Quantum Simulations Tell The Atomic-Level Story

With quantum molecular dynamics simulations, scientists can get an accurate picture of what happens to individual atoms during an experiment.

FOR almost as long as Lawrence Livermore has existed, scientists have been experimenting with materials to learn what happens to them under high pressure. In the brief instant of a high-explosive detonation, for example, shock waves produce pressure up to 500,000 times that of Earth's atmosphere, detonation waves travel as fast as 10 kilometers per second, and temperatures soar to 5,500 kelvins.

Early high-pressure experiments were designed to investigate the properties of weapon materials under these mind-boggling conditions and thus support the development of new weapons. Today, experiments seek out the fundamental properties of such deceptively simple materials as water and hydrogen. This very basic information is being applied to work in high explosives, planetary science, and materials science.

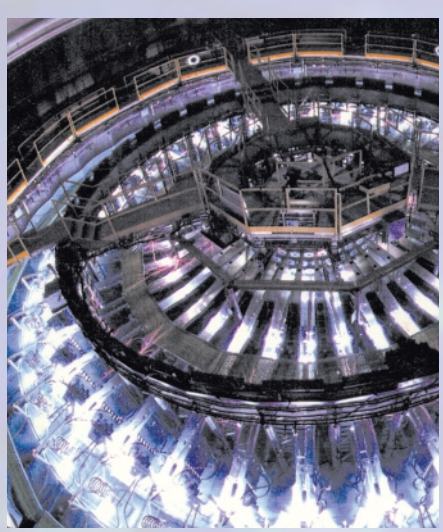
Experiments with a gas gun that shocks a sample or with a diamond anvil cell that applies static pressure demonstrate the changes brought about by pressure—the "after" conditions that scientists can compare to the "before." Now, for the first time, using computer simulations, researchers can get an accurate look at what happens to individual atoms and molecules during those experiments.

Simulations based on quantum molecular dynamics make it possible to view experimental activity as it happens. Quantum molecular dynamics is quite different from classical molecular dynamics, which is primarily concerned with the classical motion of atoms interacting with a given potential. The interesting chemistry and physics of many molecules take place at the atomic and subatomic level. But Newton's laws of classical mechanics no longer apply here. Physicists developed quantum mechanics early in the 20th century to appropriately describe the physics and chemistry of matter at the microscopic level. Quantum molecular dynamics focuses on all the interactions between atoms and electrons and does not involve fitting interactions to experimental data.

First-principles, or ab initio, molecular dynamics models use only the laws of quantum mechanics, the fundamental physics equations that describe electrons. (See the box on p. 8.) These models in combination with Livermore's powerful computers allow scientists to create accurate, reliable simulations of complex physical phenomena.

Physicist Giulia Galli leads the Quantum Simulations Group at Livermore. In the four years since this group was established, it has explored entirely new territory. Early work included simulations of the mixing of water and hydrogen fluoride, DNA, and the elasticity of silicon carbide, a semiconductor material. (See *S&TR*, July/August 1999, pp. 20–22.) Their more recent simulations of shocked liquid hydrogen were the largest ab initio simulations to date on Livermore's terascale computers, which are part of the National Nuclear Security Administration's Advanced Simulation and Computing (ASCI) program. "Our hydrogen simulations were the first to look at an experiment in action," says Galli. "We could actually see how a real experiment had gotten from 'before' to 'after.'"

Quantum simulations are an excellent tool for predicting the properties of materials that cannot be measured directly. They provide accurate information about the properties of materials subjected to extreme conditions (for example, high temperature or high pressure) that are difficult to achieve experimentally. Simulations also help experimental physicists to interpret their results. "Simulation results neatly complement experimental results and may also guide the choice of new experiments," says Galli.



Experiments on (left) Livermore's Nova laser and (right) Sandia National Laboratories' *Z* accelerator shocked liquid deuterium, an isotope of hydrogen. In both experiments, a short, intense shock caused the hydrogen to form a hot plasma and, very briefly, become a conducting metal. The experiments found different compressibilities, which could affect the equation of state for hydrogen and its isotopes. Quantum simulations sought to point out physical reasons for the differences.

Codes Make It Work

The computer code used to simulate dynamic processes is JEEP, which physicist Francois Gygi began developing about eight years ago when he was at the Swiss Federal Institute of Technology. Some physical properties of matter, such as optical properties, can be obtained more accurately using static calculations performed with quantum Monte Carlo codes, which are the specialty of physicists Andrew Williamson, Jeff Grossman, and Randy Hood.

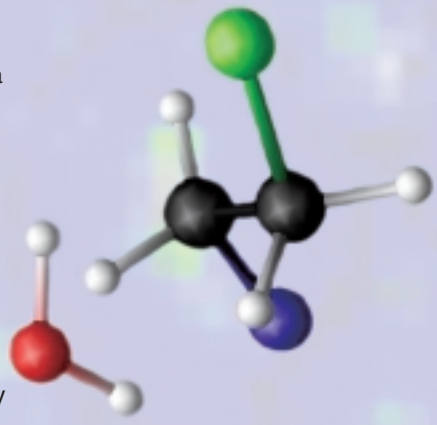
JEEP and quantum Monte Carlo codes operate differently. Both have to make approximations in their equations, but quantum Monte Carlo codes make very few. JEEP operates faster and excels at deriving the location of atoms and molecules. The more accurate quantum Monte Carlo simulations cannot give dynamic properties but are a better tool for determining the optical properties of molecules. Quantum Monte Carlo calculations are also useful for testing the validity of approximations made in the JEEP code's theory and for improving the accuracy of this theory.

Simulations Resolve Differences

Quantum simulations by Galli and Gygi may point out the differences found during two sets of high-pressure experiments on deuterium, an isotope of hydrogen with one proton and one neutron. One set of experiments was performed on Lawrence Livermore's Nova laser. The other set was performed on Sandia National Laboratories' *Z* accelerator, the world's most energetic pulsed-power machine, in Albuquerque, New Mexico.

The Livermore experiments in 1997 and 1998 and the Sandia experiment in 2001 subjected a sample of liquid deuterium to a short, intense shock that caused the hydrogen to form a hot plasma and, very briefly, become a conducting metal. In the Nova experiments, a laser beam produced a steady shock wave aimed at the target cell holding the sample. The wave was smoothed to ensure a spatially planar and uniform shock front, critical for obtaining accurate measurements.

The experiment at Sandia used an entirely different technique for producing a shock wave. Pulsed-power machines have large banks of capacitors used to accumulate electrical charges over many hours. All of that stored energy is discharged in one enormous pulse that lasts for a fraction of a microsecond. The pulse creates a powerful electromagnetic field that slams a flyer plate into the deuterium sample capsule. Sandia's magnetically driven plate is faster



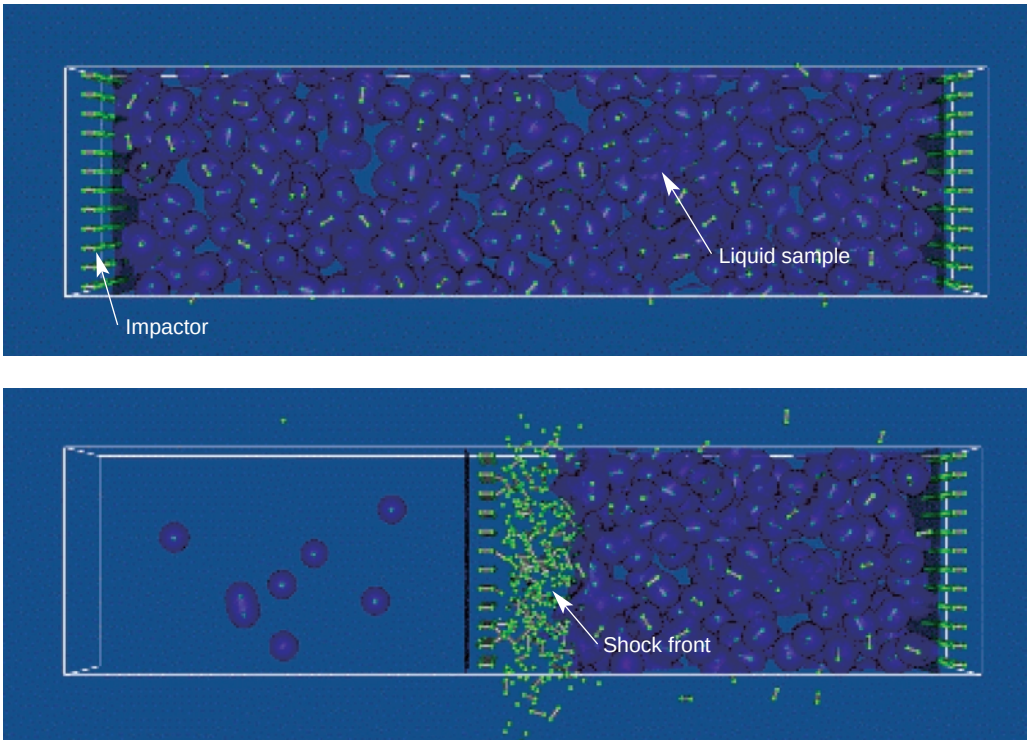
although smaller than the flyers used by Livermore's two-stage gas guns for shock experiments. It thus results in higher shock pressures. The *Z* accelerator also sustains a shock for a longer time than the Nova laser.

The two sets of experiments on the Nova laser showed that the deuterium samples were compressed to a density much higher than anyone had expected. These data differed from those used to predict the then-current model of the equation of state (EOS) for hydrogen and its isotopes. An EOS is a mathematical representation of a material's physical state as defined by its pressure, density, and either temperature or energy. It is a necessary constituent of all calculations involving material properties. Predictions concerning the formation and evolution of large planets, such as Jupiter, strongly depend on the EOS of hydrogen at pressures reached in the Nova experiments.

The *Z* flyer data reached pressures up to 70 gigapascals, which overlapped part of the pressure regime of the Nova laser experiments. The Nova experiments determined the EOS by using an x-ray probe and x-ray microscope to look into the deuterium as it was being shocked. The Sandia experiments simultaneously shocked a deuterium sample and a foil of aluminum. Researchers then found the EOS by comparing deuterium's behavior with that of aluminum. Although the Sandia EOS data required the comparison with aluminum, the *Z* flyer produced a shock in the deuterium that held a constant pressure for much longer than did the experiments with the Nova laser.

At a pressure of 40 gigapascals, the Nova and *Z* data agree, showing that the hydrogen EOS is about 20 percent more compressible than it was earlier thought to be. In other words, at this pressure, hydrogen will squeeze into a smaller volume with a higher density than previous models had predicted. At a pressure of 70 gigapascals, the Nova data show an even larger compressibility compared with equilibrium theory—almost 50 percent higher—while the *Z* flyer data are about 7 percent higher than theory predicted. "This is a considerable and important discrepancy," says Livermore physicist Robert Cauble, who oversaw the experiments on both the Nova laser and the *Z* accelerator.

Galli and Gygi performed two sets of simulations as they sought an explanation for the experimental results. The first simulations were of hydrogen under fixed pressure and temperature. The pressure values ranged from 20 to 120 gigapascals while temperatures ranged from 5,000 to 12,000 kelvins. Galli and Gygi then simulated the behavior of liquid deuterium during a shock experiment. Although the simulations of static conditions gave results that agreed with Sandia's data,



Quantum simulations of shocked hydrogen reveal the atomic-scale structure of the shock front. (top) Thirteen hundred and twenty deuterium atoms are arranged in a periodically repeating molecular dynamic cell that contains an impactor, a wall, and a liquid sample. Four computer experiments used different impactor velocities in an effort to mimic experimental results. (bottom) The shock front and the compression of the deuterium atoms are shown from one computer experiment.

the simulation of a shock in deuterium gave results that agreed with the Livermore Nova shocks.

Gygi notes that the conditions of the Nova and *Z* accelerator experiments differed. For one thing, the time scales of the pulse were different: 2 to 4 nanoseconds in Nova and about 30 nanoseconds in the *Z* machine. "Another variable may be that a laser beam is very different from a magnetic pulse," says Gygi.

Although the simulations did not supply a full explanation for the difference between the two sets of experimental results, Galli and Gygi's calculations did help to point out possible important differences. "In the past," says Gygi, "experimentalists with different results just pointed fingers at each other. Now, we hope that simulations will help to explain the physical reasons causing disagreement between different experiments. Also, big experiments are often expensive to repeat. The Nova laser is gone completely, so reproducing part of the Nova results with simulations can be very useful."

Water, Water Everywhere

Recent experiments also explored one of the most common liquids—water. "You would think that everybody knows everything about water," says Galli, "but that is far from the truth. And water is in practically everything in our world." Water is in many materials studied at Livermore: Biological systems are largely water, high explosives contain water, and water vapor may accumulate inside an aging nuclear weapon.

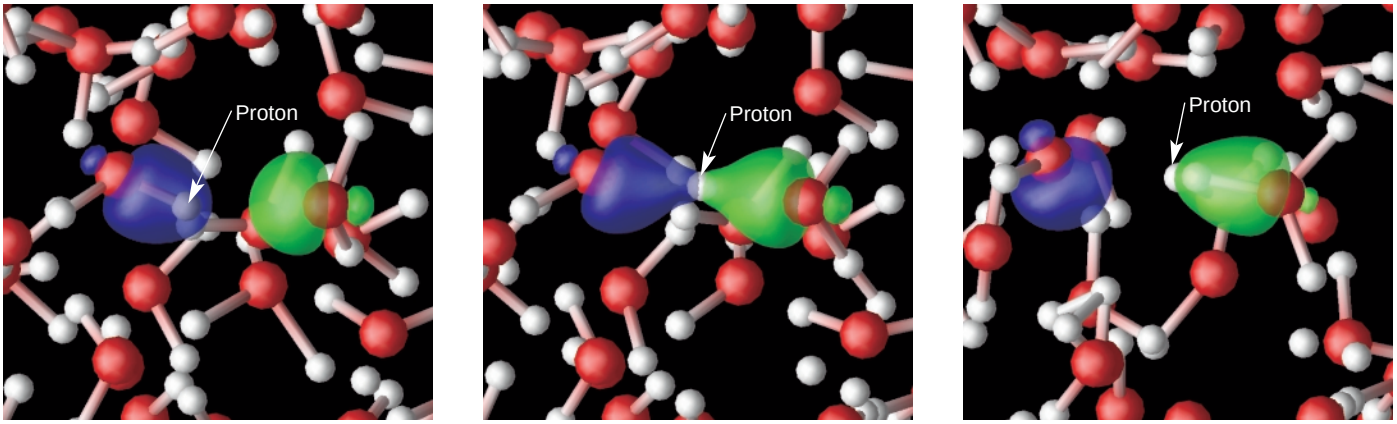
Physicist Eric Schwegler, Galli, and Gygi were interested in what happens to water under pressure, information important to Livermore's U.S. nuclear weapons stockpile stewardship mission. In particular, they were interested in learning how the water molecule comes apart under high-pressure conditions.

First, they developed a model of liquid water at ambient conditions, which compared favorably with recent x-ray data gathered at the University of California at Berkeley and with neutron diffraction data gathered in England. Then they modeled water at moderate pressure and found structural data that agreed with recent diamond anvil cell experiments performed at Commissariat à l'Énergie Atomique (CEA) in France.

Scientists already knew that under ambient conditions, water molecules rarely dissociate (come apart)—just once every 11 hours. When dissociation does occur, two water (H_2O) molecules become hydroxide (OH^-) and hydronium (H_3O^+), with one proton hopping to the other H_2O molecule. How increased pressure affects dissociation has long been debated.

Experiments on water at extreme temperatures and pressures have been few. One pioneering 1985 experiment at Livermore used a two-stage gas gun to shock water with pressures up to 26 gigapascals and temperatures to 1,700 kelvins. This experiment did not find any evidence of H_3O^+ under pressure. These data led to the suggestion that the dissociation mechanism at high pressures might be different from the one at ambient conditions, that perhaps a single H_2O molecule dissociates to H^+ and OH^-.

In quantum simulations of static pressure conditions ranging up to 30 gigapascals, Schwegler's team found that the dissociation process begins in earnest at 14 gigapascals. By 30 gigapascals, dissociation is occurring once every billionth of a second. The team was surprised to discover the same dissociation process that occurs at ambient conditions in which a proton jumps across to another water molecule. The simulations also indicated why the 1985 experiment did not reveal this process. At very high pressures, the lifetime of a H_3O^+ molecule is on average only 9.8 trillionths



Snapshots of the dissociation of a water molecule at high pressure. (left) As the water molecules dissociate, (middle) a proton is transferred to a neighboring water molecule so that (right) a hydroxide (OH^-) and a hydronium ion (H_3O^+) are formed.

of a second, too short to be observed in the 1985 experiment with detection technologies available then.

For Better Health

Schwegler, Galli, and Gygi are also working with researchers in Livermore's Biology and Biotechnology Research Program (BBRP) Directorate to simulate the dynamic behavior of DNA and other biomolecules. The goal is to combine Livermore's expertise in biology, simulation methods, and high-performance computing to nurture a new Laboratory core competency in computational biology. (See *S&TR*, April 2001, pp. 4–11.)

The simulations of water at ambient conditions were a necessary jumping-off point since all biomolecules contain a high percentage of water. Such liquid-phase simulations are far more complicated than those of isolated molecules in the gas phase because of the increased number of atoms that must be modeled.

"Getting water right made our future work much easier," says Schwegler. "And there are lots of experimental data to compare."

Subsequently, the team developed first-principles simulations of the dissolution of sodium and magnesium ions in water. In each case, their simulations agreed with numerous experimental investigations by others, but they also found several interesting features that had not been seen before.

That work was preparation for quantum simulations of the DNA sugar–phosphate backbone connecting the millions of base pairs that make up our genetic code. The flexibility of DNA in solution is central to the formation of DNA–protein complexes, which in turn mediate the replication, transcription, and packaging of DNA. Part of this flexibility comes from rotations around the bonds found in the backbone.

To learn more about how these rotations work, the team modeled the

Simulating Quantum Molecular Dynamics

In the classical molecular dynamics approach, a model of interactions between atoms is supplied as input before a simulation can be carried out. Such models are based on a priori knowledge of the physical system being studied. "Those models work if you know the chemical bonds already," says physicist Francois Gygi.

In contrast, first-principles, or ab initio, molecular dynamics does not require any a priori knowledge of interatomic interactions. These simulations use only the laws of quantum mechanics, the fundamental physics equations that describe electrons. The existence of chemical bonds is the result of electron interactions and the laws of quantum mechanics. Quantum simulations can describe the forming and breaking of chemical bonds, which cannot be done using classical molecular dynamics. Thus, classical molecular dynamics cannot explain complex states of matter such as hot, compressed fluids in which molecules come apart and regroup. Quantum molecular dynamics, however, is an ideal method for showing what happens to fluids under pressure.

The fundamental physics equations that must be solved in quantum simulations are extraordinarily complex. Until powerful computers such as Livermore's ASCI White came along, ab initio quantum molecular dynamics simulations could handle only a few atoms. Even now, a model of a few hundred atoms over less than a millionth of a second takes days of computing time to complete on Livermore's huge computers.

Modeling the behavior of molecules at the quantum level requires not only unprecedented computational power and speed but also specially designed simulation codes. One such code is JEEP, which Gygi began developing when he was at the Swiss Federal Institute of Technology.

JEEP is based on density functional theory, which describes the electronic density of a molecular or condensed system. Walter Kohn of the University of California at Santa Barbara won the Nobel Prize for Chemistry in 1998 for his development of density functional theory. In its original form, this theory was confined to ground-state properties of molecules. Since then, it has been expanded and made applicable to the study of atomic motion and complex dynamic effects of matter. Kohn's work on density functional theory has revolutionized the way scientists approach the electronic structure of atoms, molecules, and solid materials in physics, chemistry, and materials science.

Since coming to Livermore, Gygi has adapted and optimized JEEP for use on the massively parallel computers of ASCI. Now, with ASCI computers, he can examine materials systems with hundreds of atoms and thousands of electrons extremely accurately.

Monte Carlo codes are more accurate but have been extremely demanding of computing time. Every increase in the number of particles (N) being modeled requires N^3 more computing time. Twice as many electrons requires 8 times more computing time, 3 times as many electrons requires 27 times more computing time, 4 times as many electrons requires 128 times more computing time, and so on. Modeling more than a few atoms requires prohibitively long periods of computing time. Recently, however, physicists Andrew Williamson, Jeff Grossman, and Randy Hood developed a technique that allows for linear scaling of computing time for quantum Monte Carlo calculations. In other words, doubling the number of electrons only increases computing time by a factor of two instead of a factor of eight. This important breakthrough is based on techniques also used in some quantum molecular dynamics codes.

smallest part of the DNA backbone, the dimethyl phosphate anion (DMP^-). They observed changes in the shape of DMP^- when it was exposed to a sodium cation, changes that had not been seen in any previous classical molecular dynamics simulation of DMP^- in water. In future simulations, they plan to examine the influence of magnesium and other cations on the shape and flexibility of DNA.

Schwegler's team has also been collaborating on studies of cancer-fighting drugs known as phosphoramides being done by Mike Colvin and his associates in BBRP. These nitrogen-mustard-based drugs have been used to treat cancer for 50 years, so there is plenty of experimental data to compare with simulations. By examining how the phosphoramide molecules are activated, this team hopes to find ways to improve the drug and to make it more effective. (See *S&TR*, April 2001, pp. 9–10.)

Mustard drugs are believed to work by forming cross-links between the two strands of a cancer cell's DNA. Because the cell cannot easily eliminate the cross-links, the cell cannot replicate itself and dies. Before the drug can attach itself to the cancer cell's DNA, it has to lose chlorine ions. With his quantum simulations, Schwegler is learning more about the activation process, examining how the drug loses the chlorine ions and how much energy is required.

Surface Chemistry Is Key

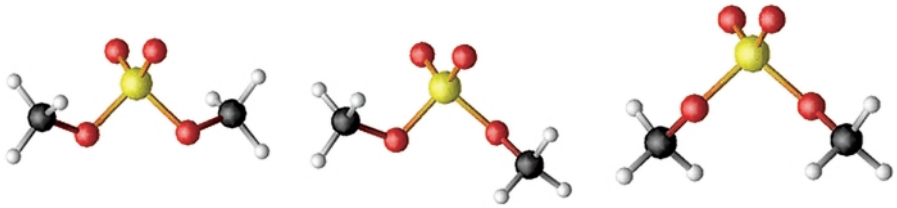
Livermore researchers used both density functional theory (on which the JEEP code is based) and quantum Monte Carlo codes to perform first-principles calculations of silicon nanoclusters, or quantum dots, which are tiny silicon molecules just a few nanometers in size, about 100,000 times smaller than the width of a human hair. These nanoclusters produce different colors of light depending on their diameter and are being considered as replacements for the fluorescent markers that researchers now use to tag proteins during experiments. With the markers, scientists can locate specific proteins and watch them as they go about their business.

Existing fluorescent dyes work well as markers. But they are short-lived. Their fluorescence rapidly fades until they are no longer detectable. They also have to be excited by a specific wavelength of laser light that matches their absorption. If researchers are studying more than one protein at a time and use multiple fluorescent markers, they must also use as many lasers as there are different markers.

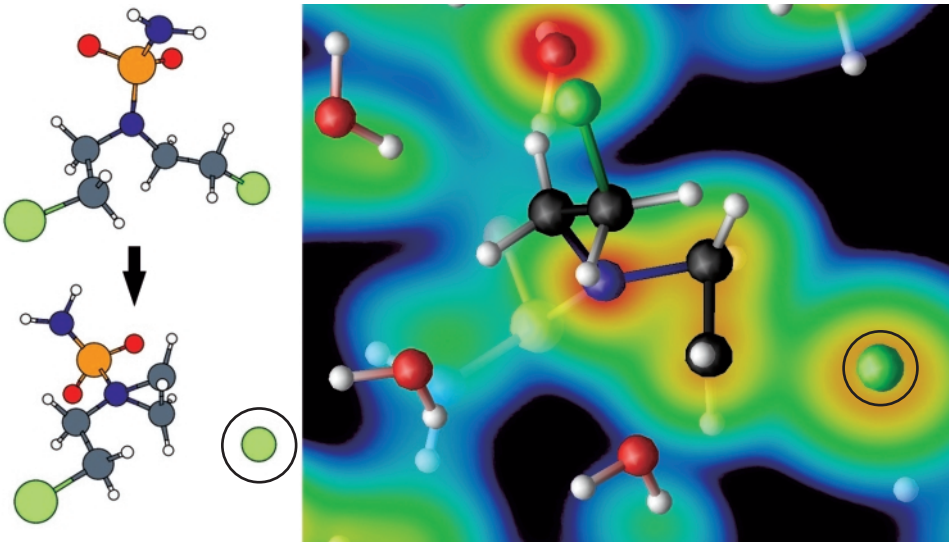
Silicon quantum dots have several advantages as biomarkers. They do not bleach out, and multiple markers can be excited by a single laser. "Given their small size, they would be a gnat on the side of a protein," says Williamson, "and the protein should continue to act and react normally."

The synthesis of silicon dots is still in its infancy. Livermore has several experimental efforts under way to synthesize them. A long-term goal is to use silicon nanoparticles in biosensors to detect biological and chemical warfare agents.

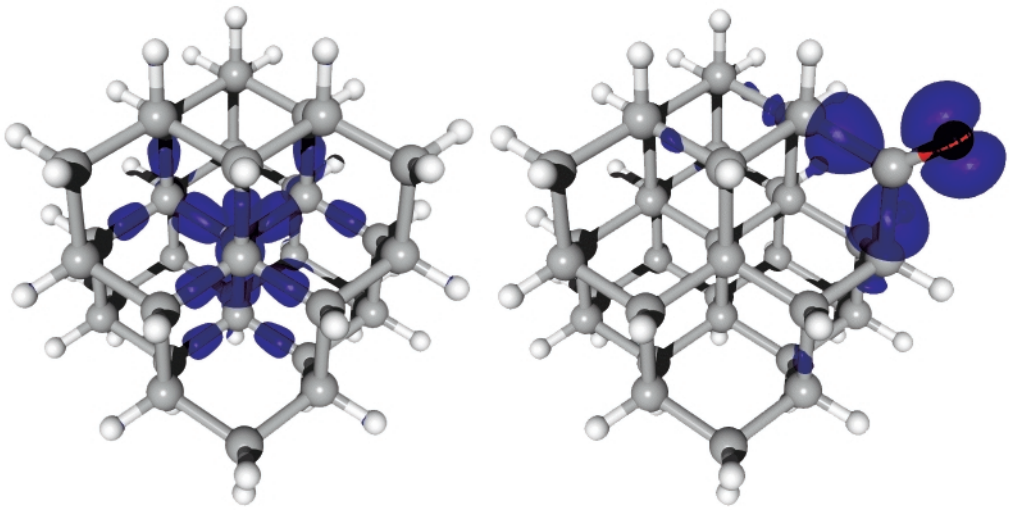
During the manufacture of the quantum dots, contamination is a



Part of the flexibility in DNA comes from rotations around the bonds found in the backbone, which consists of deoxyriboses linked together by phosphodiester bridges. Shown here is a simple model of the phosphodiester linkage found in the backbone of DNA. The molecule can adopt a variety of conformations by rotations around the phosphorus–oxygen bonds.



The cyclization of phosphoramide mustard in solution. (left) As the new carbon–nitrogen bond is formed, a chloride ion (circled) leaves the mustard and (right) is solvated by the surrounding water molecules.



(left) In a 71-atom silicon quantum dot, the white atoms are hydrogen atoms bonded to the surface that are "passivating" the dot and making it less reactive. A silicon dot that is completely passivated by hydrogen will have all its electrons in the center. (right) When two of the hydrogen atoms are replaced by a more reactive oxygen atom, the electron charge cloud is drawn toward the oxygen atom. This dramatically changes the optical properties (wavelength) of the silicon quantum dot.

concern. Oxygen, especially, can be a killer for silicon, notes Williamson. Recent Livermore simulations examined the effect of oxygen on silicon particles. A single oxygen atom, as well as many other contaminants, can make a big difference on a quantum dot because of the dot's large ratio of surface area to volume. Surface chemistry plays a big role in the study of these tiny particles.

The effects of surface chemistry are illustrated in the figure above. The left portion of the figure shows a nanometer-size silicon quantum dot made up of 71 atoms. The white atoms on the surface are hydrogen atoms bonded to the dot in such a way as to "passivate" the surface. This means they attach themselves to the highly reactive surface silicon atoms (gray). The purple cloud shows the region where the electrons that will absorb light are most likely to be located in this silicon quantum dot. For a silicon dot completely passivated by hydrogen, the electrons are located in the center of the dot. The right portion of the figure above shows how the situation changes when two of the hydrogen atoms are replaced by a more reactive oxygen atom. The electron charge cloud is drawn toward the oxygen atom, and this change in the electron density dramatically changes the optical properties of the silicon dot.

The team is currently broadening the scope of its nanostructure investigations to include other semiconductor materials such as germanium and cadmium–selenide.

Bigger and Better

One goal of Galli's group for the next few years is to apply quantum simulations to a wider and broader set of problems and to use quantum simulations on a par with laboratory experiments as a tool for research in science and engineering. Quantum simulations are a fully predictive approach that will provide a new window through which scientists can observe the world at the atomistic level in exquisite detail, avoiding uncontrolled approximations. Galli's group will focus on fluids under extreme conditions—for example, water under shocked conditions—and on building knowledge and expertise in the field of nanoscience, in particular, modeling artificial and biological nanostructures for labeling and sensing applications.

Because of the success of their quantum simulations, Galli and Gygi are working with IBM on the design of the next-generation ASCI computers. When these monster computers arrive, extremely complex simulations may be able to answer questions that cannot now be answered.

—Katie Walter

Key Words: hydrogen, JEEP, nanostructures, quantum dots, quantum molecular dynamics, quantum Monte Carlo calculations, quantum simulations, water.

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