: Auger decay in benzene



Energy of Auger electrons: $E^{DIP} - E_{core}$

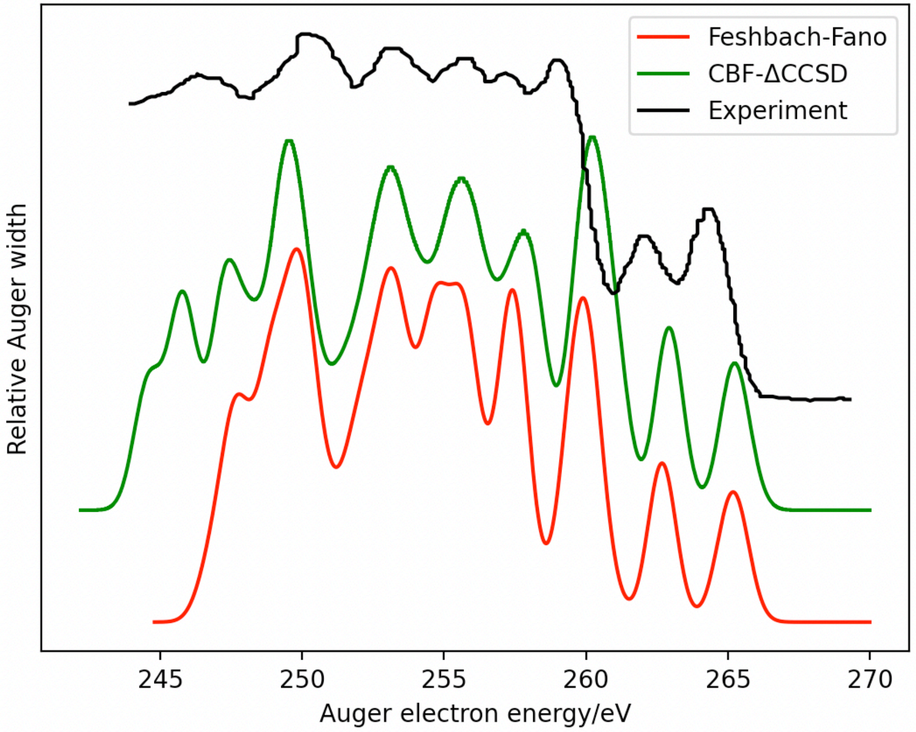
Peak intensity: $\tilde{\Gamma}$

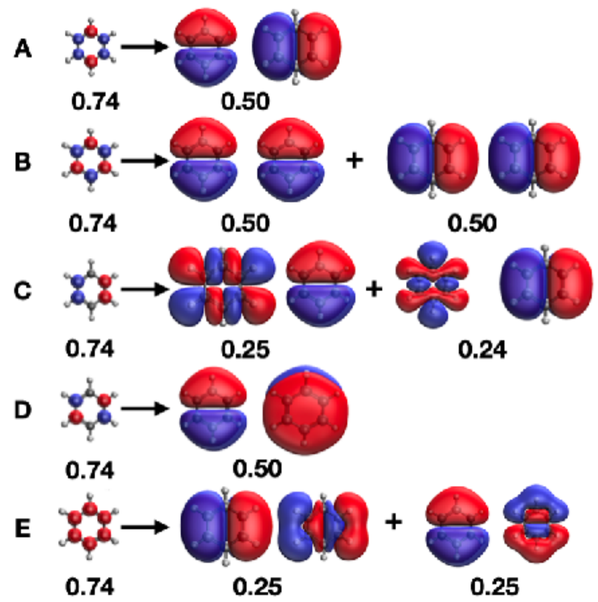
Number of decay channels ~6x15x15=1,350

143 DIP states between 24-43 eV

Feshbach-Fano and complex basis functions approaches agree with each other and with exp-t

Natural Auger orbitals help assign the peaks





Jayadev, Ferino-Prez, Matz, Krylov, Jagau, JCP **158** 064109 (2023); Jayadev, Skomorowski, Krylov, JPCL **14** 8612 (2023)

Conclusions

1. EOM-CC is an excellent framework for many-body calculations in the bound and unbound domains, expecially in the context of spectroscopy modeling

2. Outstanding problems

- Better treatment for free-electron states
- Reduced cost/scaling for higher-order variants
- Some multi-configurational cases are beyond reach of current methods
- Some issues with conical intersections

$$\Psi = \mathrm{Re}^{T}\,\Phi_0$$
$$\overline{H} = \exp(-T)H\exp(T)$$
$$\overline{H}R\Phi_0 = ER\Phi_0$$