Homework 3

Due: 11:59 PM, Tuesday, September 15. Submit your homework via Canvas.

10 points   **Problem 1:** Numerically solve the differential equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \left(2E - x^2\right)\psi = 0 \tag{1}$$

with the initial conditions $\psi(0) = 1$ and $\frac{\mathrm{d}\psi}{\mathrm{d}x}(0) = 0$.[1] Describe what happens as you tune E in the domain $0 < E < 3$, and compare with what you know about the quantum harmonic oscillator.

10 points   **Problem 2:** Consider a one dimensional particle of mass m in the potential

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2 x^2 & x \geq 0 \\ \infty & x < 0 \end{cases}. \tag{2}$$

Find the allowed eigenvalues and eigenstates of the Hamiltonian for this system.[2]

10 points   **Problem 3:** Consider the following one dimesional quantum mechanical problem,

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - Fx \tag{3}$$

corresponding (loosely speaking) to a harmonic oscillator pushed by a constant force F.

(a) Define the operator $\bar{x} = x + c$, for any constant c. Show that $[x, p] = [\bar{x}, p] = \mathrm{i}\hbar$.

(b) By choosing a clever value of c, describe how you can find raising and lowering operators which lead to an exact algebraic solution of this problem, as with the conventional harmonic oscillator. Write the exact eigenstates and eigenvalues of H.

10 points   **Problem 4 (van der Waals interactions):** A crude model for intermoleclular interactions is the following. Let us consider two molecules a distance R apart. Assume each molecule has a single mobile electron, which for simplicity moves only along a single direction. The electrons are located at positions $x = x_1$ and $x = x_2 + R$: see Figure 1. We assume the Hamiltonian is

$$H = \frac{p_1^2 + p_2^2}{2m} + \frac{k}{2}\left(x_1^2 + x_2^2\right) + \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{R} - \frac{1}{R - x_1} - \frac{1}{R + x_2} + \frac{1}{R + x_2 - x_1}\right]. \tag{4}$$

The Coulomb terms above correspond to the electrical interaction energies between the electrons and molecular ions. You should assume that the ions are completely stationary. You should treat electron 1 and electron 2 as distinguishable particles, for simplicity.

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[1] *Hint:* I suggest using `NDSolve` in `Mathematica`. If you have never used this function before, its documentation will be useful. You should be able to straightforwardly modify the example given for the purposes of this problem.

[2] *Hint:* What must the wave function do as $x \to 0$? Very little calculation is required for this problem.

(a) Assume $R \gg x_1, x_2$. Approximate the potential energy by a second order Taylor expansion in $x_{1,2}$ near 0.

Figure 1: Positions of the electrons and atoms along the one dimensional line.

(b) Show that the ground state energy of the resulting electrons is (up to a constant offset) proportional to R^{-6}. This is the van der Waals interaction between neutral atoms. Are van der Waals forces repulsive or attractive?

Problem 5 (Methane): Methane (CH_4) is a relatively simple polyatomic molecule, depicted in Figure 2. The atoms in this figure are labeled by numbers 1 to 5; do not worry about the indistinguishability of hydrogen atoms in this problem. As a crude model for covalent bonding, let us suppose that the potential energy of a C-H bonded pair is the following simple function of the absolute distance r between the C and H atoms:

$$V_{CH}(r) = \frac{k}{2}(r - R)^2. \tag{5}$$

Due to the repulsion of the negatively charged electrons in the covalent bonds (whose dynamics we do not consider microscopically), we also propose the following crude potential energy for two hydrogen pairs:

$$V_{HH}(r) = -gr. \tag{6}$$

In this cartoon, a stable molecule will form. The total Hamiltonian describing the nuclear motion is then given by

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2 + \mathbf{p}_3^2 + \mathbf{p}_4^2}{2m_H} + \frac{\mathbf{p}_5^2}{2m_C} + \sum_{i<j} V_{HH}(r_{ij}) + \sum_{i=1}^{4} V_{CH}(r_{i5}). \tag{7}$$

Figure 2: The equilibrium positions of the 5 atoms in CH_4, with H labeled 1 to 4 and C labeled 5.

Note that $m_C \approx 12m_H$ and $r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$. Set $m_H = k = 1$, $g = 0.05$, and $R = 0.877525512861$. One classically stable configuration of the methane molecule in our crude model is approximately

$$(x_1, y_1, z_1) = \left(\frac{\sqrt{8}}{3}, 0, -\frac{1}{3}\right), \tag{8a}$$

$$(x_2, y_2, z_2) = \left(-\frac{\sqrt{2}}{3}, \sqrt{\frac{2}{3}}, -\frac{1}{3}\right), \tag{8b}$$

$$(x_3, y_3, z_3) = \left(-\frac{\sqrt{2}}{3}, -\sqrt{\frac{2}{3}}, -\frac{1}{3}\right), \tag{8c}$$

$$(x_4, y_4, z_4) = (0, 0, 1), \tag{8d}$$
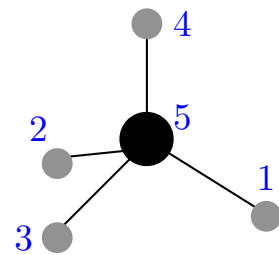
$$(x_5, y_5, z_5) = (0, 0, 0). \tag{8e}$$

Download the affiliated `Mathematica` notebook for this problem, wherein the Taylor expansion of $V(\mathbf{x}_1, \ldots, \mathbf{x}_5)$ has been carried out for all $3 \times 5 = 15$ coordinates about the equilibrium point (8): the K matrix in the notebook is defined as

$$V \approx V_0 + \frac{1}{2}K_{AB}\delta x_A \delta x_B, \tag{9}$$

where here, V_0 is a constant and δx_A denotes the 15-component vector of small perturbations to all 5 atomic positions away from equilibrium.

2

(a) Numerically implement the algorithm we developed in lecture to obtain the frequency of oscillation of every normal mode of the molecule.

(b) You should find there are some modes that oscillate at zero frequency. Explain why – part of your explanation should account for the number of zero modes that you find.

(c) There are also a number of degenerate normal modes which oscillate at the same finite frequency. These are a consequence of the high symmetry of the methane molecule. To see that the symmetry is responsible, replace atom 1 in Figure 2 with a chlorine atom to create chloromethane (CH_3Cl). Approximating $m_{Cl} = 35m_H$, determine the new spectrum of normal mode frequencies, and comment on the result. For simplicity, you do not need to change the potential energy terms in (7).[3]

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[3] *Hint:* This requires an extremely minor modification to your numerical code from part (a).