Computational Nanoscience
NSE C242 & Phys C203
Spring, 2008

Lecture 28:

Wish-list, Reactions, and X-Rays

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We Know this Class Has Been Perfect….

…BUT, just supposed for a moment that it hadn't been. How can you imagine it changing? (I know, I know, but *stretch* your imagination!)

We'll help get started. For example, you could say that this class has been "A technological and pedagogical tour-de-force"…you wouldn't change a thing, you just wish we had even more lectures, like a whole lecture on:

- Interfaces, Doping (e.g., p-n junction, Schottky barrier)

- Optical properties (more details on LDOS/DOS/etc)

- Surfaces/Adsorption

- Finite-element and more on mesoscale modeling

We Know this Class Has Been Perfect....

From the crowd:

Quantum chemistry approaches, like post-HF (since HF was already old news)

More tight binding? A tight binding code?

Helpful with examples – real world examples tied everything together well. On each code, some examples were ok but some didn't get realistic enough…more explanation on connection of results to materials.

In-class simulations very helpful. More instruction on the nanoHUB about what the parameters mean, simple tutorials for the toolkit, etc.

Intro to quantum mechanics, then QMC, but needed much more intro if didn't know QM so the lecture kind of useless…

Covered DFT but still much more to learn for DFT – aux text or citations to books, etc. would be helpful. (short ie 10 pages references would be useful)

We Know this Class Has Been Perfect….

From the crowd (continued):

References to good texts on coding, and more CS aspects of course

Would like to see more of the "guts" of these tools…one possibility make it 3 or 4 units but allow for time to play with code, get into how the codes work, etc.

With a discussion section that time could be spent doing simulations and talking about the codes more.

Should have been 3 units.

Online breeze presentations, or podcasts would have been nice.

Modeling Chemical Reactions

Most reactions of interest take place in some kind of medium, such as in a solvent, in an enzyme, or on the surface of a catalyst.

This environment can have a significant impact on the reaction (e.g., speeding it up, slowing it down, etc.).

Isolated systems are a good place to start, i.e., with no medium or environment.

Sometimes these "gas phase" reactions represent the actual system, but in most cases one needs to take careful account of the surroundings.
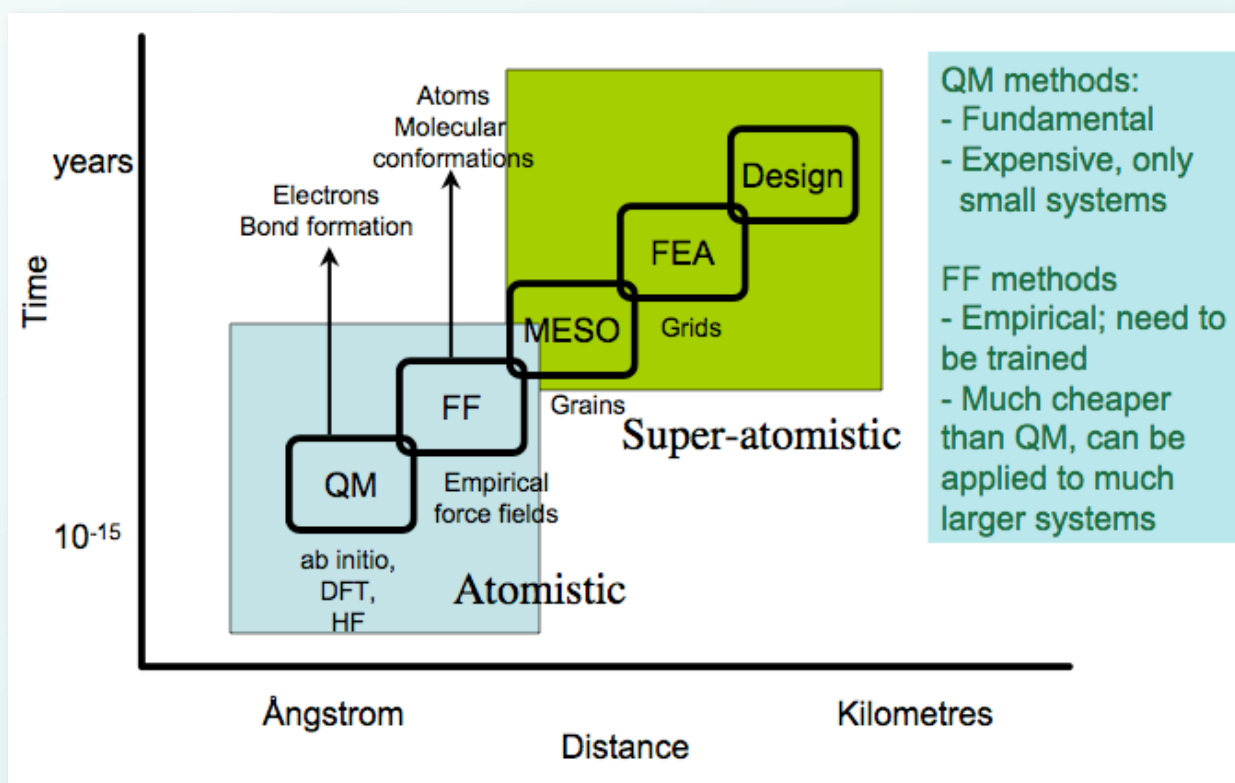
So…the place to begin is to choose which method is appropriate. And that would be?

Yes, a good start could be to use quantum mechanics, at least when possible. Why?

Still, there are many cases where an empirical approach can give satisfactory results.

Modeling Chemical Reactions

As usual, it depends what kind (in this case that means size) problem we need to solve.

Nudged Elastic Band

If only the reactant and product are known, the Nudged Elastic Band approach can give good results for the transition state.

In this approach, the path between the reactants and products is split up into a sequence of "images" which are equally spaced along the reaction coordinate.

Each image is then optimized but only in the direction perpendicular to the negative gradient of the energy.

In this manner, a saddle point, at least near one or another equilibrium geometry, can be approximated.

You've already learned about this in much more detail during a wonderful lecture by Elif.

Molecular Dynamics

Using MD to study reactions is perhaps the most accurate overall approach, since:

One can assess the effects of temperature

One can allow the full reaction to evolve in real time, obtaining (possibly even physical!) dynamical information.

Unexpected events may be observed. In other words, nothing need be known about the transition state or the products.

Modeling Chemical Reactions

If one is interested in modeling a reaction using molecular dynamics, there are effectively three options:

Fully quantum mechanical MD (major CPU burning will ensue!)

Use empirical assumptions (semi-empirical methods), e.g.,
- CINDO/MINDO/AM1/MOPAC
- Tight-binding
- Analytical Bond Order Potentials

Add ability to simulate reactions to force-field method (empirical bond-order based force fields)
- Tersoff-potential
- Brenner/REBO/AIREBO
- ReaxFF

Empirical Approaches for Reactions

Many groups have developed force-field models for studying reactions.

The model specifically designed for reactions is usually derived by extending an existing force field to enable the structures and relative energies of transition structures to be determined.

The main approach is the following:
- Take some "core part" of a reaction, e.g., without substitutions
- Compute all possible "sterio-isomers" for the reactions (stable products) and the corresponding transition states.
- Re-fit the potential to be sure that these data agree well with experiment.

Now apply the new potential to a more complicated reaction with any substitution…and keep your fingers crossed!

Modeling Chemical Reactions

Sophisticated empirical methods, such as "Airebo" and "ReaxFF" have progressed quite a bit and can in many cases reproduce experiment or DFT.

- Reactive force field can be used to simulate the entire reaction pathway
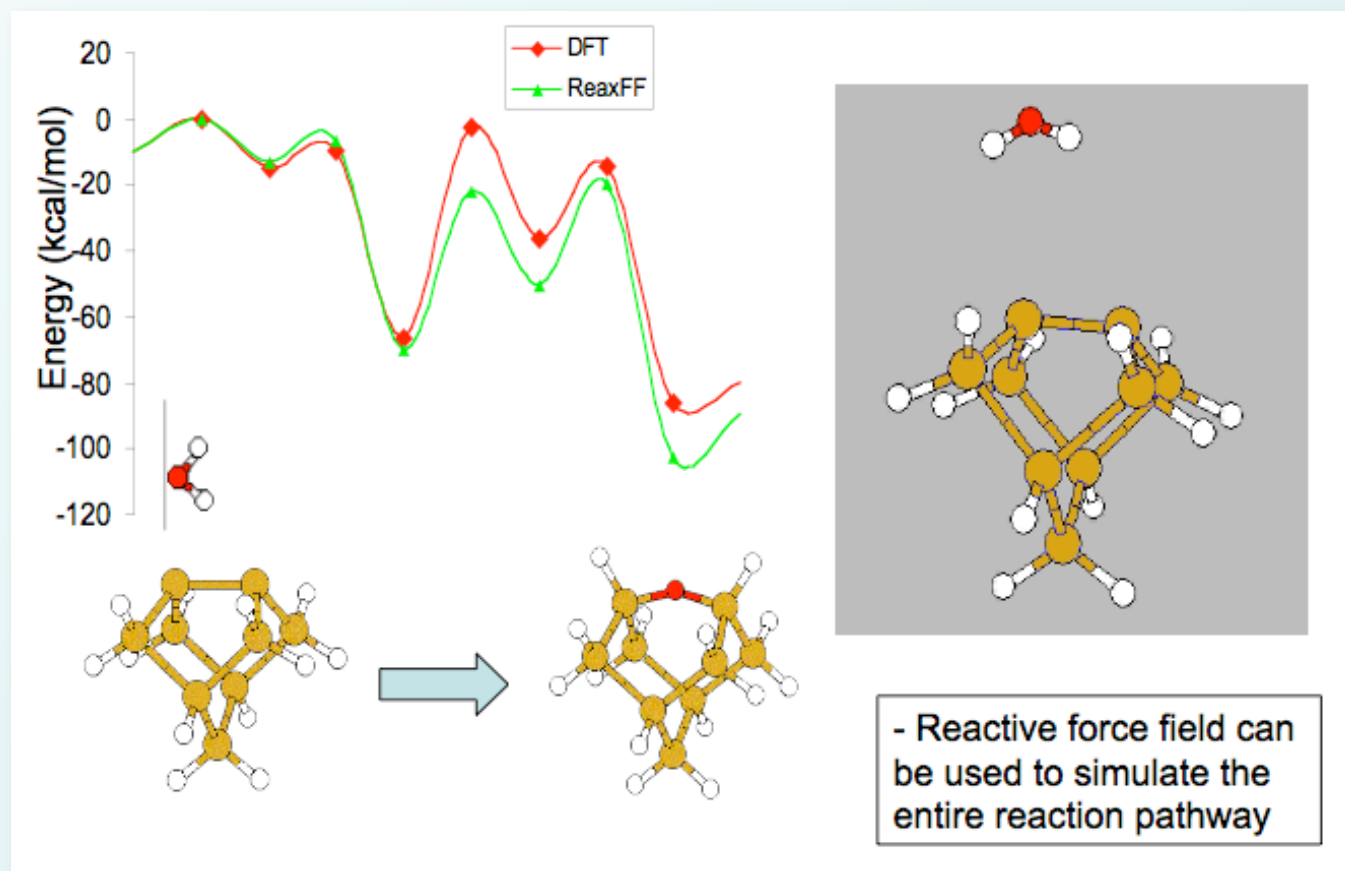
QM/MM

One approach to simulate chemical reactions, especially in solution, is to use a combination of quantum mechanics and molecular mechanics.

The "reacting" parts of the system are treated quantum mechanically, with the rest of the system being modeled using force fields.

Then, the total energy is E = E(QM) + E(MM) + E(QM/MM)

Perhaps the best known QM/MM approach is the "ONIOM" method developed by Morokuma.

One of the "hot" areas of research that employs these hybrid methods is in the simulation of enzyme reactions. (see, e.g., Warshel et al).

Reaction Examples

Let's spend some time doing a real calculation or two.

First, we'll start with something very simple (or seemingly so!) - the H2 molecule.

Then we'll move from there to water.

Then, we'll probably already be out of time, which is too bad since those are kind of model problems…but hopefully it will give you a good sense of how to do this kind of thing.

Reaction Example: H2

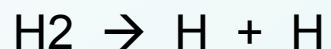How do we compute the dissociation curve for an H2 molecule??

First step is to choose a code and a level of theory.

We'll start with GAMESS and Hartree-Fock.

We know that in Hartree-Fock the hydrogen atom has an energy of exactly -0.5 Hartree.

H2 Dissociation

Example Reaction:

H2 → H + H

Once we have the relaxed H2 molecule (for the given method and basis), we can begin to dissociate it by hand.

That is, we could simply compute a series of total energies for the system as the H atoms drift apart.
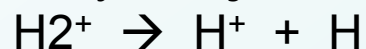
Will this work?

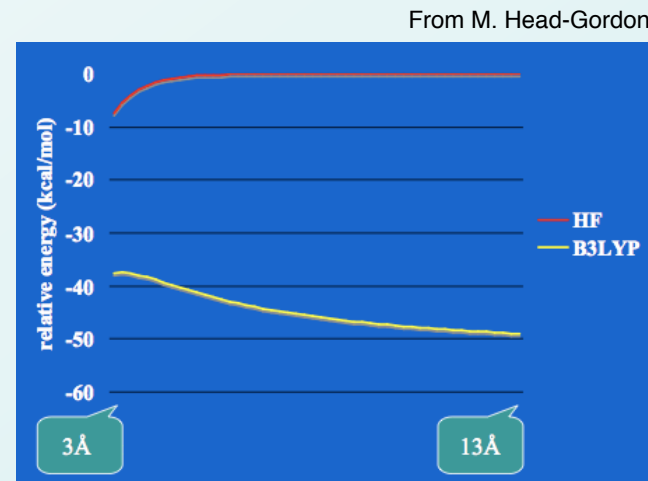> Yikes! The self-interaction problem (remember that?) is coming back to haunt us!
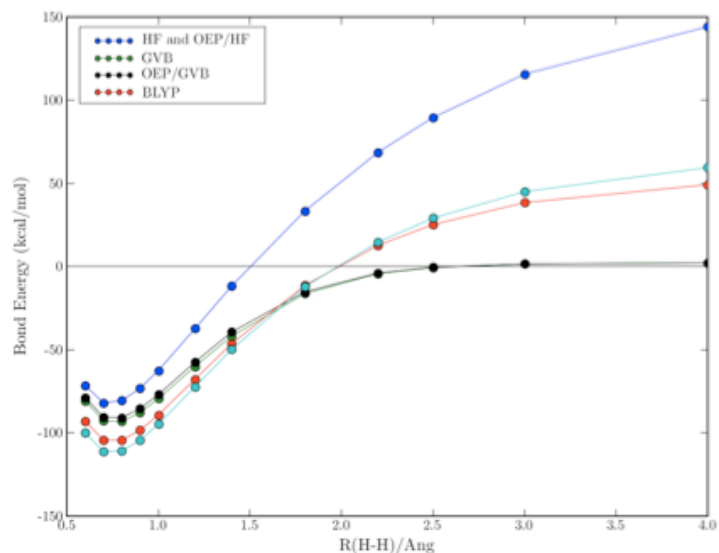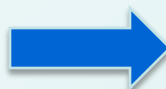
H2+ Dissociation

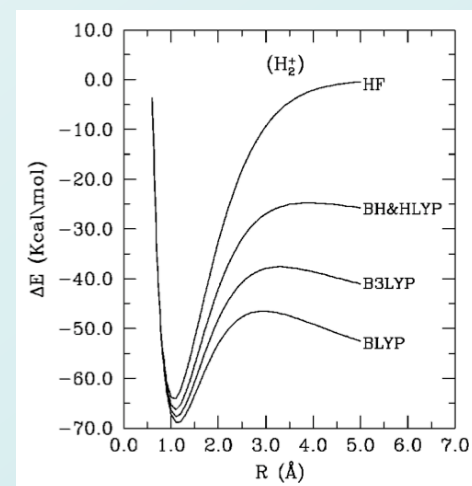Well, certainly with **just 1 electron** it must be easier for DFT, right…??

$H2^+ \rightarrow H^+ + H$

From M. Head-Gordon
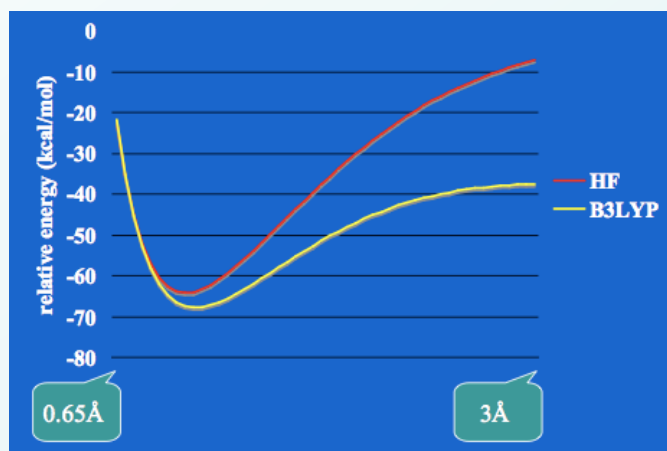
Sort of close-looking…kind of.

…actually, disastrous!

This is a very active area of research!

Jeffrey C. Grossman and Elif Ertekin, *NSE C242 & Phys C203, Spring 2008, U.C. Berkeley*

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Water Formation

Let's move on to a more complicated reaction:

H2 + O2 → H2O ….ok, actually 2H2 + O2 → 2H2O, right?

So, where do we start on this one?
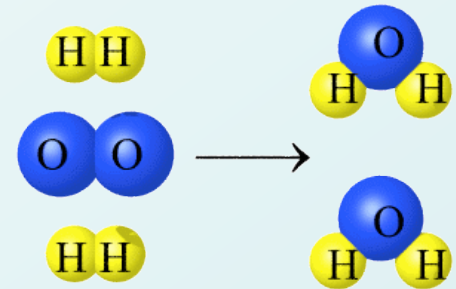
Water Formation

Hartree-Fock, Post-HF, etc., differ substantially

DFT shows NO barrier!!