Beyond Basic Molecular Dynamics: New tools for the study of molecules in motion

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Molecular Dynamics

More than 75 years after the first molecular dynamics trajectory was calculated, many fundamental challenges remain the same.

Chemistry is often said to be the science of change, and change inherently involves time evolution. It is important to have theoretical, as well as experimental, tools to study the time evolution of chemical systems.

Theoretical tools provide an important complement to experiments by allowing us to:
- look directly at the mechanisms of chemical phenomena at resolutions in time and space that aren't accessible to experiments
- understand exactly what physics underlie to different chemical processes

Molecular dynamics (MD) is one of the most widely-used theoretical approaches to study the time evolution of chemical systems. The basic principle of MD is the idea that we can define a potential energy surface — a landscape which describes the forces felt by the atoms due to the underlying quantum interactions of the electrons. Once these forces are defined, MD is just the process of applying classical dynamics (essentially, Newton's famous $F = ma$) to that surface.
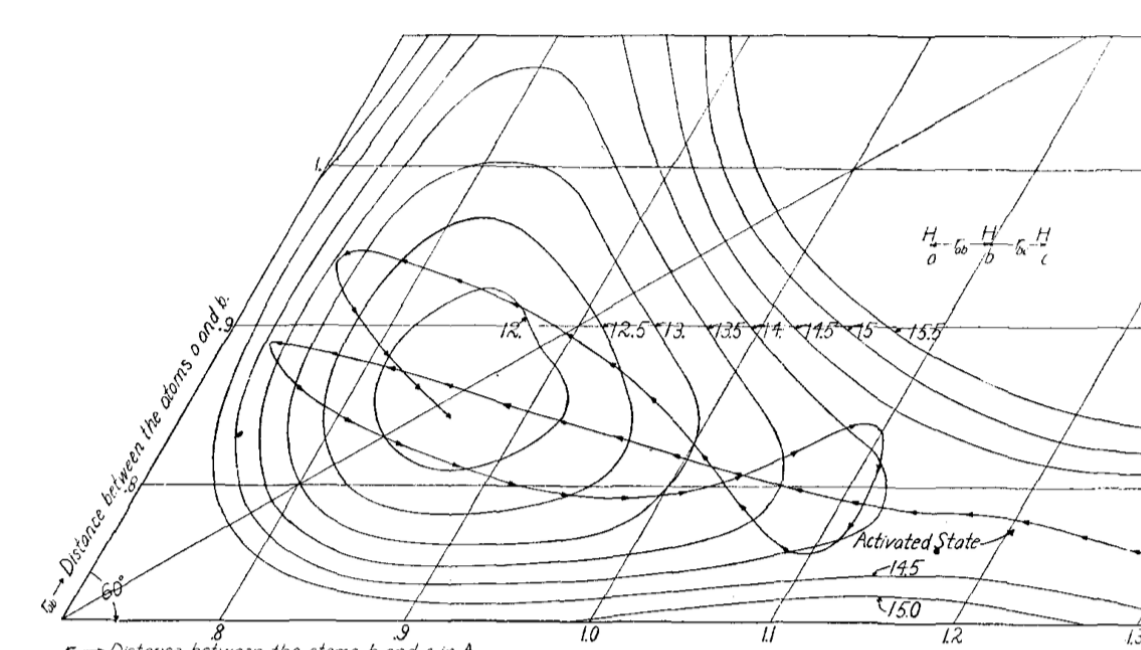
My research projects have addressed aspects of all three of these challenges.

Fig. 3. A detailed vibrational trajectory for linear H_3 is indicated by the line with arrows.
The first molecular dynamics trajectory. Hirschfelder, Eyring, Topley. JCP **4**, 170 (1936).

Three challenges which we still face in MD were present even in the first MD trajectory:

1. Accurate Potential Energy Surfaces.
This potential energy surface has a nonphysical metastable H_3 state, known as "Lake Eyring."

2. Quantum Effects.
This calculation does not include any nuclear quantum effects, which are important for reactions between light species like these.

3. Rare Events.
The trajectory gets stuck in "Lake Eyring," unable to overcome the barrier to escape to either products or reactants within the available simulation time.

Pushing the frontiers of "molecular" dynamics

Studying electron flow in nanoelectronics and molecular electronic devices using classical dynamics.

I developed the Dynamics for Classically Mapped Fermions (DCMF) semiclassical approach to study molecular electronics. The DCMF maps second-quantized operators (including Hamiltonians) to classical action-angle variables:

$$\hat{a}_i^\dagger \hat{a}_i \mapsto n_i$$

$$\hat{a}_i^\dagger \hat{a}_j \mapsto \sqrt{\left(n_i^2 + n_i + \lambda\right)\left(n_j^2 + n_j + \lambda\right)} \times e^{i(q_i - q_j)}$$

$$\hat{a}_i^\dagger \hat{a}_i \hat{a}_j^\dagger \hat{a}_j \mapsto e^{-\alpha^2 (n_i - 1)^2} e^{-\alpha^2 (n_j - 1)^2}$$

An important aspect of this is that instead of trying to describe arbitrary potential energy surfaces in terms of second quantization, we bring second quantization into the realm of classical molecular dynamics. We have tested the DCMF, with good results, on three models of molecular electronics:

Landauer   Holstein   Anderson
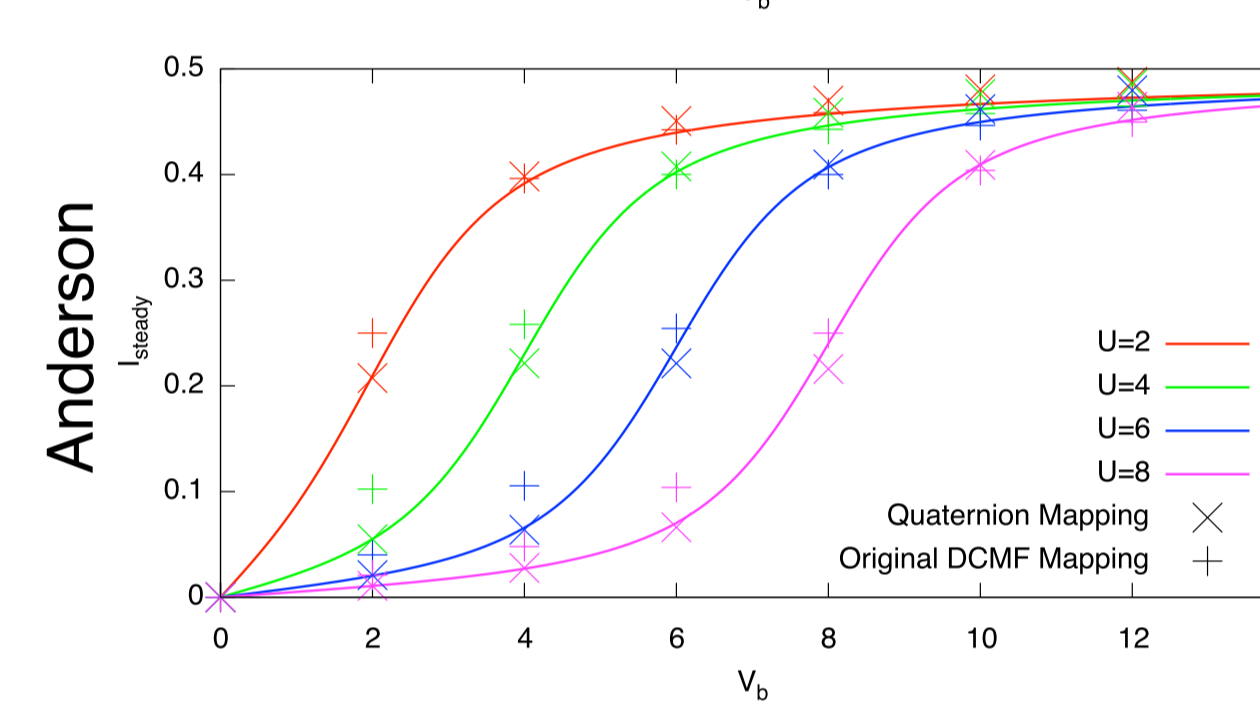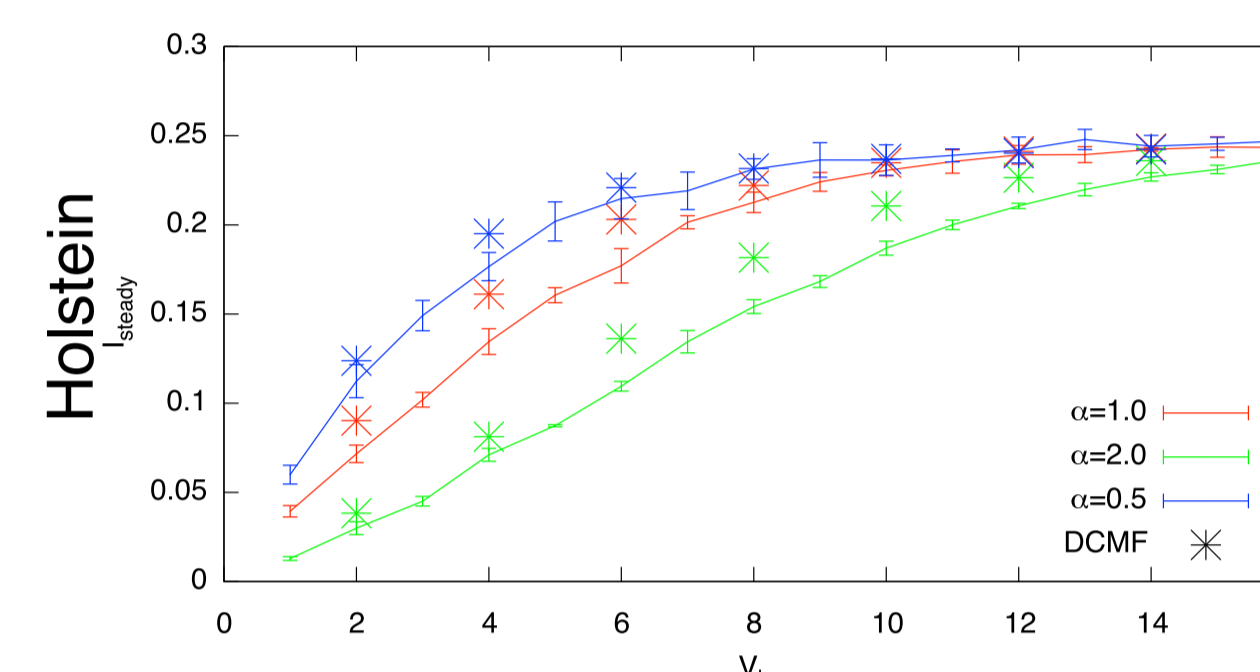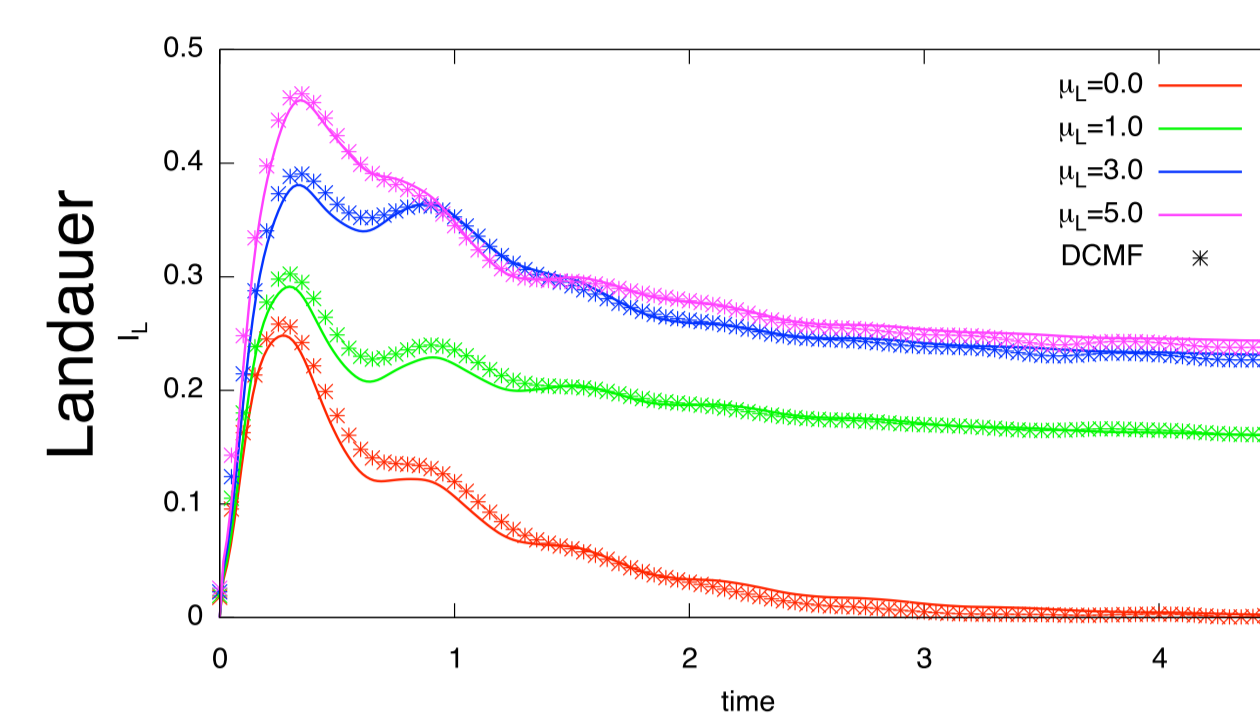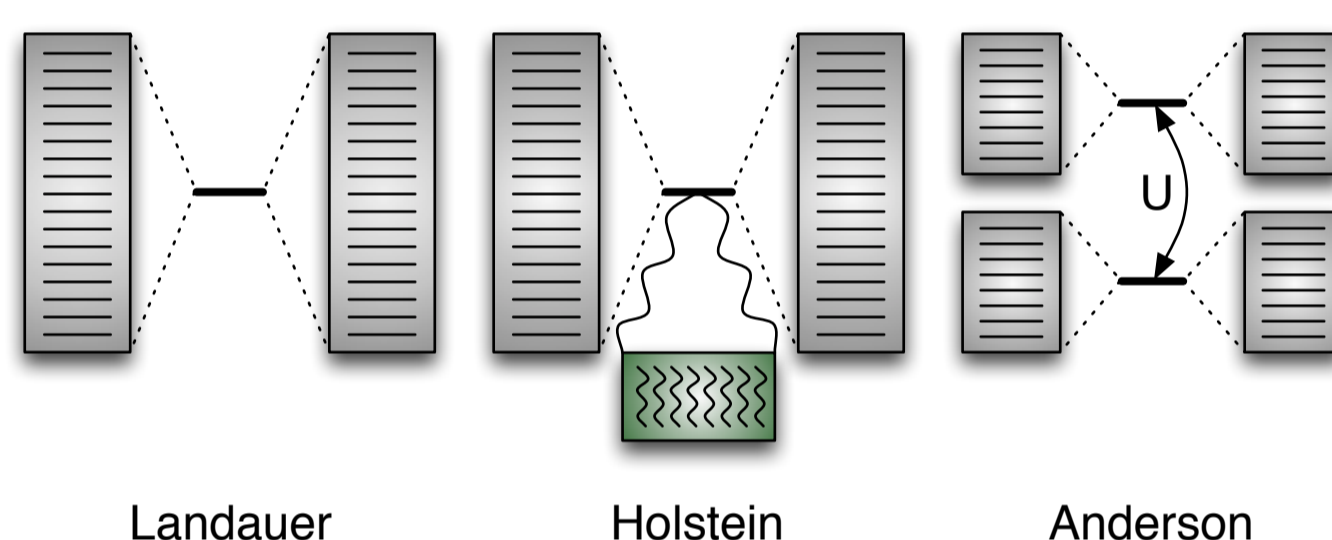
A new perspective on quantum effects

Deepening our understanding of the role of quantum dynamics, including in energy transfer processes and photosynthesis.

The double Herman-Kluk semiclassical initial value representation (DHK-IVR) approximates the quantum time correlation function for operators A and B as:

$$C_{AB}(t) \approx \int d\mathbf{\Omega}_0 \int d\mathbf{\Omega}_0' \, A(\mathbf{\Omega}_0, \mathbf{\Omega}_0') \times B(\mathbf{\Omega}_t, \mathbf{\Omega}_t') \, C(\mathbf{\Omega}_t, \mathbf{\Omega}_t') e^{i\Delta S}$$

where each of the integrals is over a full phase space, the functions A and B are the coherent state matrix elements for those operators, and the function C contains information from the semiclassical prefactor.

I am developing ideas based on the "important initial phase space distribution" (IIPSD): the set of points in the phase space at $t=0$ that make significant contributions to the integral. Using the idea that individual functions can be see as envelopes over their products, the IIPSD approach finds evidence of quantum coherences much faster than it would normally take to calculate them.

These ideas can be applied very broadly. I'm currently using them to explain some paradoxes in energy transfer processes.
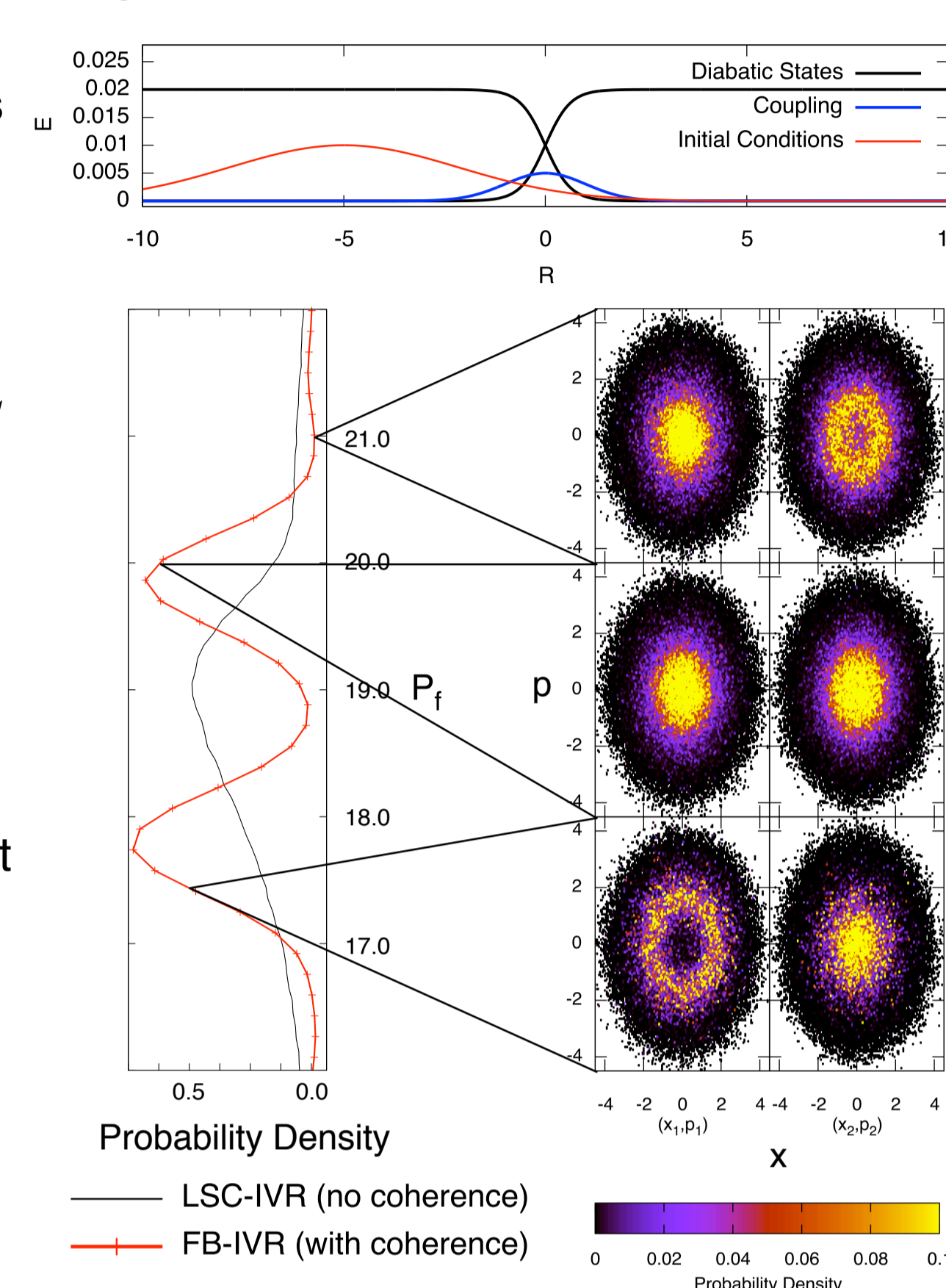

The structure in the IIPSD moves from one electronic state degree of freedom to the other, depending on the final momentum measured.


Methods for studying networks of rare events

Creating new and efficient tools to study the networks of rare event transitions that occur in systems with multiple states.

Correlated Rare Events

Transition interface sampling (TIS) is an efficient method for calculating rates of chemical processes. We are extending TIS to situations with correlated rare events: where a previous transition can affect a later transition. In the process, we have developed multiple interface set TIS.
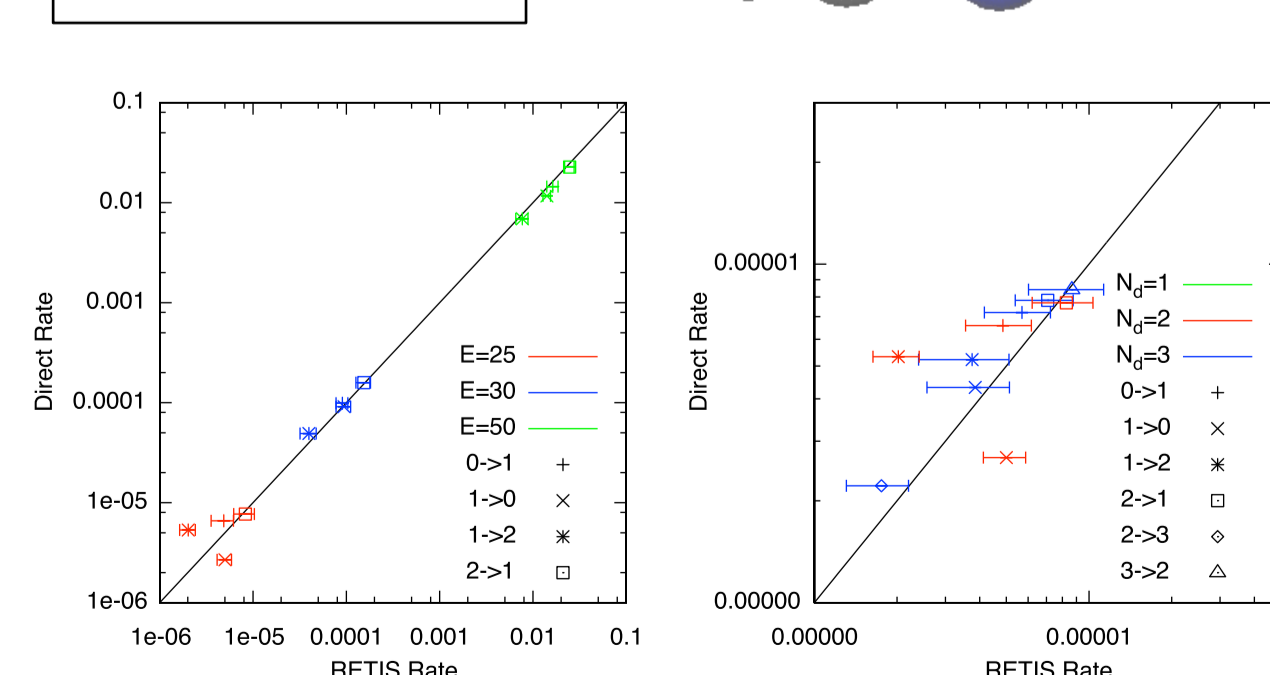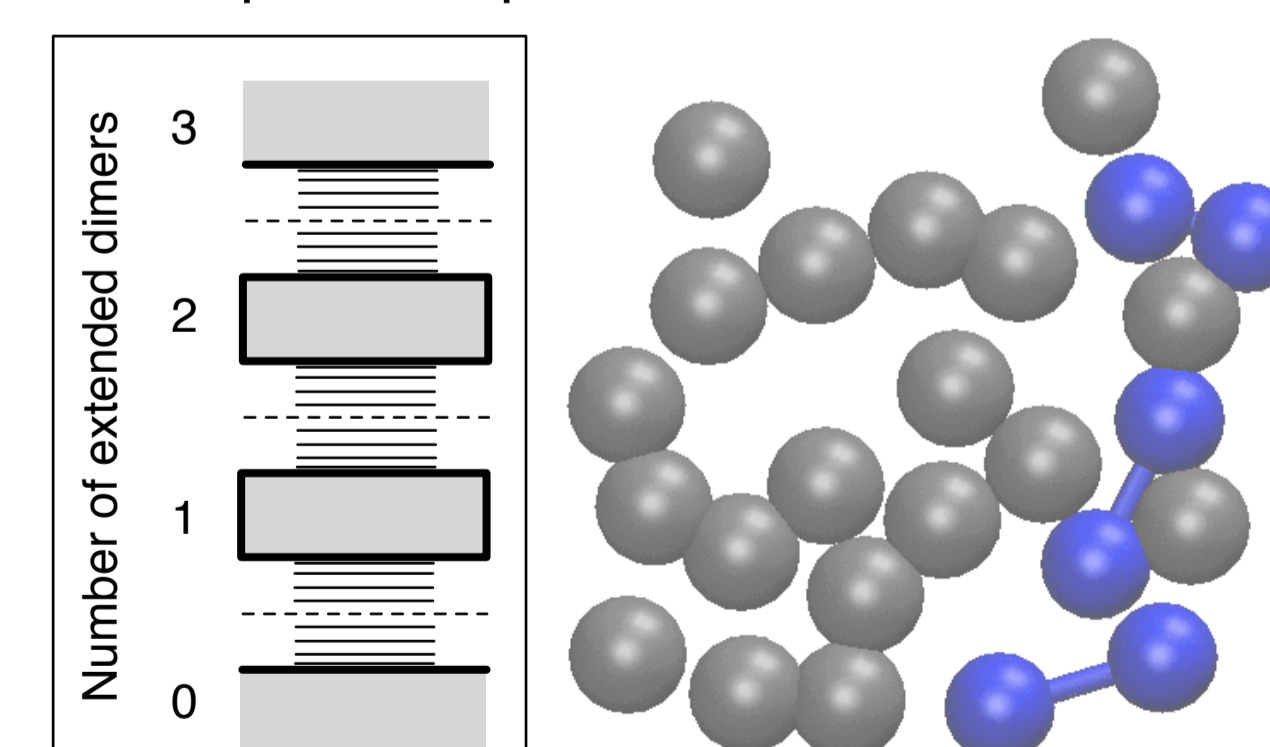
### "Push" vs. "Pull" Interfaces for Rarer Events
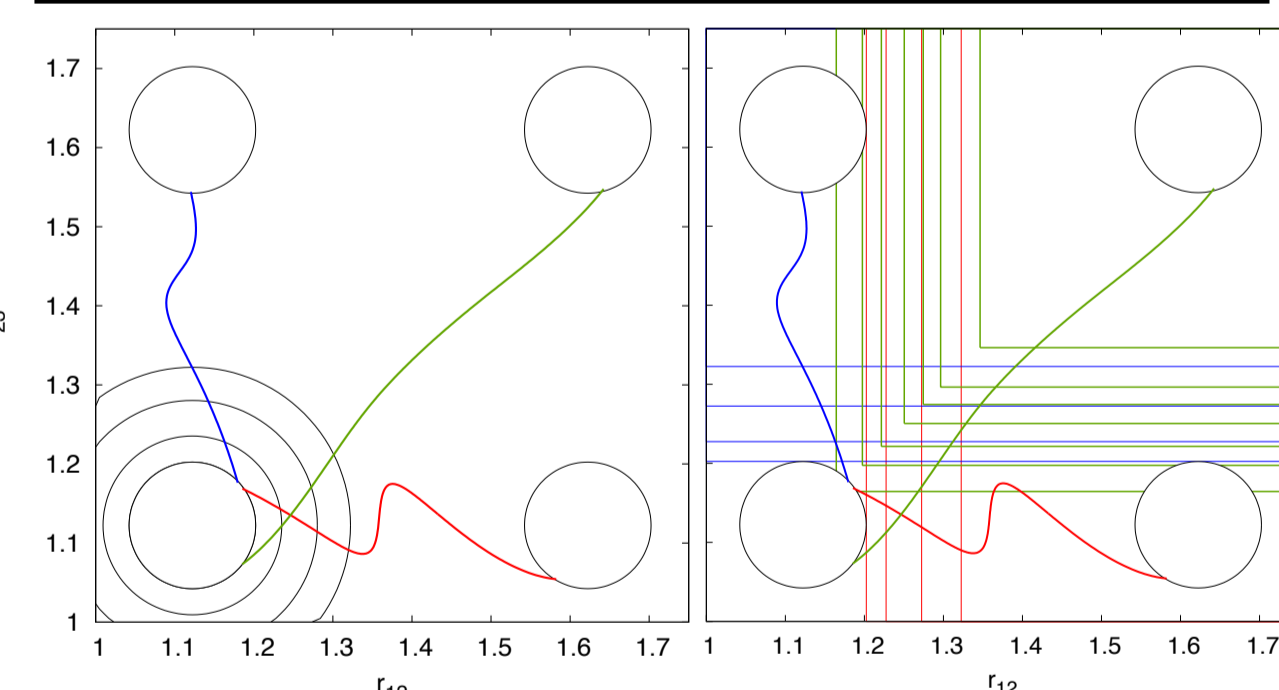
Rates for different transitions can vary widely, making it difficult to efficiently sample them all in one calculation. In this example, the diagonal transition is less likely than the other transitions. By using multiple interface sets, we can efficiently calculate the rates for all transitions at once.
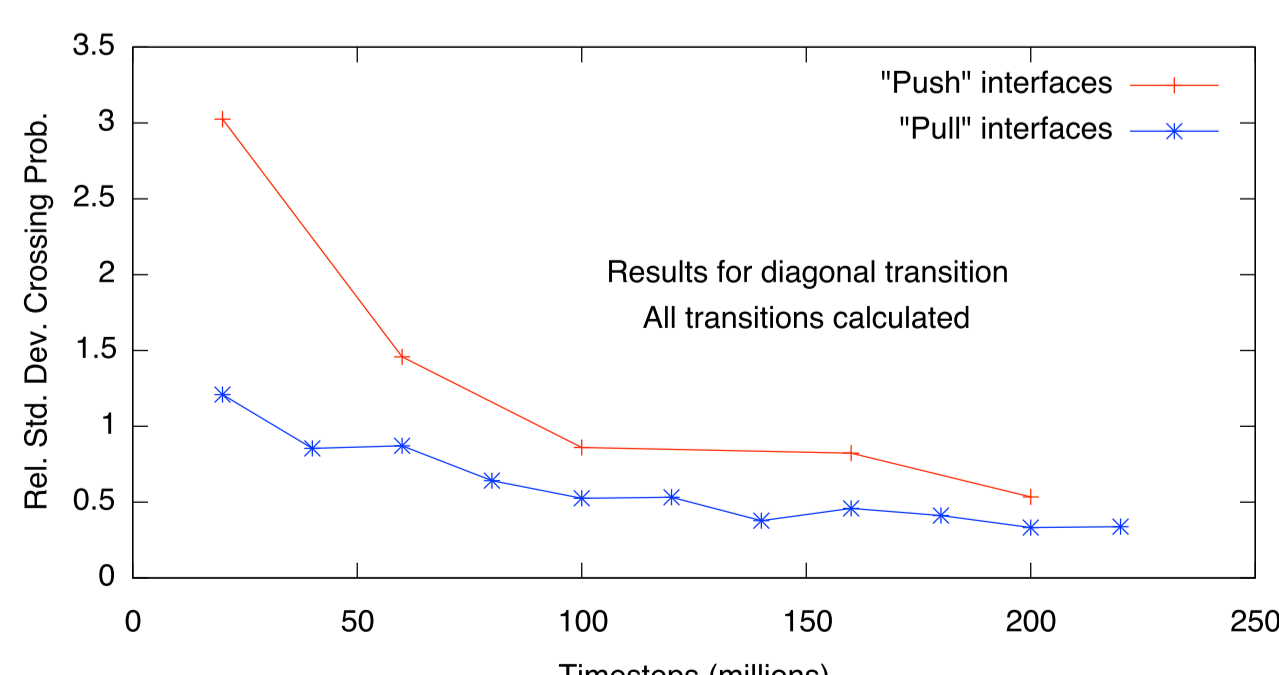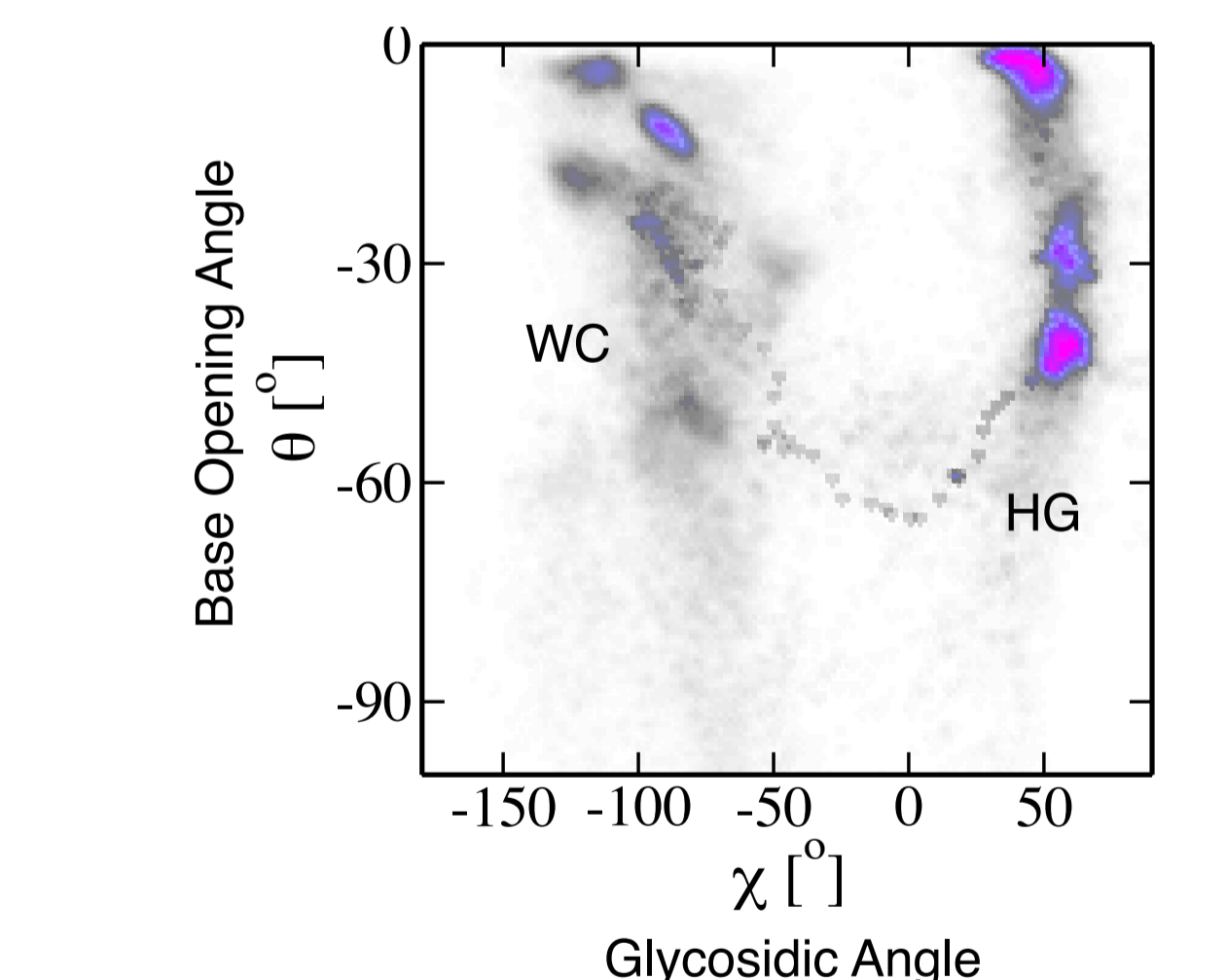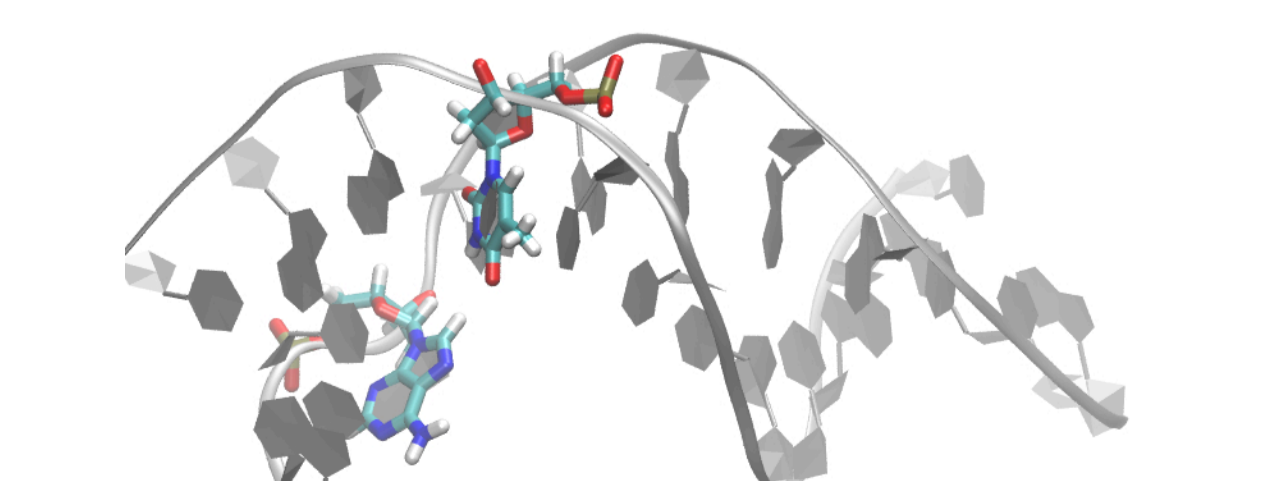

Simulating DNA

Learning about the processes of life at the scale of atomic motion.

Nikolova et al. Nature. **470** 498 (2011)
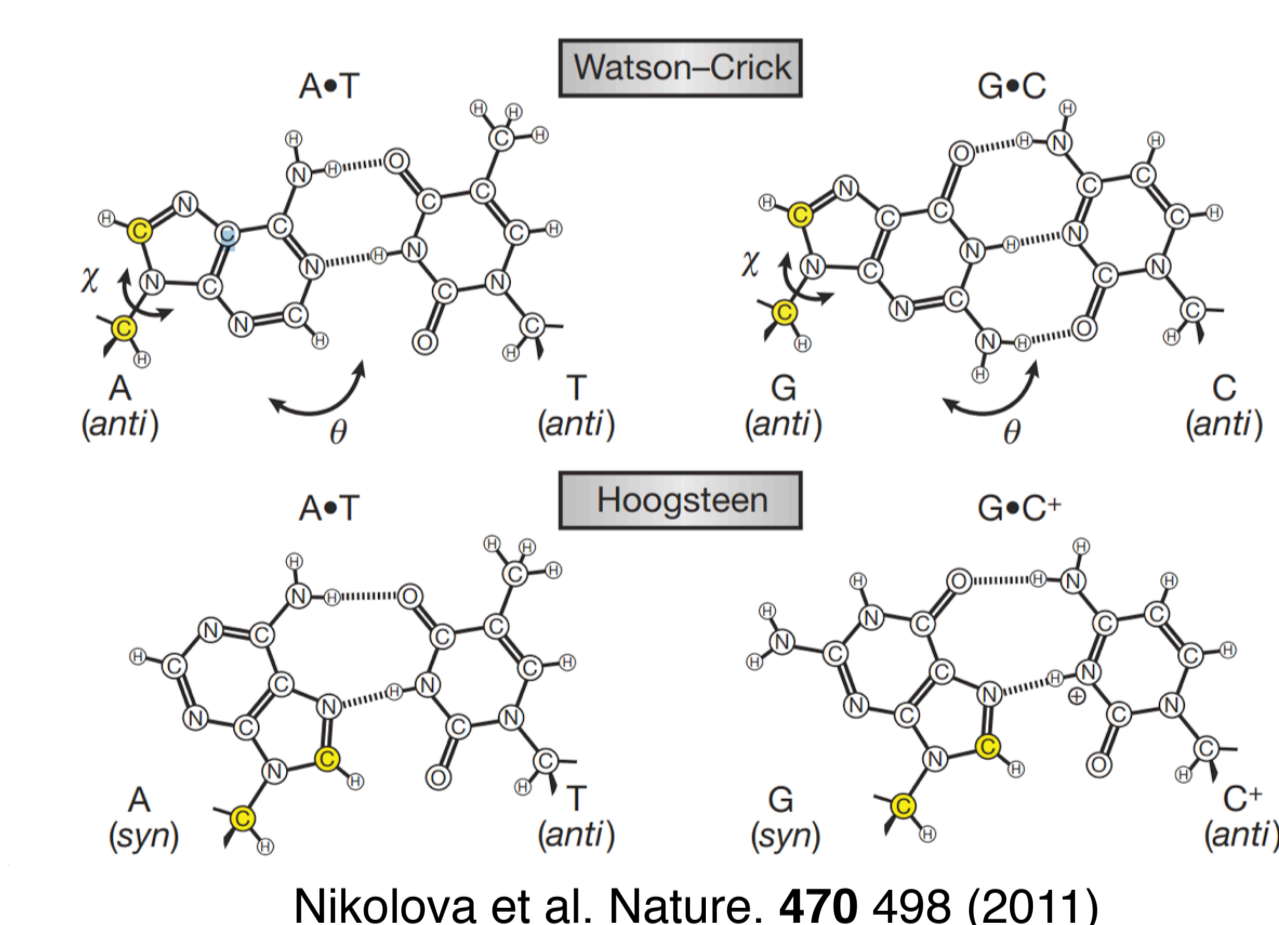
The Watson-Crick (WC) DNA base pairing motif is one of the most familiar topics in biochemistry. However, it was only recently shown that an alternate motif, Hoogsteen (HG) base pairing, occurs at physiological conditions. We are using path sampling methods to study the mechanism and rate of the conversion between WC and HG motifs.

Path density plot from 854 transition paths of the WC→HG transition.

Future Work:

I am planning to simulate other processes involving DNA. The Hoogsteen pairing motif also appears in DNA triplex formation, a topic in which I am interested. I would also like to simulate the recognition process in DNA-binding proteins. The transition interface sampling tools I have developed may be useful for these studies as well.

Teaching

Educating students at all levels, from high schoolers likely to drop out to graduate students at top universities.

I help students at the top and at the bottom with extra materials.
When I teach a course, I develop two kinds of extra materials for students: for the students who are struggling, I prepare review packets on basic concepts. For advanced students, I prepare extra challenge questions aimed at deepening their understanding of the subject.

I use new technology when appropriate.
Technology has enabled all sorts of new teaching methods. I take an approach of cautious optimism: I'm eager to use technology in my teaching, but I always ask whether it will help the students learn, not whether I think it is fun.

I use faculty research and current events to show the relevancy of the course.
When possible, I try to connect the lectures and problems to topics from current events. I also try to emphasize when a subject is close to the research interests of a professor they might know, and I bring in recent scientific articles that highlight subtle aspects of the material from the course.

Examples of teaching materials I have developed are available at http://www.hyperblazer.net/teaching/

Universiteit van Amsterdam
Second-Year Student Project
Supervisor. Designed and planned a research project for undergraduates in chemistry.

Molecular Simulation Tutorial
Teaching Assistant. Guided several computer lab sessions.

University of California, Berkeley
Advanced Quantum Mechanics
Teaching Assistant. Served as the only TA for a class of about 40 chemistry grad students.

Physical Chemistry
Teaching Assistant. Undergraduate course introducing the principles of quantum mechanics.

General Chemistry
Teaching Assistant. Led discussion and lab sections in a course for non-majors.

Lycée Le Corbusier (Illkirch, France)
English Assistant
Taught English at a French high school to students who ranged from housepainter apprentices to future architects.

Colorado College
Chemistry and Physics Tutor