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

Anna I. Krylov
University of Southern California, Los Angeles

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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 wavefunctions.
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

gaseous electrons, ions, radicals, photons
multi-phase processes
electrolytic reactions
radiation processes
dissolved radical chemistry
thermal energy deposition

(a)

Bulk Plasma
M\(^+\) e\(^-\) M\(^+\) hv

Vapor Layer

Bulk Liquid

reactions
cations/anions/precursors

~1000 V

~1000 V

(left)
plasma anode
(liquid cathode)

(right)
plasma cathode
(liquid anode)

plasma cathode

liquid anode

jet of basic solution

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.

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.

$$\psi_R(t) = \exp(-iE_Rt/\hbar)\psi_R(0) \quad E_{\text{res}} \text{ resonance energy}$$

$$E_R = E_{\text{res}} - i\Gamma/2 \quad \Gamma \text{ resonance width (~1/lifetime)}$$

**Non-Hermitian QM:**

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

Complex absorbing potential (CAP) approach

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

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


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 $\eta \rightarrow 0$. Need to work with finite $\eta$. This introduces the need to compute eta-trajectories and perturbs the results.

   **Solution:** De-perturbative correction.

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

\[
\Psi = \text{Re}^T \Phi_0 \\
\overline{HR\Phi_0} = E\text{R}\Phi_0 \\
\overline{H} = \exp(-T)H \exp(T)
\]
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

\[ \overline{H} R \Phi_0 = E R \Phi_0 \]

Different target states 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

Figure 14: Potential energy curve and resonance width for the \( ^{12}g \) resonance of \( N_2 \) computed at the UHF (left), UCCSD and EOM-EA-CCSD (right) levels of theory. Potential energy curves for the \( N_2 \) ground state are shown as well. UHF and to a lesser extent UCCSD deliver inconsistent descriptions of the conversion of the resonance into a bound state since the resonance width becomes zero albeit the \( N_2 \) curve is still above the \( N_2^- \) curve.

\[ E(R)/eV = 0.42 \text{ eV} \]
\[ \Gamma(N_2^-)/eV = 0.40 \text{ eV} \]

Figure 15: Dyson orbitals for attachment to various transient anions. The upper and lower plots in each panel show the real and imaginary parts, respectively. For N-methylformamide (lower right panel), the Dyson orbital for attachment to the dipole-bound \( ^{2}A' \) state is shown as well. In part reproduced from Ref. 36.

CAP-Hartree-Fock PES are not internally consistent
CAP calculations of complex potential energy surfaces

**Figure 14:** Potential energy curve and resonance width for the \( \text{N}_2 \)\(^{1}\g\) resonance of \( \text{N}_2 \) computed at the UHF (left), UCCSD and EOM-EA-CCSD (right) levels of theory. Potential energy curves for the \( \text{N}_2 \) ground state are shown as well. UHF and to a lesser extent UCCSD deliver inconsistent descriptions of the conversion of the resonance into a bound state since the resonance width becomes zero albeit the \( \text{N}_2 \) curve is still above the \( \text{N}_2 \) curve.

\[
\begin{align*}
\text{CO} / \text{N}_2 & \quad E_{\text{R}} = 2.46 \text{ eV} \\
\text{H}_2 / \text{N}_2 & \quad E_{\text{R}} = 2.02 \text{ eV} \\
\text{CuF} / \text{N}_2 & \quad E_{\text{R}} = 1.68 \text{ eV} \\
\text{C}_6\text{H}_4\text{O} / \text{N}_2 & \quad E_{\text{R}} = 2.88 \text{ eV} \\
\text{C}_6\text{H}_6 / \text{N}_2 & \quad E_{\text{R}} = 1.64 \text{ eV} \\
\text{C}_2\text{H}_3\text{CHO} / \text{N}_2 & \quad E_{\text{R}} = 0.63 \text{ eV} \\
\text{C}_2\text{H}_5 / \text{N}_2 & \quad E_{\text{R}} = 2.25 \text{ eV} \\
\text{CH}_3\text{NHCHO} / \text{N}_2 & \quad E_{\text{R}} = 0 \text{ eV} \\
\end{align*}
\]

**Figure 15:** Dyson orbitals for attachment to various transient anions. The upper and lower plots in each panel show the real and imaginary parts, respectively. For N-methylformamide (lower right panel), the Dyson orbital for attachment to the dipole-bound \( \text{N}_2 \)\(^{2}\g\) state is shown as well. In part reproduced from Ref. 36.

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?
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.

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\[ \text{CuF (E = 0) } \]
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:
\[ \Phi_0 = | \phi_1 \phi_2 \ldots \phi_n \rangle \]

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: \( \Psi_{k_f}^e (n) \)

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

\[
P \sim |D_k^{IF}|^2 \quad D_k^{IF} = u \langle \Psi_I^N | r | \Psi_F^{N-1} \cdot \Psi_k^e \rangle
\]

Probability \( \rightarrow \) cross section (experimental observable).

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

\[
D_k^{IF} = u \langle \Psi_I^N | r | \Psi_F^{N-1} \cdot \Psi_k^e \rangle = u \langle \phi^d | r | \Psi_k^e \rangle
\]

Where \( \phi_{IF}^d \) is a Dyson orbital:

\[
\phi^d (1) = \sqrt{N} \int \Psi_I^I (1, 2, \ldots, N) \Psi_F^F (2, \ldots, N) d2 \ldots dN
\]
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 a 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.

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

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

Dyson orbitals for various temporary anions computed with CAP-EOM-EA-CCSD. The upper and lower plots show the real and imaginary parts, respectively.

C\(_6\)H\(_4\)O\(_2\) /\(^2\)A\(_u\)  
\[ E_R = 2.88 \text{ eV} \]  
\[ \Gamma = 0.012 \text{ eV} \]

C\(_6\)H\(_6\) /\(^2\)E\(_{2u}\)  
\[ E_R = 1.64 \text{ eV} \]  
\[ \Gamma = 0.04 \text{ eV} \]

C\(_6\)H\(_6\) /\(^2\)B\(_{2g}\)  
\[ E_R = 6.75 \text{ eV} \]  
\[ \Gamma = 0.35 \text{ eV} \]

CH\(_3\)NHCHO\(^-\)  
\[ ^2\text{A}' \]  
\[ E = -0.015 \text{ eV} \]  
\[ E_R = 2.91 \text{ eV} \]  
\[ \Gamma = 0.27 \text{ eV} \]

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

\[
\Psi_F^{Re} = \sum_{pq} \gamma_{pq}^{Re} p^\dagger q \Psi_I + \text{higher excitations}
\]

\[
\Psi_F^{Im} = \sum_{pq} \gamma_{pq}^{Im} p^\dagger q \Psi_I + \text{higher excitations}
\]

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):

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

Or give most compact representation of the transition:

$$\Psi_F = \sum_K \sigma_K a_K^\dagger i_K \Psi_I + \text{higher excitations}$$

And are related to the observables:

$$\langle \Psi_F | \mu | \Psi_I \rangle = \text{Tr} [\gamma \mu] = \sum_K \sigma_K \langle \tilde{\phi}_K^h | \mu | \tilde{\phi}_K^p \rangle$$

Resonance wave-functions: Real and imaginary excitons

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

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


[Image of molecular structures and energy levels]

- AB
- $[AB^-]^*$
- AB
- AB$^-$

Studied by Neumark (exp), Simons, Sommerfeld, Crawford (theory), and others.
In this part of report electronic structure of C\textsubscript{N}−C\textsubscript{N}\textsubscript{−} are mentioned in the table below. The above observed molecular orbitals are similar in nature as we expect to happen in conjugated alkenes. After this analysis, EOM-IP-CCSD(aug-cc-pVTZ) calculations were performed on the same geometry of anion. The aim for this calculation was to understand the vertical detachment energy (VDE) of electron to neutral molecule. VDE and dipole moments are mentioned in the table below.

<table>
<thead>
<tr>
<th>Bond</th>
<th>C\textsubscript{N}−C\textsubscript{N}\textsubscript{−}</th>
<th>\textsubscript{IP}(eV)</th>
<th>\textsubscript{VDE}(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{1}−C\textsubscript{2}</td>
<td>9.170 (</td>
<td>\textsubscript{Koopmans})</td>
<td>7.374 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
<tr>
<td>C\textsubscript{2}−C\textsubscript{3}</td>
<td>6.449 (</td>
<td>\textsubscript{Koopmans})</td>
<td>5.243 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
<tr>
<td>C\textsubscript{3}−C\textsubscript{4}</td>
<td>7.809 (</td>
<td>\textsubscript{Koopmans})</td>
<td>6.551 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
<tr>
<td>C\textsubscript{4}−C\textsubscript{5}</td>
<td>10.802 (</td>
<td>\textsubscript{Koopmans})</td>
<td>10.060 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
<tr>
<td>C\textsubscript{5}−C\textsubscript{6}</td>
<td>10.802 (</td>
<td>\textsubscript{Koopmans})</td>
<td>10.060 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
<tr>
<td>C\textsubscript{6}−C\textsubscript{7}</td>
<td>10.802 (</td>
<td>\textsubscript{Koopmans})</td>
<td>10.060 (\textsubscript{RI-MP2(aug-cc-pVTZ)})</td>
</tr>
</tbody>
</table>

After comparison, bond lengths reported in reference 2 were used due to high level theory calculations. Important hartree-fock molecular orbitals and their energy are shown below.

\(\text{Transition} \rightarrow \text{Symmetry} \rightarrow \text{MO} \rightarrow \text{Bond Length (A)} \rightarrow \text{Bond Length } (x, y, z) \rightarrow \text{Dipole Moment (Debye)} \rightarrow \text{Vertical Detachment Energy (eV)} \rightarrow \text{Ionization From } \sigma \text{ orbital} \rightarrow \text{Ionization From } \pi \text{ orbital} \rightarrow \text{Plenty of resonances including } \text{CN}^-\rightarrow \text{Resonances are stabilized and become bound states in longer cyanopolyynes}\)
Electron-detached states of the $C_nN$ anions

$CN^-$
- 4.00 eV
- 1.37 D
- 5.33 eV
- 0.20 D

$C_3N^-$
- 4.67 eV
- 3.86 D
- 4.72 eV
- 0.14 D

$C_5N^-$
- 4.98 eV
- 5.84 D
- 4.70 eV
- 0.11 D

$C_7N^-$
- 5.21 eV
- 7.94 D
- 4.70 eV
- 0.03 D

Large electron affinities/detachment energies;
Detachment from $\sigma$ orbital leads to large dipole moment;
Detachment from $\pi$ orbital: small dipole moment;
$\sigma$ orbital is stabilized in longer chains by increased dipole moment
Orbital characterization of the excited states

Resonances correspond to valence transition of the type $\pi^* \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$.

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)

$\text{C}_3\text{N}^- \quad \mathbf{^1\Delta}$

$\text{PR}_{\text{NTO}}=2$

$\text{C}_7\text{N}^- \quad \mathbf{^1\Sigma^+}$

$\text{PR}_{\text{NTO}} \,(\text{Re})=2.9$

$\text{PR}_{\text{NTO}} \,(\text{Im})=1.4$
Huckel model explains trends in resonances and bound states in cyanopolyyenes

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

![Diagram showing excitation energies for different cyanopolyynes](image-url)
Resonances and bound states in cyanopolyynes

Trends in all ππ* states can be fit to Hückel model with β=3.2-4.1
Conclusions


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)
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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)
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