Computational Studies *of* New Materials II

**From Ultrafast Processes and Nanostructures to
Optoelectronics, Energy Storage and Nanomedicine**

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From Ultrafast Processes and Nanostructures to
Optoelectronics, Energy Storage and Nanomedicine

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COMPUTATIONAL STUDIES OF NEW MATERIALS II From Ultrafast Processes and Nanostructures to Optoelectronics, Energy Storage and Nanomedicine

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Preface

In 1999 at the request of World Scientific, Daniel Jelski and Thomas F. George edited a book entitled *Computational Studies of New Materials* consisting of fourteen chapters written by leading experts on topics including fullerenes, semiconductors, fractals, polymers and nonlinear optical processes. In 2008, Dr. Zvi Ruder, senior executive editor at World Scientific, approached us about editing a sequel, or second volume. We agreed to this venture with two additional editors — Renat R. Letfullin and Guoping Zhang — and decided upon the title *Computational Studies of New Materials II*.

While the 1999 book was quite timely when it was published, much has evolved during the past decade in the development of new materials and appropriate computational techniques, especially with the “explosion” of interest and activity in nanoscience and nanotechnology. It is worth noting that the stage was set for this from a federal perspective when in 1999 US President Bill Clinton’s science advisor, Neal Lane, rated nanotechnology as one of the government’s 11 inter-agency R&D priorities for the purpose of planning the FY 2001 budget.^a

Nanomaterials, i.e., materials with dimensions on the scale of a nanometer, play a prominent role in this current 2010 book. This includes ultrafast processes stimulated by short laser pulses, such as in connection with fullerenes, and the exciting field of nanomedicine, such as selective laser cancer therapy using gold nanospheres and nanorods. Topics in addition to nanomaterials include energy storage and optoelectronics, such as in connection with polymeric light-emitting

^a *OE Reports*, Number **188** (Society of Photo-Optical Instrumentation Engineers, August 1999).

diodes, semiconductor quantum wells, and tailored negative-index metamaterials and microdevices.

We ourselves have authored a number of the chapters and have invited various outstanding scientists throughout the world to serve as chapter authors. We are most impressed by the extremely high caliber of research and its presentation in the chapters by our colleague contributors. We thank the staff in the chancellor's office at UM–St. Louis for their help throughout the editorial process. We also thank Ms. Hwee Yun Tan (editor) and Ms. Jen Nie Kasim (marketing) at World Scientific for their role in producing and promoting this book.

Thomas F. George
Daniel Jelski
Renat R. Letfullin
Guoping Zhang

March 2010

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Introduction

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In the world of science, ten years is a very long time!

Back in 1999, World Scientific published a volume entitled *Computational Studies of New Materials* [1] for which two of us served as the editors. A decade later, we were approached by World Scientific about editing a second volume. Adding two more editors, the four of us discussed the relationship between the first volume and this current second volume. Has the world changed so much that we need a new title? Or is this a continuation of what was done before?

This is, after all, a Rip Van Winkle experience. It's as if we had gone to sleep for ten years and awoke to find the world a completely different place. The original title was carefully chosen, where the emphasis was on the materials, and less on the computational algorithms. New materials in

those days included semiconductor surfaces and doped semiconductors, fullerenes (both C_{60} and nanotubes), fractal clusters, and aperiodic crystals, among others.

In the introduction to the 1999 volume [1], we remarked at how much the world had changed since the 1970s:

Once upon a time, not too terribly long ago, materials science and solid-state physics were roughly synonymous. In those days a volume such as this would have bristled with terms such as "Brillouin zone" and "Wigner-Seitz cells." Then crystals were periodic, solids stretched infinitely in all directions, polymers consisted of monomer units, and polarizability was simply proportional to the volume. The world was simple and wonderful.

This ancient terminology, residually present in the first volume, has completely disappeared from the current text. There are several reasons for this. First, chemistry, physics and engineering are merging into a new discipline called *nanotechnology*. This is the mesoscopic size range – larger than the small molecules a chemist handles, but much smaller than the macroscopic crystals traditionally studied by physicists. In this region, solid-state terminology is no longer very helpful, but neither is the traditional language of chemistry. A new language is being invented. Biochemistry has long dealt with matter at this scale, so it should not be a surprise that our current volume includes articles of medical and biochemical interest.

Second, the state of the experimental art has changed significantly. Today we live in the era of ultrafast lasers (pulses as short as a femtosecond). Table 1 in Chapter 1 by Nánai *et al.* provides a helpful table listing the properties of modern laser. Chemists use these tools to probe molecular transition states on very short timescales. Materials science can use these tools effectively as well: it is possible to distinguish the temperature difference between electrons and phonons in the same material within the nanosecond timeframe that it takes for it all to equilibrate.

Finally, computers are much faster and software is vastly improved than 10 years ago. Of course, this is strikingly apparent to any average citizen, but it is nonetheless worth reviewing. The first volume still had some articles on the methods of quantum chemistry, e.g., detailing basis sets and algorithms. All of this is now in the background, readily

available in commercial software, abbreviated by the phrase "level of theory." Quantum chemistry is no longer a task for the materials scientist except in very special circumstances. Indeed, it shows up in our volume in only one chapter by Chu and Telnov (Chapter 4) — appropriately about density functional theory approaches for probing molecules in intense, ultrashort laser fields.

These changes mean that we can now better deliver on our promise to focus on the materials, letting the algorithms live in the background. And in regard to materials, there is something new and something old. The new is, as already mentioned, the advent of nanotechnology. What is nanotechnology? It is the manipulation of matter and energy on the nanometer scale, or roughly 10 to 100 atomic radii. For structures on this scale, surfaces become very important, for either chemical, optical or physical properties.

Chapter 1 (Nánai *et al.*) is an excellent overview of laser-matter interactions at the nanoscale. After reviewing the mathematics of light-matter interactions, with special attention to the high-intensity, nonlinear case, the article considers laser-exciton-phonon interactions for nanoparticles. This includes an interesting discussion of the two-temperature model, where electrons and phonons form separate heat baths. Finally, laser-induced methods of producing nanostructures are reviewed.

An interesting contrast is Chapter 2 by Letfullin and George, which investigates ultrashort laser interactions with metal nanoparticles and argues that a one-temperature model suffices. The goal is to show how gold particles can be heated up very quickly — explosive heating.

Quantum wells, or quantum dots, are a phenomenon whose name predates the term nanotechnology, but which are indeed an excellent example of the latter. As far back as the 1980s, Louis Brus developed "quantum dots," an early example of nanotechnology. By tuning the size and chemical composition of the quantum dot, we can create a light source of any visible frequency desired; they are becoming popular as light bulbs [2].

Chapter 11 by Park *et al.* discuss quantum wells of wurtzite ZnO-based structures with magnesium doping. As the magnesium concentration rises, the materials demonstrate high internal electric fields, leading to piezoelectric and polarizability effects.

Chapter 12 looks at how modifying the chemistry of a titanium oxide nanostructures changes the optical response. The authors computationally investigate different structures: zero-dimensional clusters, 1D rods, 2D layers, and 3D bulk. These structures are doped with nitrogen and boron. This yields a thorough description of the electronic and optical characteristics TiO_2 clusters, which is computational materials science at its finest!

One novel theme of the current volume concerns medicine — a topic unmentioned ten years ago. This, frankly, is astonishing, for until very recently medicine has been a purely experimental art. The computational study of medical materials is surely a very impressive, recent and pregnant development.

Letfullin and George contribute three, directly relevant chapters. The first (Chapter 5) is an overview of the importance of nanomaterials in medicine. This reviews the properties of nanoparticles as a function of impinging wavelength, pulse duration and single vs. multipulse modes.

The second (Chapter 6) is a model for how nanomaterials can be used to treat cancer. This builds on both Chapters 2 and 5. These nanoparticles have two features: first, on the surface are antibodies that bind specifically to cancer cells; and second, the interior of the particle, typically a gold cluster or rod, strongly absorbs a particular laser frequency. Thus large amounts of energy can be focused on cancer cells, destroying those with minimal collateral damage to the rest of the body. The third (Chapter 8) concerns the ablation of tissue by laser light — using the laser as a very fine, potentially non-invasive scalpel.

Proteins are nanoscale molecules and thus have become part of the overall discipline of materials science. While the famous protein folding problem is beyond our scope, the way proteins change shape upon binding with particular ligands is very important. A useful chapter by Huang and Chung (Chapter 9) describes methods by which this problem can be approached. There are a number of methods using classical force fields that work. Much work has been put into discovering methods for realistically modeling protein-ligand interactions that work and are inexpensive to run. Sometimes science really is indeed an art.

Chapter 7 by Braescu *et al.* investigates numerically the effect of argatroban, hirudin and melagatran on thrombin formation.

Fullerenes and other carbon structures were a topic ten years ago, and they remain of interest today. Zhang and George (Chapter 3) discuss the excitation of infrared normal modes in C_{60} . They use a tight-binding model for the electronic structure and a three-parameter harmonic force field for the phonons. These are coupled by laser light. There are two ways to excite normal modes — one is through the resonant electronic excitation that depends on the laser frequency. The second is through an off-resonant excitation that depends on the laser pulse duration.

The optical properties of light-emitting conjugated polymers are explored in Chapter 10 by Li *et al.* By contrast, Chapter 14 by Li *et al.* explores just bulk optical properties, without any specific reference to a material.

Chapter 13 by Popov and George focuses on tailoring of linear and nonlinear optical properties of a novel class of extraordinary artificial nanostructured electromagnetic materials – negative-index metamaterials. The feasibility of the design of a generation of unique nanophotonic microdevices with enhanced functionality is numerically simulated.

Chapter 15 is a second contribution by Zhang and George. This is a very interesting application of ultrafast lasers to manipulate spins on an unprecedented short time scale — laser-induced femtosecond magnetism. A magnetic field can be created by the symmetry-breaking caused by spin-orbit coupling. This phenomena, discovered in 1996, has applications to writing on magnetic media.

A fifth contribution by Letfullin and George, Chapter 16, is about metal nanoparticles in chemical lasers, where the gas medium is HF/DF. Within this are dispersed a cloud of metal nanoparticles (aluminum with a radius of $0.09\ \mu\text{m}$), which are ablated by an infrared laser. The result is the chemical creation of photons, resulting in a huge gain.

Finally, it is very appropriate that the book closes on some straight chemistry, namely the computational discovery of new hydrogen compounds (Chapter 18). An example of such a compound is $\text{Ca}(\text{BH}_4)_2$. A quantum calculation is used to determine the ground-state electronic structure of these compounds on a molecular scale. This result is then used to produce a simple classical force field that reproduces the essential properties under consideration. Obviously, charge distribution is an important component. The super-molecular structure is then modeled using this simple force field.

In conclusion, let us point out some intriguing trends. One stands out very dramatically — with a few specialized exceptions, nobody is working on quantum chemistry. The computational tools used in these papers are all decades old and are very well established. CHARMM is used to model proteins. A tight-binding calculation reproduces the electronic structure in C_{60} . Standard density functional calculations yield the charge density in borohydrides. In ten years, quantum chemistry has gone from being at the forefront of research to being a routine calculation. This is surely progress.

Second, the right tools are brought to bear on the problem at hand. Why use some computationally intensive, *ab initio* model when tight binding works just as well? CHARMM has been so well optimized for protein structure that one can use it for this application with confidence. In short, simple tools that are calibrated for the problem are found to be far superior to complex tools that attempt to be general.

This means that the problems can become much more complex and sophisticated. With today's computer power and the just mentioned ability to precisely limit the complexity, it is possible to consider complex chemistry and sophisticated structures. Of course, computational protein chemists — represented here by Huang and Wong — have been doing some of this for years. But many other articles in this volume depend on the excellent tools developed over the past decade. We do, indeed, stand on the shoulders of giants.

And as for the title? We have chosen to keep the same title. *Computational Studies of New Materials* seems even more apt today than ten years ago. We really are able to keep our promise to leave algorithms in the background. We can now use them in ever more clever and sophisticated ways in the service of materials science.

Light reading? Probably not. Depending on your background, some chapters will be more accessible than others. So don't be shy — make no effort to read the book from cover to cover. Read what catches your fancy — and enjoy.

1. D. Jelski and T. F. George, *Computational Studies of New Materials* (World Scientific, Singapore, 1999).
2. A quantum leap for lighting, *The Economist* **394** (Issue 8672), 18–19 (March 6, 2010).