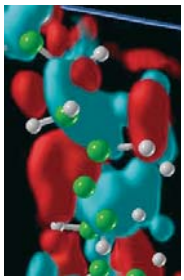

FOLLOW THE ENERGY

SIMULATIONS ARE UNRAVELING THE DETAILS OF ENERGY TRANSFER IN PHOTOSYNTHESIS

Photosynthesis may hold the key to solving one of humanity's most pressing problems: finding a clean, efficient, carbon-neutral, and sustainable source of energy to replace fossil fuels and slow down global warming.

While commercially available photovoltaic cells in solar panels convert only 9 to 14 percent of the sunlight they absorb into electrical energy, the initial photosynthetic steps of energy and electron transfer in green plants and cyanobacteria are 97 percent efficient. Photosynthesis also removes some carbon dioxide, the most important greenhouse gas, from the atmosphere, converting the carbon to carbohydrates.

Nature has a lot to teach us, if we can figure out how photosynthesis works at the level of electrons in molecules.

Researchers are taking a big step toward that understanding with the project "Quantum Monte Carlo Study of Photoprotection via Carotenoids in Photosynthetic Centers," one of the first projects funded by the DOE Office of Science's Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. Led by theoretical chemist William Lester, Jr. of the University of California, Berkeley and Lawrence Berkeley National Laboratory, the project used about 1.4 million processor hours on NERSC's IBM supercomputer, Seaborg, in 2004. (The "quantum Monte Carlo" in the project title is a statistical model for studying strongly correlated systems such as electrons in molecules. "Photoprotection" is a defense mechanism within the photosynthetic system that protects plants from the oxidation damage that would otherwise result from absorbing more solar energy than they can immediately utilize.)

"The theory behind energy transfer in photosynthesis is more than 50 years old, but some aspects have never been quantitatively tested," says research team member Graham Fleming, who is Berkeley Lab's Deputy Director and a chemistry professor at UC Berkeley. "We need the capabilities of NERSC to provide crucial quantities to test our models for energy transfer in photosynthetic complexes."

Lester says, "Before we had computational capabilities such as those at NERSC, it was not possible to model the energy and electron transfer processes we want to study. NERSC is providing us with the computers and software support that enable us to run codes developed in my laboratory that will give us the information we need and could not otherwise obtain."

Life on Earth depends on the photosynthetic reactions that green plants and cyanobacteria use to convert energy from sunlight into chemical energy. Among other things, these reactions are responsible for the production of all of our planet's oxygen. In high school biology, students learn that nature uses chlorophyll, the family of green pigment molecules, as a light absorber and energy-transfer agent, but the physics and chemistry behind the overall process are extremely complicated. What's more, the elementary photosynthetic steps take place on times as short as a few tens of femtoseconds (a femtosecond being one millionth of a billionth of a second).

"According to the first law of photosynthetic economics, a photon saved is a photon earned," Fleming says. "Nature has designed one of the most exquisitely effective systems for harvesting light, with the reactions happening too fast for any light to be wasted as heat. Current synthetic light-harvesting devices, however, aren't following nature's model.

"The photosynthetic light-harvesting system is so sensitive to changing light conditions, it will even respond to the passing of clouds overhead," Fleming adds. "It is one of nature's supreme examples of nanoscale engineering."

Photosynthesis starts with a light harvesting system, which consists of two protein complexes, Photosystem I and Photosystem II. Each complex features light-absorbing antennae made up of members from two families of pigment molecules, chlorophylls and carotenoids. These pigment antennae are able to capture photons of sunlight over a wide spectral and spatial cross-section.

The chlorophyll and carotenoid molecules gain extra "excitation" energy from the captured photons that is immediately funneled from one neighboring molecule to the next, until it arrives at another molecular complex, which serves as a reaction center for converting energy from solar to chemical (Figure 1). This transfer of excitation energy involves several hundred molecules and hundreds of individual steps along different electronic pathways, yet still transpires within 30 picoseconds for Photosystem I and 200 picoseconds for Photosystem II. By human standards of time, that's instantaneous.

"If we can follow the steps in transferring energy from donor to acceptor molecules, we might be able to design new and much more effective strategies for synthetic light harvesters," Fleming says.

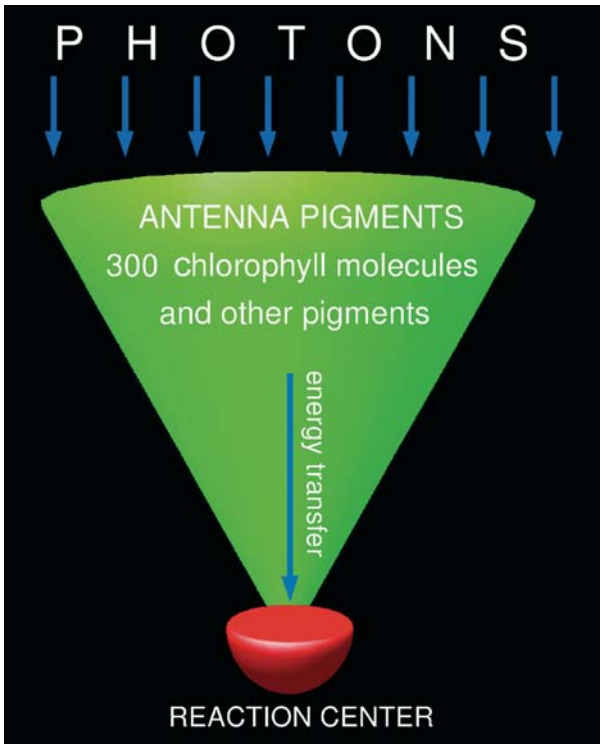

FIGURE 1 A simplified schematic of photon harvesting and energy transfer to the photosynthetic reaction center.

Because the extra energy being transferred from one molecule to the next changes the way each molecule absorbs and emits light, the flow of energy can be followed spectroscopically. However, to do this, Fleming and his experimental research team need to know what spectroscopic signals they should be looking for. This is where the INCITE grant is helping. Lester, Alán Aspuru-Guzik, and other collaborators have developed and are running a quantum Monte Carlo computer code called Zori[1] on NERSC's

[1]Alán Aspuru-Guzik, Romelia Salomón-Ferrer, Brian Austin, Raul Perusquía-Flores, Mary A. Griffin, Ricardo A. Oliva, David Skinner, Dominik Domin, and William A. Lester, Jr., "Zori 1.0: A parallel quantum Monte Carlo electronic structure package," J. Comp. Chem. (in press). Harsha Vaswani and Michael Frenklach contributed to the photoprotection application of Zori. The Zori code and documentation are available at http://www.zori-code.com/.

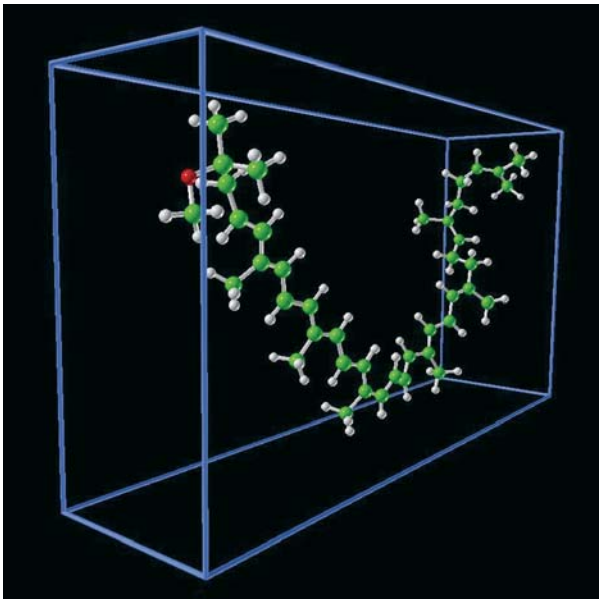

FIGURE 2 Nuclei of the spheroidene molecule, $C_{41}H_{60}O$. Carbon is shown as green, hydrogen as gray, and oxygen as red.

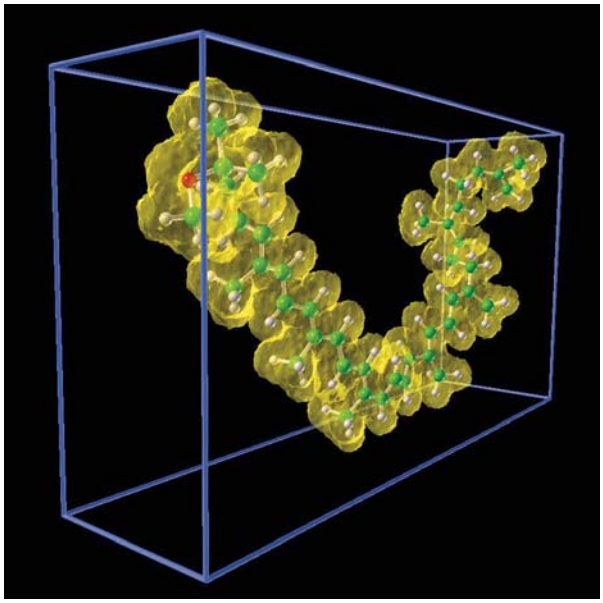

FIGURE 3 Electron density of the spheroidene molecule.

Seaborg computer to predict the optimal electronic pathways for photosynthetic energy transfer. NERSC consultant David Skinner helped optimize the code to take full advantage of Seaborg's capabilities.

Says Lester, "Most people have long thought of computational chemistry as only being able to tackle simple systems reliably, but we've come a long way with improved implementation of our algorithms in recent years."

Rather than tackling the entire complex process of photosynthesis, Lester's team wanted to work on a manageable piece of the puzzle, so Fleming suggested studying the electronic structures behind photoprotection. Research into photoprotection has focused on the carotenoids in Photosystem II, which appear to be the regulatory agents that dissipate excess energy, thus preventing oxidation damage. (Carotenoids such as beta-carotene and lycopene from the vegetables and fruits we eat perform a similar antioxidant function in the human body, protecting us from a variety of illnesses.)

When green plants and photosynthetic bacteria (including the cyanobacteria and purple bacteria families) absorb more energy than they can use, the chlorophyll molecules can undergo a transition to a "triplet" state — a kind of variation in their energy state. This state is very dangerous because it, in turn, can excite molecular oxygen to its excited "singlet" state — an exceedingly reactive chemical that destroys the photosynthetic proteins and, in the end, will kill the plant or bacterium.

Carotenoid molecules are ubiquitous in photosynthetic organisms because they can remove ("quench") chlorophyll triplets, leading to harmless generation of heat instead of dangerous singlet oxygen. In green plants, an additional process called "feedback de-excitation quenching" takes place, in which carotenoids detect changes in the rate of photosynthesis via pH

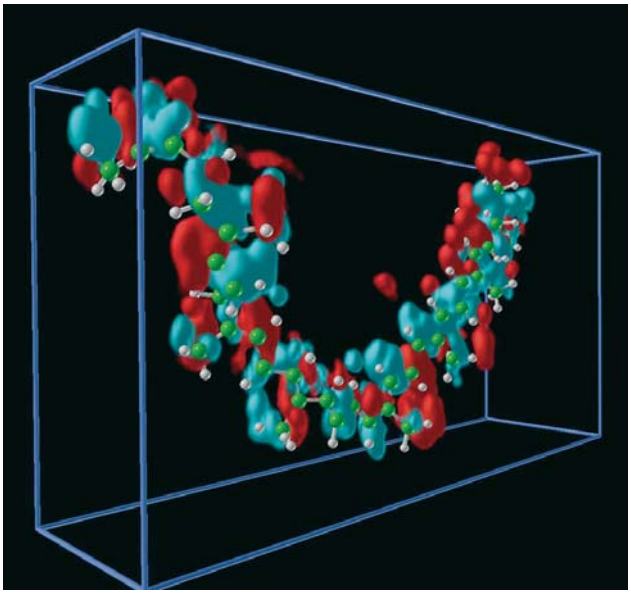

FIGURE 4 Spin density of the spheroidene molecule.

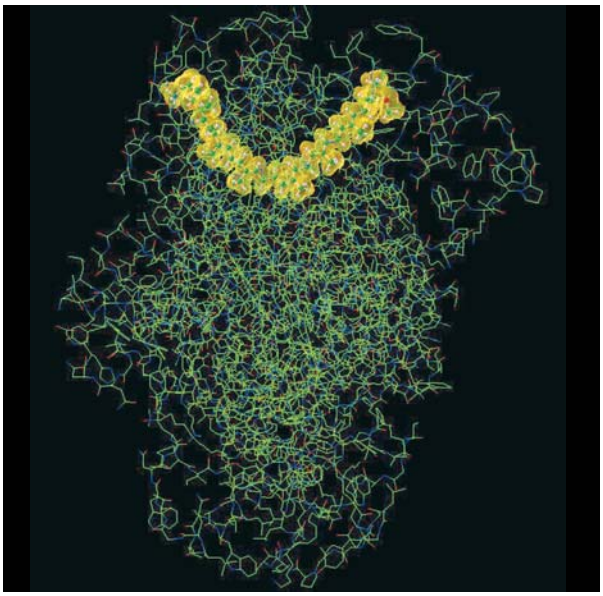

FIGURE 5 The spheroidene molecule in the protein environment. The Lester group is developing methods for approximate treatment of the chemical environment of the region surrounding the molecule studied with the accurate quantum Monte Carlo method.

levels (the feedback mechanism) and stop the excitation from reaching the reaction center where oxidizing compounds could be formed. Instead, the excitation is dissipated from one molecular system to another and the energy is safely released as heat.

Earlier studies had already identified spheroidene as a photoprotective carotenoid in bacteria, so Lester's research team set out to calculate the excitation energies and rate of triplet energy transfer between bacteriochlorophyll (a close chemical relative of the chlorophyll in green plants) and spheroidene. They have developed a linear diffusion Monte Carlo method that has high accuracy, scalability, and relative speed. The optimized Zori code now runs 10 times faster than the researchers' original algorithm, and they are now able to study systems 4 times larger than those they worked on before the INCITE grant.[2]

To make the results of their calculations more understandable, the Berkeley Lab/NERSC Visualization Group worked with the researchers to create visual images and movies of the simulation data (see Figures 2–5 and http://www-vis.lbl.gov/Events/SC04/Incite1/). As the research progresses, the visualization techniques developed for this project will be able to illustrate the energy transfer pathways of photosynthesis.

The next step for Lester's research group is to implement an electron pair localization function that describes the pairing of electrons in the spheroidene–bacteriochlorophyll molecular system, further clarifying the energy transfer pathways. Then they will apply their method to other components of photosynthetic processes, such as zeaxanthin, a carotenoid in green plants that was recently proven

[2] A. Aspuru-Guzik, R. Salomón-Ferrer, B. Austin, and W. A. Lester, Jr., "A sparse algorithm for the evaluation of the local energy in quantum Monte Carlo," J. Comp. Chem. (in press).

by Fleming's experimental group to play a photoprotective role in green plants.

The computational scientists are also aiming to develop optimal quantum Monte Carlo methods to calculate the excited state of even larger molecules involving thousands of electrons — a task that will require the capabilities of the next generation of supercomputers. Although the focus of this project is photosynthesis, the work itself is fundamental electron chemistry, so the computational methods and codes developed in this project are likely to find applications in a much wider range of chemical research.

Research funding: BES, INCITE
(Organizational acronyms are spelled out in Appendix H.)