The University Of Sheffield.

Research Councils UK Energy For a Low Carbon Future

Modelling the interactions between polymer solar cells

A feasibility study into the use of Avogadro software for polymer solar cell modelling applications

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E-Futures

Project outline

- Investigating the use of the modelling software Avogadro: a freeware open source chemistry platform. does it have features that are useful for polymer solar cell research?

Polymer solar cells

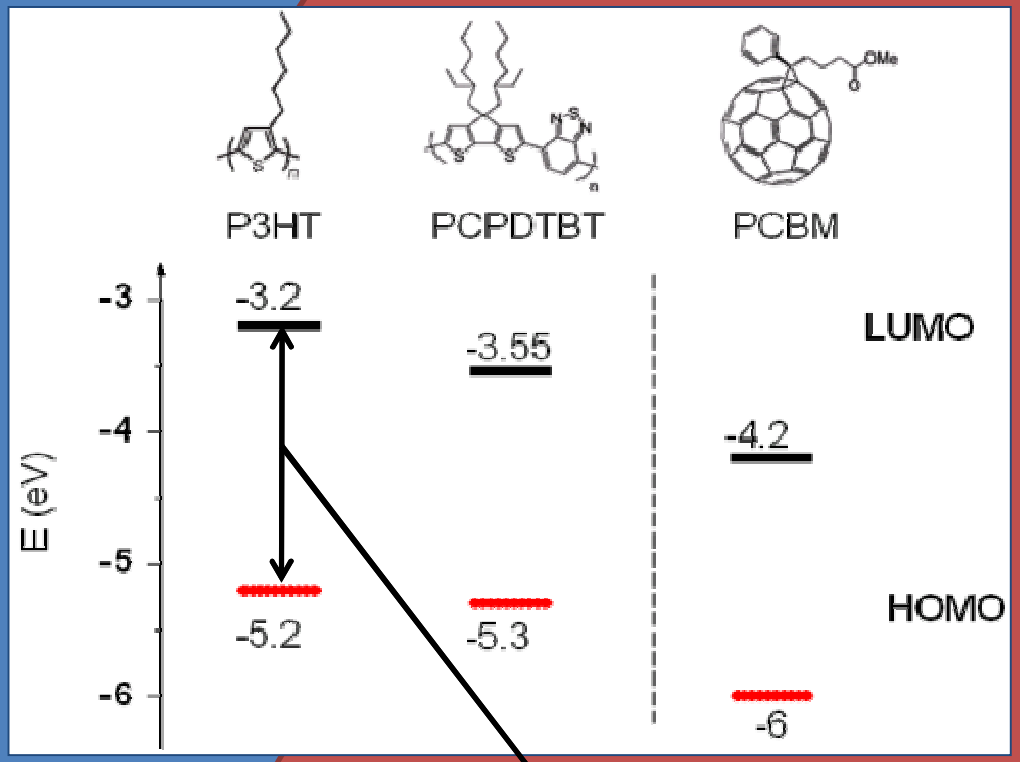
- Incident photons are absorbed by the cell, generating an electron-hole pair, or exciton.

- Photon absorption is affected by the macroscopic surface properties: the phase separation of the different polymers, and their vibrational spectra.

- Exciton generation is influenced by the molecular orbital structure of the polymer.

P3HT:PCBM solar cells

- Currently the most prevalent organic photo-cell blend.
- P3HT is the electron donor in this mix, from the excitation of a pi-orbital electron.



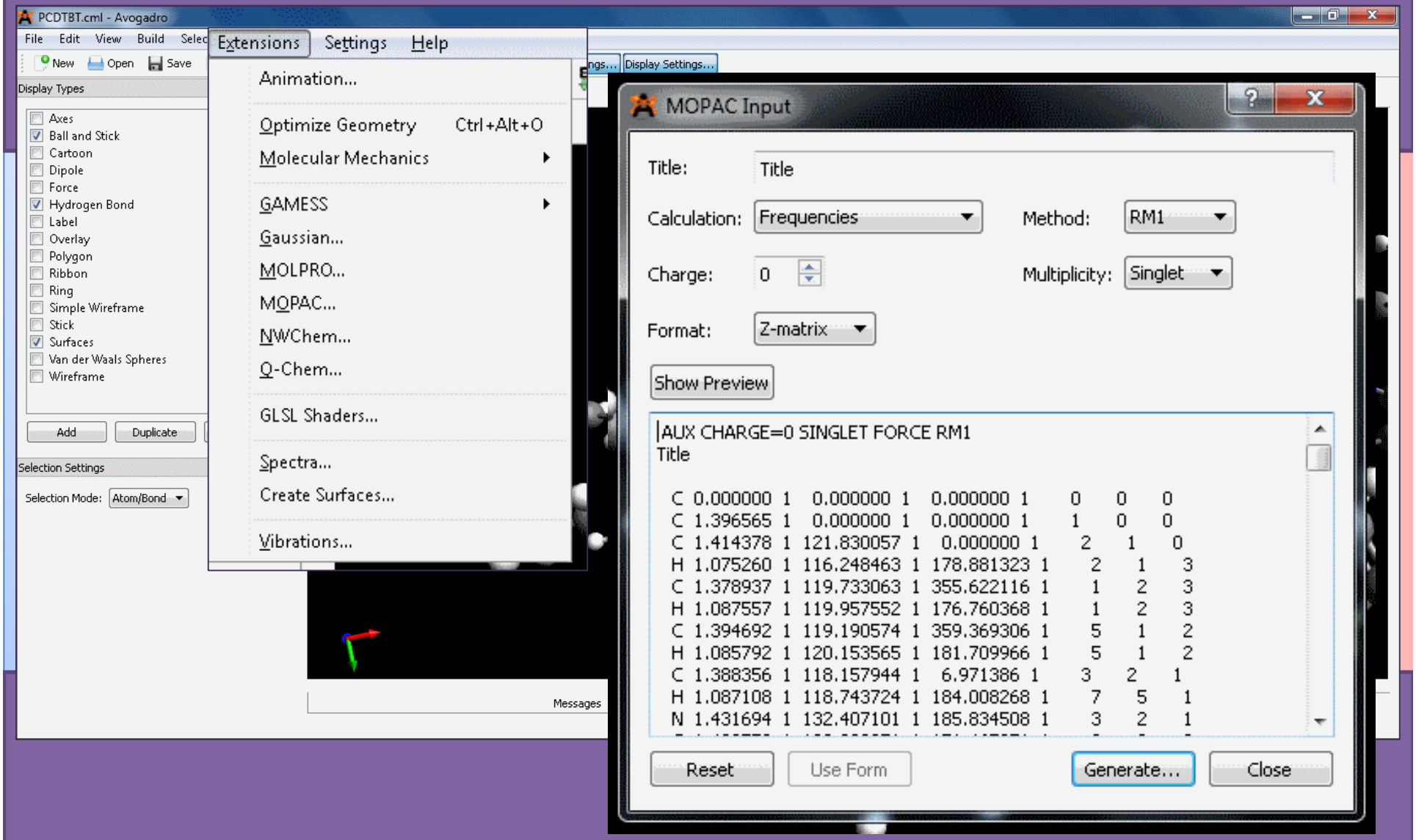
Modelling Aims

- To predict the molecular interactions in the P3HT:PCBM blend: how the molecules stack and if the phase separation can be better understood.
- To compare calculated physical/chemical properties with experimental data, to see if it is acceptable for similar applications.

Avogadro

- Avogadro writes output files for different ab initio quantum chemistry packages:
  - GAMESS, MOPAC, Gaussian, NWChem, Qchem, MOLPRO
- Of those, academic licenses could only be obtained for MOPAC and GAMESS, the others being too expensive.

Avogadro


PCDTBT.cml - Avogadro
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C 1.378937 1 119.733063 1 355.622116 1 1 2 3
H 1.087557 1 119.957552 1 176.760368 1 1 2 3
C 1.394692 1 119.190574 1 359.369306 1 5 1 2
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H 1.087108 1 118.743724 1 184.008268 1 7 5 1
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Computation

- The extensions solve quantum chemical functionals to generate optimal geometry, frequencies and single point energies for a structure.

- *Ab initio* or *semi-empirical* approaches are used, with necessary compromises being made to reduce the required computational effort.

Hamiltonians

- The calculations are solved with Hamiltonians, which have been developed from observed data. There are a number of them, each more suited to certain applications.
- In most cases, PM6 is considered the most advanced due to the vast amount of data used to develop it.

- RM1
- MNDO
- MNDO-d
- PM3
- PM6
- RM1

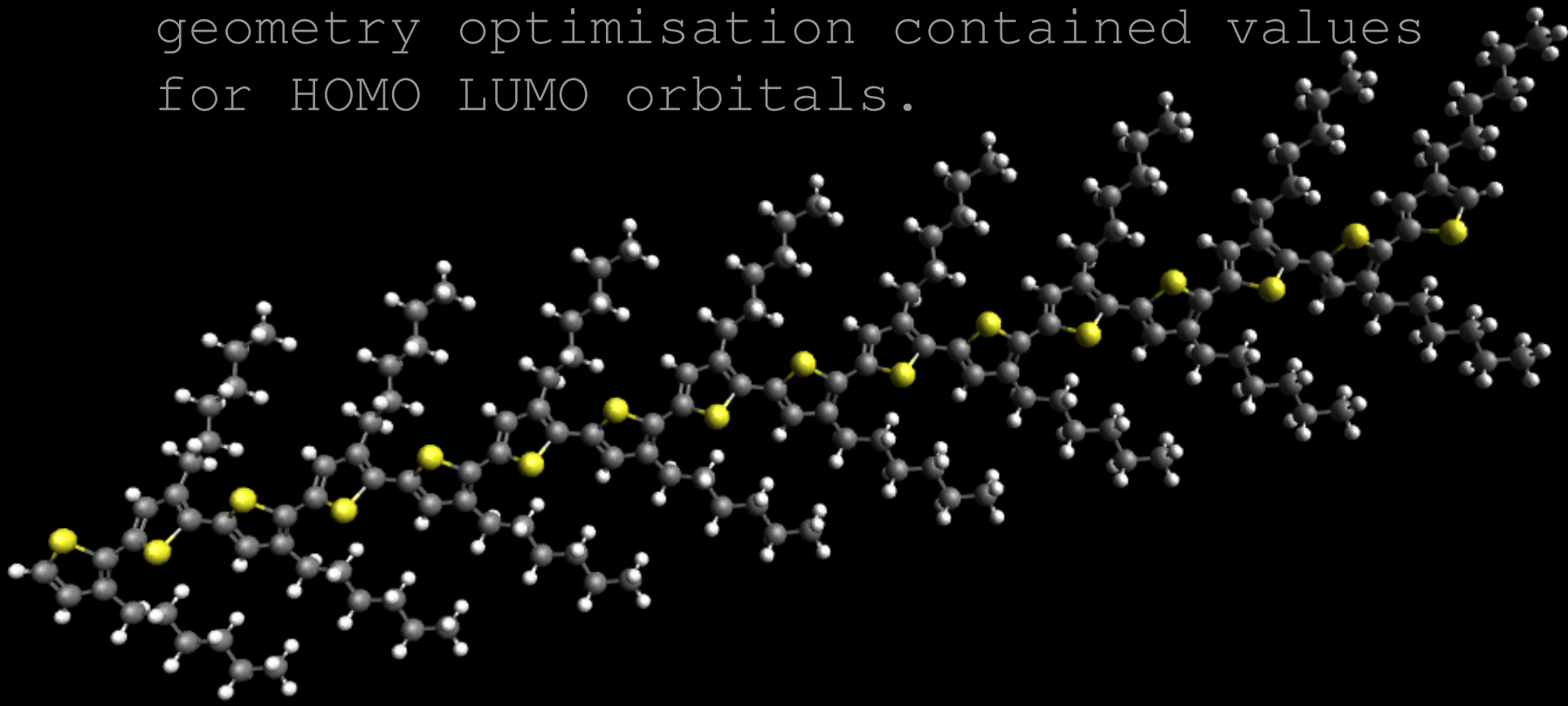
P3HT and MOPAC

- MOPAC selected for use (GAMESS technical problems prevented it being used effectively: user input syntax errors).
- MOPAC is able to calculate molecular orbitals and vibrational spectra, so it should be possible to relate the gap between the HOMO and LUMO levels to absorption spectra for P3HT.
- P3HT molecules of different lengths were simulated using the softwares different functions.

> . . .

Results

> The output files generated by MOPAC for geometry optimisation contained values for HOMO LUMO orbitals.

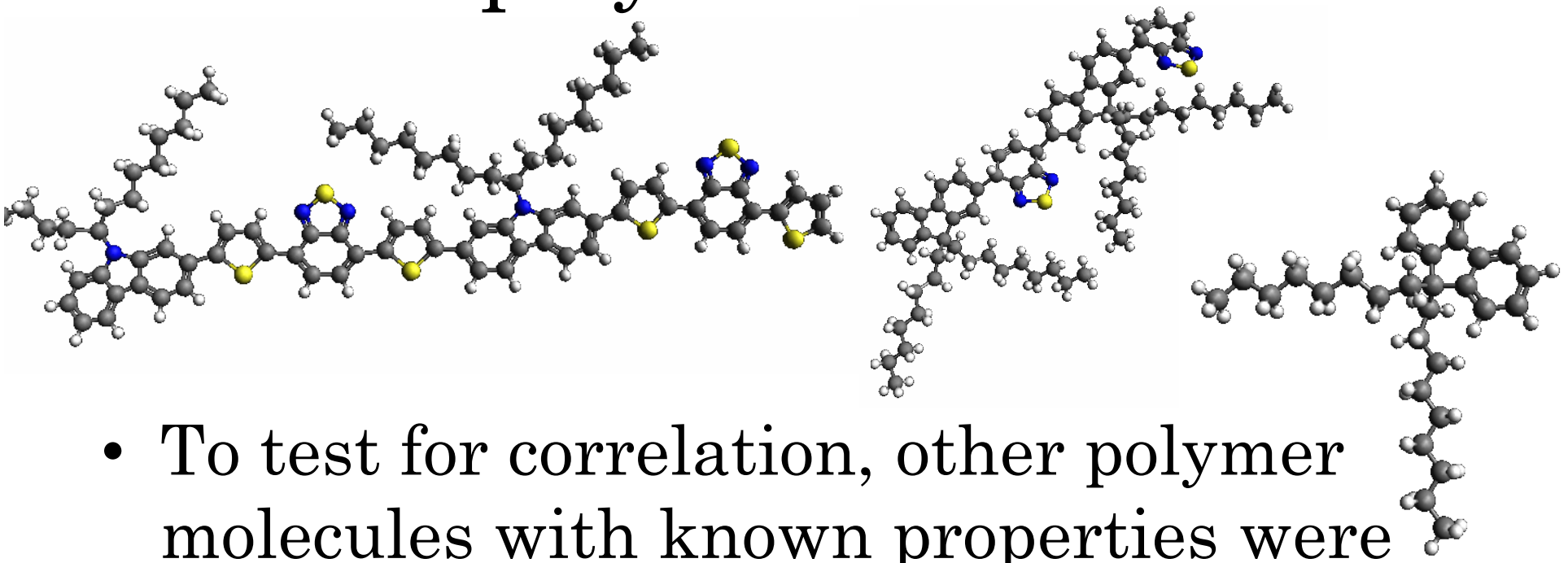


> The modelled gap differed from the experimental by between 7 and 4 eV.

Analysis

- As expected an increase in chain length improved the accuracy, but computation time increased exponentially.
- The error could also be accounted for in the ‘multiplicity’ choice, where a triplet value improved accuracy (default setting: singlet).
- Even for the smallest iteration of P3HT, a triplet was very computationally expensive.

Other polymer molecules…



- To test for correlation, other polymer molecules with known properties were similarly modelled:
  - PCDTBT, F8BT and F8.
- A similar difference was observed, with increasing accuracy with molecule size.

Overall results

Polymer	Chain length	Energy gap (modelled) eV	Energy gap (observed) eV	Error
P3HT	2	8.43	1.90	**6.42**
	4	7.88	1.90	**5.88**
	8	6.99	1.90	**4.99**
F8 (singlet)	1	8.44	≈ 2.0	**6.44**
	4	7.22	≈ 2.0	**5.22**
F8 (triplet)	1	7.49	≈ 2.0	**5.49**
F8BT	1	8.16	≈ 2.0	**6.16**
	2	7.88	≈ 2.0	**5.88**
PCDTBT	1	6.45	1.88	**4.57**
	2	6.45	1.88	**4.57**

Next steps…

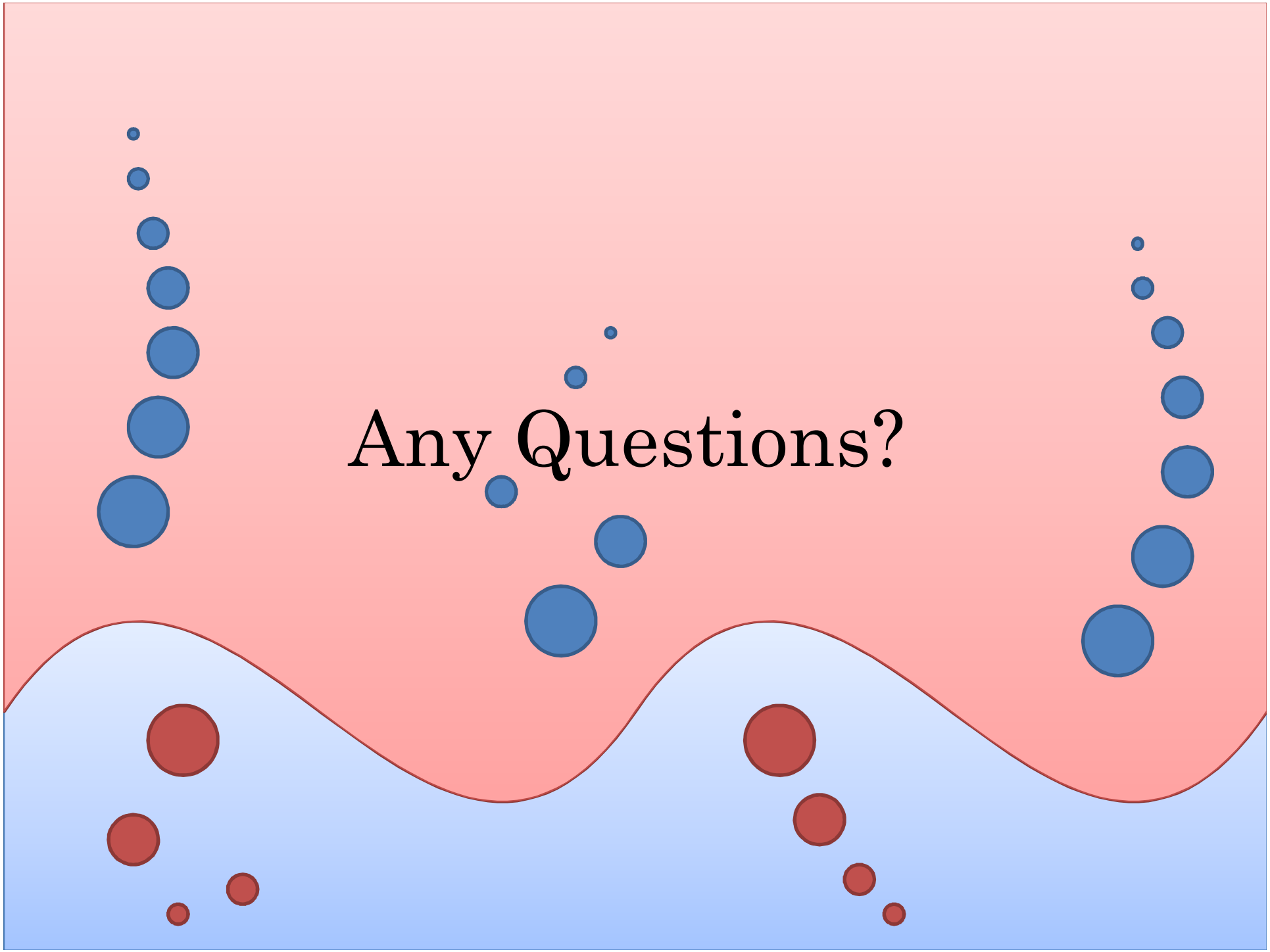
- MOPAC and GAMESS are well spoken of in the literature, but require an in-depth knowledge to operate fully. With further training, better results could be obtained.

- The academic license of MOPAC limits computation time to 2 days: this severely limits the size of calculation that can be done. A full license purchase would allow larger molecules to be processed.

Next steps…

- Within Avogadro it seems possible to generate spectra from the output files, but the documentation doesn't yet say how. This would generate more useful data if it could be done.

- In summary: as a freeware platform the software works well, but has limitations. Further online support is necessary for inexperienced users.


Any Questions?