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5a. CONTRACT NUMBER W911NF-04-1-0243
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER 4D10S7
5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

6. AUTHORS David N. Beratan, Weitao Yang, Michael J. Therien, Koen Clays

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Duke University
Office of Research Support
Duke University
Durham, NC 27705

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The aim of this project was to develop inverse design methods capable of designing optimized molecular species and materials. The project involved the development of continuous, integer, and hybrid molecular optimization methods that allow the identification of optimal target species. A component of this project involves the synthesis and characterization of these candidate materials. The target property in this project is the nonlinear optical response of organic species. The outcome of this project was a suite of methods useful for the design and

15. SUBJECT TERMS
inverse design, nonlinear optics, optimization, molecular design, structure-function relations

16. SECURITY CLASSIFICATION OF:
a. REPORT UU
b. ABSTRACT UU
c. THIS PAGE UU

17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON David Beratan
19b. TELEPHONE NUMBER 919-660-1526
The aim of this project was to develop inverse design methods capable of designing optimized molecular species and materials. The project involved the development of continuous, integer, and hybrid molecular optimization methods that allow the identification of optimal target species. A component of this project involves the synthesis and characterization of these candidate materials. The target property in this project is the nonlinear optical response of organic species. The outcome of this project was a suite of methods useful for the design and optimization of molecular materials.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)


(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)


Number of Papers published in non peer-reviewed journals: 1.00

(c) Presentations

XIANGQIAN HU
Oct. 2009, Hong Kong University.

DAVID BERATAN
University of North Carolina - Chapel Hill, 1/09

MICHAEL THERIEN
National American Chemical Society Meeting, Philadelphia, August 18th, 2008.
Department of Chemistry, University of Leuven, Leuven, BELGIUM, October 20th, 2008.
University of Hasselt, Hasselt, BELGIUM, November 6th, 2008.
University of Hasselt, Hasselt, BELGIUM, November 20th, 2008.

Number of Presentations: 8.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

“Methods and systems for selecting molecular structures,” provisional patent application, submitted 2/16/07; patent filed 6/12/08.

Patents Awarded

Graduate Students
### Names of Post Doctorates

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<tr>
<td>Xiangqian Hu</td>
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<td>Paula Mori-Sanchez</td>
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<td>Aron Cohen</td>
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<td>Shahar Keinan</td>
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<td>Ravindra Venkatramani</td>
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<td>Mingliang Wang</td>
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<td>Inge Asselberghs</td>
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**FTE Equivalent:** 2.41  
**Total Number:** 9

### Names of Faculty Supported

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<tr>
<td>David Beratan</td>
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<td>No</td>
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<tr>
<td>Weitao Yang</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Michael Therien</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Donald Rose</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Koen Clays</td>
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**FTE Equivalent:** 5  
**Total Number:** 5

### Names of Under Graduate students supported

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**FTE Equivalent:**  
**Total Number:**
**Student Metrics**
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ...... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: ...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: ...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: ...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... 0.00

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### Names of Personnel receiving masters degrees

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### Names of personnel receiving PHDs

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<tr>
<td>Dequan Xiao</td>
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<td>Timothy Heaton-Burgess</td>
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### Names of other research staff

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<tr>
<td>Cecilia Eichenberger</td>
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<td>Michael Peterson</td>
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Sub Contractors (DD882)
hyper-Rayleigh scattering characterization of nonlinear optical materials

Inventions (DD882)
Statement of the problem studied.
This project, supported from 2004 to 2009, aimed at developing theoretical tools to assist in the design of real optimal molecular structures and materials. That is, the project combined state of art quantum chemical methods with newly developed approaches to property optimization in order to establish an “inverse design” framework for designing optimal molecular structures. The majority of the research was theoretical in nature and was performed at Duke University. A limited investment was made in synthetic methodology and in the development of state-of-art characterization methods (through collaborations with the Therien and Clays groups). Our targeted property was the molecular first hyperpolarizability, known as $\beta$.

Summary of the most important results and Bibliography
Our progress on the theoretical front was particularly noteworthy. In this final report, we present a chronological summary of our project, emphasizing our key developments and discoveries in the context of our published contributions:

2006

Our first, and perhaps our key contribution, was to establish a new theoretical methodology to map the challenge of discrete chemical optimization onto a problem of continuous optimization. This was accomplished with our “linear combination of atomic potentials” (LCAP) approach, described in a 2006 Journal of the American Chemical Society publication. To date, this paper has been cited 37 times, and it was highlighted in numerous periodicals. This contribution defined the core continuous optimization approach used in much of the project.

2007

In 2007, we expanded the LCAP approach to semiempirical electronic structure methods, allowing the exploration of much larger molecular spaces. This paper also provided the first exploration of mixed discrete optimization methods with property gradient guided approaches.

2008
- S. Keinan, W.D. Paquette, J.J. Skoko, D.N. Beratan, W. Yang, S. Shinde, P.A. Johnston, J.S. Lazo, and P. Wipf, “Computational design, synthesis and biological evaluation of


2008 saw a considerable expansion of our optimization approach into property gradient biased Monte Carlo methods, providing a marriage between our continuous (property derivative LCAP) methods and discrete optimization. We also provided quantitative benchmarks among discrete, continuous, and hybrid optimization methods in 2008. This year also saw the synthetic program come on line, and we began to perform the optimization of realistic families of nonlinear optical chromophores that were found to have predicted order of magnitude property enhancements compared to prior benchmark structures. We also showed that our methods could explore molecular spaces of astronomical size when the chemical species are closely related structurally.

2009


2009 saw continued development of gradient-guided Monte Carlo optimization approaches, broadening the applicability of our methodology.

2010


Finally, studies of 2009-10 established firm links between our optimization approach and experiment. Perhaps the most exciting development in our formalism was a Thomas-Kuhn sum
rule method that predicts the frequency dispersion of $\beta$ based purely on experimental linear spectroscopy and a limited number of $\beta$ values at specific frequencies. This could prove a breakthrough, as chromophore design will be of the greatest utility when it can address design as specific telecom wavelengths. In addition, we performed molecular optimization in specific rich “structural subspaces” that can be accessed by our experimental collaborators. Indeed, the predicted structures discovered in the computations are expected to produce order of magnitude enhancements of molecular hyperpolarizabilities above those accessible in currently existing structures.