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Electronic and Nonlinear Optical Materials: The Role of Theory and Modeling

Theory and modeling have played an important role in many areas of science and engineering since the availability of modern computing machines. However, nowhere has their role been so important and critical as in the development of new materials. The development of new materials is driven by anticipated new technology and/or perceived improvement in existing technology. In both cases, however, two major factors, namely, improved technology and potential economic payoff, guide the search and development of new materials. It is natural then that any approach that reduces the cost of materials development based upon the traditional experimental trial and error approach is not only highly desirable but also a preferred one. But the theory and modeling of new materials are not merely cost reducing tools. They provide a detailed physical understanding of the phenomenon and required materials properties for technological applications. Such an understanding, in addition to improving our fundamental knowledge of the chemistry and physics of materials, constitutes the foundation of the applications of materials to contemporary and future technologies. Therefore, the role of theory and modeling in materials development spans from providing a comprehensive understanding of the physics underlying a technologically useful or debilitating phenomenon to identifying systems exhibiting appropriate device properties. It is toward achieving such broad goals that a special symposium with a focus on the "Electronic and Nonlinear Optical Materials" was organized, first in 1994 and second in 1999 at American Chemical Society (ACS) National Meetings. The 1994 ACS symposium, held in Washington, DC, was dominated by contributions to the theory and modeling of organic nonlinear optical materials. The contributions to the 1994 symposium were published by the American Chemical Society in a book, appropriately titled, *Nonlinear Optical Materials: Theory and Modeling*.[1]

The 1999 ACS symposium, held in New Orleans, which provided the basis for the present Special Issue of The Journal of Physical Chemistry, focused equally on the electronic and NLO materials. The electronic materials, especially the inorganic semiconductor and semiconductor-insulator systems have dominated the materials science research for most of the second half of last century. Rapid advancement in the complementary metal-oxide-semiconductor (CMOS) technology leading to the present day microcomputers is a testimony to the research and developments dedicated to the electronic materials in the past 30 years. Yet, a number of issues relating point defects and impurities to the reliability of the metal-oxide-semiconductor (MOS) field-effect transistors (FETs) have remained either unresolved or ignored. Perhaps such issues were not considered crucial to the device performance in the past, as the oxide thickness in previous generation MOSFETs allowed some tolerance against defects and impurities. However, a continued trend toward miniaturization of the CMOS devices toward submicron technology,[2] has underscored the need for understanding the nature, microscopic properties, and the role on device performance of the defects in MOS systems. Most often, the defects affecting the device properties are those at or near the $Si-SiO_2$ interface and in the gate dielectric (SiO_2). Unfortunately, microscopic characterization of point defects in $Si-SiO_2$ systems has been the toughest challenge facing solid-state physics community since past 30 years. Spectroscopic techniques, such as the electron spin resonance, photoluminescence spectroscopy, and deep-level transient spectroscopy, to name but a few, are often used to detect various defects in $Si-SiO_2$ systems. But for obvious reasons, the experimental techniques alone fail to provide the details of the chemical nature, atomic structure, and most importantly the mechanisms of generation and annealing of these defects. In principle, such details can be obtained from accurate quantum mechanical calculations. However, the traditional solid-state electronic structure techniques based upon periodic boundary conditions for perfect crystals are not suitable for treating localized defects and charge traps in semiconductor and semiconductor-insulator systems. Furthermore, due to a lack of periodicity in amorphous silicon-dioxide (a-SiO_2), **k**-space (periodic lattice) based theories, which have been enormously successful in the development of solid state physics for nearly 50 years, are hardly useful for providing microscopic details of the dielectric in MOS system. These are only a few of the problems faced by the solid-state physics community that have contributed to a rather persistent lack of fundamental understanding of defects in MOS devices.

Fortunately, a number of fundamental issues related to the defects can be conveniently addressed with the help of ab initio quantum chemical studies on finite size clusters. Because of the localized nature of the defects in $Si-SiO_2$ systems, it is possible to obtain a great deal of information related to the fundamental properties, such as the chemical nature, local atomic structure, electronic and spin properties, etc., from accurate calculations on atomic clusters representing a small region of space in close vicinity of the defect centers in the solid. This permits quantum chemists to accurately study and probe the defect centers using model clusters of finite size. Of course,

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for improved accuracy, the cluster size must be sufficiently large to adequately describe the local chemistry and physics. This approach, though costly, has become quite attractive due to the advancements in computational methods, availability of super fast computing machines, and the accuracy of the results obtained from such calculations. A testimony to this approach is the number of papers in this issue dedicated to the study of defects and other materials characteristics in $Si-SiO_2$ systems. I anticipate that in the coming years more quantum chemists will become involved in addressing fundamental problems related to semiconductor materials for the contemporary and future technological applications.

The drive toward miniaturization of electronic devices has renewed interest in the feasibility and applications of molecular electronics.[3,4] One anticipates that the wires, logic elements, and other components of conventional electron devices can be replaced by organic molecular units. Obviously, an electronic device based upon molecular units would be considerably smaller and faster than permitted by the current technology. However, a number of issues need to be addressed in order to achieve the level of understanding required for molecular electronics technology. These issues relate to the mechanism of electron transport across molecular units, at molecule−metal junctions, control of electron transport by external source, dependence of carrier (electron−hole) mobility on the geometrical and electronic structure of molecular units, etc. In this case, not only extensive modeling and computations of structure−property relationships are required but a good amount of physics via existing and new theoretical approaches needs to be developed. Considering the rapid growth in the research activities on molecular electronics in the past several months, I anticipate many exciting developments in the theory and computational approaches in the coming years as well as the applications of these tools to the advancement of this rapidly growing field. The articles in the present issue dedicated to molecular electronics will provide a starting point for the present and future researchers in the field.

NLO materials, especially organic and polymeric ones, have continued to be at the forefront of research activities since the mid-1980s. High NLO susceptibility, fast response time, virtually endless possibilities of structural modification, and ease in processability are some of the properties of conjugated organic systems uniquely suited for their applications in photonic devices, such as the frequency converters, electrooptic modulators, optical switches, etc. However, the ad hoc trial-and-error methods used to design appropriate systems proved to be insufficient for a satisfactory progress in the field. In the mid 1980s a comprehensive time-dependent Hartree−Fock (TDHF) theory,[5] developed by Hideo Sekino and Rodney Bartlett at Quantum Theory Project, University of Florida, provided a basis for modeling NLO materials by ab initio methods. The Sekino−Bartlett method, however, proved to be too expensive (from the point of view of the software and hardware available at that time) to be used for organic molecules of practical interest. It is important to point out that semiempirical methods, used by several groups, most notably by Henk Hameka at the University of Pennsylvania and by Mark Ratner at the Northwestern University, did provide physically useful data, but the information content was limited and the reliability of the methods was not always up to expectation. Therefore, development of first-principles based methods to conveniently and reliably predict structure−NLO property relationships in organic materials became the focal point in several laboratories and Sekino−Bartlett TDHF theory formed the starting point for many of them. These activities led to a number of new developments in the late 1980s and early 1990. A few notable ones are introduction of the $(2n+1)$ rule in TDHF theory,[6] which considerably reduced computational steps for predicting higher-order effects; "direct" computation of time-dependent Fock matrices,[7] which obviated the need for storing two-electron integrals and also allowed for parallel computations of Fock matrices across several processors; and inclusion of electron correlation effect,[8,9] which could provide much improved results than generally available from the TDHF theory. The TDHF theory has been recently extended to open-shell case,[10] which is particularly useful for studying NLO properties of paramagnetic radicals and ions. It is fascinating to note that the development such as the introduction of the $(2n+1)$ rule, which was intended for TDHF theory, has also been successfully adapted in density functional theory (DFT) based approaches.[11] These and other new developments have made first-principles modeling of organic NLO materials straightforward and easy. Yet, a number of issues, such as the molecular vibrational effect and influence of the medium on NLO phenomena in molecular materials, cannot be conveniently addressed by the traditional TDHF or DFT theories. In recent years, several groups have been involved in addressing these issues. For example, the vibrational NLO effects have been extensively treated by Bernie Kirtman (University of California, Santa Barbara), David Bishop (University of Ottawa, Canada), and colleagues. Theories dealing with the effect of the medium and local field effects on NLO properties have been developed by Roberto Cammi (University of Parma, Italy) and Hans Ågren (Royal Institute of Technology, Stockholm, Sweden) and their groups. Applications of these theoretical methods and computational approaches to organic systems have provided valuable new insights into the physics underlying NLO response of organic and polymeric materials. These subjects, which are of interest to both theory and experimental communities, are adequately represented in this issue. One can only expect that in the coming years faster and more accurate theoretical methods and integrated computational algorithms will be available to model organic materials, not only for NLO but also for electronics applications.

While current theoretical methods are able to treat nonresonant NLO processes conveniently, there seems to be a lack of those treating resonant phenomena, such as the two- and three-photon absorptions. Multiphoton absorption processes have important applications in power-limiting and sensor-protection devices. Considering the intense activities in the experimental community to develop suitable resonant NLO materials, I expect the theoretical community to rise to the occasion and provide an accurate and reliable theory and convenient computational algorithm to calculate multiphoton absorption cross section and resonant NLO properties.

A discussion of NLO materials will be incomplete without mentioning silica glass. First discovered in the mid-1980,[12] the second-order NLO response in doped silica glass has been an area of intense research activity. However, the activity has been mostly confined to the physics and electrical engineering communities. While tremendous achievements have been made toward enhancing the NLO susceptibility and response time in different materials configurations, the physical mechanism(s) underlying the observed effect has (have) been not fully understood. The role of defects and impurities are often mentioned, but no conclusive data exists due to a lack of systematic study. Similar to what happened with organic NLO materials then, the quantum chemistry can make valuable contributions toward understanding the origin and mechanism

of second-order effects in silica glass. Any progress made in that direction would be extremely valuable due to the technological applications of silica fiber.

As in most such endeavor, an effort toward bringing a group of scientists together, to motivate them to engage in mutual dialogue, and persuade them to contribute their time and technical data to the special issue, requires the involvement and helping hands of many people than a few. In this particular case, I am extremely grateful to Professor Rodney Bartlett, Professor Mostafa El-Sayed, and Professor George Schatz for encouragement and guidance. Interests of Dr. Dominic Ryan and the Late Professor Mike Zerner in the symposium have been invaluable to its success. I am thankful to Dr. Walter Shedd and Dr. Robert D. Pugh at the Space Electronics and Protection Technologies Branch of the Air Force Research Laboratory, Space Vehicles Directorate, for their encouragement and support. I express my special thanks to Dr. Prakashan Korambath for providing me with invaluable assistance in this endeavor. Finally, I thank the PHYS and COMP divisions of the American Chemical Society for their help and all the contributors to this special issue.

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