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RPPR Final Report
as of 03-Dec-2019

Agency Code:

Proposal Number: 67443CH **Agreement Number: W911NF-16-1-0232**
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Country: USA
DUNS Number: 072933393 EIN: 951642394
Report Date: 08-Aug-2019 Date Received: 28-Nov-2019
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Title: Metastable Autoionizing States of Molecules and Radicals in Highly Energetic Environment
Begin Performance Period: 09-May-2016 **End Performance Period:** 08-May-2019
Report Term: 0-Other
Submitted By: Anna Krylov Email: krylov@usc.edu
Phone: (+12) 137-404929
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STEM Degrees: **STEM Participants:**

Major Goals: The scope of this grant was electronic structure method development targeting electronic states that are metastable with respect to electron detachment and computational studies of fundamental chemical processes involving molecules and radicals in highly excited states. Such metastable electronic states, which lie above the ionization (or electron-detachment) continuum, are called resonances; they are common in energetic environments such as plasma, which is generated in electric arcs, supersonic combustion, fusion reactors, plasma displays, extremely hot flames, lightning, polar aurorae, etc. Plasmas (and, consequently, these metastable states) play an important role in technology. Moreover, the quantum mechanical description of resonances is of fundamental importance on its own — it is a prerequisite for understanding chemical dynamics in plasmas and matter in high-energy environments.

The research program was built upon our previous work on developing the ideas of non-hermitian quantum mechanics into quantum chemistry methods by using complex absorbing potentials and equation-of-motion coupled-cluster theory.
The main technical goals were: (i) extension to core-ionized states via new iterative diagonalization approaches; (ii) improvement of computational efficiency and extending these tools for larger molecules via resolution-of-identity (RI) and Cholesky decomposition (CD) techniques as well as parallelization; (iii) development of the formalism and codes for calculations of properties (such as transition dipole moments and Dyson orbitals) and integration with our code for calculating photoionization/photodetachment cross sections; and (iv) development of the conceptual framework for the analysis of complex densities and density currents.

Accomplishments: We considerably extended the methodology by extending it to various domains. The most important development is extension of the theory to describe properties of resonances and to analyze the wave functions in terms of molecular orbital theory. We also improved performance of solvers, the efficiency of the codes, and computational infrastructure. We also carried out several illustrative calculations. The most important results are described in the attached report.

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Training Opportunities: The research in my group provides training for students and postdocs in the theoretical and computational foundations of electronic structure; it also includes a strong component of computer code design and implementation, preparing students for careers in high-tech industries. My former postdocs and students are very successful pursuing careers of their choice (ranging from Google, Exxon Mobil, and investment banks to academia).
My achievements in mentoring were recognized by the Melon Mentoring Award and Hanna Reisler Mentoring Award.

A few highlights concerning careers of the ARO supported personnel:
- Ksenia Bravaya is now an Assistant Professor at Boston University.
- Thomas Jagau is pursuing habilitation in Munich. He has received several awards, including Emmy Noether award, EU start-up grant, and the Hellman Award from the German Theoretical Chemistry Society.
- Dmitri Zuev is now employed at Citadel LLC.

Results Dissemination: The ARO-funded research resulted in nine original papers and one review (the list is uploaded). The ARO support was acknowledged in numerous invited talks and university seminars. The computer codes were integrated in the Q-Chem package and in open-source libtensor library.

Honors and Awards: 2019 Earle K. Plyler Prize for Molecular Spectroscopy and Dynamics, APS
2018 Simons Fellow in Theoretical Physics
2018 Mildred Dresselhaus Award, CUI, Hamburg, Germany
2018 Mainz Guestprofessorship, Mainz, Germany
2017 Hanna Reisler Mentoring Award, WiSE, USC
2016 Phi Kappa Phi Faculty Recognition Award, USC

Protocol Activity Status:

Technology Transfer: The codes developed under the ARO support are integrated into the Q-Chem package. There were released in Q-Chem 5.0.The modules are also available as open source (upon request) and can be integrated in other packages (integration in Cfour and Psi4 is planned).

PARTICIPANTS:

Participant Type: PD/PI
Participant: Anna Krylov
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
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Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Kaushik Nanda
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:

International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
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Person Months Worked: 5.00 **Funding Support:**
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International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Sahil Gulania
Person Months Worked: 5.00 **Funding Support:**
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International Collaboration:
International Travel:
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Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Pavel Pokhilko
Person Months Worked: 3.00 **Funding Support:**
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Participant Type: Graduate Student (research assistant)
Participant: Anastasia Gunina
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Participant: Wojciech Skomorowski
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Date Submitted: 11/20/19 12:00AM Date Published: 5/7/17 3:18PM
Publication Location: Los Angeles, CA, USA
Article Title: Extending Quantum Chemistry of Bound States to Electronic Resonances
Authors: Thomas-C. Jagau, Ksenia B. Bravaya, Anna I. Krylov
Keywords: metastable states, coupled-cluster theory
Abstract: Electronic resonances are metastable states with finite lifetime embed- ded in the ionization or detachment continuum. They are ubiquitous in chemistry, physics, and biology. Resonances play a central role in processes as diverse as DNA radiolysis, plasmonic catalysis, and at- tosecond spectroscopy. This review describes novel equation-of-motion coupled-cluster (EOM-CC) methods designed to treat resonances and bound states on an equal footing. Built on complex-variable techniques such as complex scaling and complex absorbing potentials that allow resonances to be associated with a single eigenstate of the molecular Hamiltonian rather than several continuum eigenstates, these methods extend electronic-structure tools developed for bound states to elec- tronic resonances. Selected examples emphasize the formal advantages as well as the numerical accuracy of EOM-CC in the treatment of electronic resonances.
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Article Title: Autocorrelation of electronic wave-functions: a new approach for describing the evolution of electronic structure in the course of dynamics
Authors: Barak Hirshberg, R. Benny Gerber, Anna I. Krylov
Keywords: Molecular orbitals, electronic wave-function, autocorrelation functions, Born Oppenheimer approximation, molecular dynamics
Abstract: We introduce a new approach for analysing changes in electronic structure in the course of ab initio molecular dynamics simulations. The analysis is based on the time autocorrelation function of the many-body electronic wave-function. The approach facilitates the interpretation of dynamical events that may not be easily revealed by consideration of nuclear configurations alone. We apply the method to several illustrative examples: the shared proton vibration in the F?(H2O) complex, representing changes in strength of non-covalent interactions; proton transfer in the water dimer cation, as an example for chemical reactions in weakly bound systems; and the intramolecular proton transfer in malonaldehyde. In all cases, we observe distinct features in the time autocorrelation function when chemical changes occur. The autocorrelation function serves as an effective reaction coordinate, incorporating all degrees of freedom, including electronic ones. The method is also sensitive to changes i
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Article Title: Real and Imaginary Excitons: Making Sense of Resonance Wave Functions by Using Reduced State and Transition Density Matrices
Authors: Wojciech Skomorowski, Anna I. Krylov
Keywords: EOM-CC methods
Abstract: Within non-Hermitian quantum mechanics, metastable electronic states can be represented by isolated L2-integrable complex-valued wave functions with complex energies. An analysis scheme of the real and imaginary parts of resonance wave functions by using reduced transition density matrices and natural transition orbitals is presented. While the real parts of excitons describe changes in the electron density corresponding to the bound part of the resonance, the imaginary excitons can be interpreted as virtual states facilitating one-electron decay into the continuum. The different nature of real and imaginary excitons is revealed by exciton descriptors, in particular hole-particle separation and their correlation. Singular values and respective participation ratios quantify the extent of collectivity of the excitation and a number of distinct decay channels. The utility of the new tool is illustrated by the analysis of bound and metastable excited states of cyanopolyyne anions.
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Article Title: Same but Different: Dipole-Stabilized Shape Resonances in CuF– and AgF–
Authors: Thomas-C. Jagau, Diep B. Dao, Nicholas S. Holtgrewe, Anna I. Krylov, Richard Mabbs
Keywords: photoelectron spectroscopy, resonances, transient anions, silver fluoride, copper fluoride
Abstract: Electron attachment to closed-shell molecules is a gateway to various important processes in the gas and condensed phases. The properties of an electron-attached state, such as its energy and lifetime as well as the character of the molecular orbital to which the electron is attached, determine the fate of the anion. In this experimental and theoretical study of copper and silver fluoride anions, we introduce a? new type of metastable anionic state. Abrupt changes in photoelectron angular distributions point to the existence of autodetaching states. Equation-of-motion coupled-cluster singles and doubles calculations augmented by a complex absorbing potential identify some of these states as ? and ? dipole-stabilized resonances, a new type of shape resonance. In addition, these molecules support valence and dipole-bound states and a ? resonance of charge-transfer character. By featuring five different types of anionic states, they provide a vehicle for studying fundamental properties of
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Article Title: Conversion of He(23S) to He2(a3?u +) in Liquid Helium
Authors: P. Nijjar, A. I. Krylov, O. V. Prezhdo, A. F. Vilesov, C. Wittig
Keywords: EOM-CC methods
Abstract: The report of an anomalously intense He4+peak in electron impact mass spectra oflarge helium droplets created a stir 3 decades ago that continues to this day. When the electron kineticenergy exceeds 41 eV, an additional pathway opens that yields He4+predominantly in an electronicallyexcited metastable state. A pair of He*(23S) atoms has been implicated based on the isolated He*energy of 19.82 eV and the 41 eV threshold, and the creation of He4+has been conjectured to proceedvia a pair of He2*(a3?u+) precursors. The mechanism whereby He*converts to He2*in liquid heliumhas remained a mystery, however. High level ab initio theory combined with classical molecular dynamics has been applied tosystems comprising small numbers of He atoms. The conversion of He*to He2*in such systems is shown to be due to a simplemany-body effect that yields He2*rapidly and efficiently.
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Article Title: Channel branching ratios in CH2CN- photodetachment: Rotational structure and vibrational energy redistribution in autodetachment
Authors: Justin Lyle, Olivia Wedig, Sahil Gulania, Anna I. Krylov, Richard Mabbs
Keywords: Radioactive decay, Absorption band, Autoionization, Excitation energies, Coupled-cluster methods, Rotational spectra, Oscillator strengths, Photoelectron spectroscopy, Correlation-consistent basis sets, Electrostatics
Abstract: We report photoelectron spectra of CH2CN?, recorded at photon energies between 13 460 and 15 384 cm?1, which show rapid intensity variations in particular detachment channels. The branching ratios for various spectral features reveal rotational structure associated with autodetachment from an intermediate anion state. Calculations using equation-of-motion coupled-cluster method with single and double excitations reveal the presence of two dipole-bound excited anion states (a singlet and a triplet). The computed oscillator strength for the transition to the singlet dipole-bound state provides an estimate of the autodetachment channel contribution to the total photoelectron yield. Analysis of the different spectral features allows identification of the dipole-bound and neutral vibrational levels involved in the autodetachment processes. For the most part, the autodetachment channels are consistent with the vibrational propensity rule and normal mode expectation. However, examination of t
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Article Title: Bound and continuum-embedded statesof cyanopolyyne anions
Authors: Wojciech Skomorowski, Sahil Gulania, Anna I. Krylov
Keywords: EOM-CC methods
Abstract: Cyanopolyyne anions were among the first anions discovered in the interstellar medium. The discovery has raised questions about the routes of formation of these anions in space. Some of the proposed mechanisms assumed that anionic excited electronic states, either metastable or weakly bound, play a key role in the formation process. The verification of this hypothesis requires detailed knowledge of the electronic states of the anions. Here we investigate the bound and continuum states of four cyanopolyyne anions, CN?, C3N?, C5N?, and C7N?, by means of ab initio calculations. We employ the equation-of-motion coupled-cluster method augmented with complex absorbing potential. We predict that already in CN?, the smallest anion in the family, there are several low-lying metastable states of both singlet and triplet spin symmetry. These states, identified as shape resonances, are located between 6.3–8.5 eV above the ground state of the anion (or 2.3–4.5 eV above the ground state of the paren
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Article Title: EOM-CC guide to Fock-space travel: the C2 edition
Authors: Sahil Gulania, Thomas-C. Jagau, Anna I. Krylov
Keywords: EOM-CC methods
Abstract: Despite their small size, C2 species pose big challenges to electronic structure methods, owing to extensive electronic degeneracies and multi-configurational wave functions, which lead to a dense manifold of electronic states. We present detailed electronic structure calculations of C2, C2?, and C22?, emphasizing spectroscopically relevant properties. We employ the double ionization potential (DIP) and ionization potential (IP) variants of the equation-of-motion coupled-cluster method with single and double substitutions (EOM-CCSD) and a dianionic reference state. We show that EOM-CCSD is capable of describing multiple interacting states in C2 and C2? in an accurate, robust, and effective way. We also characterize the electronic structure of C22?, which is metastable with respect to electron detachment.
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Article Title: Triplet Excitons in Small Helium Clusters
Authors: Parmeet Nijjar, Anna I. Krylov, Oleg V. Prezhdo, Andrey F. Vilesov, Curt Wittig
Keywords: EOM-CC methods
Abstract: An electron traveling through liquid helium with sufficient kinetic energy can create a low-lying triplet exciton via inelastic scattering. Accompanying repulsion between the exciton and nearby atoms results in bubble formation. That is not all, however. Repulsion compresses an "incipient He2* exciton", pushing it into a region where an He2* moiety commences evolution toward its potential energy minimum. The above picture follows from ab initio calculations of the two lowest adiabatic potential energy surfaces for collinear three-atom systems and dynamics studies launched on the lowest adiabat that calculate said surface on the fly. The timescale for launching trajectories toward the He2* moiety is significantly shorter than the timescale for pushing helium away from the exciton in large systems, making results with three atoms relevant to liquid helium. This explains how He2* might be created in the aftermath of electron-impact excitation of He*. Interplay between the lowest adiabats

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Results from the ARO support, "Metastable autoionizing states of molecules and radicals in highly energetic environments", 2015-2019

Building on our formalism and production-level computer codes for CS and CAP-augmented EOM-CCSD,[1] during the previous funding period we developed several snew tools for modeling resonances.[1–4] Our main focus was on extending the theory to calculation of *properties* of metastable states and extracting insight from resonance wave functions. We also conducted computational studies of resonances in various systems of increasing complexity;[5–9] some in collaborations with the experimental groups.[5–7] The ARO support has been acknowledged in nine original papers[2–10] and one review,[1] and in numerous invited talks and university seminars. In 2016, Krylov's work on resonances (which is exclusively funded by ARO) was recognized by the Phi Kappa Phi Faculty Recognition Award from USC. Krylov has also recieved prestigeous Simons Fellowship, Mildred Dresselhaus Award, and Mainz Guestprofessorship, which supported her full-year sabatical stay in Germany in 2018-2019. Finally, Krylov has been selected as 2020 Earle K. Plyler Prize for Molecular Spectroscopy and Dynamics from APS (https://www.aps.org/programs/honors/prizes/plyler.cfm).

Our most important achievement in the past 3 years is the extension of the CAP-augmented EOM-CC methods to calculations of electronic properties of metastable states and experimental observables. Specifically, we extended the concepts of Dyson orbitals,[11–14] reduced one-particle density matrices,[15–20] and Natural Transition Orbitals (NTOs)[20–24] to the domain of metastable states.[2,4]

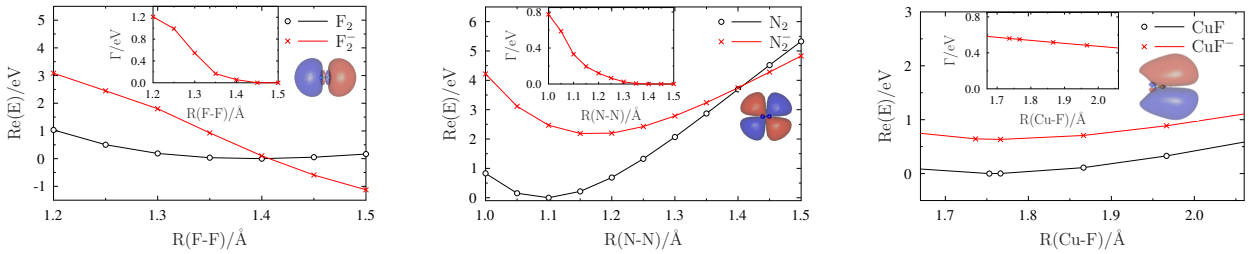

Figure 1: Extension of the Dyson orbitals to the domain of metastable states allows us to rationalize chemical changes induced by electron attachment. The three panels show the connection between the shape of the Dyson orbital and the shape of the PES for the σ^* valence, π^* valence, and π dipole-stabilized resonances in F_2^-, N_2^-, and CuF^-, respectively. Resonance widths as a function of bond distance and Dyson orbitals are displayed in insets. Attachment to anti-bonding orbitals (F_2^- and N_2^-) leads to significant change in the potential energy slope and strong dependence of the lifetime on the internuclear distance, whereas attachment to a dipole-stabilized orbital does not perturb the molecular core resulting in nearly constant lifetime and parallel potential energy curves of the neutral and the anion (CuF^-).

Dyson orbital,[11–14] ϕ^d, is the key quantity in processes involving electron ejection or electron attachment:

$$\phi^d(1) = \sqrt{N} \int \Psi_I^N(1,\ldots,n)\Psi_F^{N-1}(2,\ldots,n)d2\ldots dn \tag{1}$$

It connects the initial (N-electron) and final ($N-1$-electron) states. In the context of photoionization, Dyson orbitals appear in the so-called photoelectron matrix element:[25–27]

$$D^{IF} = (\phi^d|\mu|\xi_\omega) \tag{2}$$

that determines the cross sections and angular distributions of photoelectrons (ξ_ω denotes the wave function of the ejected electron).

Dyson orbitals are also useful for deriving qualitative insight from many-body calculations, because they extend simple molecular orbital theory to correlated wave functions. For example, the shapes of Dyson orbitals can be used to explain main features of potential energy surfaces of various

shape resonances, as illustrated in Fig. 1. Distinctly different shapes of the Dyson orbitals in F_2^-, N_2^-, and CuF^- allow one to classify these shape resonances as of σ^*-, π^*-, and dipole-stabilized π-type. In the σ^* and π^* resonances, the curvature of the neutral and anionic PES are very different, whereas in the dipole-stabilized case the two PES are nearly parallel because the extra electron resides outside of the molecular core. Likewise, the shape of the Dyson orbital explains the observed different dependence of the lifetime on the internuclear distance in these shape resonances. Quantitatively, complex Dyson orbitals can be used for calculating partial widths corresponding to different detachment channels, as was done in Ref. 9. As described below, in the next funding period we will extend the theory of calculating photoionization/photodetachment cross sections using Dyson orbitals[27,28] to describe autoionization.

The key objects in properties calculations are reduced state and transition density matrices:[15–20]

$$\gamma_{pq}^{IF} = (\Psi^I | p^\dagger q | \Psi^F) \tag{3}$$

where Ψ^I and Ψ^F are the initial and final states, respectively (if $I \equiv F$, one obtains a state density matrix). For example, dipole (or transition dipole) is computed as contraction of such one-particle density matrices with the matrix of dipole moment. Due to c-product normalization, density matrices become complex in non-Hermitian extensions of quantum mechanics. We have implemented and validated computer code for computing these quantities using the CAP-EOM-CCSD wave functions.[2,4]

Transition density matrices are similar to Dyson orbitals defined above, in a sense that they connect initial and final states and determine the probabilities of one-photon transitions between these states. Transition density matrices can be interpreted as amplitudes on one-electron excitation operator mapping Ψ^I onto Ψ^F. If the initial state Ψ^I is bound (and its wavefunction is real, $\Psi^I \equiv \Psi_I^{Re}$) and the final metastable excited state is represented by complex-valued wavefunction Ψ^F, then the expressions for transition one-particle density matrix $\gamma_{pq}^{Re}(FI)$ and $\gamma_{pq}^{Re}(FI)$ contain only one term with $\Psi_I^{Re} \equiv \Psi^I$ and Ψ^F can be represented as:

$$\Psi_F^{Re} = \sum_{pq} \gamma_{pq}^{Re}(FI) p^\dagger q \Psi_I \quad + \quad higher \quad excitations \tag{4}$$

$$\Psi_F^{Im} = \sum_{pq} \gamma_{pq}^{Im}(FI) p^\dagger q \Psi_I \quad + \quad higher \quad excitations \tag{5}$$

Thus, γ^{Re} and γ^{Im} can be interpreted as real and imaginary amplitudes of a single excitation operator that generates a correlated many-body Ψ^F from Ψ^I. Because γ describes the changes in electron density upon excitation, it can be interpreted as exciton wavefunction[17–20] when expressed in coordinate space. This analysis provides a roadmap for interpreting the physical meaning of complex transition densities in non-Hermitian theories.[4]

NTOs, which are defined by singular value decomposition of the transition density matrix, allow one to describe electronic transitions in terms of pairs of hole and particle orbitals.[17–21,24] We extended[4] this powerful and rigorous theory to metastable states, enabling the description of resonances in a simple molecular orbital framework (particularly important is the ability to visualize the decay channels). In analogy with real-valued theories, γ^{Re} and γ^{Im} can be used to define real and imaginary parts of the exciton's wavefunction:

$$\chi^{Re/Im}(r_p, r_h) = \sum_{pq} \gamma_{pq}^{Re/Im} \phi_p(r_p) \phi_q(r_h), \tag{6}$$

We showed[4] that while real parts of excitons describe changes in the electron density corresponding to the bound part of the resonance, the imaginary excitons can be interpreted as virtual states facilitating one-electron decay into the continuum. Fig. 2 shows bound and imaginary NTOs for the $^1\Sigma^+$ resonance in C_7N^-. While the shape of the real and imaginary holes are very similar, the

particle states are very different. As one can see from the NTOs and the respective singular values, the real part of the resonance can be described as $\pi \rightarrow \pi^*$ excitation, whereas the main decay channel is the transition from a lone-pair to an s-like orbital, with minor contributions of the $\pi \rightarrow p$ type.

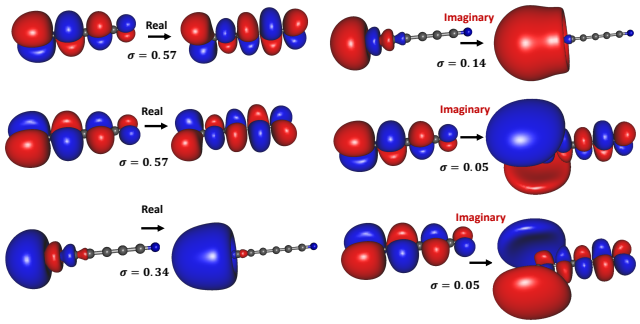

Figure 2: Real and imaginary NTOs and the respective singular values for the $^1\Sigma^+$ resonance in C_7N^-. The singular values enable the evaluation of partial widths corresponding the channels producing Σ and Π neutral states: Γ_Σ=0.10 eV and Γ_Π=0.03 eV. *From Ref. 4*

Among various applications,[5–9] I would like to highlight our calculations[9] of a metastable dianion, C_2^{2-}. Neutral and anionic C_2 species play a role in combustion,[29] plasma,[30–32] and astrochemistry.[30,33] Fig. 3 shows potential energy curves of C_2^{2-} and C_2^-. The resonance, located 3.2 eV above the ground state of C_2^-, can decay into three channels. The norms of the corresponding Dyson orbitals (shown in Fig. 3) are close to one, indicative of one-electron process. Despite very similar shapes of the Dyson orbitals, the computed partial widths are vastly different because of the energy dependence of the outgoing wave.

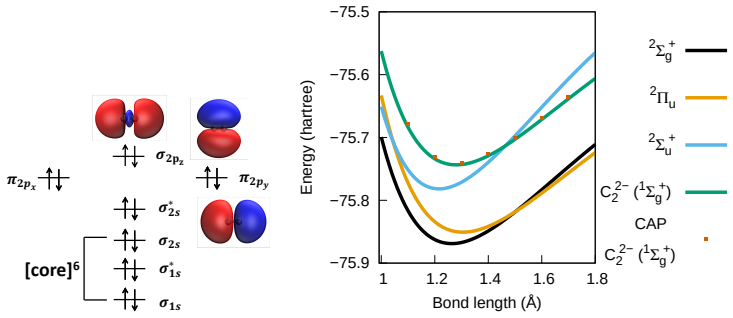

Figure 3: Left: Electronic configuration of C_2^{2-}. Electronic states of C_2^- are derived by removing electron from one of the three Dyson orbitals shown in the left panel. Computed partial widths for the 3 channels are: $\Gamma(^2\Sigma_g^+)$=0.21 eV, $\Gamma(^2\Pi_u)$=0.04 eV and $\Gamma(^2\Sigma_u^+) \sim 0$. Right: Potential energy curves of C_2^{2-} and C_2^- illustrating its resonance nature. *From Ref. 9*

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