AFRL-AFOSR-VA-TR-2021-0093

Ab Initio Molecular Dynamics Above the Ionization Threshold

Benjamin Levine
MICHIGAN STATE UNIVERSITY
426 AUDITORIUM RD RM 2
EAST LANSING, MI, 48824
USA

08/04/2021
Final Technical Report

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
04-08-2021	Final	30 Sep 2017 - 29 Sep 2020

4. TITLE AND SUBTITLE
Ab Initio Molecular Dynamics Above the Ionization Threshold

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-17-1-0411

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
Benjamin Levine

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
MICHIGAN STATE UNIVERSITY
426 AUDITORIUM RD RM 2
EAST LANSING, MI 48824
USA

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St. Room 3112
Arlington, VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR RTB2

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-VA-TR-2021-0093

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
We developed theoretical methods aimed at modeling the nonadiabatic dynamics of molecules in dense manifolds of electronic states, with an eye toward modeling processes involving ionization that are of interest to AFOSR (e.g. endothermic dissociative recombination). In particular, we have developed two distinct methods: 1) We developed a time-dependent multireference configuration interaction singles to model the electronic dynamics of systems during ionization. 2) We developed the Ehrenfest molecular dynamics with collapse to a block method for modeling molecular
dynamics on many electronic states. Together, these methods enable accurate modeling of dynamics in dense manifolds of states.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			MICHAEL BERMAN
U	U	U	UU	6	**19b. TELEPHONE NUMBER** *(Include area code)* 426-7781

Standard Form 298 (Rev.8/98)
Prescribed by ANSI Std. Z39.18

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATE COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33315-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report. e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/ monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

1. Final Report

In this project, we developed theoretical methods aimed at modeling the nonadiabatic dynamics of molecules in dense manifolds of electronic states, with an eye toward modeling processes involving ionization that are of interest to AFOSR (e.g. endothermic dissociative recombination). In particular, we have developed two distinct methods:

1) We developed a time-dependent multireference configuration interaction singles (TD-MRCIS) method to model the electronic dynamics of systems during ionization.

2) We developed the Ehrenfest molecular dynamics with collapse to a block (TAB) method for modeling molecular dynamics on many electronic states.

Together, these new simulation methods will enable modeling the dynamics of systems with dense manifolds of electronic states, including those undergoing ionization, with greater accuracy than previously possible. During this project, we published three papers describing our work, including an Editors' Choice paper in the Journal of Chemical Physics.[1-3]

1.1. Development of TD-MRCIS

A precursor to the proposed TD-MRCIS code is a fast, GPU-accelerated time-dependent complete active space configuration intersection (TD-CASCI) code. In the initial stage of this project, we completed, tested, and published results from this code. The performance of our code is excellent. We can perform a 100 fs TD-CASCI calculation of decacene ($C_{42}H_{24}$), correlating 12-electrons in 12-orbitals (12/12), employing the 6-31G* basis, and using a 1 attosecond time step, in 20.1 hrs on a single NVidia K40 GPU. This is an unprecedentedly large calculation that can now be performed on routine desktop computer resources in less than a day.[3]

In addition, we have added single excitations to our TD-CASCI code, yielding a functioning TD-MRCIS code. In addition, this code has been optimized to run efficiently on GPU. Performance is excellent. Times for computation of a single $\boldsymbol{\sigma} = \mathbf{Hc}$ product are shown in Figure 1 for pentacene ($C_{22}H_{14}$) and decacene, using active spaces ranging from (4/4) on the left to (10/10) on the right. A single $\boldsymbol{\sigma} = \mathbf{Hc}$ product corresponds to the time to perform half a time step in our TD-MRCIS algorithm. Even pentacene with an 8/8 active space plus single excitations to the virtual space can be simulated for

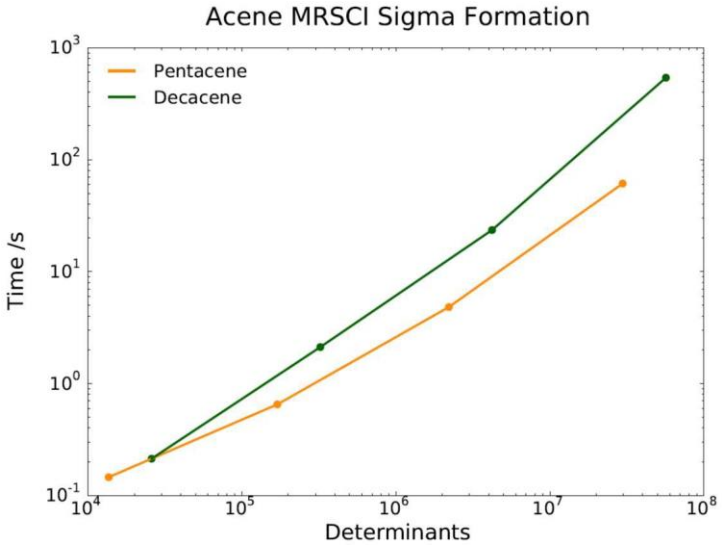

Figure 1. Times for a single MRCIS $\boldsymbol{\sigma} = \mathbf{Hc}$ build operation as a function of configuration space size, as described in the main text. A 6-31G* basis was used, and all virtual orbitals are included

100 fs in approximately one week on a single GPU.

We have extended the MRCIS algorithm to enable modeling ionization by adding complex absorbing potential (CAP). A CAP is a complex potential that is zero in the immediate vicinity of the molecule of interested, but is finite and imaginary in some surrounding region. Because it is non-Hermitian, the CAP annihilates population that reaches it, preventing the electron from leaving the immediate vicinity of the molecule. This widely used scheme enables us to model ionization processes (such as those involved in $Sm + O \rightarrow SmO^+ + e^-$). Our CAP code has been thoroughly tested and is ready for use.

We have tested the code in two contexts. We have used the TD-MRCIS code to model dynamics of molecules interacting with light. In addition to allowing ionization (when combined with a CAP and a large, molecule-centered basis), TD-MRCIS incorporates state-dependent orbital relaxation to first order. Thus, we expect it to provide a more accurate treatment of dynamics than TD-CASCI methods. Figure 2 shows a computed spectrum of Ag_4, with the lowest peaks in excellent agreement with time-independent calculations. In addition, utilizing the $\boldsymbol{\sigma} = \mathbf{Hc}$ code described above, we have been testing the ability of MRCIS to treat high excitations in a time-independent context. Combined with efficient geometry optimization schemes, we have identified pathways for Auger recombination in a small silicon clusters. Here, the singly-external determinants of the MRCIS ansatz enable the description of high-lying single excitations essential to the process.

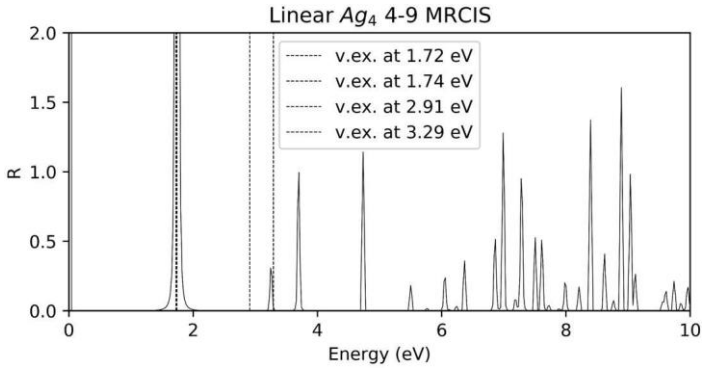

Figure 2. Electronic absorption spectrum of linear Ag_4 computed at the MRCIS level, with the field polarized along the linear axis of the molcule. The results of time-independent calculations (regardless of polarization) are shown by vertical dashed lines.

1.2. Development of Nonadiabatic Molecular Dynamics Method for Many Electronic States

As mentioned above, our goal is to develop a nonadiabatic molecular dynamics method that, unlike existing methods, accurately incorporates decoherence effects without complete knowledge of the electronic eigenspectrum. This enables more accurate modeling of nonadiabatic dynamics in dense manifolds of states than is currently possible. Our work in this direction focused on three related goals:

a) Defining and testing a stochastic procedure for modeling decoherence as a sudden change in the electronic wave function (that is, as a wave function collapse).

b) Defining and testing the decoherence time to be used in this procedure.

c) Defining and testing a scheme for approximating the electronic eigenspectrum from time-dependent wave function data (to be obtained by TD-MRCIS).

In our original plan, we intended to utilize existing definitions from the literature for a) and b). However, during the first year of support we carefully tested these definitions and found that they behave pathologically in some cases. In response, we have developed more promising strategies.

We found that the most widely employed stochastic procedures for collapse of the Ehrenfest wave function (here collectively referred to as "collapse to a state" or TAS methods), which are based on the collapse of the entire wave function into a single eigenstate, exhibits pathological behavior when applied to systems where more than two electronic states are populated.[2] Specifically, they incorrectly predict fast decoherence between pairs of parallel states (which should, in principle, remain coherent forever) when a third non-parallel state is populated. In reality, the rate of decoherence between any pair of parallel states should be independent of the existence of additional states. To correct this systematic and qualitative error, we devised a solution which we called independent pairwise stochastic collapse (IPSD).[2] In this procedure, the electronic wave function collapses to a carefully defined linear combination of eigenstates rather than a single eigenstate.

In order to thoroughly test IPSD, we first developed a series of one-dimensional models.[2] These models mimic dynamics on states with three or more differently sloped PESs. These models have usefulness outside of our own tests, as many methods (including trajectory surface hopping and decoherence-corrected Ehrenfest methods) share the flaws of CAS and IPSD, to varying degrees.

Upon application to this series of models, IPSD was found to be deficient.[2] Specifically, in cases involving dynamics on several electronic states with very different potential energy surfaces (pertinent to ionization), the pairwise collapse approach resulted in a pathological overestimation of some decoherence rates.

In response, we developed a new method we call Ehrenfest dynamics with collapse *to a block* (TAB), which is inspired by the same ideas as pairwise collapse, but more thoughtfully constructed. TAB correctly describes the loss of coherence following a nonadiabatic transition between electronic states. This

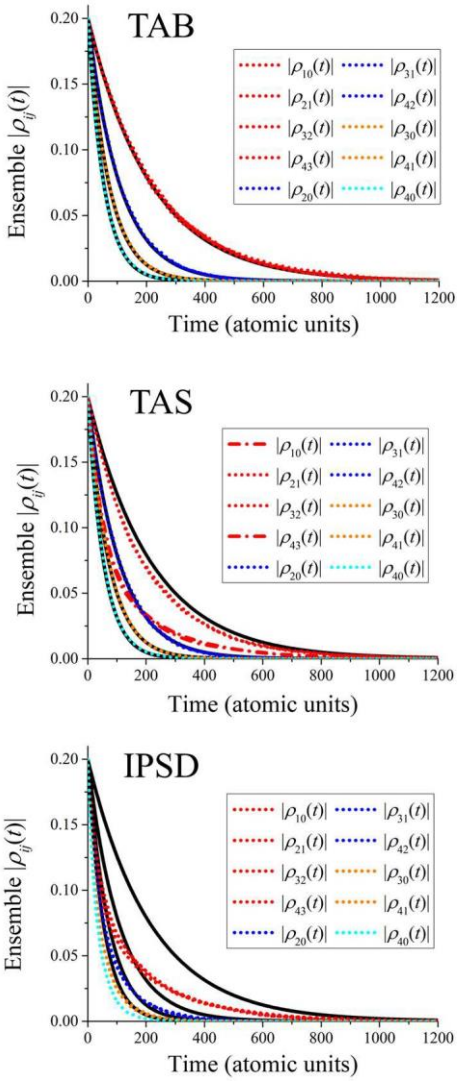

Figure 3. Time dependent coherences (colored lines) compared to reference exact decays (black).

can be seen in Figure 3, which presents the state pairwise coherences as a function of time for a simple model of non-parallel PESs.

Having identified a decoherence-corrected Ehrenfest molecular dynamics scheme that accurately describes coherence loss in systems with more than two electronic states, we turned our attention to adapting this method to operate on many electronic states, where we define "many electronic states" to mean "more states than we can reasonably compute PESs for at every time step." To this end, we employ the history of our time-dependent electronic wave function to build a restricted basis in which to compute approximate electronic eigenstates. Our basis spans a Krylov-like subspace created by operating the Hamiltonian on the present wavefunction. As such, it provides a reasonably efficient description of the occupied electronic states.[1]

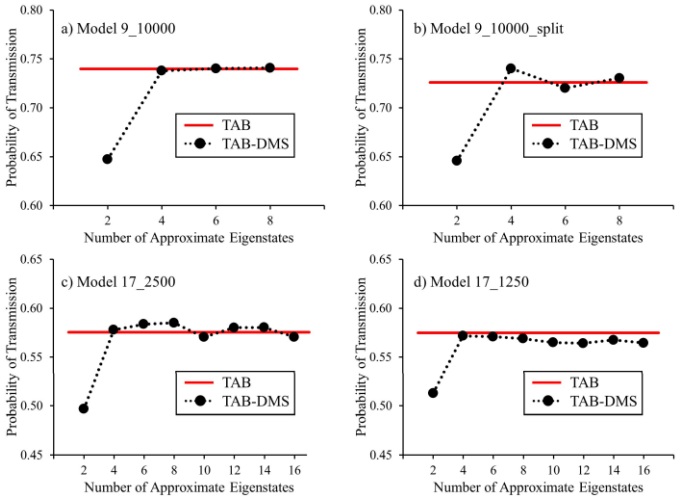

Figure 4. The convergence of transmission probabilities of TAB-DMS simulations to the exact TAB limit, as a function of number of approximate eigenstates. Panels a-d correspond to four different models, described in ref [1].

We have shown the resulting method (TAB in dense manifolds of states, or TAB-DMS) to provide an accurate description of the transmission of population through one or more dense bands of parallel PESs in a series of one-dimensional models.[1] This approach is systematically improvable to the exact TAB limit by increasing the number of exact eigenstates. Figure 4 shows that, for a series of models with differing densities of states, the transmission probabilities converge rapidly with increasing number of approximate eigenstates.

1.3. Impact

The above reflects several important steps towards the efficient and accurate first principles simulation of the nonadiabatic dynamics of molecules in dense manifolds of electronic states. Specifically, we have:

a) developed an efficient algorithm for propagating CI wave functions in large configuration spaces using a direct CI strategy,

b) developed the TAB method, which (to the best of our knowledge) is the first nonadiabatic molecular dynamics method that provides a proper treatment of the state pairwise coherences between populations on more than two electronic states, and

c) developed the TAB-DMS method, an extension to TAB that can accurately describe nonadiabatic molecular dynamics in systems where the sheer number of electronic states renders the calculation of all PESs at all points in time impossible.

1.4. References

(1) Esch, M. P.; Levine, B. G. Decoherence-corrected Ehrenfest molecular dynamics on many electronic states. *Journal of Chemical Physics* **2020**, *153*, 11, 114104. http://dx.doi.org/10.1063/5.0022529

(2) Esch, M. P.; Levine, B. G. State-pairwise decoherence times for nonadiabatic dynamics on more than two electronic states. *Journal of Chemical Physics* **2020**, *152*, 9. http://dx.doi.org/10.1063/5.0010081

(3) Peng, W. T.; Fales, B. S.; Levine, B. G. Simulating Electron Dynamics of Complex Molecules with Time-Dependent Complete Active Space Configuration Interaction. *Journal of Chemical Theory and Computation* **2018**, *14*, 4129. http://dx.doi.org/10.1021/acs.jctc.8b00381

Response Summary:

If you have any questions, please contact your Program Officer.

Air Force Office of Scientific Research
875 N Randolph Street
Suite 325 Room 3112
Arlington, VA 22203

**All material posted to this site should be ready for public release. If you feel your material is not ready for public release, please work directly with your Program Officer to submit your report via email.

Q1. Award Number (Federal Award Identification Number XXXXXX-XX-X-XXXX)
FA9550-17-1-0411

Q3. Report Type

- Final Performance

Q4. Principal Investigator
Benjamin G. Levine

Q5. Principal Investigator Email
ben.levine@stonybrook.edu

Q6. Principal Investigator Phone
631-632-2381

Q7. Project Title
Ab Initio Molecular Dynamics above the Ionization Threshold

Q8. Recipient Organization
Michigan State University

Q310. Business Office Email
Proposalteam2@osp.msu.edu

Q9. Report Due Date
12/30/2020

Q10. Report Period Start Date
10/01/2017

Q11. Report Period End Date
09/30/2020

Q297. Current Program Officer
Michael Berman

Q298. Please list any other Co-Program Officers (if applicable)
N/A

Q395. Please confirm the report type you are submitting is: Final Performance

- Yes, that is correct.

Q12. Is this survey being submitted by someone other than the Principal Investigator?

- No

Q407. How many participants worked on the grant during this period of performance?
This number includes all PIs and each person who worked, and was funded by the project during this reporting period.

You will be asked to provide the following information for: (1) PDs/PIs; and (2) each person who worked, and was funded by the project, during this reporting period. Please note that such reporting does not constitute a formal institutional report of effort on the project, but rather is used by agency program staff to evaluate the progress of the project during a given reporting period.
(Max 20 participants)
7

Q401#1. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- Name

	Last Name, First Name
Participant 1	Esch, Michael
Participant 2	Peng, Wei-Tao
Participant 3	Fales, Brian Scott
Participant 4	Liang, Fangchun
Participant 5	Durden, Andrew
Participant 6	Humphries, Kathryn
Participant 7	Levine, Benjamin
Participant 8	N/A
Participant 9	N/A
Participant 10	N/A
Participant 11	N/A
Participant 12	N/A
Participant 13	N/A
Participant 14	N/A
Participant 15	N/A
Participant 16	N/A
Participant 17	N/A
Participant 18	N/A
Participant 19	N/A
Participant 20	N/A

Q401#2. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- Months Worked

	#
Participant 1	24
Participant 2	24
Participant 3	12
Participant 4	3
Participant 5	3
Participant 6	3
Participant 7	1.5
Participant 8	N/A
Participant 9	N/A
Participant 10	N/A
Participant 11	N/A
Participant 12	N/A
Participant 13	N/A
Participant 14	N/A
Participant 15	N/A
Participant 16	N/A
Participant 17	N/A
Participant 18	N/A
Participant 19	N/A
Participant 20	N/A

Q401#3. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- Describe briefly how this person contributed to the project

Participant 1	Primary developer of the TAB and TAB-DMS methods, manuscript preparation
Participant 2	Primary developer of TD-CASCI, manuscript preparation
Participant 3	Primary developer of MRCIS
Participant 4	Aided in development of TAB/TAB-DMS
Participant 5	Aided in development of TD-CASCI/TD-MRCIS
Participant 6	Aided in application work
Participant 7	Oversaw project, manuscript preparation, aided in software development
Participant 8	N/A
Participant 9	N/A
Participant 10	N/A
Participant 11	N/A
Participant 12	N/A
Participant 13	N/A
Participant 14	N/A
Participant 15	N/A
Participant 16	N/A
Participant 17	N/A
Participant 18	N/A
Participant 19	N/A
Participant 20	N/A

Q401#4. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- Project Role

Participant 1	Grad Student (Research Assistant)
Participant 2	Grad Student (Research Assistant)
Participant 3	Grad Student (Research Assistant)
Participant 4	Grad Student (Research Assistant)
Participant 5	Grad Student (Research Assistant)
Participant 6	Non-Student Research Assistant
Participant 7	Principal Investigator

Q401#5. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- International Business during Reporting Period. 1) Did the individual collaborate with individuals located in a foreign country? 2) Did this individual travel to a foreign country as part of the collaboration?
N/A

Q401#6. Please answer the following for each participant.
(Currently our system has a maximum allowable entry of 20 participants)
- Add'l Funding Source(s)

Participant 1	Yes
Participant 2	Yes
Participant 3	No
Participant 4	No
Participant 5	No
Participant 6	No
Participant 7	No

Q403. Please confirm whether any of your participants had any international business associated with this grant during this reporting period.
(If you input any information on the above International Business question, you should select yes.)

- No, none of the participants had international business

Q412. Abstract

Please submit your report abstract below.

We developed theoretical methods aimed at modeling the nonadiabatic dynamics of molecules in dense manifolds of electronic states, with an eye toward modeling processes involving ionization that are of interest to AFOSR (e.g. endothermic dissociative recombination). In particular, we have developed two distinct methods: 1) We developed a time-dependent multireference configuration interaction singles to model the electronic dynamics of systems during ionization. 2) We developed the Ehrenfest molecular dynamics with collapse to a block method for modeling molecular dynamics on many electronic states. Together, these methods enable accurate modeling of dynamics in dense manifolds of states.

Q413. Distribution Statement

-Please verify that the report you are about to upload is cleared for public release.
-In order to upload a PDF, your report must be publicly releasable.
-Please click the YES radio button below to confirm that your report is publicly releasable, then you will be able to upload a PDF copy of your report.
-You are allowed to upload one report document. If you need to change the file upload, re-click the submission box and select your correct file upload.

- Yes- Approved for Public Release

Q414. Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 100MB.

NOTE: Once you submit this survey below, you will NOT be able to go back and make changes.
[Click here]

Q353. Archival Publications (published) during reporting period: State "Nothing to Report" if nothing to report

(1) Esch, M. P.; Levine, B. G. Decoherence-corrected Ehrenfest molecular dynamics on many electronic states. Journal of Chemical Physics 2020, 153, 11, 114104. http://dx.doi.org/10.1063/5.0022529
(2) Esch, M. P.; Levine, B. G. State-pairwise decoherence times for nonadiabatic dynamics on more than two electronic states. Journal of Chemical Physics 2020, 152, 9. http://dx.doi.org/10.1063/5.0010081
(3) Peng, W. T.; Fales, B. S.; Levine, B. G. Simulating Electron Dynamics of Complex Molecules with Time-Dependent Complete Active Space Configuration Interaction. Journal of Chemical Theory and Computation 2018, 14, 4129. http://dx.doi.org/10.1021/acs.jctc.8b00381

Q354. New discoveries, inventions, or patent disclosures to report for this period? This question is required.

- No

Q355. Changes in research objectives (if any):

N/A

Q356. Change in AFOSR Program Officer, if any:

N/A

Q357. Extensions granted or milestones slipped, if any:

N/A

You are about to submit your AFOSR deliverable report. Please use the back button if you would like to review your submission before formally submitting your AFOSR deliverable report.

Embedded Data:

Date Stamp	6/1/2021