Marking Scheme - CHEM1030 Quantum Chemistry Practical C: Equilibrium geometry and chemical shielding of modafinil

Feature	Maximum mark out of 100
Introduction: objectives and problem setting	5
Introduction: description of methods	10
Molecule drawing in GaussView	5
Energy and gradient convergence plots	10
Bond length plot (X-ray against PM6)	5
Bond length accuracy discussion	15
Chemical shift comparison with experiment	10
Chemical shift accuracy discussion	15
Report: quality of writing	10
Report: quality of typesetting	5
Report: quality of references	10

Introduction: objectives and problem setting [5 points]

The introduction should contain the following statements or their equivalents:

1. The objective of the work is to determine the minimum energy geometry of modafinil and to use that geometry to determine its chemical shifts.
2. The work starts from a schematic drawing of the modafinil molecule and proceeds in two stages: energy minimisation and calculation of chemical shifts.
3. Some of the resulting chemical shifts are compared to the experimental data and conclusions are drawn about their accuracy.

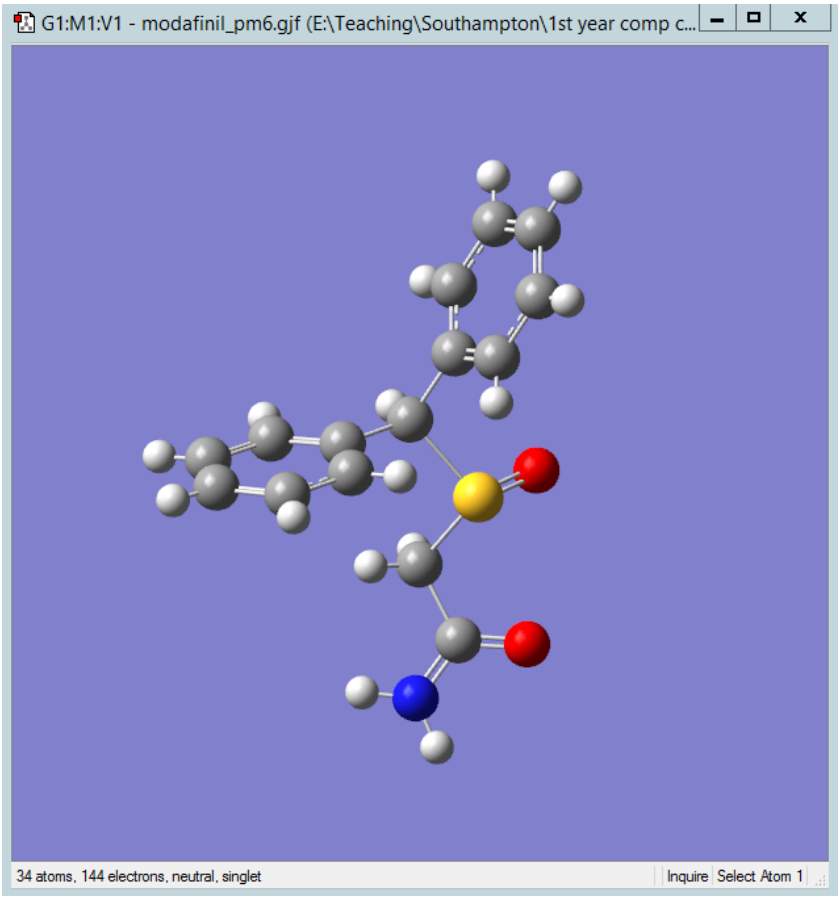
Introduction: description of methods [10 points]

The introduction should contain the following statements or their equivalents:

1. The software package used is Gaussian09, with its graphical user interface called GaussView.
2. The method used for the calculation of energies is PM6, which is a semi-empirical method that differs from the full quantum mechanical treatment in that it replaces complicated integrals with empirical parameters that are derived from experimental databases.
3. Geometry optimisation is performed using a variant of the gradient descent algorithm: at each point in the optimisation process, the gradient of the energy with respect to nuclear coordinates is calculated and the program makes a step down that gradient until a minimum of the energy is located.
4. The chemical shifts are calculated in two stages: first, chemical shielding values is obtained by calculating the second derivative of the energy with respect to the applied magnetic field and the nuclear magnetic moment; then chemical shift values relative to TMS (tetramethylsilane) are obtained by subtracting the chemical shielding of TMS.

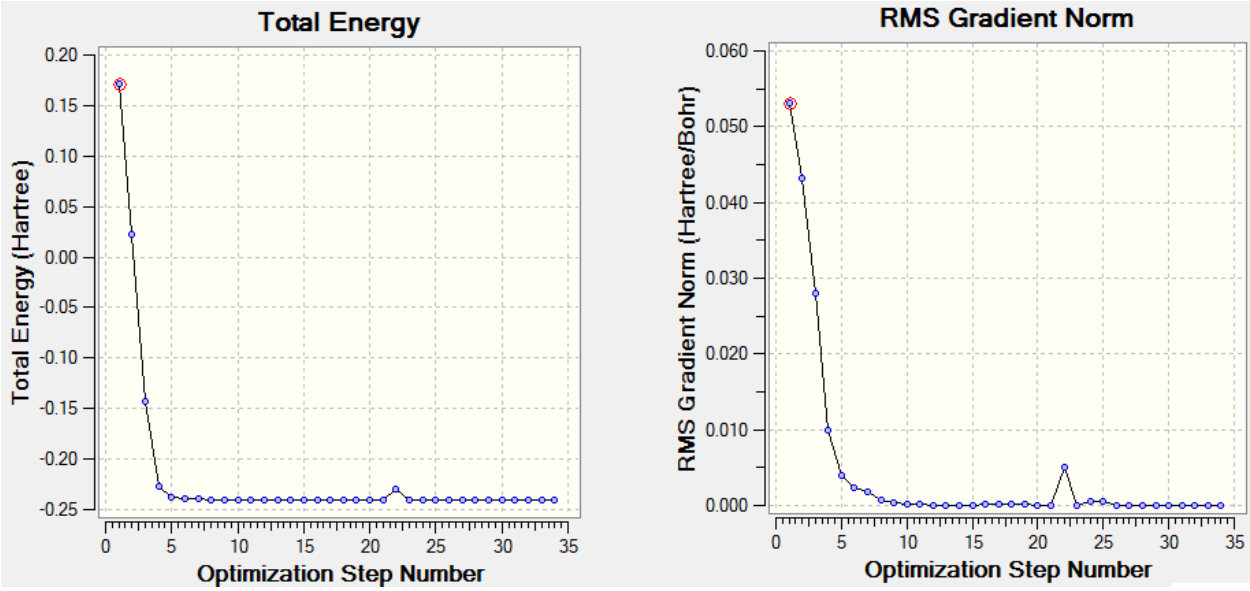
Molecule drawing in GaussView [5 points]

A picture similar to the following should be included



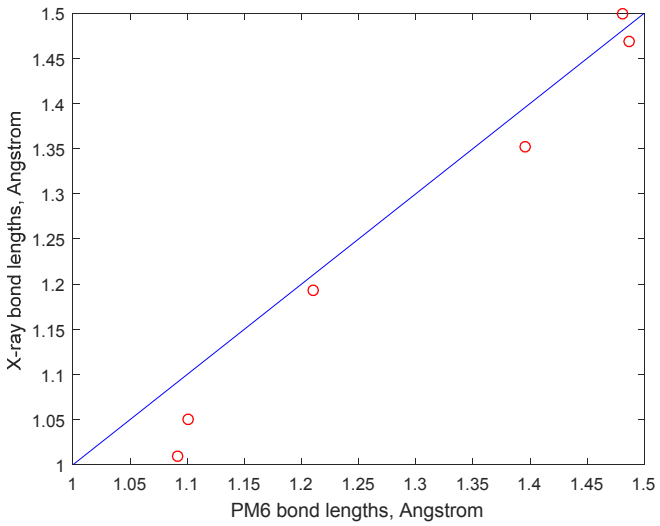
Energy and gradient convergence plots [10 points]

Pictures similar to the following should be included



Bond length plot

A few bond lengths should be extracted from the optimized geometry and the X-ray crystallography data provided. The bond lengths from the PM3 optimization should be plotted against the bond lengths from the X-ray data to produce a plot that looks similar to the following:



Bond length accuracy discussion [15 points]

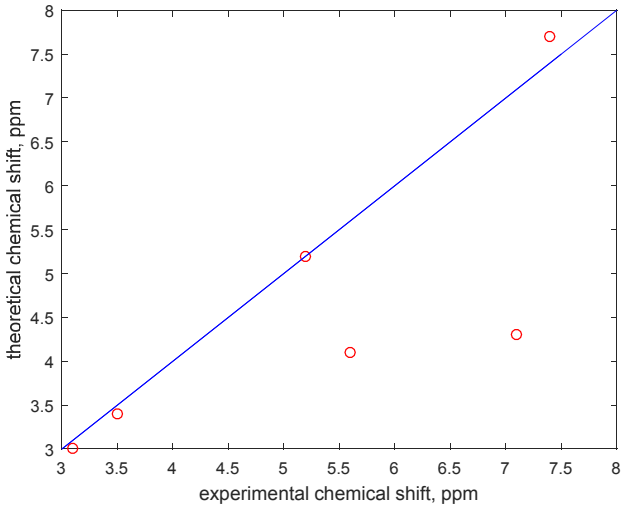
Students are expected to observe that

1. The agreement between PM6 and X-ray data is not particularly good.
2. The error is most likely to be on the PM6 side because of its approximate nature.
3. The disagreement is of the order of 5% of the bond length.
4. Any applications that require bond lengths to precision greater than about 10% should be using more sophisticated methods than PM6.
5. For the purposes of rough geometry optimization, PM6 is adequate.

Chemical shift comparison with the experiment [10 points]

Students are expected to examine the experimental dataset and

1. Correctly identify the atoms involved (NH protons at 5.6 and 7.1 ppm; CH_2 protons at 3.1 and 3.5 ppm; aromatic protons around 7.4 ppm; CH proton at 5.2 ppm).
2. Plot or tabulate the theoretical chemical shifts against the experimental ones and conclude that the agreement is reasonably good



Chemical shift accuracy discussion [15 points]

Students are expected to observe that:

1. Chemical shifts are conformation-dependent, but only one conformation is used in the calculation and that is likely to limit the accuracy.
2. Chemical shifts depend on solvent interactions and hydrogen bonding patterns, but the calculation is carried out in vacuum. That is likely to limit the accuracy – the biggest deviations are, in fact, observed for the atoms that are likely to be affected the most by polar solvents.
3. A semi-empirical method that was found to not be particularly accurate in the previous section was used to obtain the molecular geometry. That is likely to limit the accuracy.
4. Proton chemical shifts are generally within 1 ppm of their experimental value, except for the NH protons. That appears to be the reliability range of the method used.

Report: quality of writing [10 points]

The report should:

1. Be neatly formatted.
2. Not use screenshots of equations instead of correctly entered equations.
3. Use academic English (third person, past tense, neutral and factual).
4. Be written clearly and succinctly.

Report: quality of typesetting [5 points]

Bonus points should be awarded for the use of LaTeX and Origin, as well as for use of consistent, readable and elegant formatting and presentation.

Report: quality of references [10 points]

References should:

1. Only include academic sources (textbooks, peer reviewed journals).
2. Use a consistent referencing style (any style is fine).
3. Not contain any web links.
4. Not include any non-peer-reviewed sources.