Prof. Thomas Prisner, Dr. Deniz Sezer

Physikalische Chemie III für Lehramt

Übungsblatt 4

(12.05.2023)

Besprechung 25.05.2023

The Google Colab notebook that we created in our last meeting is here:
https://colab.research.google.com/drive/1u0FRaeIO25HEvKIqezFVFPrjFKt3uMp7?usp=sharing

1 Molecular vibration in classical mechanics

Let us consider the molecule Cl−H. For concreteness, assume that we deal only with the isotope ^{35}Cl.

(a) Calculate the reduced mass

$$\mu = \frac{m_{\mathrm{Cl}} m_{\mathrm{H}}}{m_{\mathrm{Cl}} + m_{\mathrm{H}}} \tag{1}$$

in atomic mass units (amu) and in kilograms.

(b) Given that the force constant characterizing the covalent bond of Cl−H is $k = 477.8\ \mathrm{J\,m^{-2}}$, calculate the (angular) frequency of vibration

$$\omega_0 = \sqrt{\frac{k}{\mu}}. \tag{2}$$

(c) Use the relationship

$$\nu_0 = \frac{\omega_0}{2\pi} \tag{3}$$

to transform your result to (regular) frequency. What is the numerical value of ν_0 in units of Hz?

2 Molecular vibration in quantum mechanics

The Schrödinger equation for a particle of mass μ in the harmonic potential

$$V(x) = \frac{1}{2}kx^2 \tag{4}$$

is

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\psi_\nu(x) = E_\nu \psi_\nu(x). \tag{5}$$

In class we showed that the wave function

$$\psi_0(x) = A\mathrm{e}^{-\alpha x^2} \tag{6}$$

satisfies the Schrödinger equation when the parameter α is selected such that

$$\alpha = \frac{\sqrt{k\mu}}{2\hbar}. \tag{7}$$

The corresponding energy was found to be

$$E_0 = \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{1}{2}\hbar\,\omega_0, \tag{8}$$

where $\omega_0 = \sqrt{k/\mu}$ was the angular frequency of oscillation according to classical mechanics (Eq. (2)).

(a) Calculate the constant A in Eq. (6), from the normalization condition

$$\int_{-\infty}^{\infty} \psi_0(x)\psi_0(x)\mathrm{d}x = 1. \tag{9}$$

Use the fact that

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2}\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}. \tag{10}$$

(b) Repeat the analysis we carried out in class to show that the wave function

$$\psi_1(x) = Bx\mathrm{e}^{-\beta x^2}, \tag{11}$$

where B and β are some constants, also satisfies the Schrödinger equation when β is chosen appropriately. Identify the proper β. Is it different from α in Eq. (7)?

(c) Using the β that you identified, show that the energy that corresponds to the wave function in Eq. (11) is

$$E_1 = \left(1 + \frac{1}{2}\right)\hbar\,\omega_0, \tag{12}$$

where ω_0 was defined in Eq. (8).

(d) Obtain the constant B in Eq. (11) such that the normalization condition

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_1(x)\mathrm{d}x = 1 \tag{13}$$

holds.

3 Wave functions of molecular vibration

In fact, there are infinitely many wave functions that satisfy the Schrödinger equation (5), with ψ_0 and ψ_1 being only two of them. All functions can be written collectively as follows:

$$\psi_\nu(x) = N_\nu\, H_\nu\left(\frac{\sqrt{k\mu}}{\hbar}x\right)\mathrm{e}^{-\frac{\sqrt{k\mu}}{2\hbar}x^2}, \qquad \nu = 0, 1, 2, 3, \ldots. \tag{14}$$

Here N_ν is the normalization constant and $H_\nu(z)$ is the Hermite polynomial of order ν. As an example, the first few Hermite polynomials are

$$\begin{aligned}
H_0(z) &= 1 \\
H_1(z) &= 2z \\
H_2(z) &= 4z^2 - 2 \\
H_3(z) &= 8z^3 - 12z \\
H_4(z) &= 16z^4 - 48z^2 + 12.
\end{aligned} \tag{15}$$

The energy that corresponds to $\psi_\nu(x)$ is

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\,\omega_0. \tag{16}$$

(a) Using the numerical values of k and μ from question **1**, plot the wave functions $\psi_0(x)$, $\psi_1(x)$ and $\psi_3(x)$ describing the vibration of the molecule Cl−H.

(b) For these three wave functions, plot the probabilities

$$p_\nu(x) = |\psi_\nu(x)|^2. \tag{17}$$