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Molecular mechanics

Introduction to molecular mechanics and force fields [edit]

History of Molecular Modelling and Molecular Mechanics [edit]

The origins of the molecular mechanics method can be traced to work done by Barton in the late 1940s, as well as Bright-Wilson (Molecular Vibrations, 1938. DOI: 10.1063/1.1750232) and others in the late 1940s and early 1950s and e.g. Allinger (starting in 1959, DOI: 10.1021/ja01530a049) and the MM2/3/4 force fields and Kollman/Amber in the 1970s-80s.

Norman Allinger

The Force Field [edit]

The **steric energy** of a molecule is defined by the following terms (normally five, but can be more). These terms are independent, and each relate to transferable properties of molecules. The constants in these equations together constitute what is called a mechanics **force field** (notice how there are no terms relating to electrons, apart from being implied in the charges $\mathbf{q}_i$ on the atoms!).

$$E_{\text{steric}} = \sum_{\text{bonds}} K_r(r - r_{eq})^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}[1$$

https://wiki.ch.ic.ac.uk/wiki/index.php?title=Mod:mechanics

DON'T PANIC

A Beginner's Guide to Computational Chemistry Module 1 and Beyond

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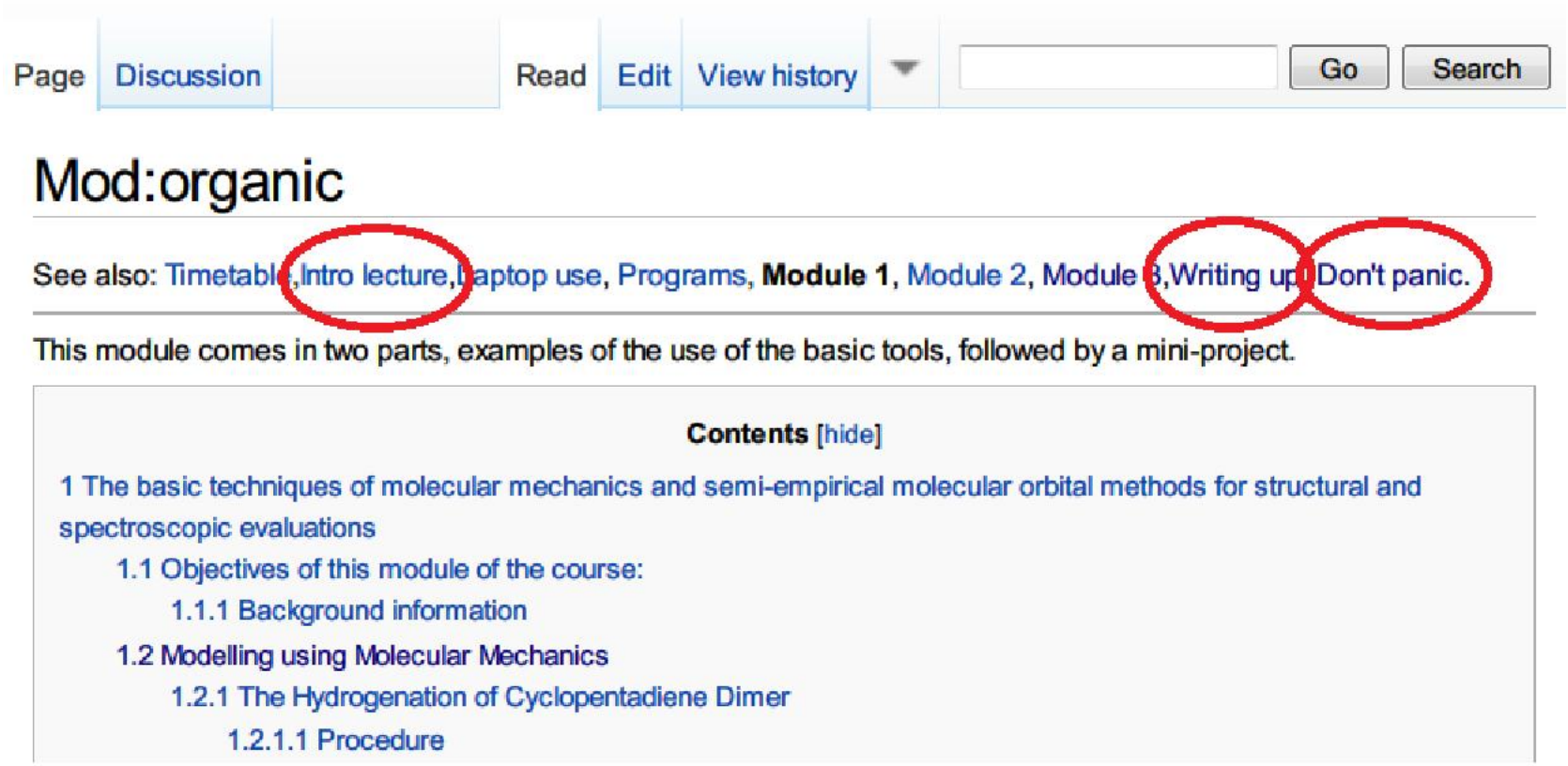
Where to get help?



Why Wiki: it's an efficient way to communicate your results.

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Computational Chemistry Techniques

- Molecular mechanics: balls and sophisticated springs.
- Semi-empirical calculations: make approximation to cut computational cost.
- *Ab initio* calculations: (almost) full quantum mechanics, time and resources consuming.

Each of these techniques has strengths and weaknesses, and evaluating them is an essential part of your assignment.

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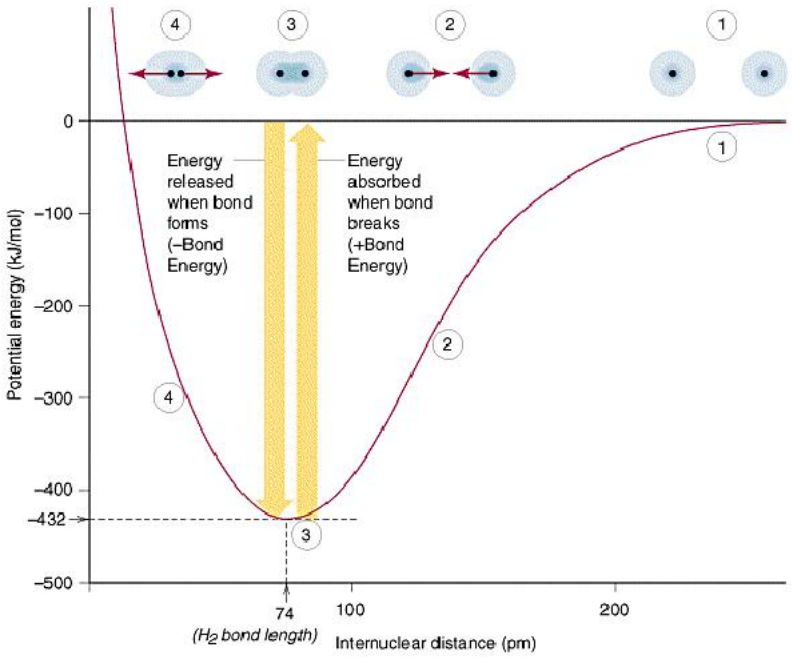
Molecular mechanics



- Balls and sophisticated springs.
- Carefully calibrated force field parameters
- Can only calculate what it has been instructed how to. Purely organic technique.
- Cannot handle orbital interactions, bond forming/breaking processes.
- Can handle VERY LARGE MOLECULES.

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Molecular mechanics

Cyclopentadiene

Stretch:	1.2855	
Bend:	20.5794	
Stretch-Bend:	-0.8381	
Torsion:	7.6571	
Non-1,4 VDW:	-1.4171	
1,4 VDW:	4.2322	
Dipole/Dipole:	0.3776	
Total Energy:	31.8766	kcal/mol

- Energy is calculated by how much deviation from the perfect structural parameters.
- The breakdown of different types of energy is very important for analysis and identifying why one structure is more stable than another.
- You are expected to understand the meaning of each of these terms (see Intro Lectures page).

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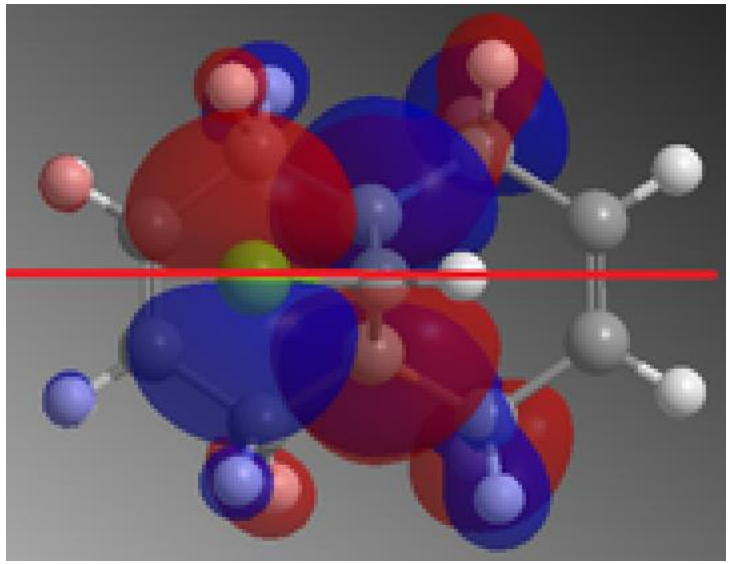
Semi-empirical methods



- Fast
- Can optimise structures, calculate MOs, electron density and distribution and a range of physical properties.
- Can competently handle organometallic compounds.
- Can model electronic effects, H-bonding, orbital interactions, transition states.
- Pay for speed with accuracy!

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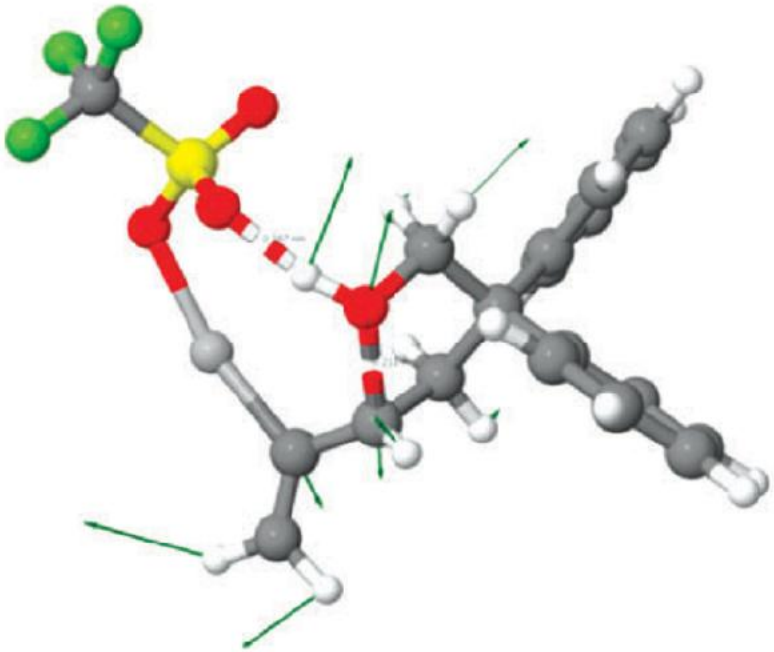
Ab initio methods



- Full quantum mechanics calculation, with some minor ‘approximation’.
- Accuracy depends on the basis set and the method (HF, DFT, MP4, CCSD).
- Basis set: a finite set of functions used to create MOs.
- Computational cost increases exponentially with number of electrons and size of basis set.
- NEED A SUPERCOMPUTER!

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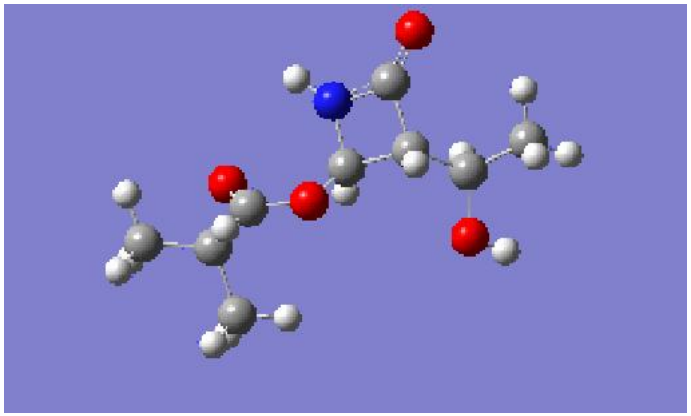
Ab initio methods



- Density Functional Theory calculation is your main tool for mini project
- Can competently handle all type of compounds and transition states.
- Can calculate energy, enthalpy, entropy, solvent effect, NMR chemical shifts and coupling constants, circular dichroism, optical rotation, IR vibrational frequency.
- Fairly fast compared to other *ab initio* methods.

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Warnings

- The software packages don't come with an AI.
- Only good starting structures will give good optimised structures. Local minima can lead you astray.
- Beware of the Visual Editing – Calculation – Visual Display cycle. What you see on screen isn't always the true results.
- Use your chemical intuition.

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What is expected of you?

1. The module is problem-oriented, you get to decide which technique to use.

2. We give guidelines and suggestions, but you decide.

3. ANALYSIS trumps results. Watch out for:

   - Energies
   - Bond angles and dihedral angles
   - Molecular orbitals (bonding, anti-bonding)
   - Bond strength, bond lengths and vibrational frequencies

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Data presentation

- No special award for the best wiki page
- We want clear, concise description of your work.
- If we can't see something clearly, we can't give it marks! Some visual aids often help.
- For you mini project, tell us exactly what question you are trying to answer.
- Keep Chem3D files of your work, you might be asked for them.

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TALK TO US!

- We're here to help you.
- Mini project must be discussed with us before attempted.
- Our advice is to start your mini project as early as next Monday. Many things can go wrong in research!
- Write your wiki as you go along, don't leave it until the last day to learn.
- If you can finish your four questions by Friday, send your link to me and I'll give you some feedback, without any penalty to your final mark.

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TALK TO US!

- Matt Hughes, Demonstrator, in room 232 between 12.00 and 17.00

- Dr Bao Nguyen, between 14.00 and 15.00
  Email: b.nguyen@imperial.ac.uk, at any time.