Computational and Theoretical Chemistry 2 (NWI-MOL176) computer assignment I

Gerrit C. Groenenboom, Theoretical Chemistry, Radboud University Nijmegen, 20-Apr-2025

Question 1: Numerical solution of quantum harmonic oscillator

The harmonic oscillator Hamiltonian $\hat{H}_0$ is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x), \tag{1}$$

with $V(x) = \frac{1}{2}kx^2$ and $\hbar = 1$ in atomic units. For $\mu = 1$ and $k = 1$, solve numerically the harmonic oscillator time independent Schrödinger equation,

$$\hat{H}_0\phi_n(x) = \epsilon_n\phi(x). \tag{2}$$

on a grid,

$$x_i = x_0 + i\Delta, \qquad \text{for } i = 1, 2, \ldots, n. \tag{3}$$

The potential energy is represented by a diagonal matrix with matrix elements

$$V_{ij} = V(x_i)\delta_{ij}. \tag{4}$$

1a. Use the second order finite difference approximation of d^2/dx^2 to set up a kinetic energy matrix.

1b. Find a grid such that the error in the lowest 4 eigenvalues is less than 0.01. Remember that you must find a grid spacing that is small enough to properly represent the kinetic energy, but at the same time have a range that is sufficiently large.

1c. Tabulate the eigenvalues and make a plot of the corresponding eigenvectors on the grid.

For arbitrary k and μ, the exact energies are

$$\epsilon_n = (n + 1/2)\hbar\omega \tag{5}$$

with

$$\omega = \sqrt{\frac{k}{\mu}}. \tag{6}$$

1d. Check this expression numerically for $k = 8$ and $\mu = 2$. How do you adapt the grid of question **1b** so it works in this case without trial and error?

Question 2: Morse potential for HF

The harmonic oscillator is a simple model to describe vibrations of a diatomic molecule. The Morse potential allows for a more accurate desciption:

$$V(r) = V_e + D_e[1 - e^{-\alpha(r-r_e)}]^2. \tag{7}$$

The parameters in this model are the equilibrium distance r_e, the dissociation energy D_e, and the value of the potential at the equilibrium distance $V_e = V(r_e)$, which we set to zero here. Near the equilibrium the potential can be approximated as a harmonic oscillator. These are the spectroscopic constants of HF and conversion factors for atomic units:

$$\omega_e = 4138 \text{ cm}^{-1} \qquad\qquad 1 \text{ cm}^{-1} = 1/219\,474.63 \text{ E}_h \text{ (hartree)}$$
$$\omega_e x_e = 90 \text{ cm}^{-1} \qquad\qquad 1 \text{ Å} = 1.889\,7261 \; a_0 \text{ (bohr)}$$
$$D_e = 47\,633 \text{ cm}^{-1} \qquad\qquad 1 \text{ a.m.u.} = 1822.8885 \text{ m}_e \text{ (electron mass)}$$
$$r_e = 0.91680 \text{ Å}.$$

The force constant k (see question 1) is the second derivative of the potential in the minimum and it depends on D_e and the exponent α.

2a. Using the given constants, find the exponent α and plot the Morse potential together with the harmonic approximation of the potential.

2b. Use the finite difference method to compute the first six vibrational energy levels for the Morse potential.

2c. Compute the energies of the rotational states for angular momentum quantum number $J = 0, 1, 2, 3, 4$ for the $v = 0$ vibrational ground state.

Rotation-vibration energy levels $E_{v,J}$ of diatomic molecules are often reported in this form

$$E_{v,J} = E_0 + G(v) + F_v(J) \tag{8}$$
$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 \tag{9}$$
$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2, \tag{10}$$

where ω_e, $\omega_e x_e$, B_v, and D_v are spectrocopic constants.

2d. For $J = 0$ find the constants E_0, ω_e, and $\omega_e x_e$ from a linear fit to your results for question **2b**.

2e. For $v = 0$ find the spectroscopic constants B_v and D_v from a linear fit to your results of question **2c**.

The rotational constant B_v for $v = 0$ can be computed by perturbation theory as the expectation value

$$B_0 = \langle v = 0, J = 0 | \frac{\hbar^2}{2\mu r^2} | v = 0, J = 0 \rangle. \tag{11}$$

2f. Compute B_0 by perturbation theory for the $v = 0, J = 0$ wave function of question **2b**.