

**DUE BEFORE WORKSHOP 3 - May 19th**

Write a report addressing the following problems. All computational exercises must be completed in Fortran. Submit a **PDF** of your report via Blackboard, along with any Fortran files, input and output files, gnuplot scripts, and anything else required to run your programs and replicate your results in a separate zipped directory.

**Marking:** There are ten marks in total. One mark is for presentation (readability, figure formatting etc), and the remaining nine marks will be split unevenly amongst the problems. For computational problems half the available marks are for the implementation, and the other half are for the discussion of theory and explanation of results wherever appropriate. A marking rubric is available on Blackboard.

**Problem 1 -  $\text{H}_2^+$  potential-energy curves (6 marks)**

Following the lecture slides, write a program to calculate the Born-Oppenheimer electronic energies of the  $\text{H}_2^+$  molecule. Your code will need to take the same radial grid and basis parameters as the hydrogen exercise from assignment 1, but now rather than specifying a single  $\ell$  you need to specify  $\ell_{\text{max}}$ . For simplicity, every  $\ell$  can use the same  $N$  and  $\alpha$

To run the calculation at multiple  $R$  values, either implement the loop over  $R$  in your Fortran code, or use a Bash script.

Include the following in your report:

- details of the relevant theory and your code.
- A figure comparing your  $1s\sigma_g$  potential-energy curve (the lowest state) for increasingly accurate bases (play around with  $N$  and  $\ell_{\text{max}}$ ), compared with the accurate curve provided in the `PEC.1ssg` file. Do not expect perfect agreement with the accurate curves – a demonstration that your results get closer to the accurate results as you improve the basis is fine.
- The same for the  $2p\sigma_u$  state (the second state).

**Problem 2 -  $\text{H}_2^+$  vibrational wave functions (3 marks)**

Copy your hydrogen code from assignment 1 and modify it so the analytical  $V$  matrix is replaced by a numerically-evaluated  $V$  matrix:

$$V_{ij} = \int \varphi_{k_i \ell_i}(R) \epsilon(R) \varphi_{k_j \ell_j} dR, \quad (1)$$

where  $\epsilon(R)$  is the accurate  $1s\sigma_g$  potential-energy curve provided. The potential-energy curve must be read in from the `PEC.1ssg` file and interpolated onto the radial grid defined in your code using the supplied `intrpl` subroutine. Run the code with  $\ell = 0$  and print the wave functions and energies to file. You will also need to read in the reduced mass of the molecule and modify the Hamiltonian matrix to take this into account. The values of  $\mu$  for  $\text{H}_2^+$  and its isotopologues are given here:

Molecule	$\mu$ (atomic units)
$\text{H}_2$	918.07635
HD	1223.89925
HT	1376.39236
$\text{D}_2$	1835.24151
DT	2200.87999
$\text{T}_2$	2748.46079

Include the following in your report:

- details of the relevant theory and your code.
- A figure similar to what is in the lecture slides showing a few vibrational wave functions inside the  $1s\sigma_g$  potential-energy curve. To visualise the energies corresponding to each wave function the waves should be shifted by their energy (i.e. if the energy for a state is -0.597 then plot using `1:($2-0.597) w l`).

- A figure comparing the  $v = 0$  vibrational wave functions for each of the 6 isotopologues. Comment on the differences.

*Extension (optional):* The vibrational Schrödinger equation including the dependence on rotational levels is

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1)}{2\mu R^2} + \epsilon_n(R) \right] \Phi_v^n(R) = \varepsilon_{nvJ} \Phi_v^n(R). \quad (2)$$

How large do you have to make  $J$  before you see the number of bound vibrational levels decrease? Reproduce the figure on Page 38 of the slides for this  $J$ , but instead of the potential energy curve plot the effective potential

$$V_{\text{eff}}(R) = \frac{J(J+1)}{2\mu R^2} + \epsilon_n(R). \quad (3)$$