Prof. Thomas Prisner, Dr. Deniz Sezer

Physikalische Chemie III für Lehramt

Übungsblatt 6

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Complete the plotting exercise from Übungsblatt 4. The notebook we created for Übungsblatt 5 is here: https://colab.research.google.com/drive/1QizC6rjhJWbqYLRmD1d-yzWXcEAmDWAQ?usp=sharing

1 Morse potential

For the simple harmonic oscillator with potential energy

$$V^{\text{sho}}(x) = \frac{1}{2}kx^2 \tag{1}$$

the energies of the different levels predicted by the Schrödinger equation are

$$E_\nu^{\text{sho}} = \left(\nu + \frac{1}{2}\right)\hbar\omega_{\text{vib}}, \qquad \nu = 0, 1, 2, 3, \ldots. \tag{2}$$

While the above potential approximates well the stretching of a covalent bond between two atoms, the following Morse potential is even better:

$$V^{\text{Morse}}(x) = D_e(1 - \mathrm{e}^{-ax})^2. \tag{3}$$

The Morse potential leads to the energies

$$E_\nu^{\text{Morse}} = \left(\nu + \frac{1}{2}\right)\hbar\omega_{\text{vib}} + \left(\nu + \frac{1}{2}\right)^2\hbar\omega_{\text{vib}}\,\chi_e, \qquad \nu = 0, 1, 2, 3, \ldots, \tag{4}$$

where

$$\chi_e = \frac{\hbar\omega_{\text{vib}}}{4D_e} \ll 1. \tag{5}$$

a. Plot the dimensionless ratio

$$\frac{E_\nu^{\text{sho}}}{\hbar\omega_{\text{vib}}} = \nu + \frac{1}{2} \tag{6}$$

against the index ν for the first 21 energy levels (i.e., for $\nu = 0, 1, 2, \ldots, 19, 20$) of the simple harmonic oscillator. (Your plot should be similar to the one shown in Fig. 1 below.)

b. On the same figuure, plot the dimensionless energies

$$\frac{E_\nu^{\text{Morse}}}{\hbar\omega_{\text{vib}}} = \left(\nu + \frac{1}{2}\right) + \left(\nu + \frac{1}{2}\right)^2\chi_e \tag{7}$$

of the lowest 21 levels of the Morse potential for $\chi_e = 0.04$.

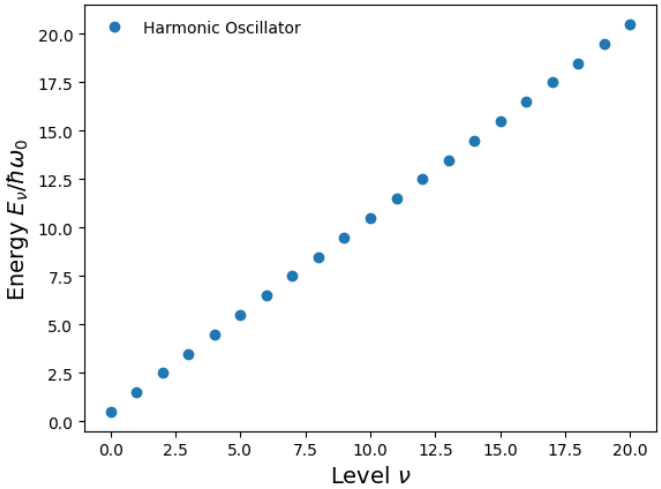


Figure 1: Energies of the lowest 21 levels of the simple harmonic oscillator.

How do the energies of the Morse potential compare to those in Fig. 1?

2 Degrees of freedom and molecular vibrations

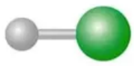
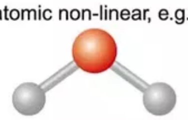
Type of molecule	N	Degrees of freedom	Modes
Monatomic, e.g. Ne 	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl 	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO_2 	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H_2O 	3	9	3 translational 3 rotational 3 vibrational

Figure 2: Degrees of freedom of molecules with N atoms.

a. Figure 2 shows how the total degrees of freedom of a molecule with N atoms are distributed among translations, rotations and vibrations. After studying the examples in the figure, determine the degrees of freedom of the following small molecules: (i) oxygen gas, (ii) methane, (ii) methanol and (iv) methanoic acid.

b. Indicate which of these molecules (including the ones in Fig. 2) have a permanent dipole moment.

3 Black body radiation and Earth's temperature

In this question you will calculate the temperature that the surface of the Earth would have in the absence of its atmosphere.

According to the Stefan-Boltzmann law, a body of absolute temperature T emits electromagnetic radiation whose total power (across all wavelengths) is

$$P_{\text{emit}} = \sigma\, A\, T^4, \tag{8}$$

where $A = 4\pi R^2$ is the area of the body, assumed to be a sphere of radius R, and

$$\sigma = 5.67 \times 10^{-8}\ \frac{\text{W}}{\text{m}^2\,\text{K}^4} \tag{9}$$

is a constant that is independent of the body.

a. In the case of the Sun,

$$R_S = 6.957 \times 10^8\,\text{m} \qquad \text{and} \qquad T_S = 5772\,\text{K}. \tag{10}$$

Using these numbers, calculate the power of electromagnetic radiation emitted by the Sun, $P_{S,\text{emit}}$.

b. From the power $P_{S,\text{emit}}$ only a small fraction reaches the surface of the Earth. Let us denote the power that reaches the Earth by P_{SE}. Calculate P_{SE} if the distance from the Sun to the Earth is

$$D = 1.496 \times 10^{11}\,\text{m} \tag{11}$$

and the Earth radius is

$$R_E = 6.371 \times 10^6\,\text{m}. \tag{12}$$

Hint: The power $P_{S,\text{emit}}$ spreads over an area $4\pi D^2$ and the cross-sectional area of the Earth that collects this spread-out power is πR_E^2.

c. When the temperature of the Earth's surface equilibrates with the energy that it receives from the Sun, it will be emitting all power P_{SE} back to space. (If not, the temperature of the surface will continue to either rise or fall.) Use the equality

$$P_{SE} = P_{E,\text{emit}} = \sigma\,(4\pi R_E^2)\,T_E^4 \tag{13}$$

to calculate the temperature T_E at which such equilibrium is established.
Is water frozen at this temperature?

d. Show that the following relation holds:

$$T_E = T_S\sqrt{\frac{R_S}{2D}}. \tag{14}$$

Use this relationship to obtain analogous temperatures for the planets Mercury ($D = 5.712 \times 10^{10}$ m), Venus ($D = 1.082 \times 10^{11}$ m) and Mars ($D = 2.5 \times 10^{11}$ m).
What is the physical state of water at these temperatures?