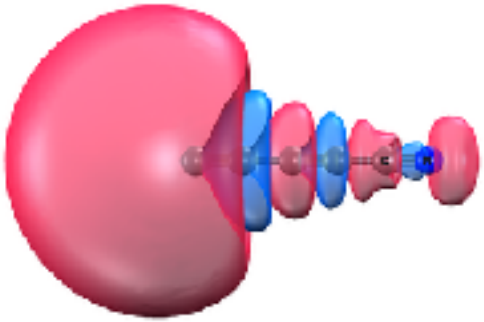
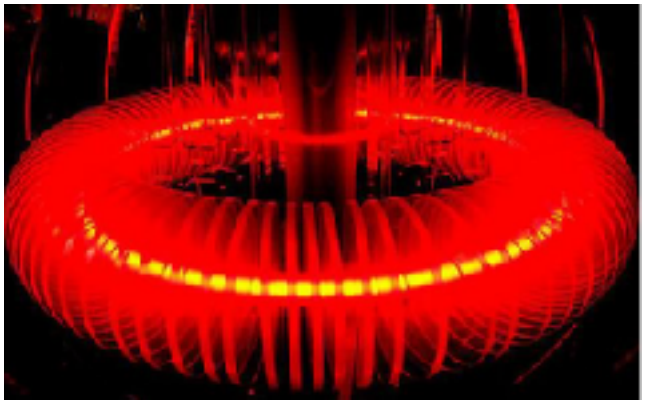
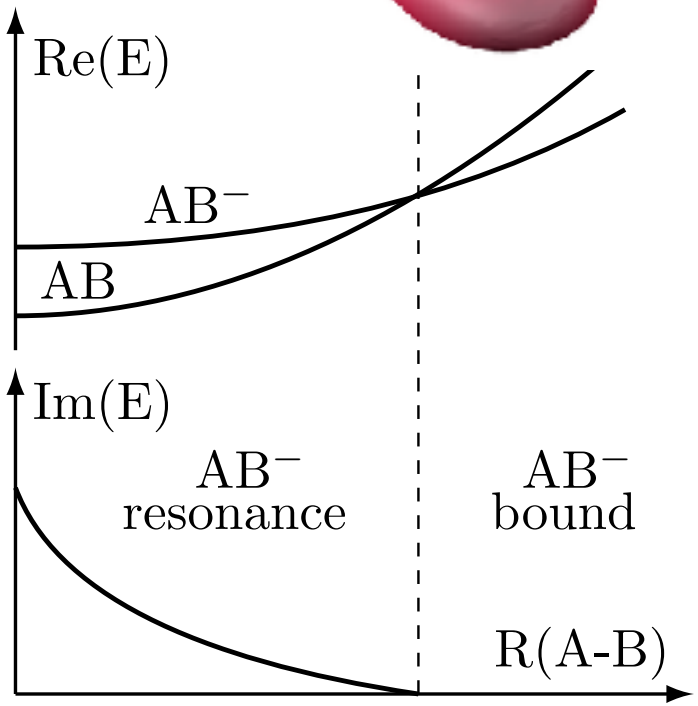
CAP EOM-CC approach for multiple bound and continuum-embedded states: Theory and examples

Anna I. Krylov
University of Southern California,
Los Angeles



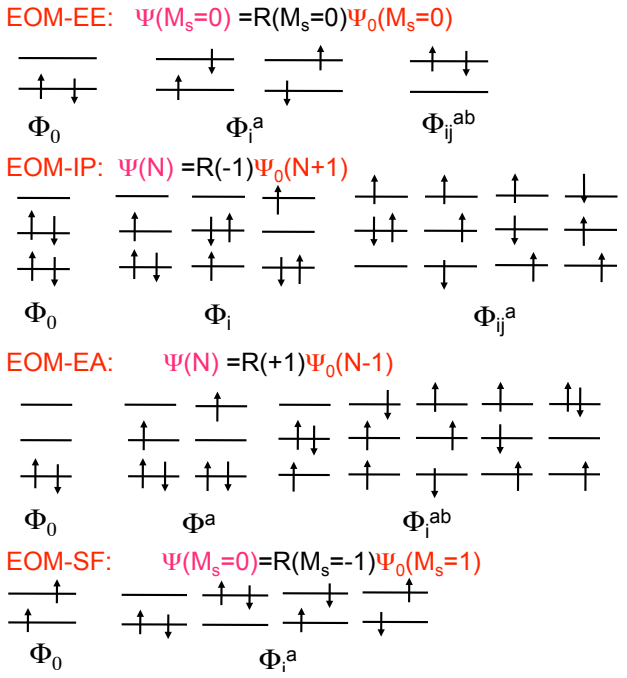




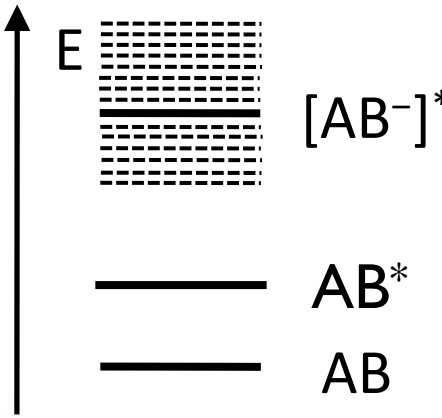
ICTP-IAEA Workshop, Trieste, Italy
April 2018

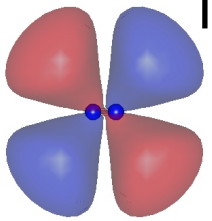
Outline

1. Electronic resonances: What are they and why they are important in chemistry.
2. Theoretical approach: Non-hermitian QM using CAP and EOM-CC.
3. How to make sense of resonance wave functions? Extension of Dyson orbitals to metastable domain.
4. Real and imaginary excitons: Natural transition orbitals for resonance wave-functions.
5. Conclusions.

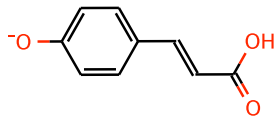


Autoionizing states: Lie above ionization/ detachment continuum

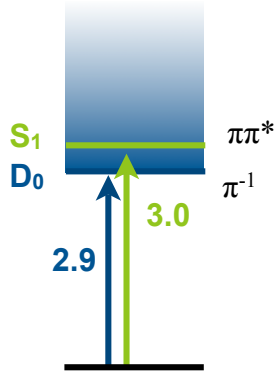




1. Transient anions: N_2^-, CO^-, uracil$^-$, etc.



2. Excited states (including core-excited) above ionization continuum.

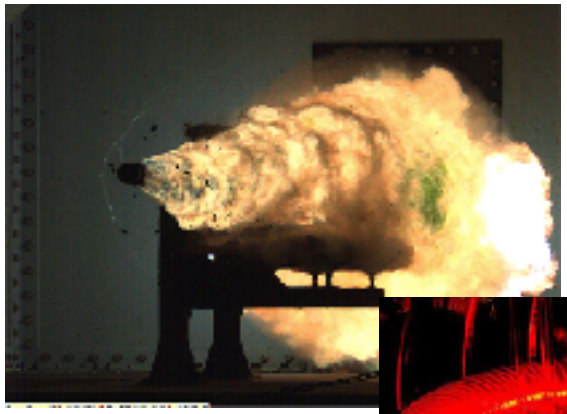
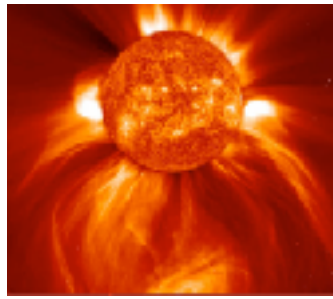


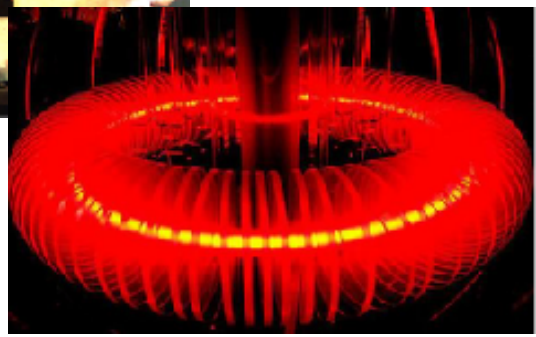
3. Core-ionized and doubly ionized states.

Finite lifetime, decay via auto-ionization/ detachment. Have distinct spectroscopic signatures. Their wave-functions are not L^2-integrable.

Metastable auotionizing states in nature and technology

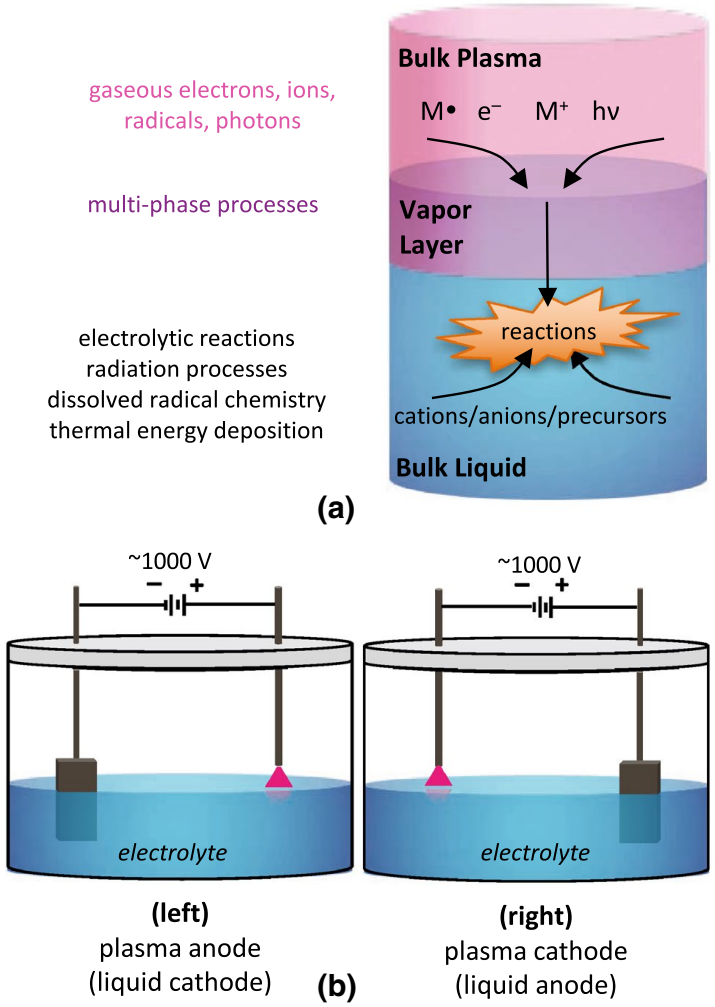


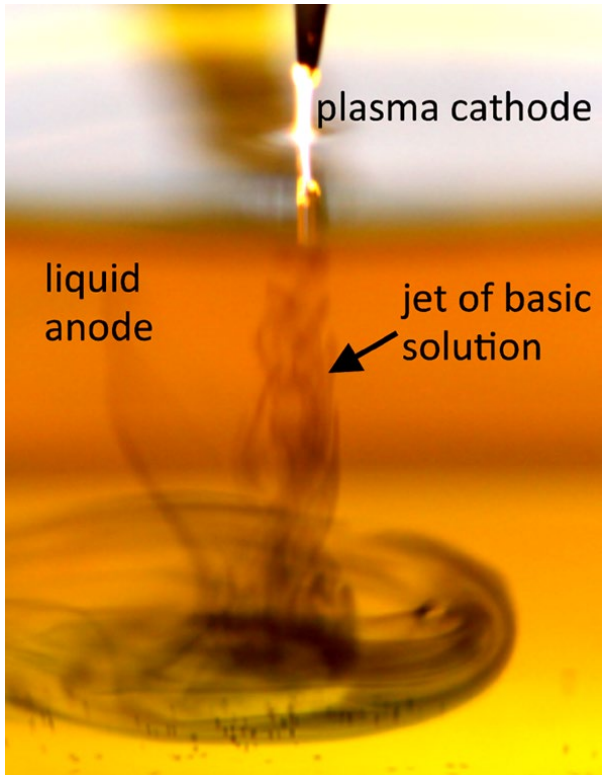



The visible Universe is 99.999% plasma (stars).
High energy environments (e.g., fusion reactors, plasma reactors).
Radiolysis, DNA damage by slow electrons proceeds through metastable electron-attached states.
Interactions of molecules with metals (e.g., electrodes).
New chemistry: Plasmonic catalysis, plasma+solvent electrochemistry; using plasma for pollution control to remove NOx and SOx (engines, power plants).
Also: new light sources and experiments.

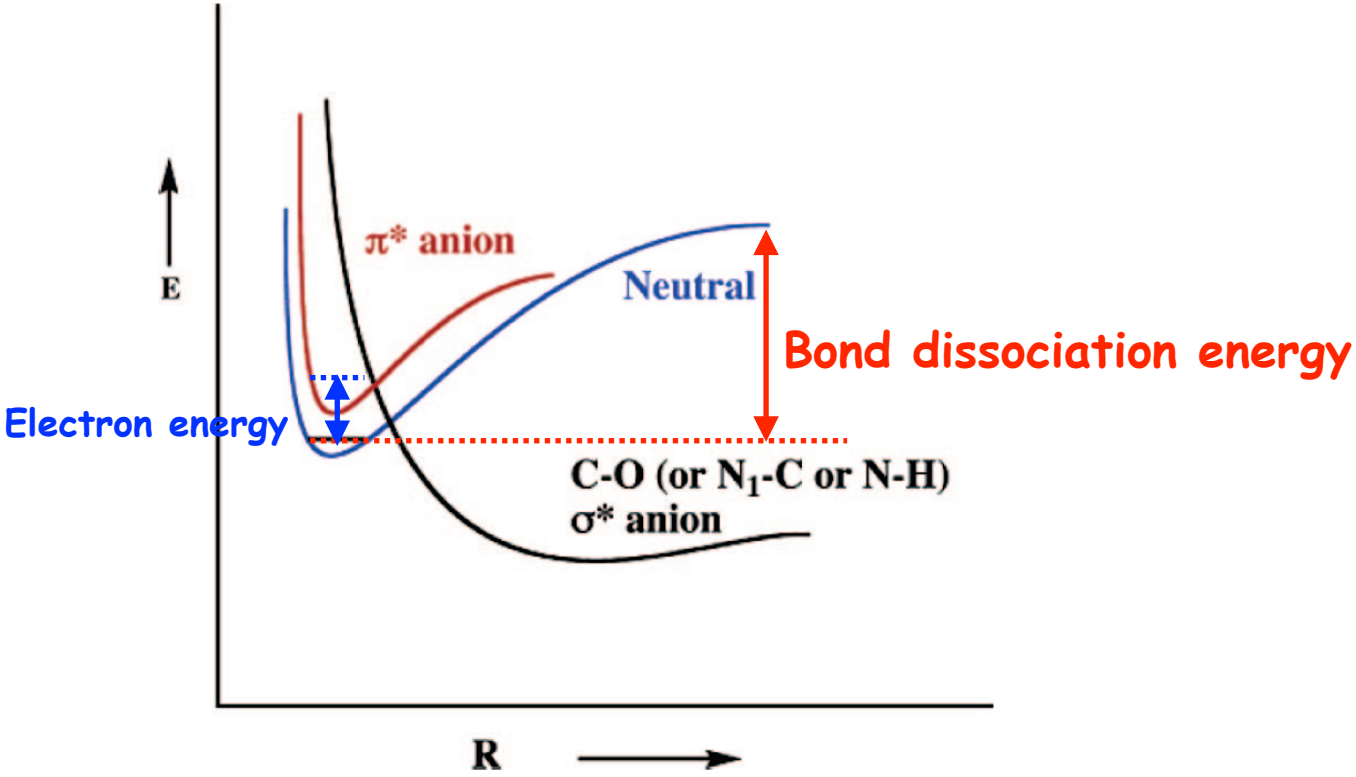
Plasma electrochemical cell





Rumbach and Go, Topics in Catalysis, Springer (2013)

New chemistry facilitated by resonances via dissociative electron attachment



Electrons can break bonds and act as catalysts.
We need new theory to develop new technologies.

Simons, J. Phys. Chem. A, **112**, 6401 (2008);
Herbert, Reviews in Computational Chemistry, **28**, 391 (2016).

Resonances in non-Hermitian QM

Resonances can be described as discrete L^2-integrable states with complex energies

$$\psi_R(t) = exp(-iE_R t/\hbar)\psi_R(0)$$

E_{res} resonance energy

$$E_R = E_{res} - i\Gamma/2$$

Γ resonance width (~1/lifetime)

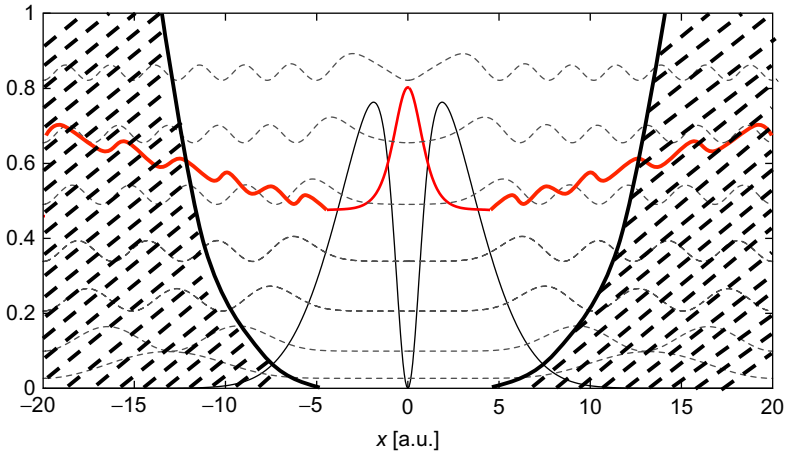
Non-Hermitian QM:

Outgoing boundary conditions, Feshbach (diabatic) formalism, and complex-variable approaches.

Reviews and books: Reinhardt Ann. Rev. Phys. Chem. **33** 232 (1982); Moiseyev, Non-Hermitian quantum mechanics; Cambridge University Press, 2011.

Complex absorbing potential (CAP) approach

$H(\eta) = H_{mol} - i\eta W(R)$,
where W(R) is a box-like potential



- CAP absorbs tails of diverging wave function;
- Eigenstates of H(η) - complex energy of the resonance E_R;
- E_{res} depends on the strengths of the potential;
- Exact E_{res} and Gamma are obtained in the limit η->0 (in the complete basis set).

Jolicard, Austin, CPL 121 106 1985; Riss, Meyer, J. Phys. B 26, 4503 (1993) and J. Phys. B 28, 1475 (1995); Sommerfeld, Cederbaum, PRL 80 3723 (1998); Sajeev, Vysotskiy, Cederbaum, Moiseyev, JCP 131 21102 (2009).

Our impl-n: Jagau, Zuev, Bravaya, Epifanovsky, Krylov, JPCL 5, 310 (2014);
Zuev, Jagau, Bravaya, Epifanovsky, Shao, Sundstrom, Head- Gordon, JCP 141, 024102 (2014).

Complex absorbing potential (CAP) approach: Important issues

1. Needs to be combined with appropriate electronic structure method (multi-state, balanced, dynamical and no-dynamical correlation, size-intensive, amendable to properties, systematically improvable, correct description of the continuum onsets).

Solution: EOM-CC family of methods.

2. In finite bases, CAP is not represented exactly. Cannot go to the limit $\eta \to 0$ Need to work with finite η. This introduces the need to compute eta-trajectories and perturbs the results.

Solution: De-perturbative correction.

Jagau, Bravaya, Krylov, Ann. Rev. Phys. Chem. **68** 525 (2017).

Ab initio methods for open-shell and electronically excited species

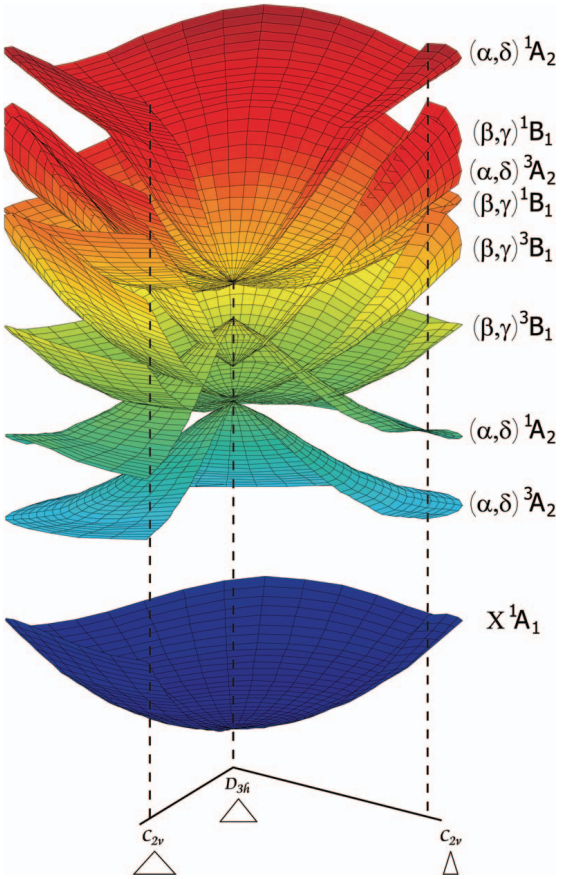
Coupled-cluster (CC) hierarchy: predictive and accurate methods for closed-shell molecules

Equation-of-motion CC (EOM-CC): Extends CC approach to excited states and multi-configurational wave functions

$$\Psi = \mathrm{Re}^{T}\,\Phi_0$$

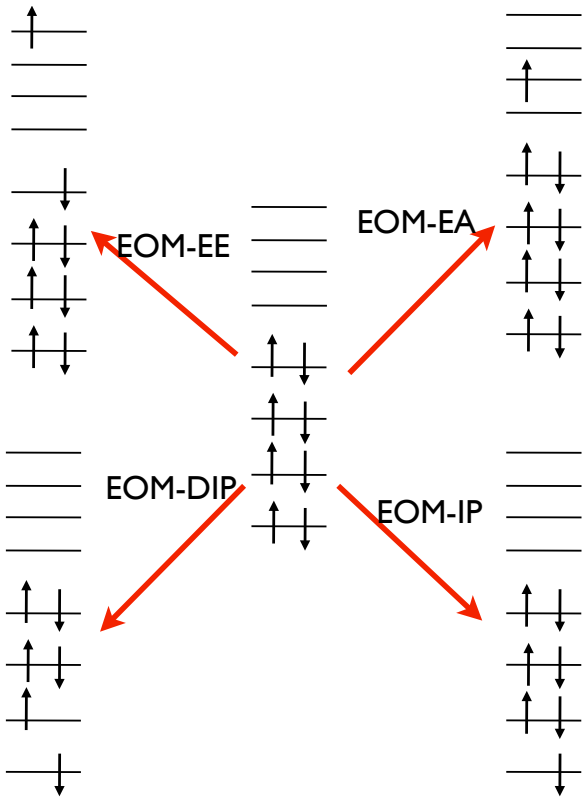
$$\overline{H}R\Phi_0 = ER\Phi_0$$

$$\overline{H} = \exp(-T)H\exp(T)$$



EOM-CC for different types of bound states and resonances

Highly excited states



Electron-attached states, transient anions

Doubly ionized states

Ionized and core-ionized states

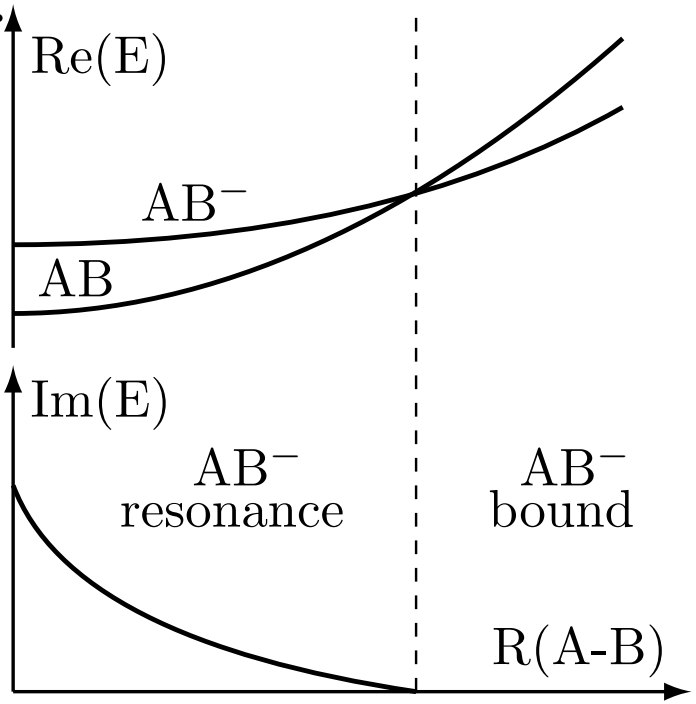
$$\overline{H}R\Phi_0 = ER\Phi_0$$

Different target stats are described by the same effective Hamiltonian

EOM-CC for complex potential energy surfaces

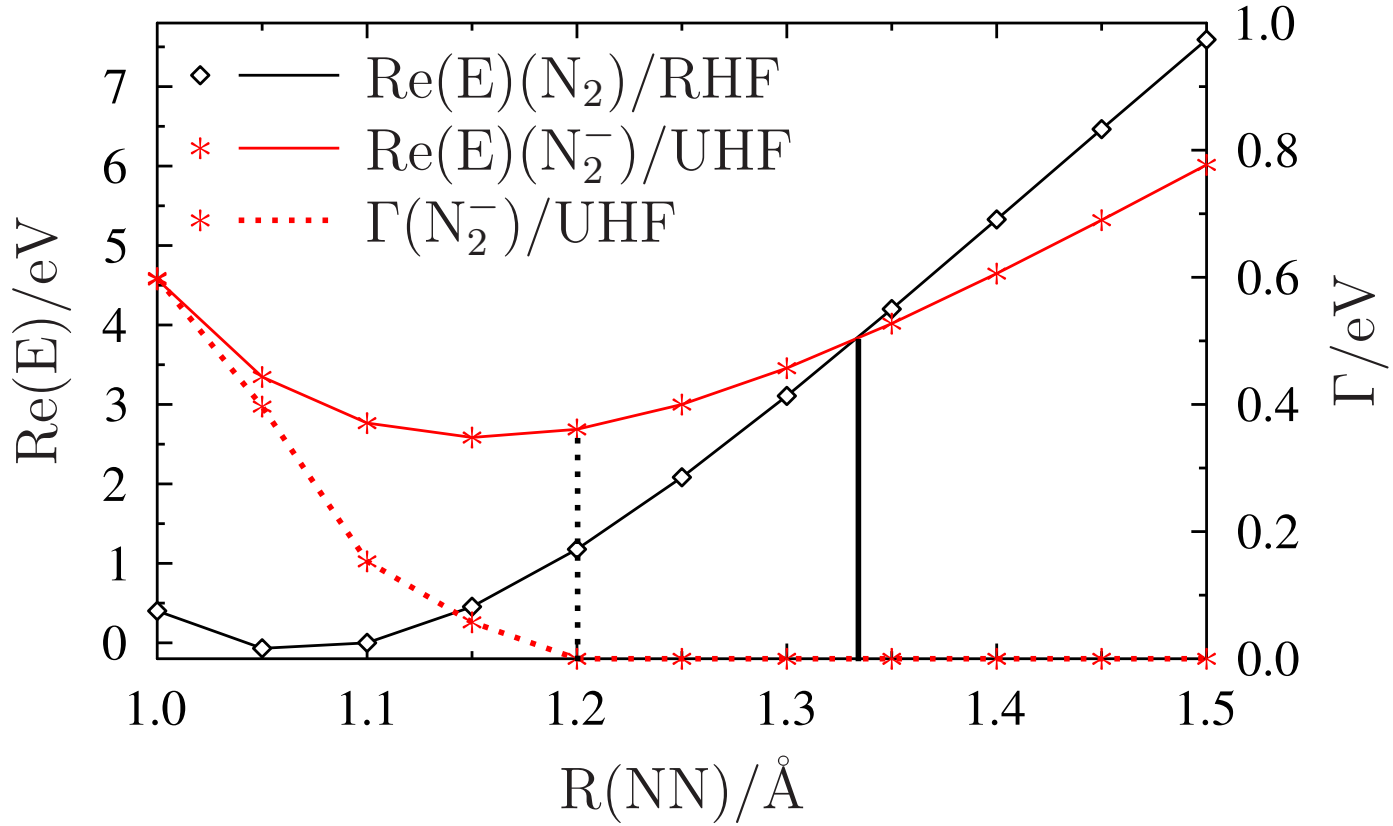
Requirements:

1. PES should be smooth (both resonance positions and widths should vary smoothly upon nuclear displacements).
2. Computed energy differences (e.g., EAs) should be consistent with the computed Gamma.



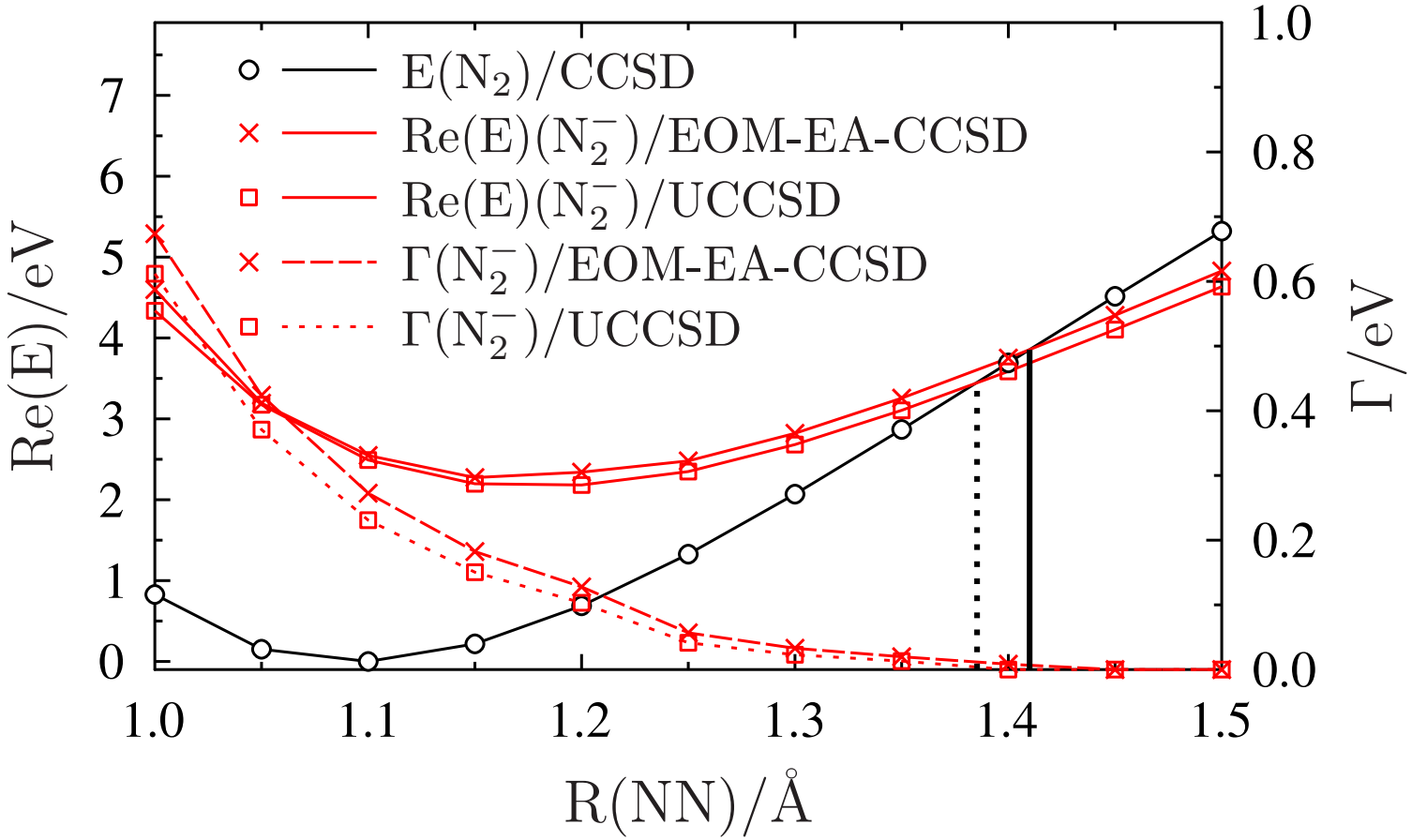
Jagau, Krylov, JPCL 5, 3078 (2014).

CAP calculations of complex potential energy surfaces



CAP-Hartree-Fock PES are not internally consistent

CAP calculations of complex potential energy surfaces



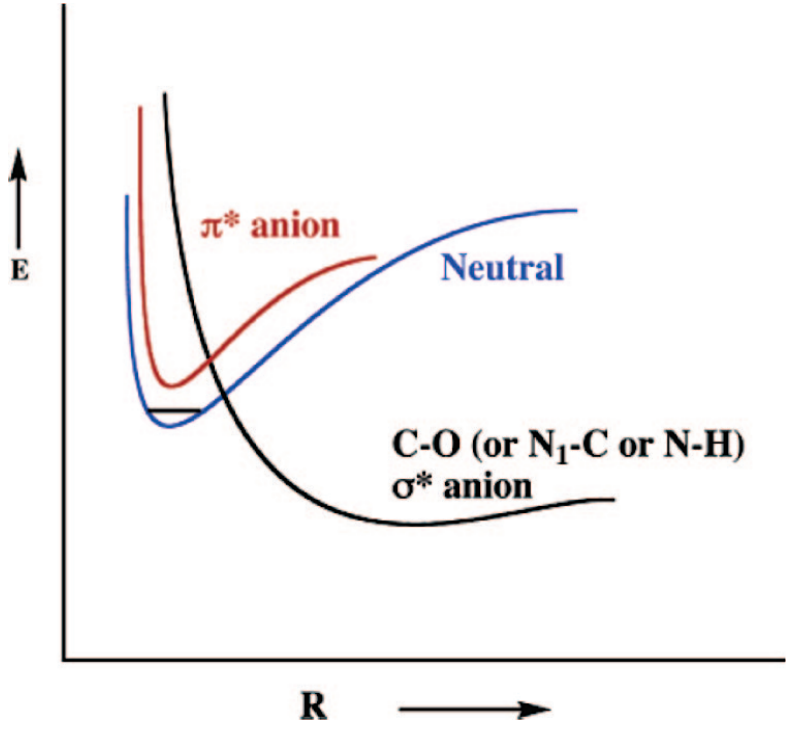
CAP-CCSD PES are less inconsistent (relative to HF)

CAP-EOM-EA-CCSD are perfectly consistent

Conclusions:

1. The robustness and accuracy of CAP in finite bases is improved by 1st order de-perturbative correction.
2. CAP-EOM-CC can be applied in a consistent black-box manner to molecular systems.
3. CAP-EOM-CC + de-perturbative correction: smooth PES and consistent dE/Gamma.
4. Recent advances in Dr. Thomas Jagau group: Analytic gradients for CAP-EOM-CCSD.

How to make sense of resonance wave functions?



How to analyze resonance wave functions? Do molecular orbitals make sense in the domain of metastable states?

Simons, JPCA **112** 6401 (2008)

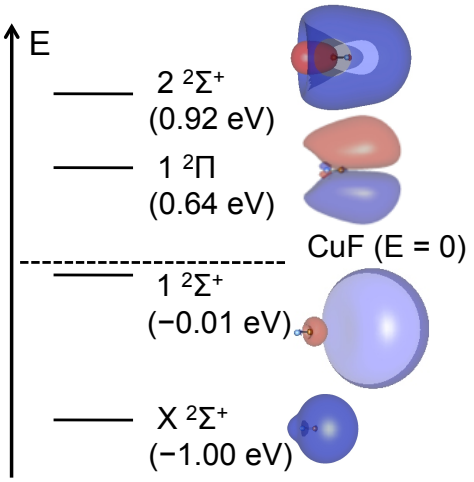
How to analyze resonance wave functions?

1. Chemical transformations induced by electrons depend on the shape of MO to which electron is attached. **But are orbitals real?**

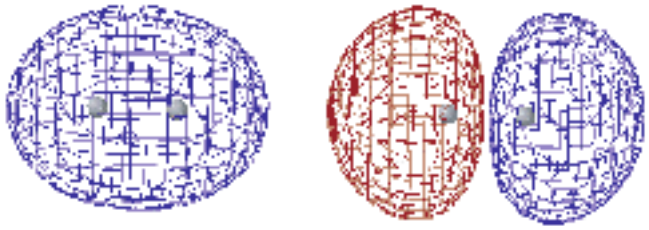
2. Dyson orbitals for bound states: rigorous molecular orbital picture of correlated wave functions. **Dyson orbitals are observables.**

3. Extension of Dyson orbitals to metastable states.

4. Exciton wave functions and Natural Transition Orbitals for metastable states.



Molecular orbitals: Appear in MO-LCAO theory



One electron systems (H_2^+):

Solving Shroedinger eqn using the basis of AOs;

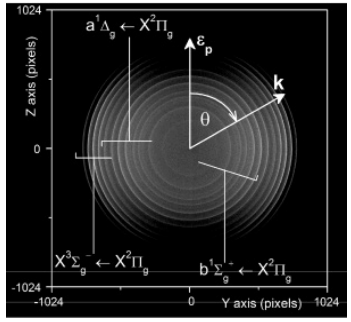
Explain bonding in molecules by electron delocalization.

Many-electron systems: MOs represent the states of pseudo-independent electrons within mean-field approximation:

$$\Phi_0 = |\phi_1 \phi_2 \dots \phi_n\rangle$$

What about correlated wave functions?

$$\Psi = \sum_K C_K \Phi_K$$



Do orbitals make sense for interacting electrons?

Are orbitals real? Do they relate to experimental observables?

Electronic wave functions, observables, and Dyson orbitals

Initial state of N-electron system: $\Psi_I^N(1,\ldots,n)$

Final state of the ionized core (N-1 electron system): $\Psi_F^{N-1}(1,\ldots,n-1)$

Final state of ionized electron with momentum k: $\Psi_{kf}^{el}(n)$

Probability of ionization event (sudden approximation, dipole approximation):

$$P \sim |D_k^{IF}|^2 \qquad D_k^{IF} = \boldsymbol{u}\left\langle \Psi_I^N | \boldsymbol{r} | \Psi_F^{N-1} \cdot \Psi_k^{el} \right\rangle$$

Probability -> cross section (experimental observable).

Using anti-symmetric properties of the wave function and one-electron nature of the dipole operator:

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

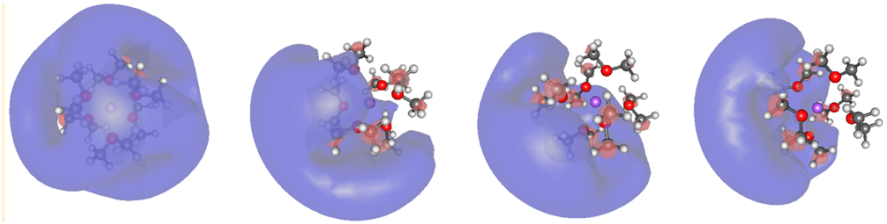
Where ϕ^d_{IF} is a Dyson orbital:

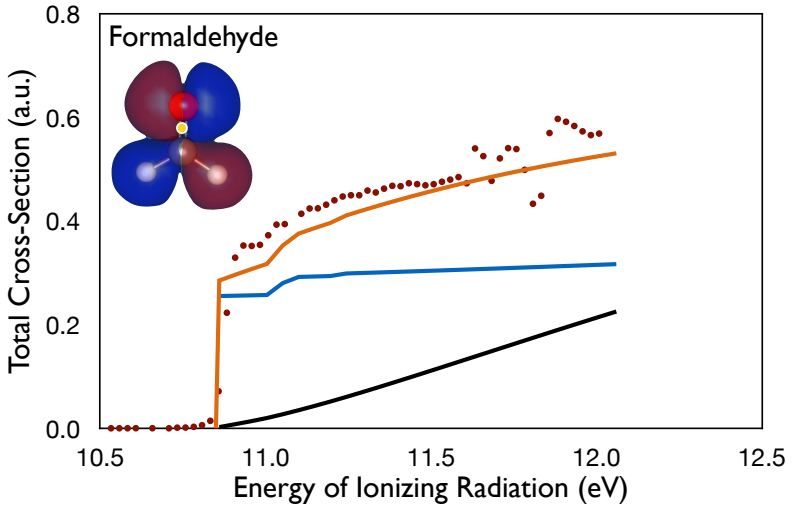
$$\phi^d(1) = \sqrt{N} \int \Psi^I(1,2,\ldots,N)\Psi^F(2,\ldots,N)d2\ldots dN$$

Dyson orbitals are experimental observables

$$\phi^d(1) = \sqrt{N} \int \Psi^I(1,2,\ldots,N)\Psi^F(2,\ldots,N)d2\ldots dN$$

DOs characterize the difference between N and N-1 electron states; they are generalization of Hartree-Fock MOs to general wave functions.
DOs enter the expressions of the cross-sections, they are observables.
PADs: sensitive measure of DO shape.

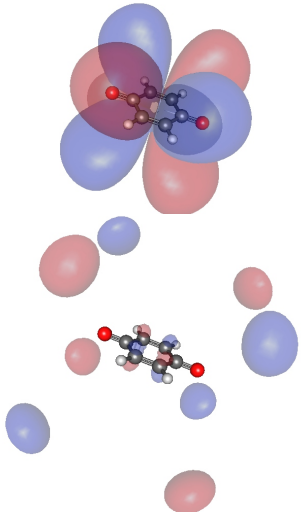




Gozem, Gunina, Ichino, Osborn, Stanton, Krylov, JPCL **6**, 4532 (2015);
Oana, Krylov, JCP **127**, 234106 (2007) and JCP **131**, 124114 (2009);
Gunina, Krylov; J. Phys. Chem. A **120**, 9841 (2016).

Dyson orbitals in CAP EOM-CC formalism enable characterization of resonances beyond energies and lifetimes.

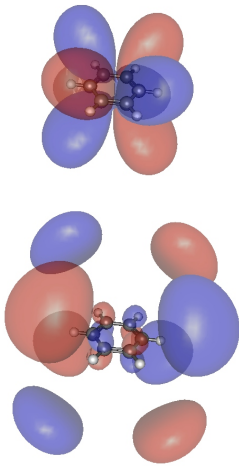
$$\phi^d(1) = \sqrt{N} \int \Psi^I(1, 2, \ldots, N)\Psi^F(2, \ldots, N)d2 \ldots dN$$



$C_6H_4O_2^-/^2A_u$

$E_R = 2.88$ eV

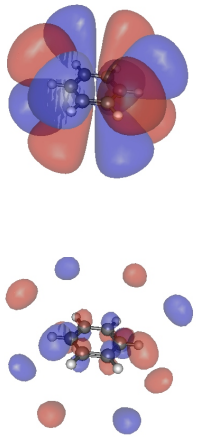
$\Gamma = 0.012$ eV



$C_6H_6^-/^2E_{2u}$

$E_R = 1.64$ eV

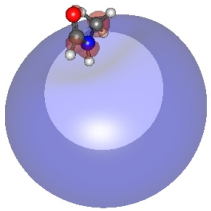
$\Gamma = 0.04$ eV

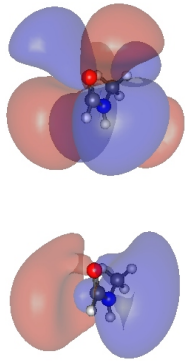


$C_6H_6^-/^2B_{2g}$

$E_R = 6.75$ eV

$\Gamma = 0.35$ eV





CH_3NHCHO^-

$^2A'$

$E = -0.015$ eV

$^2A''$

$E_R = 2.91$ eV

$\Gamma = 0.27$ eV

Dyson orbitals for various temporary anions. The upper and lower plots show the real and imaginary parts, respectively.

Jagau, Krylov, JCP 144 054113 (2016)

Exciton wave-functions within CAP EOM-CC formalism

Transition density matrix: reduced information about transition

$$\gamma_{pq}^{Re}(FI) = (\Psi_F^{Re}|p^\dagger q|\Psi_I^{Re}) - (\Psi_F^{Im}|p^\dagger q|\Psi_I^{Im})$$

$$\gamma_{pq}^{Im}(FI) = (\Psi_F^{Im}|p^\dagger q|\Psi_I^{Re}) + (\Psi_F^{Re}|p^\dagger q|\Psi_I^{Im})$$

One-electron mapping between initial and final states. For bound initial state:

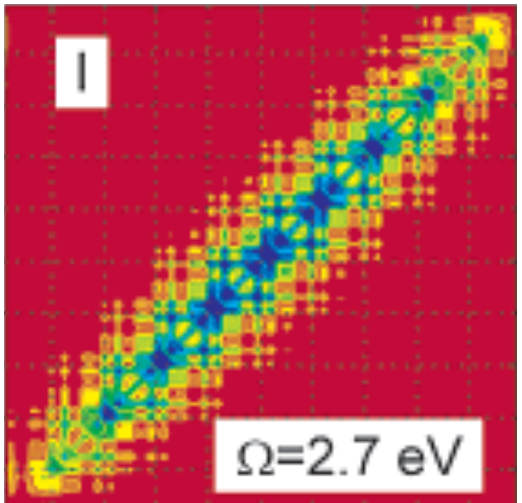
$$\Psi_F^{Re} = \sum_{pq} \gamma_{pq}^{Re} p^\dagger q \Psi_I + \quad higher \quad excitations$$

$$\Psi_F^{Im} = \sum_{pq} \gamma_{pq}^{Im} p^\dagger q \Psi_I + \quad higher \quad excitations$$

Transition density represents exciton wave-function

$$\xi(r_p, r_h) = \sum_{pq} \gamma_{pq}(FI)\phi_p(r_p)\phi_q(r_h)$$

Transition density related to observables



Natural Transition Orbitals within CAP EOM-CC

Natural Transition Orbitals: Diagonal representation of the transition OPDM (SVD of gamma):

$$\xi(r_p, r_h) = \sum_{pq} \gamma_{pq} \phi_p(r_p) \phi_q(r_h) = \sum_K \sigma_K \tilde{\phi}^p_K(r_p) \tilde{\phi}^h_K(r_h)$$

Or give most compact representation of the transition:

$$\Psi_F = \sum_K \sigma_K a^\dagger_K i_K \Psi_I + \quad higher \quad excitations$$

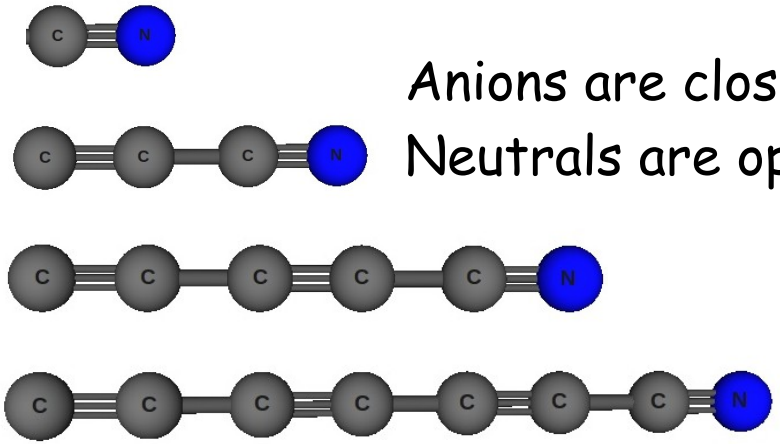
And are related to the observables:

$$< \Psi_F | \mu | \Psi_I > = Tr[\gamma \mu] = \sum_K \sigma_K < \tilde{\phi}^h_K | \mu | \tilde{\phi}^p_K >$$

Resonance wave-functions: Real and imaginary excitons

Luzanov, Zhikol, In Practical aspects of computational chemistry Springer, 2012; Plasser, Wormit, Dreuw, JCP **141** 024106 (2014); Bappler, Plasser, Wormit, Dreuw PRA **90** 052521 (2014); Head-Gordon et al, JPC **99** 14261 (1995); Martin, JCP **118** 4775 (2003).

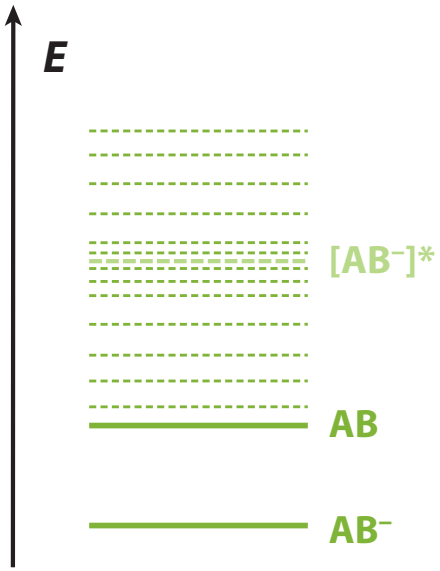
Example: Bound and metastable states in cyanopolyynes $C_{3x}N^-$



Anions are closed-shell species (singlets)
Neutrals are open-shells (doublets)

Dr. Wojtek Skomorowski

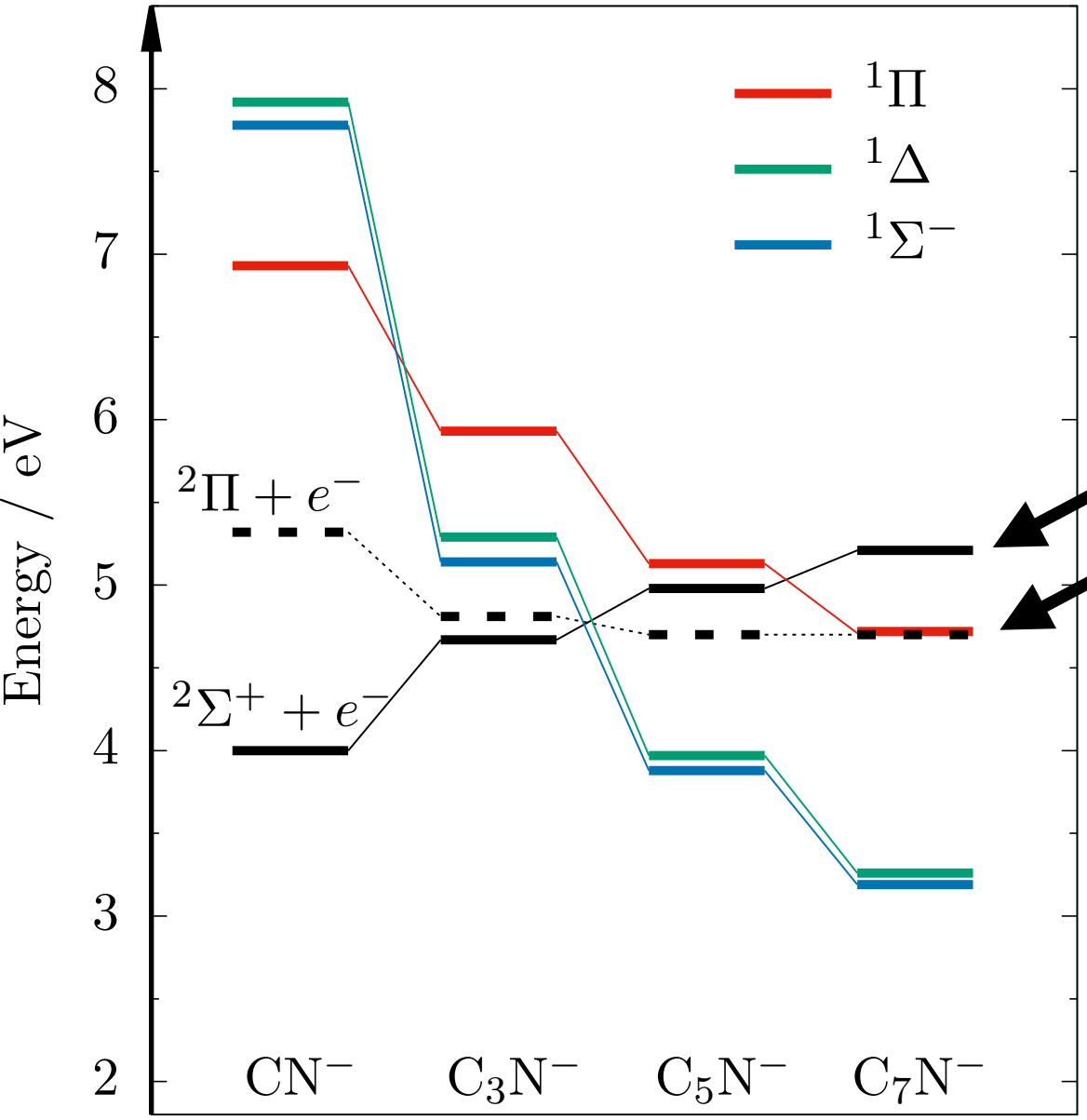
Sahil Gulania

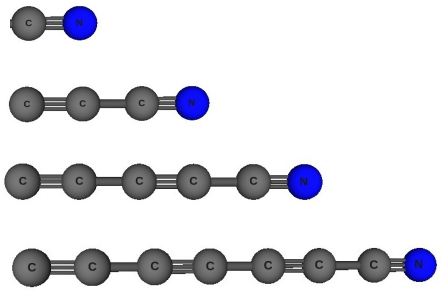


Studied by Neumark (exp), Simons, Sommerfeld, Crawford (theory), and others.

Our work: Skomorowski, Gulania, Krylov, PCCP **20**, 4805 (2018).

Resonances and bound states in cynanopolyyenes





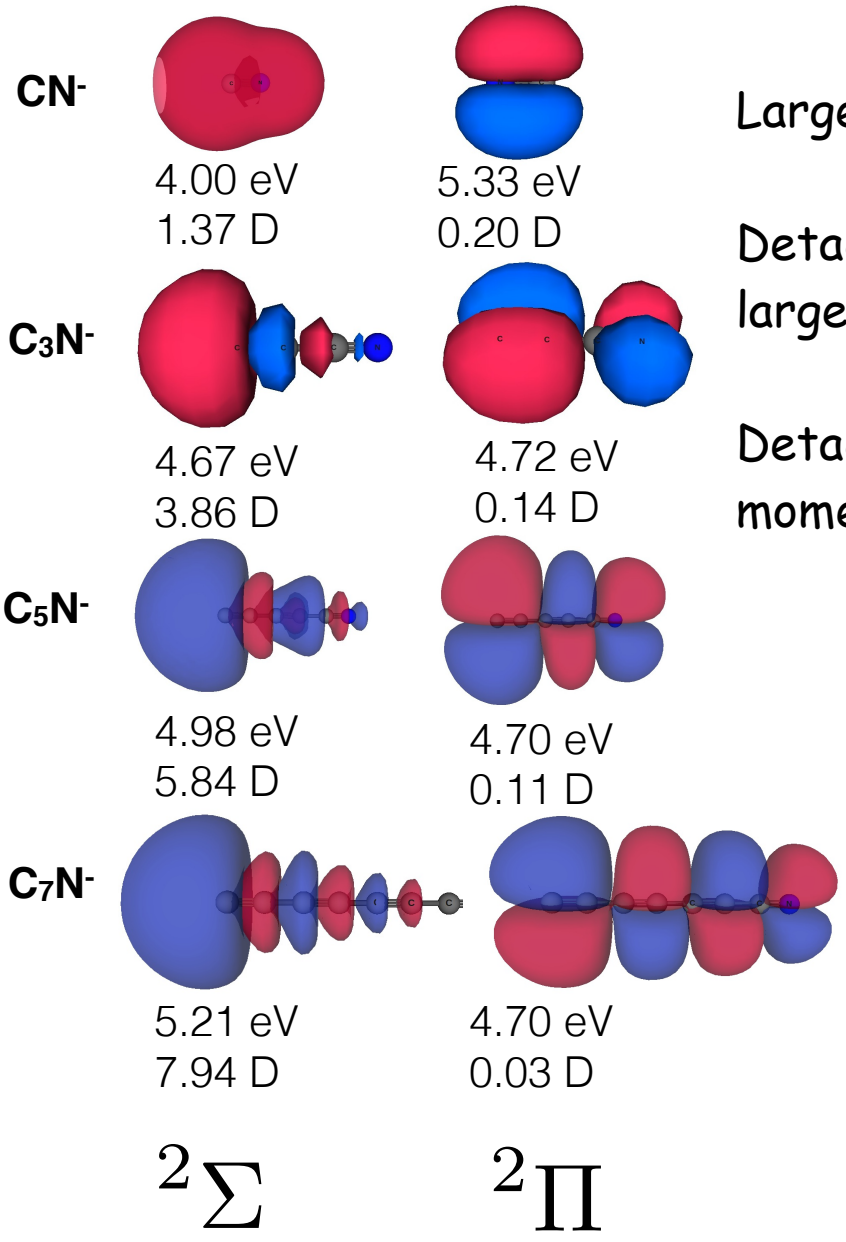
Ionization from σ orbital

Ionization from π orbital

Plenty of resonances including CN^-

Resonances are stabilized and become bound states in longer cyanopolyynes

Electron-detached states of the C_nN anions



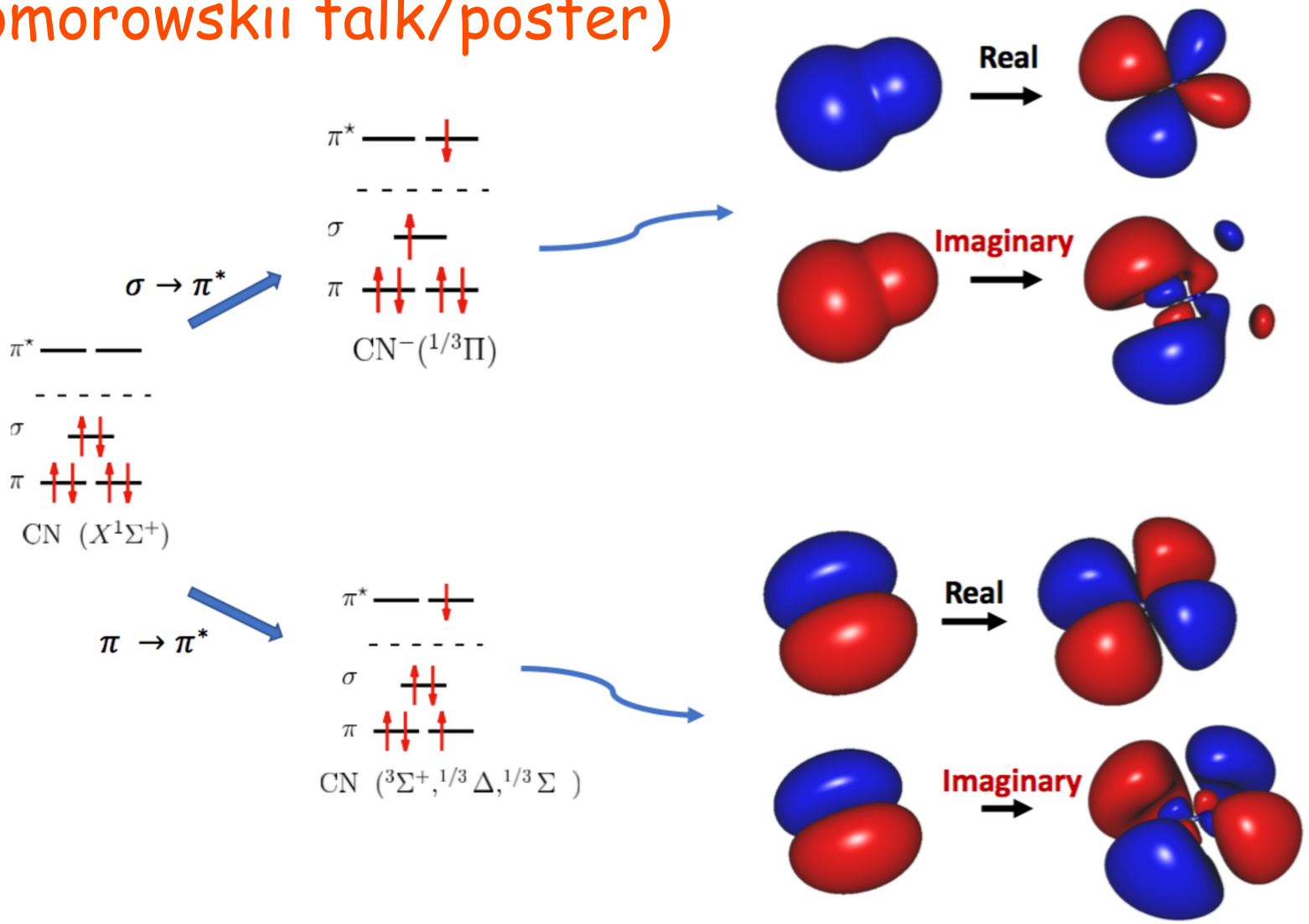
Large electron affinities/detachment energies;

Detachment from σ orbital leads to large dipole moment;

Detachment from π orbital: small dipole moment;

σ orbital is stabilized in longer chains by increased dipole moment

Example: NTOs for resonances in CN^- (more in W. Skomorowskii talk/poster)

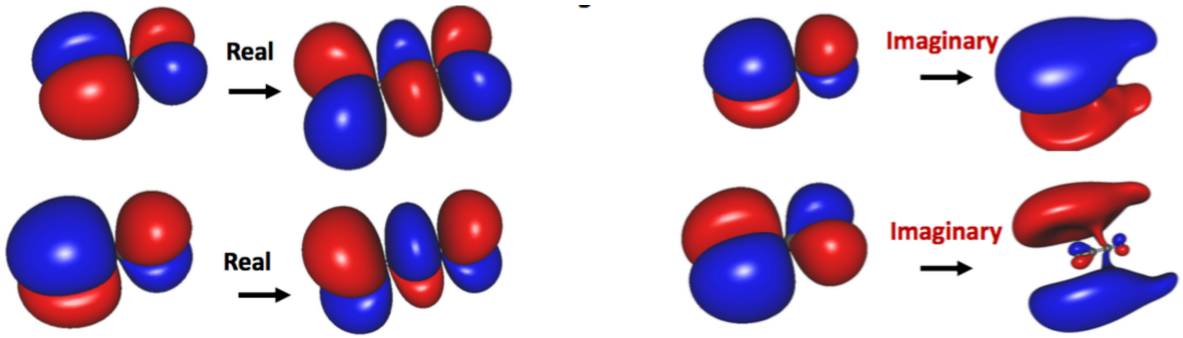


Hole orbital: Same for real and imaginary part of gamma

Particle orbital: very different!

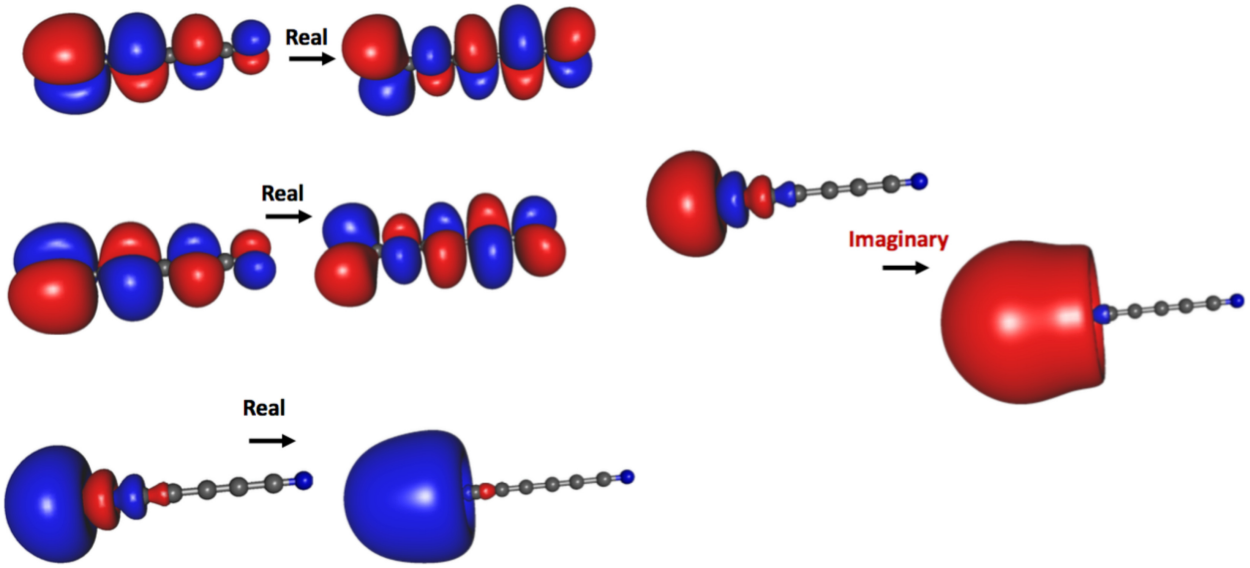
Real and imaginary excitons (more in W. Skomorowskii talk/poster)

C_3N^- $^1\Delta$



$PR_{NTO}=2$

C_7N^- $^1\Sigma^+$

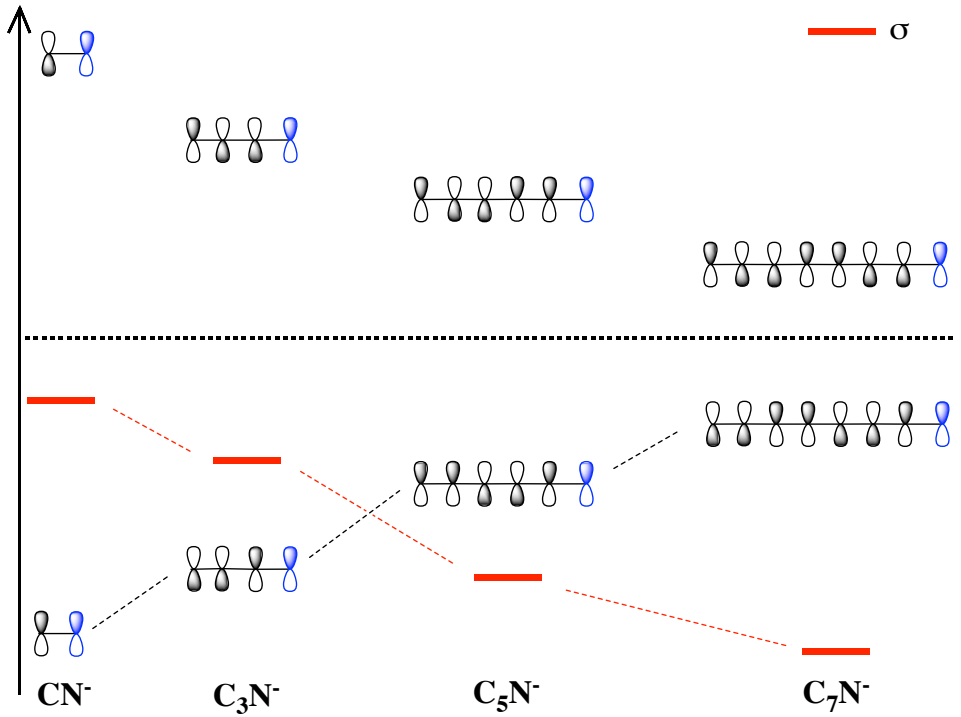


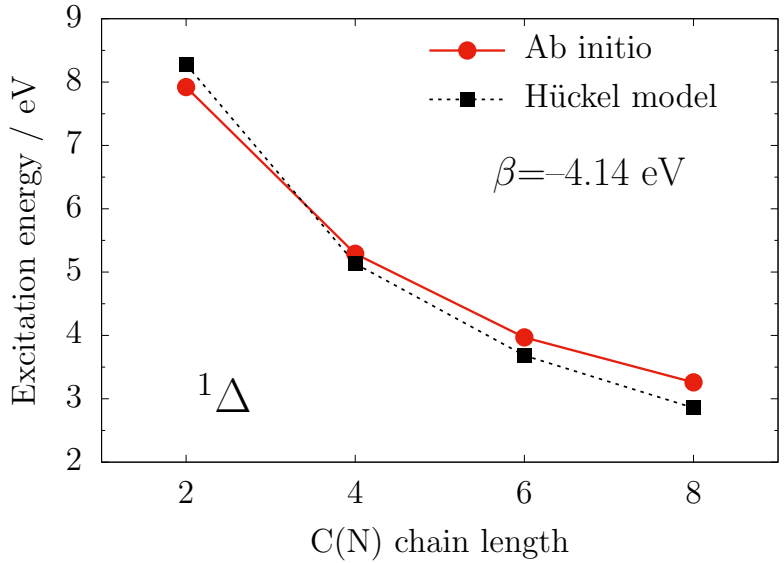
PR_{NTO} (Re)=2.9

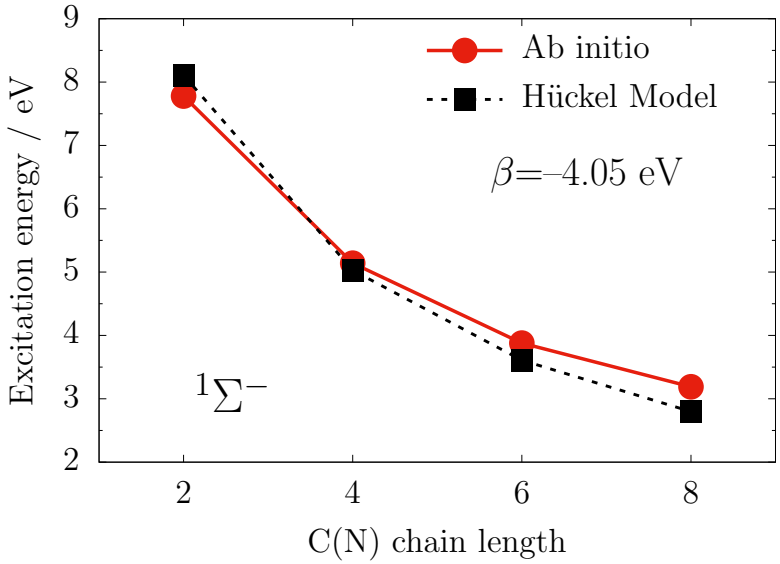
PR_{NTO} (Im)=1.4

Huckel model explains trends in resonances and bound states in cynanopolyyenes

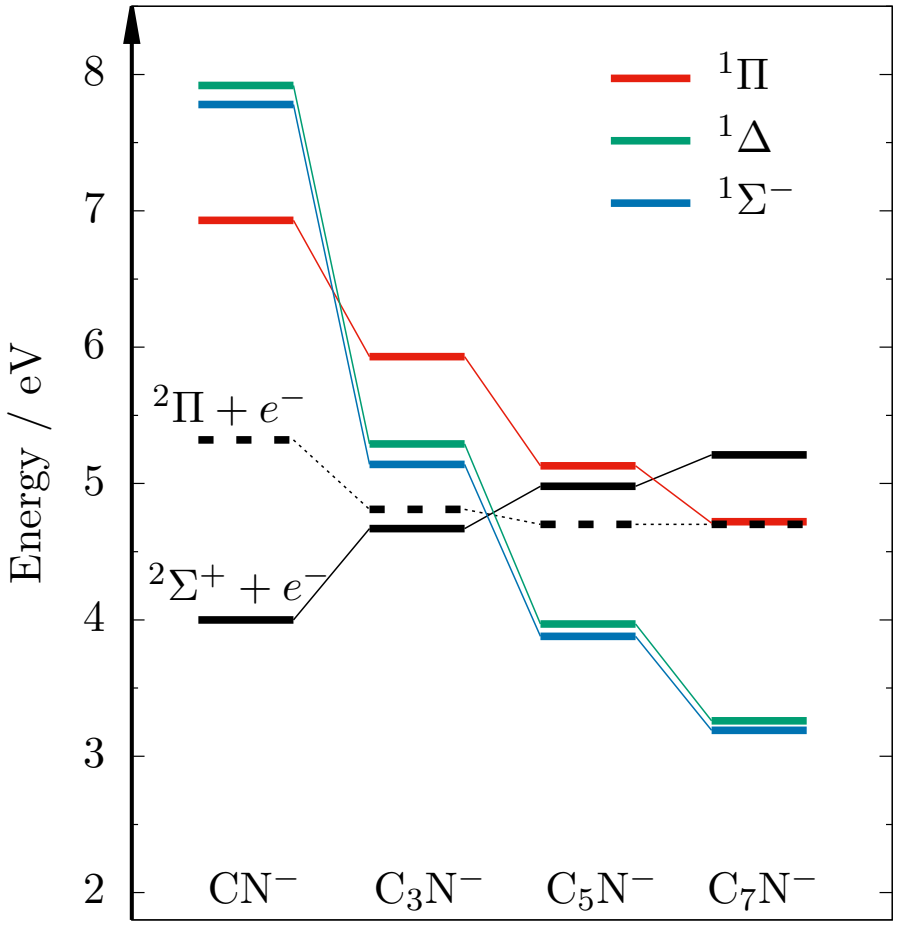
$$E_{ex}(\pi\pi^*) = -\beta \sin \frac{\pi}{2(1+N)}$$

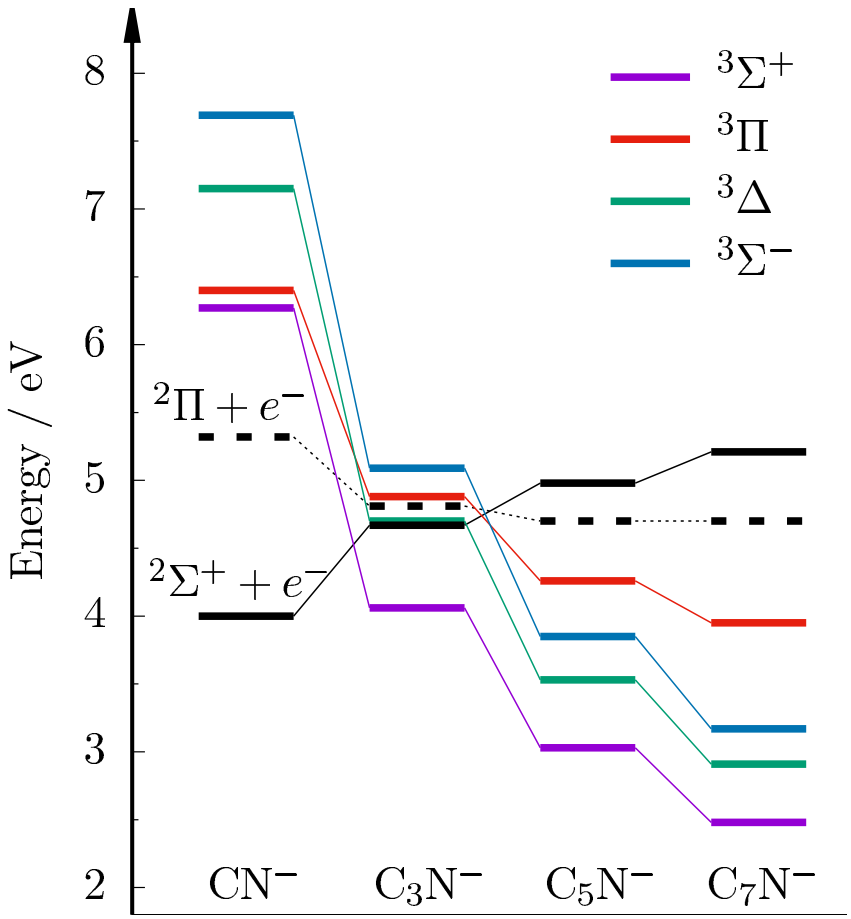






Resonances and bound states in cynanopolyyenes





Trends in all $\pi\pi^\star$ states can be fit to Huckel model with β=3.2-4.1

Conclusions

1. Resonances offer new opportunities for chemistry: New reaction pathways via electron-attached states.
2. Non-Hermitian QM: EOM-CC + CAP approaches: robust and uniform framework for bound and unbound states of different types (super-excited states, transient anions, core-level states).
3. Opportunity to test and extend important chemical concepts into a new domain. Examples: Dyson orbitals, Natural Transition Orbitals, Huckel theory, and more.

The People:

Dr. Wojtek Skomorowski (USC)
Sahil Gulania (USC)
Dr. Thomas Jagau (now Habilitant at U. Munich)
Prof. Ksenia Bravaya (now Asst. Prof. at BU)
Dr. Evgeny Epifanovsky (Q-Chem)
Dr. Dima Zuev (Citadel)

Dr. Wojtek Skomorowski

Sahil Gulania

THANKS:

Funding:

Resonances:

- Army Research Office.

Other method development:

- National Science Foundation;
- Department of Energy;
- AFOSR;
- Humboldt Foundation.