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Boston University
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881 Commonwealth Avenue
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UU	UU	UU	UU		19b. TELEPHONE NUMBER: 626-316-9231

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as of 06-Jun-2022

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INVESTIGATOR(S):

Name: Ksenia Bravaya
Email: kbravaya@gmail.com
Phone Number: 6263169231
Principal: Y

Organization: **Boston University**
Address: Office of Sponsored Program, Boston, MA 022151300
Country: USA
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Submitted By: Ksenia Bravaya Email: kbravaya@gmail.com
Phone: (626) 316-9231
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STEM Degrees: 2 **STEM Participants:** 6

Major Goals: The major goal of the proposed research program was to develop new robust electronic structure theory methods exploiting non-Hermitian quantum mechanics approaches for describing energies and widths of the metastable electronic state, as well as to implement efficient methods for describing nuclear dynamics in metastable electronic states.

Complex absorbing potential (CAP) is one of the most commonly used non-Hermitian quantum mechanics method for evaluating resonance parameters in molecular systems. The proposed developments were aimed at address two remaining challenges associated with the method. The first is the high computational cost stemming from the need for multiple electronic structure calculations for evaluating a single electronic resonance energy and width: the resonance energy and width are identified as a real and imaginary part at the stationary point of the so-called eta-trajectory, a series of complex Siegert eigenvalues computed for different values of the CAP strength parameter, eta (eta-trajectory). The second remaining challenge is often cumbersome analysis of the eta-trajectory done to locate a stationary point as the trajectories often exhibit several stationary points or do not exhibit a well-pronounced stationary point. We propose several developments that address these challenges.

Metastable electronic states often are formed in the course of the chemical reaction, and, therefore, detailed understanding of the chemical conversions that proceed through metastable electronic states requires both information on the nuclear dynamics and on electronic decay, especially considering that often both processes occur on similar time-scale. To enable simulations of nuclear dynamics in metastable electronic states for realistic molecular systems we proposed to implement a classical model, where nuclear move on a real potential energy surface (determined by a real part of the complex Siegert energy), while the imaginary part of the energy determines the probability of electron ejection and decay to the target electronic state. To benchmark this model for problems with several degrees of freedom, we proposed to implement a wave-packet dynamics scheme on complex potential energy surfaces.

Accomplishments: Uploaded as a separate document.

Training Opportunities: The program included training of graduate students. Specifically, the program supported participation in the conferences for students working on the project. PI provided a feedback on students manuscripts, software, and presentations.

Results Dissemination: The developed software is distributed as open-source at GitHub platform under MIT license. The results have been published arXiv open-access service and three manuscripts are currently in preparation for submission for publication in peer-review journals.

Honors and Awards: The PI was a recipient of the 2020 Sloan Research Fellowship in Chemistry.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Melissa Burrows
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: James Gayvert
Person Months Worked: 13.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Elizabeth Karnaukh
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Alyssa Kranc
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Soubhik Mondal
Person Months Worked: 13.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Ruslan Tazhigulov
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Participant Type: PD/PI
Participant: Ksenia Bravaya
Person Months Worked: 3.00
Project Contribution:
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Funding Support:

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Partners

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I certify that the information in the report is complete and accurate:
Signature: Ksenia Bravaya
Signature Date: 5/20/22 3:10PM

Accomplishments under Goals

The main accomplishments under the goals include development of new models and software that enable robust characterization of metastable electronic states. The developed open-source software extends the functionality of bound state methods and software to metastable electronic states and is already being used by other research groups. Below we discuss the main developments and results in more details.

To address the computational cost and software/method availability challenges associated with characterization of metastable electronic states, we have developed OpenCap software [1] that extends the functionality of the bound state electronic structure methods to resonances. The method relies on projected complex absorbing potential (CAP) approach [2] that allows one to perform an electronic structure calculation once to generate the many-electron basis of states and evaluate the CAP matrix in that basis. The following step of calculation is to combine the electronic Hamiltonian and CAP matrices (for various strength) and diagonalize the resulting CAP-augmented Hamiltonian. Considering a small size of the many-electron basis (typically 10-20 states), the post-processing steps essentially do not contribute to the overall computational cost. Therefore, the entire eta-trajectory and resonance parameters are obtained at a cost of a single electronic structure calculation. The developed OpenCAP software evaluates the CAP matrix once the many-electron basis of states is generated with an external quantum chemistry software, computes eta-trajectory, and evaluates resonance parameters real and imaginary parts of the complex energy at the stationary point of the eta-trajectory.

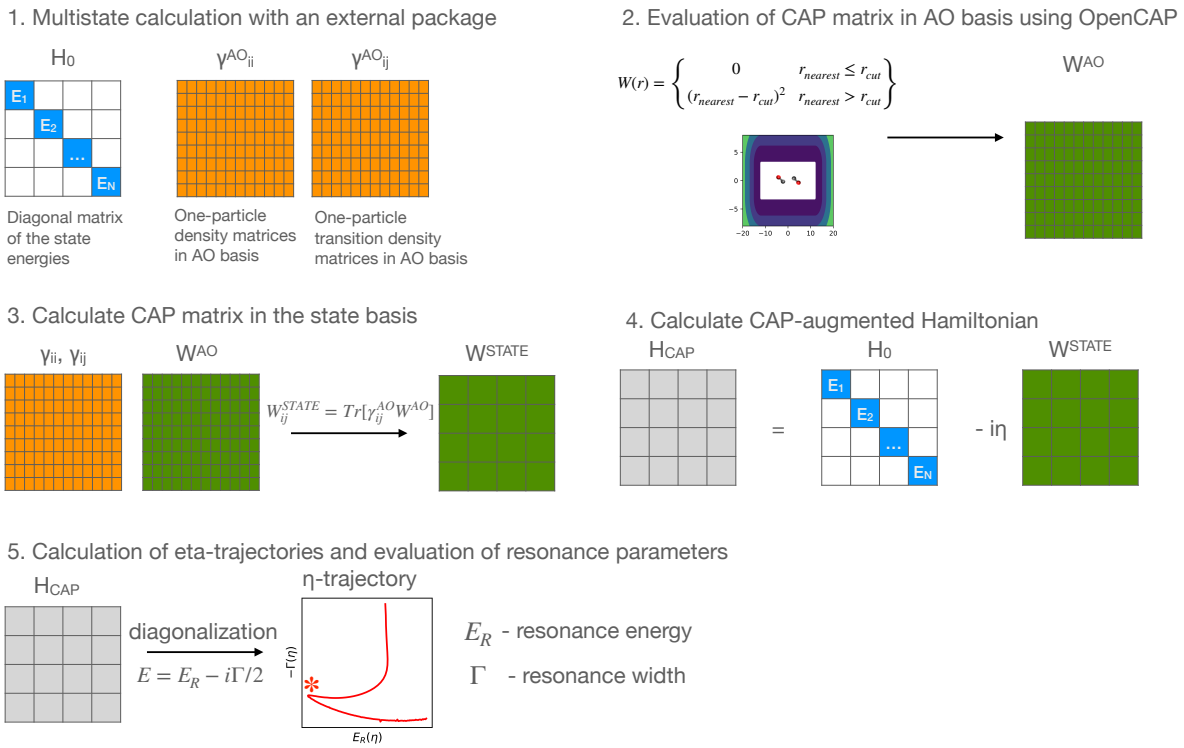

Figure 1. Workflow of OpenCAP calculation of resonance position and width.

Step 1. Calculation with bound-state method in external package (Molcas, Q-Chem, etc.) that generates the manifold of state energies (typically ~10-15), one particle density and transition density matrices in atomic orbital basis. **Step 2.** Calculation of the complex absorbing potential matrix in atomic orbital basis using OpenCap. Both Box and smooth Voronoi CAP are implemented. **Step 3.** Evaluation of complex absorbing potential matrix in the state basis. **Step 4.** Construction of the CAP-augmented Hamiltonian matrix. **Step 5.** Extracting resonance position and widths as complex eigenvalues of the so-called η-trajectories, dependencies of the eigenvalues on the CAP strength parameter, η.

The software has been interfaced with several commonly used electronic structure packages, such as Q-Chem, Psi4, and pyscf. These interfaces enable characterization of resonances with various electronic structure theory methods, including TDDFT, multireference perturbation theory, configuration interaction, and equation-of-motion coupled-cluster. The manuscript summarizing the results of this work is currently in preparation. The software is distributed as open source at GitHub (https://github.com/gayverjr/opencap). The workflow of the calculation is summarized in Fig. 1.

The reliance of CAP-based methods on computing and analyzing eta-trajectories (a series of Siegert eigenvalues as a function of the CAP strength parameter eta) is one of the disadvantage of CAP techniques as trajectories often exhibit multiple stationary points or are not well-stabilized (no pronounced stationary point). To address this challenge, we have proposed a scheme that avoids evaluation of the eta-trajectories altogether. The approach is based on Feshbach Projection theory and uses CAP to decouple localized part of the resonance from the discretized continuum states (arXiv:1906.11390). The approach has shown promising results for characterization of shape resonance in molecular systems [3].

Once the electronic structure tools for reliable and robust characterization of the energies and width of metastable electronic states are available, the next step is describing nuclear motion in metastable electronic states. We pursued two directions to describing nuclear dynamics in metastable electronic states. The first is wave-packet dynamics on complex potential energy surfaces. This approach allows one to capture quantum effects while is limited to systems with several degrees of freedom owing to the computational cost. Fig. 2 shows the computed vibrational excitation cross-sections for electron scattering on N_2. The potential energy surfaces for these calculations have been generated with XMS-CASPT2 method implemented in OpenMolcas and OpenCAP software. As one can see, the agreement between the theory and experiment is excellent. The manuscript based including these results is currently being prepared for publication. The main goal for implementing 1D and 2D wave-packet dynamics models was to obtain reference data for further benchmarking the classical approaches. The simulations with classical models for model systems as well as for molecular systems in metastable electronic states are currently underway.

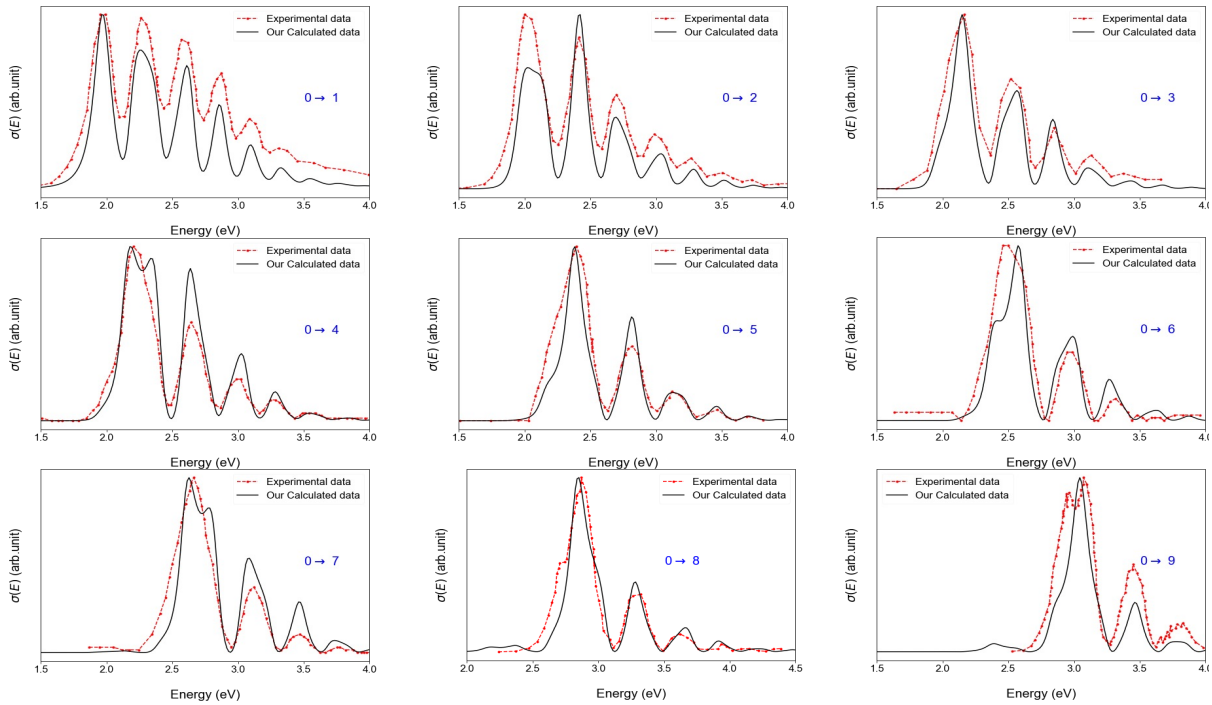

Figure 2. Computed vibrational excitation cross-section for N_2 electron scattering ($N_2(v_i=0)$ + e $\rightarrow$ N2- $\rightarrow$ $N_2(v_f)$ + e).

Overall, in the framework of this program we have developed new models and software that enable robust characterization of metastable electronic states.

1. https://github.com/gayverjr/opencap
2. M. Ehara and T. Sommerfeld, "CAP/SAC-CI method for calculating resonance states of metastable anions," Chem. Phys. Lett. 537, 107–112 (2012).
3. A.A. Kunitsa and K.B. Bravaya, "Feshbach projection XMCQDPT2 model for metastable electronic states" https://doi.org/10.48550/arXiv.1906.11390.