
Quantum dynamics (NWI-SM295) computer assignment I

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Question 1: Numerical solution of quantum harmonic oscillator

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

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

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,

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

on a grid,

$$x_i = x_0 + i\Delta, \quad \text{for } i = 1, 2, \dots, n. \quad (3)$$

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

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

- 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

$$\epsilon_n = (n + 1/2)\hbar\omega \quad (5)$$

with

$$\omega = \sqrt{\frac{k}{\mu}}. \quad (6)$$

- 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 description:

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

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:

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

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

$$E_{v,J} = E_0 + G(v) + F_v(J) \quad (8)$$

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 \quad (9)$$

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2, \quad (10)$$

where ω_e , $\omega_e x_e$, B_v , and D_v are spectroscopic 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

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

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