Indian Institute of Technology, Kharagpur

Time: 3 Hours Full Marks: 50 No. of students: 30
End semester Examination Spring, 2008-2009 Department: Chemistry
Subject: CY40014 **Introduction to Computational Chemistry**

Answer all questions

Q.1 (a) Draw the structure the molecule phenylalanine, number each atom and write down the corresponding Z-matrix.

(b) Note the following coordinates obtained by converting the z-matrix of a molecule to the Cartesian coordinates of its atoms. Write a program that
(i) reads symbols and coordinates of the atoms
(ii) calculates all the C-H bond lengths
(iii) calculates the O-C-H and O-C-C bond angles
(iv) calculates the O-C-C-H dihedral angle where H corresponds to the last entry in the given data.
5+10=15

C	0.00000	0.00000	0.00000
O	1.20000	0.00000	0.00000
H	-0.55000	0.95263	0.00000
C	-0.75000	-1.29904	-0.00000
H	-0.04293	-2.14169	-0.00000
H	-1.38570	-1.36644	0.89518
H	-1.38570	-1.36644	-0.89518

Q.2. (a) In chemical kinetics, it is often important to know the fraction of particles with a speed that exceeds a selected speed v'. According to collision theories of chemical kinetics, particles with a speed in excess of v' are energetic enough to react and those with a speed less than v' are not. Thus the fraction of particles capable of reacting in a gas phase reaction can be calculated using the Maxwell-Boltzmann distribution law as

$$f_{reactive} = 1.0 - \int_0^{v'} dv\, 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$

Write a program to compute $f_{reactive}$ numerically using Simpson's one-third rule. Explain the scaling you would use for the speed in the term involving integration on the right hand side.

(b) Set up the secular equation for an allyl fragment using the simple Huckel theory and
(i) solve it analytically;
(ii) Write a program to solve it numerically using the Newton-Raphson method.
7+8=15

Q.3. (a) During effusion, the pressure (p) of a gas varies with time (t) as $\frac{dp}{dt} = -\frac{p}{\tau}$. If the initial pressure of the gas is 5 atm, **calculate** using the 4th order Runge-Kutta method in a *single step* the pressure at time $t = 0.05\tau$.

(b) A student wrote the program shown on the right to fit a Lagrange polynomial $f(x) = \sum_{i=1}^{N} y_i \prod_{\substack{j=1 \\ j\neq i}}^{N} \frac{x - x_j}{x_i - x_j}$ of degree N through an arbitrary number of data points $\{x_i, y_i\}$ $(i = 1, N)$. Write the corrected program in your answerbook to calculate the value of *f(x)* at any value of x other than $\{x_i\}$'s given as input.

5+5=10

```
implicit real*4 (a-h, o-z)
dimension x(100),y(100)
open(unit=14,file='data.in',status='old')
read(12,*)n
do i=1,n
  read(14,*)x(i),y(i)
end do
close(14)
open(unit=12,file='ct1_3.in',status='old')
read(12,*)n
do j=1,n
  read(12,*)x(j)
end do
close(12)
read(*,*)x
sum=0.0

do i=1,n
do j=1,n
  if(i.ne.j)then
  prd=prd*((x-x(j))/(x(i)-x(j)))
  sum=sum+y(i)*prd
  end if
end do
end do

sum=fx
write(*,*)fx
stop
end
```

Q.4. In classical molecular dynamics simulation, one needs to solve the Newton's equation of motion (a second order differential equation) for a large number of particles. A computationally efficient way of integrating the equation of motion for the *i*-th particle in one dimension is to implement the following algorithm (known as the velocity Verlet algorithm)

$$r(t+\delta t) = r(t) + v(t)\,\delta t + \frac{1}{2}a(t)(\delta t)^2$$

$$v\left(t+\frac{1}{2}\delta t\right) = v(t) + \frac{1}{2}a(t)\,\delta t$$

$$a(t+\delta t) = -f[r(t+\delta t)]$$

$$v(t+\delta t) = v\left(t+\frac{1}{2}\delta t\right) + \frac{1}{2}a(t+\delta t)\delta t$$

In the above set of equations, *r*, *v* and *a* represent the coordinate, velocity and acceleration of the *i*-th particle, respectively. The force $f(r) = -12\sum_{i\neq j}\frac{1}{r_{ij}^{13}}$ is the force acting on the *i*-th particle at time *t* and the summation goes over all other particles present in the system. r_{ij} is the distance between the *i*-th and *j*-th particles at the same time.

Given the initial coordinate, velocity and accelerations of *N* particles, write a program to calculate the corresponding values for all the particles at a time $t = 10\,\delta t$. You may assume all the quantities shown above to be dimensionless. Use multiple steps to arrive at the desired time.

10

END