

Marking Scheme - CHEM1030 Quantum Chemistry Practical A: Equilibrium geometry and molecular volume of cocaine

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
Molecular volume and density figures	10
Molecular volume and density 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 cocaine and to use that geometry to determine the molecular volume.
2. The work starts from a schematic drawing of the cocaine molecule and proceeds in two stages: energy minimisation and calculation of molecular volume.
3. The resulting molecular volume is used to estimate the density of cocaine, which is compared to the experimental density obtained from the literature.

Introduction: description of methods [10 points]

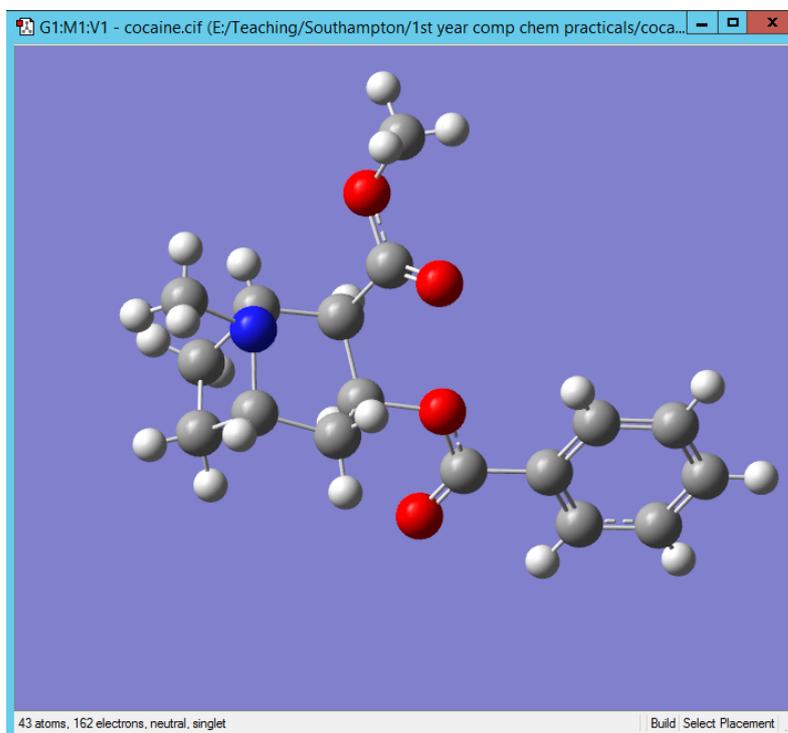
The introduction should contain the following statements or their equivalents:

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 molecular volume is calculated for the optimized geometry by associating with each atom a sphere of a certain radius (the atomic radii are determined from crystallography or DFT calculations) and calculating the total outer volume of the resulting set of interlocking spheres.
5. DFT is another quantum mechanical method that uses a simplified description of the molecule in terms of the associated electron probability density rather than the full wavefunction. In the

settings used in the work, B3LYP is a particular method for the energy calculation and cc-pVDZ is a basis set, which controls the level of detail in the calculation.

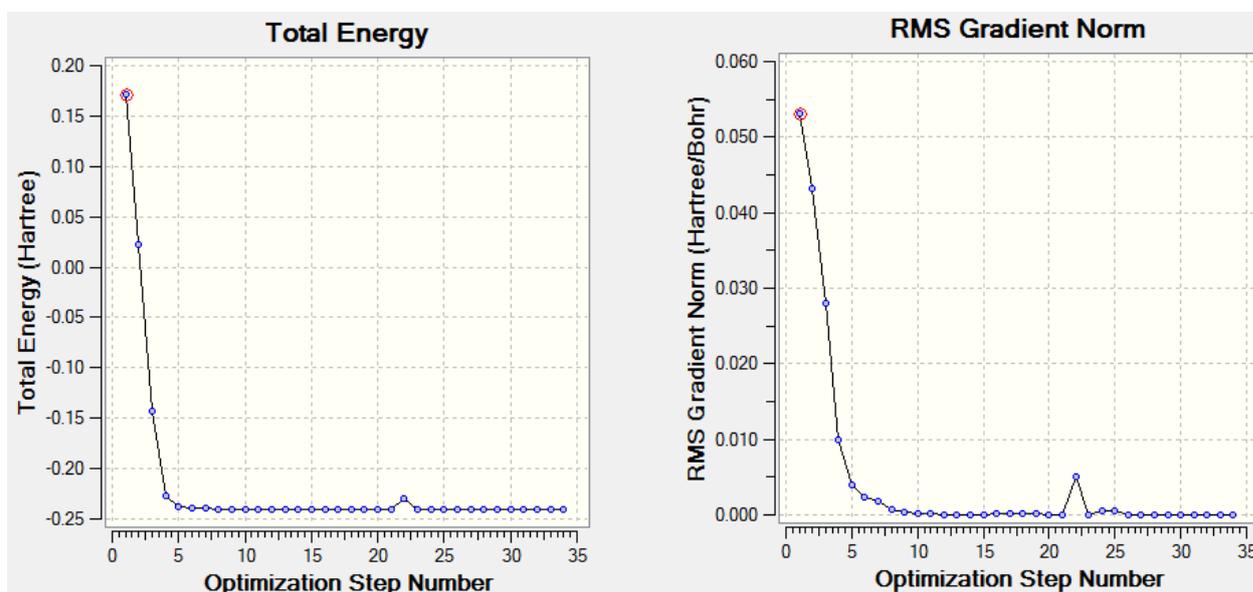
Molecule drawing in GaussView [5 points]

A picture similar to the following should be included



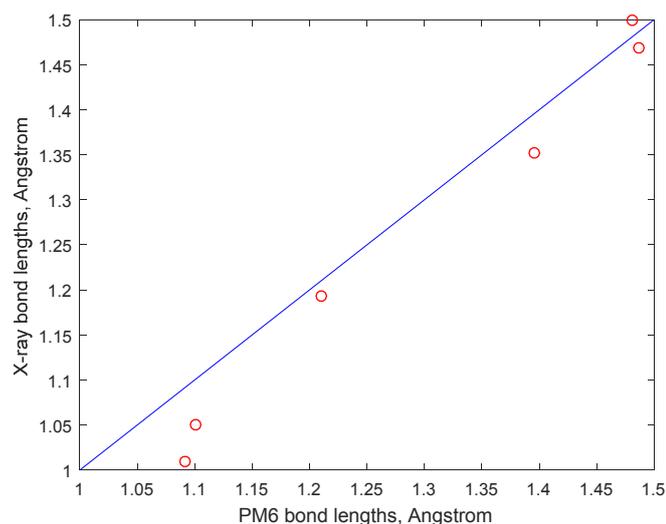
Energy and gradient convergence plots [10 points]

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.

Molecular volume and density figures [10 points]

The molecular volume that Gaussian produces at the end of the calculation should be about 420 cubic Angstroms. The students should:

1. Convert cubic angstroms into cubic metres or centimetres.
2. Find out the mass of the cocaine molecule in kilograms or grams.
3. Determine the density by dividing the mass by the volume.
4. The theoretical density should be around 1.2 g/cm^3 or 1200 kg/m^3 .

Molecular volume and density accuracy discussion [15 points]

The students are expected to observe that:

1. The theoretical density of cocaine is quite close to the experimental one (which is 1.216 g/cm^3).
2. The fact that the density matches so well indicates that cocaine crystals are well packed, with no significant voids in them.
3. The method used in this work appears to be a good one for molecular density estimation.
4. The method used implicitly assumes that a single molecule in vacuum is a good representation of the crystal structure, which is not always true.

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.