

COMPUTATIONAL CHEMISTRY I
FINAL SEMESTER EXAM
ATTEMPT ALL FOUR QUESTIONS

QUESTION ONE: (20 Marks)

What are the major numerical methods that are useful in chemical computations? Which methods require extensive memory and which methods require extensive CPU time?

Two particles interact via the potential $4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6] - 0.01e^2/(4\pi\epsilon_0 r)$. The values of ϵ , σ , e and $4\pi\epsilon_0$ are $120 k_B K$ ($k_B = 1.38 \times 10^{-23} J/K$), 3.4 \AA , $1.6 \times 10^{-19} C$, and $1.11263 \times 10^{-10} C^2/N m^2$ ($\epsilon_0 = 8.854 \times 10^{-12} C^2/N m^2$) respectively. Write a program to calculate the potential from 0.1 \AA to 10 \AA in Joules/mol. Also convert the energy values into eV, kcal/mol, hartree, a.u. and cm⁻¹.

QUESTION TWO: (20 Marks)

- a) Write a program in C/C++ to multiply two 3x3 matrices. The purpose of this is to show that the programming language is a means rather than the end. We used the compiler f77 in the chapters. Your PC/Server may have gfortran or gcc.
- b) Demonstrate that the 3rd order Lagrange interpolation for a set of equidistant points x_i for which y_i are known gives the same values as the Newton's third order interpolating polynomial. For the data, use the function $y = 0.5 x^2$ to calculate (x_i, y_i) at $x_i = 0.5, 1.0, 1.5$ and 2.0 .
- c) Find the largest eigenvalue and its corresponding eigenvector for the following matrix.
- | | | | |
|------|------|------|------|
| 1.0 | 2.0 | 3.2 | 4.5 |
| -0.3 | 0.0 | 42.3 | 9.8 |
| 0.0 | 23.0 | 3.8 | -6.8 |
| 22.0 | 17.3 | 0.2 | 50.0 |
- d) For the function $y = 0.5 x^2$ to calculate (x_i, y_i) at $x_i = 0.0$ to 10.0 at an interval of 0.01 . Obtain the integral of this set of data by using Trapezoidal rule as well as Simpson's rule and compare both these values with the analytical result.

QUESTION THREE: (20 Marks)

- a) Solve problem 6) using a set of random numbers generated from the gfortran library. Generate a set of 10000 pairs of random numbers in the range between 0 and 10 by simply scaling the random number of pairs (x_i, y_i) between 0 and 1 by a factor of 10. Among these pairs which are now between 1 and 10, count the number of pairs for which y_i is less than $(x_i)^2$. This fraction multiplied by $100/3$ is the value of the integral. Check how much the accuracy of the estimate changes by increasing the random number set to 100000.
- b) Use the Plotdigitizer software to digitize a repulsive potential energy curve given in Chapter 9. Use Gnuplot software to plot the function

QUESTION FOUR: (20 Marks)

- a) $e^2 \exp(-\kappa r)/r$ where e is the electronic charge and κ is the ionic strength. Use κ of NaCl solution of 1M. Use r in \AA . If e is in esu and r in cm, then, use $(\text{esu})^2/\text{cm} = 1 \text{ erg}$. Use Scilab software to compute the Fourier transform of the function $\exp(-2 r) + \exp(-3 r^2)$.
- b) Calculate the overlap integral between two 1s orbitals on H atoms separated by 1\AA , numerically as well as by the analytical formula as a function of r from $r = 0 \text{\AA}$ to 10\AA . Also calculate the Coulomb integral at 1\AA . Write two Slater determinants for Li atom using the 1s, 2s and $2p_x$ orbitals of Li.