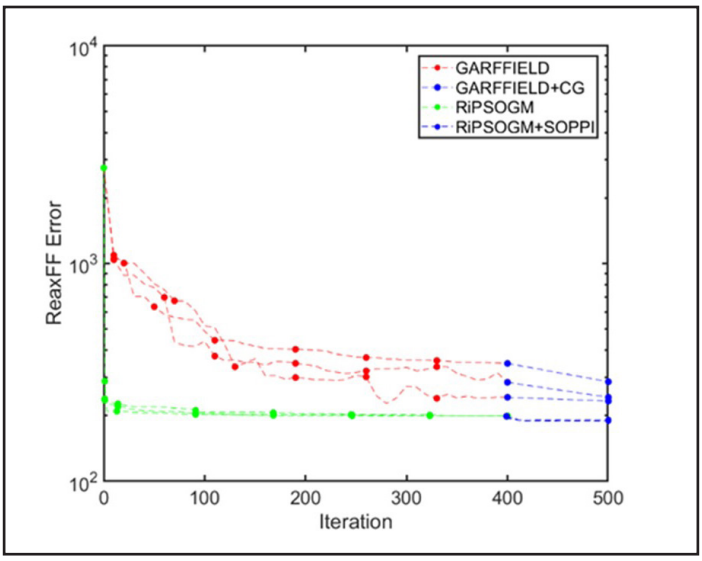

Figure 6: Comparison of our global optimization performance and the genetic algorithm based code GARFFIELD with and without a conjugate-gradient (CG) minimization. Population size in both methods is 20 agents. For each algorithm, three independent runs were performed. The y-axis is a log scale and the dots are a guide to the eye.

B. State of the Art and Technical Approach

The theoretical studies reported use mainly two methods: quantum chemical (QC) calculations and reactive molecular dynamics (RMD). These methodologies are constantly being developed and can be implemented using either commercial (QC) or open source (RMD) codes. For the QC calculations, we primarily used the Gaussian 09 commercial code [1]. In most of the implementations in this project, we employed DFT level theory with various functionals and basis sets that are suitable for the problem studied. We did comparative studies using different functionals.

In the case of RMS simulations, considerable methodological development was required. In all our studies the open source code LAMMPS was used [2]. Here, one has in many cases, to develop new implementation methodologies or force fields that are suitable to investigate the problem in question. A number of such new methodologies were developed by us during this project. Some of these were already described above:

- A method to calculate THz spectra of molecular crystals was developed by us and its implementation to TATP and RDX were published [3];
- A simple scheme that allowed us to obtain the C-J state of explosive materials rapidly and using relatively small systems was applied in the study of nanometer vacancies in ETN [4] and is also implemented in the study of liquid explosives; and
- Two new reactive force fields were developed in this project, one for the HN_3 system [5] and the other for ETN [4, 6]. In addition to these, we have developed a new code for the efficient analysis of RMD data. This approach is based on graph theory and allows us to search the LAMMPS output to identify the species at any given moment of the simulation.

At described above, recently we developed a new approach that allows for an efficient construction of reactive force fields. The development of ReaxFF for new systems constitutes two stages: 1) QC calculations of geometries, and energies of a large number of reactant configurations, intermediates, bi- and tri-molecular processes, etc; and 2) using this data baseto train an accurate ReaxFF, namely, to obtain the parameters that reproduce accurately the QC data. This stage, in most cases, used to be extremely complex and involved a very long development period. Our new approach is based on the use of population to search parameter space to obtain the global minimum. The search is based on the Particle Swarm Optimization (PSO) algorithm with a

number of improvements that markedly reduce search time and increase the probability to locate the lowest minimum.

As far as we know, we were the only group of researchers at ALERT that performs theoretical studies as those described here.

C. Major Contributions

The major contributions of this project to date include:

- Year 5:
  - Summary of the detonation properties of liquid mixtures between nitromethane and four different liquid additives (acetone, ethyleamine, methanol, and hydrogenperoxide).
  - Decomposition pathways of mixtures of H_2O_2 with urea and with erythritol.
  - Development of a new, accurate, and efficient method to search for optimal ReaxFF parameters to accurately reproduce DFT data.
- Year 4:
  - New ReaxFF parametrization for solid Erythritol tetranitrate (ETN).
  - Detonation properties of liquid mixtures.
- Year 3:
  - The role of nano-size defects simulation using a new methodology.
  - Deciphering the mechanism of laser induced ejection of molecules.
- Year 2:
  - New ReaxFF parametrization for liquid HN_3.
  - Determining the decomposition routes of HMTD for safe disposal.
- Year 1:
  - Explosive detection using 2D THz Spectroscopy.
  - Characterization of TNT detonation mechanism: bimolecular pathway.

D. Milestones

- RMD simulations of mixtures of nitromethane with four different additives: acetone, ethanolamine, methanol, and H_2O_2 were completed. Presently, we are analyzing the data with the aim to publish a paper.
- The construction of a new reactive force field for TNT was completed in Year 4. The main improvement to the existing force field is a better treatment of hydrogen bonding and dispersion forces. This improved the equilibrium density of the bulk TNT.
- The QC calculations regarding the stability, energy barrier for decomposition, and thermal decomposition pathway to obtain stable products of the three nitrified sugars were completed. The results were transferred to the experimental group of Dr. Oxley for comparison with experimental data.
- First stage of QC calculations of reactions in mixtures of H_2O_2 with urea and with erythritol were completed. The results show that in both cases, existence of enough hydrogen peroxide leads to reduced energy barriers for initial decomposition of the "fuel" molecules. These results are being substantiated at

present using more accurate calculations (i.e. using larger basis sets).

- We have not yet started the simulations of potassium chlorate mixture with wax. The study of this system will start once the calculations of H_2O_2 mixtures will end.
- The influence of nano-Al particles' addition on detonation characteristics of some of the HMEs has not started yet.
- A new efficient global search method was developed and implemented to obtain ReaxFF parameters for new systems to be used. The new approach was applied to the addition of dispersive forces to the force field for HN_3 developed by us earlier. The new force field allows to reproduce the very large difference (about 30%) between solid and liquid HN_3. The new ReaxFF is being used at present to understand the origin of this anomalous density difference.

E. Future Plans (Year 6)

As a result of the ALERT Biennial Review conducted in March of 2018, this project has been concluded and will not be funded in Year 6. As much as possible, we will complete the investigations currently in progress with the following specific objectives:

- Past Year 5, additional time and resources will be required to complete the planned study of the different improvised explosives. In particular, RMD simulations of hydrogen peroxide mixtures with urea and with sugar will be performed. These simulations will focus on the sensitivity and detonation mechanism of these mixtures.
- Our goal is to be able to simulate and predict the explosive characteristics of all improvised explosives and simulate spectroscopic characteristics for remote detection from first principles. These type of simulations require appropriate force fields. The new global optimization method we developed will allow efficient and accurate parametrization of ReaxFF for different systems. The new optimization method was already applied to improve the ReaxFF parametrization of the HN_3 system. The improvement consist of proper addition of dispersion forces and hydrogen bonding to the ReaxFF. This addition will allow to calculate accurately the vibrational characteristics of liquid and solid HN_3.
- In addition to the QC calculations related to mixtures of H_2O_2 with urea and with erythritol, we also plan to carry out RMD simulations of these systems. Reactive molecular dynamics study of oxidizer-fuel mixtures will allow for greater understanding of the sensitivity, thermodynamics, and kinetics of the detonation of these mixtures.
- We plan to initiate the study of hydrogen azide as the first member of a new family of potential improvised explosives.
- During the last 3-4 years, we studied different families of improvised explosives (i.e. peroxides, liquids, mixture of oxidizers, and fuels). The theoretical study accompanied the experimental investigation by the research group of Dr. Oxley at the University of Rhode Island. We propose that the two groups will compose a comprehensive overview of improvised explosives. This review will serve the Department of Homeland Security as a technical guide to these systems.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

1. One of the main challenges in dealing with the threat of terror is the appearance of unknown im-

provised explosives. There is a need for rapid assessment of the yield, sensitivity, and safe disposal of these explosives. In addition, procedures for detection, specifically, remote detection if possible, are needed. We suggest using computational methods as a first rapid response to these threats. We have the capability to supply such data without having to synthesize the hazardous material, which is time consuming and dangerous.

2. Our immediate goal is to advance our computational methods to address the potential hazard of explosive liquid mixtures. Currently, these liquids are hard to detect and their explosive properties are difficult to predict.

B. Potential for Transition

As a theory group, our task is to develop simulation and computational tools to be used as a base for rational design. Our tools will support experimental efforts. Our end-users are researchers, government agencies, and companies involved in security.

Computer simulations are, in most cases, the fast lane for the evaluation of unknown improvised explosives and compositions (IECs). QC and RMD calculations can identify fundamental properties, such as the detonation mechanism and yield of new materials. Experimental studies are time consuming, expensive, and potentially dangerous. Specifically, the results of the theoretical research described above can be used to guide and focus experimental efforts to synthesize, characterize, and detect materials such as IECs. For example, we have collaborated with R1 Thrust Leader, Dr. Oxley and her colleagues to validate the mechanisms of synthesis and degradation of new explosives by combining simulations and experiments.

C. Data and/or IP Acquisition Strategy

The datasets developed for modeling will be put in public domain as supplemental material.

D. Transition Pathway

Computer simulations are essential for rapid response to unknown improvised explosives. Such simulations can identify fundamental properties, such as the detonation mechanism and yield of new materials. Experimental studies are time consuming, expensive, and dangerous. Specifically, the computational results can be used to guide and focus experimental efforts to characterize materials such as HMEs. The direct outcome will be potential parameters which can be used with standard simulation platforms such as LAMPS.

E. Customer Connections

The connections to DHS, TSL, and TSA are strong. To date, the FBI is the major agency outside of DHS, which is aware of the details of this project.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Peer Reviewed Journal Articles

1. Fisher, D., Zach, R., Matana, Y., Elia, P., Shustack, S., Yarden, S., & Zeiri, Y. “Bomb Swab: Can Trace Explosive Particles Detection Be Improved?” Talanta, *174*, 1 November 2017, pp. 92–99. DOI: 10.1016/j.talanta.2017.05.085
2. Oxley, J.C., Furman, D., Brown, A.C., Dubnikova, F., Smith, J.L., Kosloff, R., & Zeiri, Y. “Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental and Computational Study.” *Journal of Physical Chemistry C*, *121(30)*, 6 July 2017, pp. 16145-16157. DOI: 10.1021/acs.jpcc.7b04668

3. Kalson, N.H., Furman, D., & Zeiri, Y. "Cavitation-Induced Synthesis of Biogenic Molecules on Primordial Earth." *ACS Cent. Sci., 3*(9), 11 September 2017, pp. 1041-1049. DOI: 10.1021/acscentsci.7b00325

Pending-

1. Furman, D., Carmeli, B., Zeiri, Y., & Kosloff, R. "Enhanced Particle Swarm Optimization Algorithm: Efficient Training of ReaxFF Reactive Force Fields." *Journal of Chemical Theory and Computation*. In press.

B. Conference Proceedings

1. Kosloff, R., Zeiri, Y., & Furman, D. "Molecular Dynamical Simulations of Energetic Materials: Mechanism, THz Spectroscopy and Laser Ablation." *The 83rd Annual Meeting of the Israel Chemical Society*, Tel Aviv, Israel, February 13-14, 2018.

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[1] Frisch, M. J.; Trucks, G. W.; et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
[2] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, J Comp Phys, 117, 1-19 (1995).
[3] G. Katz, S. Zybin, W. A. Goddard III, Y. Zeiri, and R. Kosloff. "Direct MD Simulations of Terahertz Absorption and 2-D Spectroscopy Applied to Explosive Crystals." J. Phys. Chem. Lett., 5, 772 (2014).
[4] David Furman, Ronnie Kosloff, and Yehuda Zeiri. "Effects of Nanoscale Heterogeneities on the Reactivity of Shocked Erythritol Tetranitrate." J. Phys. Chem. C, in press.
[5] David Furman, Faina Dubnikova, Adri C.T. van Duin, Yehuda Zeiri and Ronnie Kosloff. "Reactive Force Field for Liquid Hydrazoic Acid with Applications to Detonation Chemistry." J. Phys. Chem. C, (2016), 120, 4744-4752.
[6] Jimmie C. Oxley, David Furman, Austin C. Brown, Faina Dubnikova, James L. Smith, Ronnie Kosloff, and Yehuda Zeiri. "Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental and Computational Study." J. Phys. Chem. C, submitted for publication.

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