032CM - 2025

PROGRAMMING FOR COMPUTATIONAL CHEMISTRY

Normal mode analysis

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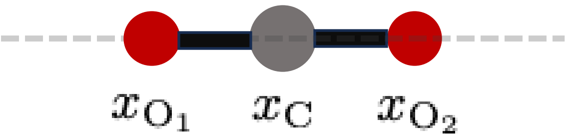
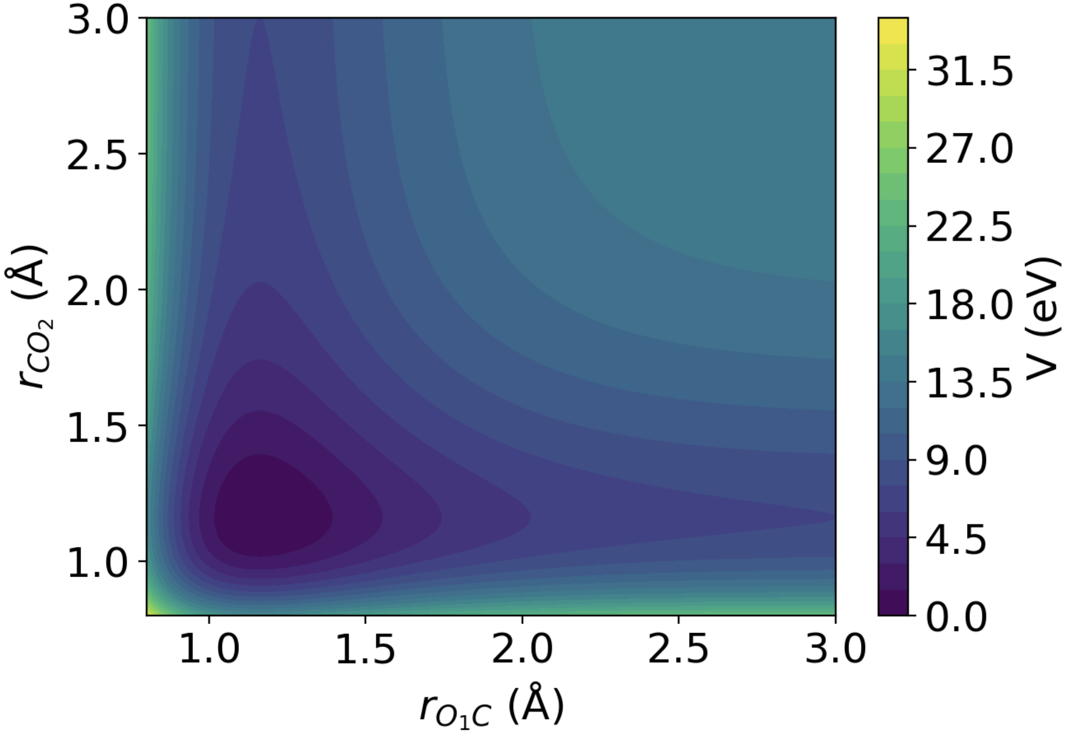
Vibrational dynamics of the CO2 molecule (Assignment 7)

Morse potential

$$V_{\mathrm{CO}}(r) = D_{\mathrm{e}}\left(1 - e^{-\alpha(r-r_e)}\right)^2$$

$$V(r_{O_1C}, r_{CO_2}) = V_{\mathrm{CO}}(r_{O_1C}) + V_{\mathrm{CO}}(r_{CO_2})$$





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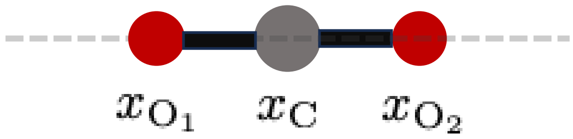

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$$F_{\mathrm{O}_1} = -\frac{\partial V}{\partial x_{\mathrm{O}_1}} = -\frac{\partial V}{\partial r_{\mathrm{O}_1 C}}\frac{\partial r_{\mathrm{O}_1 C}}{\partial x_{\mathrm{O}_1}}$$

$$F_C = -\frac{\partial V}{\partial x_C} = -\frac{\partial V}{\partial r_{\mathrm{O}_1 C}}\frac{\partial r_{\mathrm{O}_1 C}}{\partial x_C} - \frac{\partial V}{\partial r_{C\mathrm{O}_2}}\frac{\partial r_{C\mathrm{O}_2}}{\partial x_C} = -\frac{\partial V}{\partial r_{\mathrm{O}_1 C}} + \frac{\partial V}{\partial r_{C\mathrm{O}_2}}$$

$$F_{\mathrm{O}_2} = -\frac{\partial V}{\partial x_{\mathrm{O}_2}} = -\frac{\partial V}{\partial r_{C\mathrm{O}_2}}\frac{\partial r_{C\mathrm{O}_2}}{\partial x_{\mathrm{O}_2}}$$

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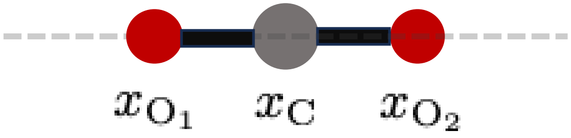

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Vibrational dynamics of the CO2 molecule (Assignment 7)

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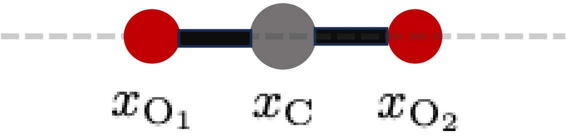

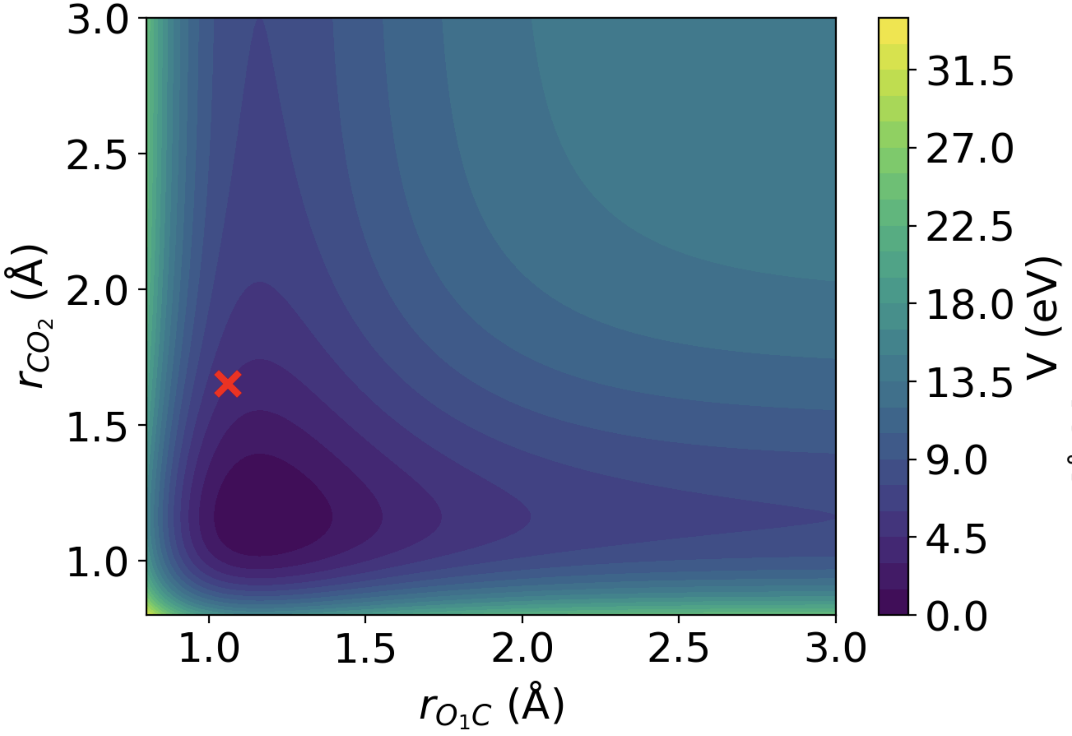

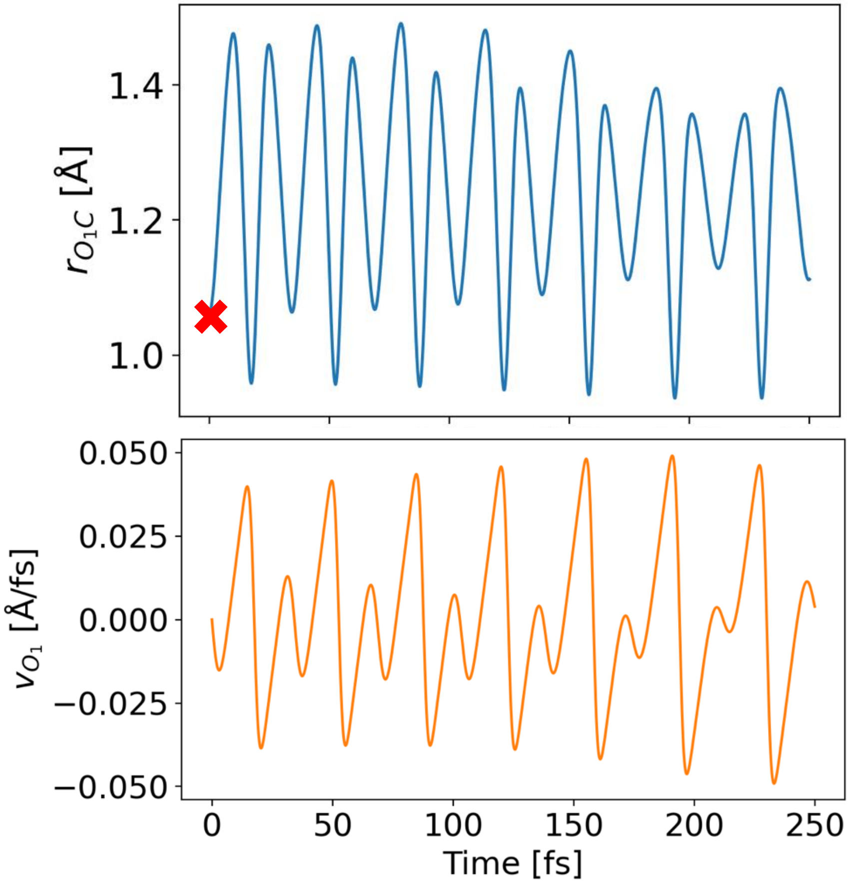

Normal modes of vibration

Potential of interaction is **harmonic**

From Taylor series about the equilibrium geometry up to second order:

$$V_{\mathrm{harm}}(x_{O_1}, x_C, x_{O_2}) = \frac{1}{2}k_{O_1C}\left(x_C - x_{O_1} - r^{\mathrm{eq}}_{O_1C}\right)^2 + \frac{1}{2}k_{CO_2}\left(x_{O_2} - x_C - r^{\mathrm{eq}}_{CO_2}\right)^2$$

$$k_{CO} = 2D_e\alpha^2$$

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$$k_{CO} = 2D_e\alpha^2$$

Find **normal coordinates** with corresponding harmonic frequencies

- Linear combination of atomic coordinates
- Satisfy independent equations of motion
- Describe collective motion (or mode) of the molecule where **all atoms vibrate in phase at one frequency**

Normal modes of vibration

Find **normal coordinates** with corresponding harmonic frequencies

$$F_{O_1} = -\frac{\partial V}{\partial x_{O_1}} = m_{O_1}\frac{d^2 x_{O_1}(t)}{dt^2}$$

$$F_C = -\frac{\partial V}{\partial x_C} = m_C\frac{d^2 x_C(t)}{dt^2}$$

$$F_{O_2} = -\frac{\partial V}{\partial x_{O_2}} = m_{O_2}\frac{d^2 x_{O_2}(t)}{dt^2}$$

Normal modes of vibration

Find **normal coordinates** with corresponding harmonic frequencies

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$$F_{O_2} = -\frac{\partial V}{\partial x_{O_2}} = m_{O_2}\frac{d^2 x_{O_2}(t)}{dt^2}$$

$$\Delta\ddot{x}_{O_1}(t) = -\frac{k_{O_1C}}{m_{O_1}}\left(\Delta x_{O_1} - \Delta x_C\right)$$

$$\Delta\ddot{x}_C(t) = -\frac{k_{O_1C}}{m_C}\left(\Delta x_C - \Delta x_{O_1}\right) - \frac{k_{CO_2}}{m_C}\left(\Delta x_C - \Delta x_{O_2}\right)$$

$$\Delta\ddot{x}_{O_2}(t) = -\frac{k_{CO_2}}{m_{O_2}}\left(\Delta x_{O_2} - \Delta x_C\right)$$

Normal modes of vibration

Find **normal coordinates** with corresponding harmonic frequencies

$$\begin{pmatrix} \Delta\ddot{x}_{O_1}(t) \\ \Delta\ddot{x}_C(t) \\ \Delta\ddot{x}_{O_2}(t) \end{pmatrix} = -\begin{pmatrix} k_{O_1C}/m_{O_1} & -k_{O_1C}/m_{O_1} & 0 \\ -k_{O_1C}/m_C & (k_{O_1C}+k_{CO_2})/m_C & -k_{CO_2}/m_C \\ 0 & -k_{CO_2}/m_{O_2} & k_{CO_2}/m_{O_2} \end{pmatrix} \begin{pmatrix} \Delta x_{O_1}(t) \\ \Delta x_C(t) \\ \Delta x_{O_2}(t) \end{pmatrix}$$

$$\Delta\ddot{\mathbf{x}}(t) = -\mathbf{K}\,\Delta\mathbf{x}(t)$$

$$\Delta\mathbf{x}(t) = \begin{pmatrix} \Delta x_{O_1}(t) \\ \Delta x_C(t) \\ \Delta x_{O_2}(t) \end{pmatrix} = \mathbf{L}\,\mathbf{Q}(t) = \mathbf{L}\begin{pmatrix} Q_1(t) \\ Q_2(t) \\ Q_3(t) \end{pmatrix}$$

Choose the columns of **L** such that they are the eigenvectors of **K**:

$$\mathbf{K}\begin{pmatrix} L_{1j} \\ L_{2j} \\ L_{3j} \end{pmatrix} = \omega_j^2 \begin{pmatrix} L_{1j} \\ L_{2j} \\ L_{3j} \end{pmatrix}, \qquad j = 1, 2, 3$$

Normal modes of vibration

Find **normal coordinates** with corresponding harmonic frequencies

ω_j^2 Eigenvalues (harmonic frequencies)

$\begin{pmatrix} L_{1j} \\ L_{2j} \\ L_{3j} \end{pmatrix}$ Eigenvectors (normal mode displacements)

$$\Delta\ddot{\mathbf{x}}(t) = -\mathbf{K}\,\Delta\mathbf{x}(t) \;\Rightarrow\; \mathbf{L}\,\ddot{\mathbf{Q}}(t) = -\mathbf{K}\,\mathbf{L}\,\mathbf{Q}(t)$$

Multiply by $\mathbf{L}^T$:

$$\ddot{\mathbf{Q}}(t) = -\boldsymbol{\Lambda}\,\mathbf{Q}(t)$$

$$\boxed{\ddot{Q}_k(t) + \omega_k^2 Q_k(t) = 0, \qquad k = 1, 2, 3}$$

Normal modes of vibration

Find **normal coordinates** with corresponding harmonic frequencies

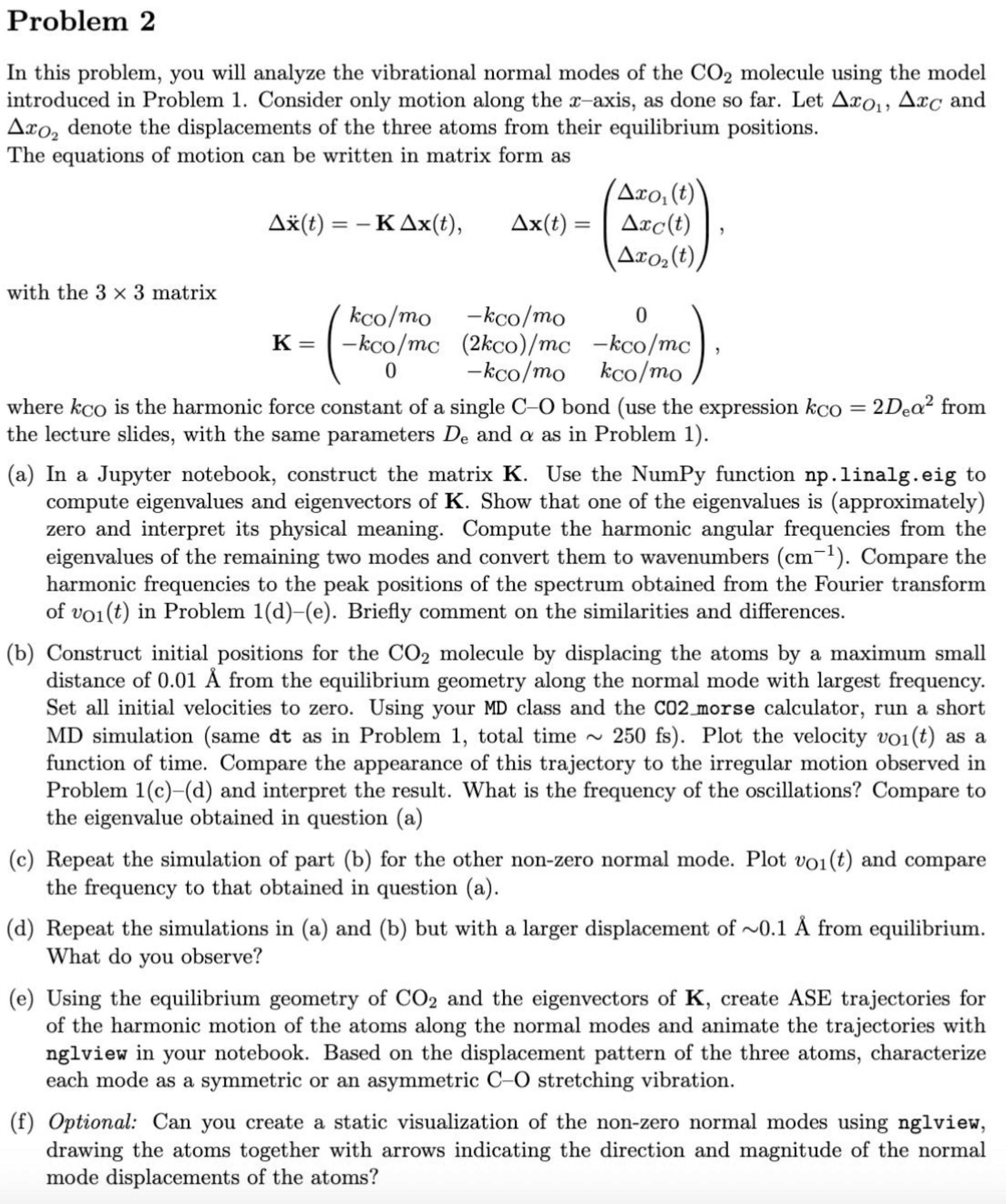
$$\boxed{\ddot{Q}_k(t) + \omega_k^2 Q_k(t) = 0, \qquad k = 1, 2, 3}$$

Normal mode coordinates

Solutions to this equation can be written as $Q_k(t) = A_k \sin(\omega_k t)$

$$\mathbf{Q}(t) = \mathbf{L}^T \Delta\mathbf{x}(t) = \mathbf{L}^T \begin{pmatrix} \Delta x_{O_1}(t) \\ \Delta x_C(t) \\ \Delta x_{O_2}(t) \end{pmatrix} = \begin{pmatrix} Q_1(t) \\ Q_2(t) \\ Q_3(t) \end{pmatrix}$$

Assignment 7



Problem 2

In this problem, you will analyze the vibrational normal modes of the CO_2 molecule using the model introduced in Problem 1. Consider only motion along the x–axis, as done so far. Let Δx_{O_1}, Δx_C and Δx_{O_2} denote the displacements of the three atoms from their equilibrium positions.
The equations of motion can be written in matrix form as

$$\Delta\ddot{\mathbf{x}}(t) = -\mathbf{K}\,\Delta\mathbf{x}(t), \qquad \Delta\mathbf{x}(t) = \begin{pmatrix} \Delta x_{O_1}(t) \\ \Delta x_C(t) \\ \Delta x_{O_2}(t) \end{pmatrix},$$

with the 3×3 matrix

$$\mathbf{K} = \begin{pmatrix} k_{\mathrm{CO}}/m_{\mathrm{O}} & -k_{\mathrm{CO}}/m_{\mathrm{O}} & 0 \\ -k_{\mathrm{CO}}/m_{\mathrm{C}} & (2k_{\mathrm{CO}})/m_{\mathrm{C}} & -k_{\mathrm{CO}}/m_{\mathrm{C}} \\ 0 & -k_{\mathrm{CO}}/m_{\mathrm{O}} & k_{\mathrm{CO}}/m_{\mathrm{O}} \end{pmatrix},$$

where k_{CO} is the harmonic force constant of a single C–O bond (use the expression $k_{\mathrm{CO}} = 2D_{\mathrm{e}}\alpha^2$ from the lecture slides, with the same parameters D_{e} and α as in Problem 1).

(a) In a Jupyter notebook, construct the matrix $\mathbf{K}$. Use the NumPy function `np.linalg.eig` to compute eigenvalues and eigenvectors of $\mathbf{K}$. Show that one of the eigenvalues is (approximately) zero and interpret its physical meaning. Compute the harmonic angular frequencies from the eigenvalues of the remaining two modes and convert them to wavenumbers (cm^{-1}). Compare the harmonic frequencies to the peak positions of the spectrum obtained from the Fourier transform of $v_{\mathrm{O1}}(t)$ in Problem 1(d)–(e). Briefly comment on the similarities and differences.

(b) Construct initial positions for the CO_2 molecule by displacing the atoms by a maximum small distance of 0.01 Å from the equilibrium geometry along the normal mode with largest frequency. Set all initial velocities to zero. Using your `MD` class and the `CO2_morse` calculator, run a short MD simulation (same `dt` as in Problem 1, total time $\sim$ 250 fs). Plot the velocity $v_{\mathrm{O1}}(t)$ as a function of time. Compare the appearance of this trajectory to the irregular motion observed in Problem 1(c)–(d) and interpret the result. What is the frequency of the oscillations? Compare to the eigenvalue obtained in question (a)

(c) Repeat the simulation of part (b) for the other non-zero normal mode. Plot $v_{\mathrm{O1}}(t)$ and compare the frequency to that obtained in question (a).

(d) Repeat the simulations in (a) and (b) but with a larger displacement of $\sim$0.1 Å from equilibrium. What do you observe?

(e) Using the equilibrium geometry of CO_2 and the eigenvectors of $\mathbf{K}$, create ASE trajectories for of the harmonic motion of the atoms along the normal modes and animate the trajectories with `nglview` in your notebook. Based on the displacement pattern of the three atoms, characterize each mode as a symmetric or an asymmetric C–O stretching vibration.

(f) *Optional:* Can you create a static visualization of the non-zero normal modes using `nglview`, drawing the atoms together with arrows indicating the direction and magnitude of the normal mode displacements of the atoms?