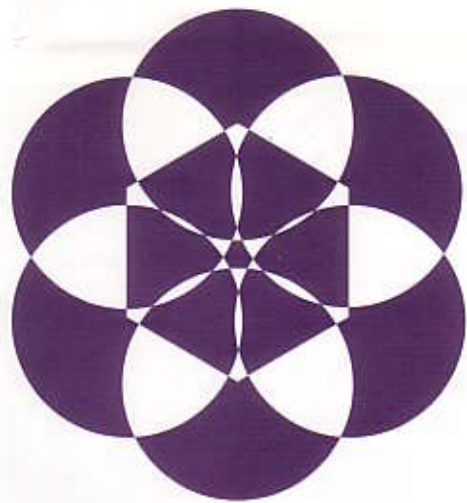


Fall 2002



Spheres

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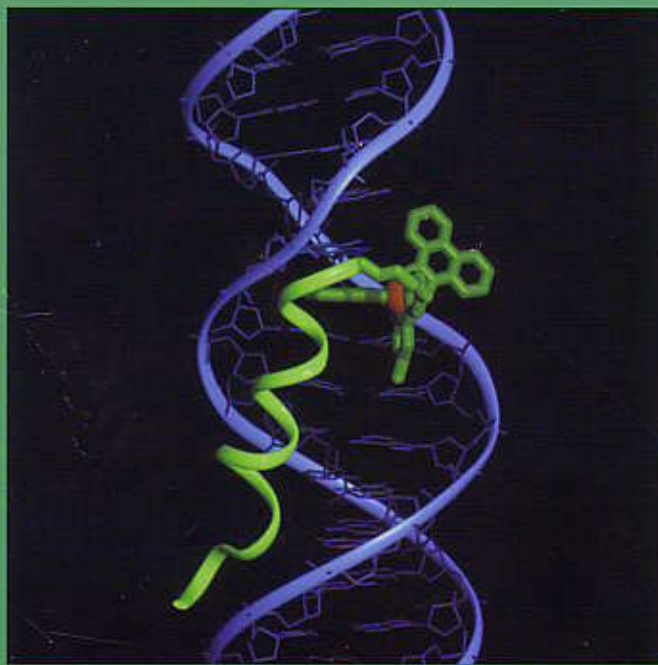
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INSTITUTE



**From
crystals full
of nothing...**



**...to DNA
charge
transfer**



Bill Goddard

De Novo Predictions of Nanoscale and Nanoelectronic Systems

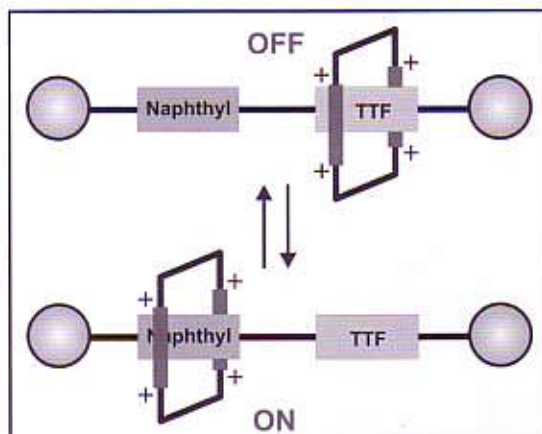
26 November 2002



First principles (de novo) calculations are another tool for the rational design of novel nanoelectronic and nanomechanical systems. Using quantum mechanics, Bill Goddard of the California Institute of Technology is investigating why and how nanosystems work – extracting the rules operating at the nanoscale level. Through collaborations with industry and universities, he has explored diverse problems including molecular switches, molecular transistors, nanomotors, DNA nanotechnology, and nanorockets.

Recently cited as a "Breakthrough of the Year" by Science magazine (*Science*, **294**, 2442 (2001)), the nanoelectronic rotaxane-based (Box 1) molecular switch devices developed by Fraser Stoddart and James Heath of the University of California, Los Angeles promise to

revolutionize computer technology. The rotaxane is comprised of a cyclo-bis(paraquat-para-phenylene) cyclophane (CBPQT⁴⁺) that is interlocked with a dumbbell component containing tetrathiafulvalene (TTF) and naphthyl groups. In the device, the location of the CBPQT⁴⁺ may be switched between the TTF and naphthyl sites using an applied bias. One configuration allows current to flow and the other does not. In collaboration with Stoddart and Heath, Goddard predicts which configuration conducts and explains the mechanism by examining the spatial distribution of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Preliminary results suggest that current flows when the CBPQT⁴⁺ ring is positioned over the naphthyl because the HOMO and LUMO are nearly degenerate and delocalized over the entire molecule. However, when the CBPQT⁴⁺ ring is positioned over the TTF, the HOMO and LUMO are spatially



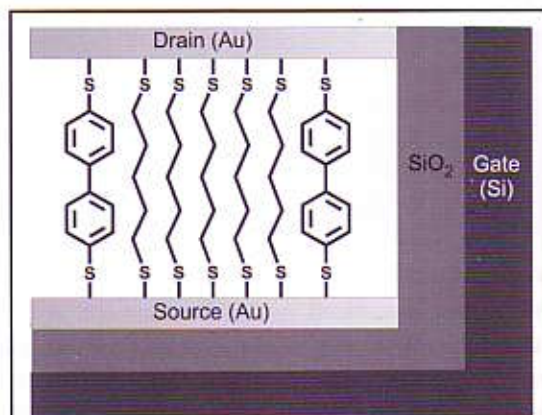
Box 1. Cartoon of a rotaxane based switch in the proposed OFF and ON configurations. Current flows only when the CBPQT⁴⁺ ring is positioned over the naphthyl group.

separated and current cannot flow. Currently, Bill Goddard is approximating the quantum mechanical behavior with force fields in order to extend the predictions to larger systems and to include finite temperatures.

In 2001, Schön et al. of Bell Laboratories proposed a molecular transistor (*Science*, **294**, 2138, (2001)). The device consists of a self-assembled monolayer of conducting 4,4'-biphenyldithiol and a non-conducting alkane attached to gold electrodes insulated by SiO₂ and gated by Si (Box 2). Much remains unknown about single molecule conductance, including how the molecules are attached to the electrodes. Excited by the possible

existence of a single molecule transistor, Goddard chose to study this system. He calculated the current versus voltage curve for a simplified transistor in which he attached gold atoms in place of the electrodes to the ends of a single 4,4'-biphenyldithiol. Goddard was unable to reproduce the experimental results for the isolated molecule case. However, he predicts that a packed monolayer of 4,4'-biphenyldithiol molecules may produce a conducting band due to the overlap of π -orbitals of the benzene rings.

Through close collaboration with experimentalists, de novo simulations have the potential to explain nanoscale phenomena and provide another means for the intelligent design of new nanoscale devices for academic and industrial problems. According to Professor Goddard, the rate limiting step



Box 2. Schematic of a single-molecule field effect transistor in which current travels through the 4,4'-biphenyldithiol but not through the simple alkane.

to future de novo predictions are "powerful computers, brilliant graduate students, and a bit of luck".

Robin Hayes (Graduate Student)
& Andrew Pelling (Graduate Student)

Review Authors



Jason Belitsky & Tae H Han



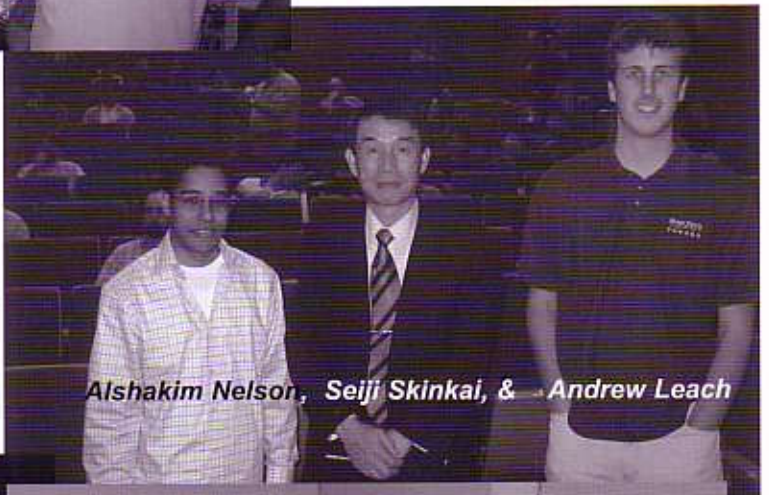
Kelly Chichak & Payam Minoofar



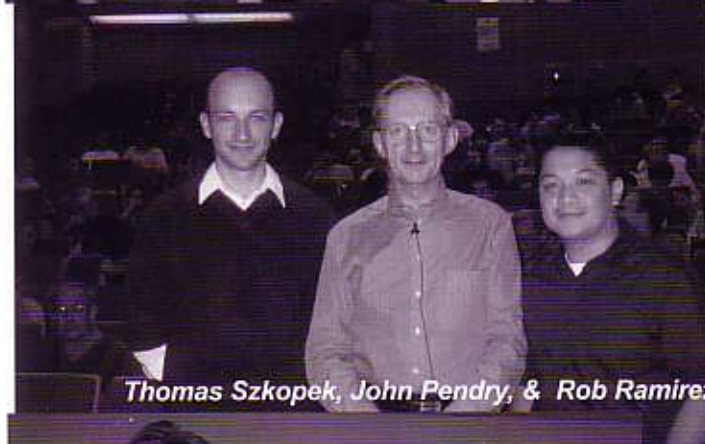
Robert Kennedy & David Steuerman



Fabien Pinaud & Emmanuel Margeat



Alshakim Nelson, Seiji Skinkai, & Andrew Leach



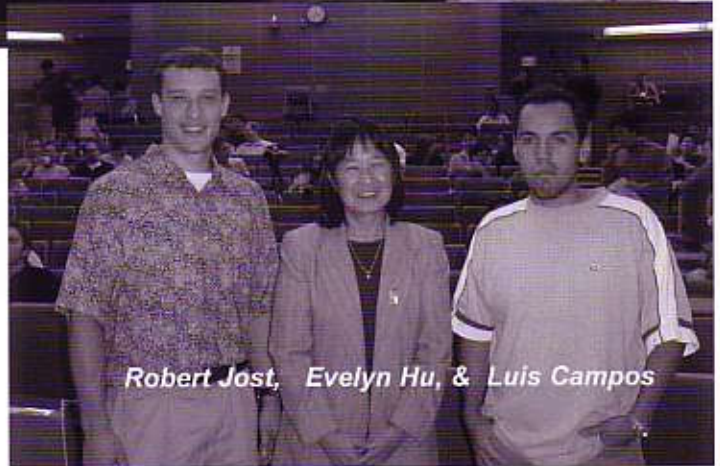
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