Linear Molecules. Math 23, Fall 2009

This note contains three homework exercises that are due on Friday November 20. This material is not covered very clearly in the text book. Therefore the exercises are followed by a detailed solution of the example of a linear molecule with three atoms that we studied in lecture.

Exercise 1. A linear molecule consists of three atoms A, B, C. Atoms A and B have mass $m = 2$, while atom C is lighter, with mass $m = 1$. Atoms A and B are linked by a spring, and so are atoms B and C. The spring connecting A and B has spring constant $k = 4$. The spring connecting B and C is weaker, with spring constant $k = 2$. Let x_1, x_2, x_3 denote the (horizontal) displacement of atoms A, B, C respectively. We do not specify the physical units of measurement in this problem.

Find the general formulas for the motions of the three atoms in the two normal vibrational modes of this molecule. You can ignore the mode in which the center of mass is in motion.

What are the angular frequencies of each of the two normal modes of this system?

Can you sketch or describe in words what each mode is like in terms of the combined motions of the three atoms?

Exercise 2. A linear molecule consists of three atoms A, B, C. The three atoms have equal mass m. Atoms A and B are linked by a spring, and so are atoms B and C. The two springs have the same spring constant k.

Derive a formula (involving the constants m and k) for the angular frequencies of the two vibrational modes of this molecule (ignoring the motion of the center of mass). **Remark.** In order to find the frequencies, you do *not* need to find any eigenvectors, only eigenvalues.

Exercise 3. If a linear molecule consists of 5 atoms, how many different normal mode frequencies can there be? Explain your answer by considering the size of the system of equations, the number of eigenvalues involved, and the way these eigenvalues translate into solutions of the system.

Example. A linear molecule consists of three atoms A, B, C. In our model, atoms A and B are linked by a spring with spring constant $k = 1$, and likewise B and C are linked by a spring with spring constant $k = 1$. The atoms A and C have mass $m = 1$, while atom B has a larger mass $M = 2$, We let x_1, x_2, x_3 denote the (horizontal) displacement of atoms A, B, C respectively. We do not specify the physical units of measurement in this problem.

The motion of the molecule is described by a linear system of second order differential equations as follows

$$\begin{aligned} mx_1'' &= k(x_2 - x_1) = -kx_1 + kx_2 \\ Mx_2'' &= -k(x_2 - x_1) + k(x_3 - x_2) = kx_1 - 2kx_2 + kx_3 \\ mx_3'' &= -k(x_3 - x_2) = kx_2 - kx_3 \end{aligned}$$

This system can be represented in vector form as $\mathbf{x}'' = A\mathbf{x}$ with coefficient matrix

$$A = \begin{pmatrix} -k/m & k/m & 0 \\ k/M & -2k/M & k/M \\ 0 & k/m & -k/m \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ 1/2 & -1 & 1/2 \\ 0 & 1 & -1 \end{pmatrix}$$

The eigenvalues of A are obtained from the characteristic equation

$$\begin{aligned}|A-\lambda\mathbf{I}| &= \begin{bmatrix} -1-\lambda & 1 & 0 \\ 1/2 & -1-\lambda & 1/2 \\ 0 & 1 & -1-\lambda \end{bmatrix} \\ &= (-1-\lambda)^3 - \frac{1}{2}(-1-\lambda) - \frac{1}{2}(-1-\lambda) \\ &= -1-3\lambda-3\lambda^2-\lambda^3+1+\lambda \\ &= -\lambda^3-3\lambda^2-2\lambda \\ &= -\lambda(\lambda+1)(\lambda+2).\end{aligned}$$

The eigenvalues of A are therefore $\lambda_1 = 0, \lambda_2 = -1, \lambda_3 = -2$. As is expected for linear molecules, all eigenvalues are negative, except for one eigenvalue that equals zero.

The eigenvector $\mathbf{v}$ for $\lambda_2 = -1$ is found by row reduction as follows,

$$|A-(-1)\mathbf{I}| = \begin{bmatrix} 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \\ 0 & 1 & 0 \end{bmatrix} \sim \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}.$$

This means that $v_2 = 0$ and $v_1 + v_3 = 0$. We can choose $\mathbf{v} = (1, 0, -1)$.

Independent solutions of the second order system of differential equations are of the form

$$\mathbf{x} = e^{rt}\mathbf{v},$$

where $r^2 = \lambda$ is an eigenvalue of A. For $\lambda_2 = -1$ we find $r = \pm i$. With $r = i$ we get

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = e^{it}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} e^{it} \\ 0 \\ -e^{it} \end{pmatrix} = \begin{pmatrix} \cos t + i\sin t \\ 0 \\ -\cos t - i\sin t \end{pmatrix} = \begin{pmatrix} \cos t \\ 0 \\ -\cos t \end{pmatrix} + i\begin{pmatrix} \sin t \\ 0 \\ -\sin t \end{pmatrix}$$

If we insert $r = -i$ we obtain the complex conjugate solution. The linear combinations of the two solutions that correspond to $\lambda = -1$, or $r = \pm i$, are therefore

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = c_1\begin{pmatrix} \cos t \\ 0 \\ -\cos t \end{pmatrix} + c_2\begin{pmatrix} \sin t \\ 0 \\ -\sin t \end{pmatrix} = \begin{pmatrix} c_1\cos t + c_2\sin t \\ 0 \\ -c_1\cos t - c_2\sin t \end{pmatrix}.$$

In terms of the motions of the molecule, each eigenvalue of A corresponds to one of the *normal modes* of vibration of the atoms in the molecule. For $\lambda = -1$ we find a normal mode in which the two outer atoms A and C vibrate in opposite directions with the same amplitude and with angular frequency $\omega = 1$, while the central atom B is at rest.

To find the other mode of the molecule we derive the solutions that corresponds to $\lambda = -2$. Following the same steps as before, first find the eigenvector,

$$|A-(-2)\mathbf{I}| = \begin{bmatrix} 1 & 1 & 0 \\ 1/2 & 1 & 1/2 \\ 0 & 1 & 1 \end{bmatrix} \sim \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1 & 1 \end{bmatrix} \sim \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 0 \end{bmatrix}.$$

This means that $v_1 + v_2 = 0$ and $v_2 + v_3 = 0$. We choose $\mathbf{v} = (1, -1, 1)$.

Solutions are of the form $\mathbf{x} = e^{rt}\mathbf{v}$ with $r^2 = \lambda = -2$, or $r = \pm i\sqrt{2}$. With $r = i\sqrt{2}$ we get

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = e^{it\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} = \begin{pmatrix} e^{it\sqrt{2}} \\ -e^{it\sqrt{2}} \\ e^{it\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \cos t\sqrt{2} \\ -\cos t\sqrt{2} \\ \cos t\sqrt{2} \end{pmatrix} + i \begin{pmatrix} \sin t\sqrt{2} \\ -\sin t\sqrt{2} \\ \sin t\sqrt{2} \end{pmatrix}$$

The linear combinations of the two solutions that correspond to $\lambda = -2$, or $r = \pm i\sqrt{2}$, are

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = c_1 \begin{pmatrix} \cos t\sqrt{2} \\ -\cos t\sqrt{2} \\ \cos t\sqrt{2} \end{pmatrix} + c_2 \begin{pmatrix} \sin t\sqrt{2} \\ -\sin t\sqrt{2} \\ \sin t\sqrt{2} \end{pmatrix} = \begin{pmatrix} c_1 \cos t\sqrt{2} + c_2 \sin t\sqrt{2} \\ -c_1 \cos t\sqrt{2} - c_2 \sin t\sqrt{2} \\ c_1 \cos t\sqrt{2} + c_2 \sin t\sqrt{2} \end{pmatrix}.$$

For $\lambda = -2$ we find a normal mode in which the two outer atoms A and C vibrate in the *same* direction with the same amplitude and same angular frequency $\omega = \sqrt{2}$, while the central atom B vibrates with same amplitude and angular frequency in the opposite direction. Because the mass of the central atom B is twice that of the two outer atoms A, C, the center of mass of the molecule remains at rest under the combined vibrations of A, B, C.

Finally, the eigenvalue $\lambda = 0$ corresponds to the motion of the entire molecule represented by the simple formulas

$$x_1 = x_2 = x_3 = c_1 + c_2 t.$$

There is no need to derive this rigorously in each case, because this particular eigenvalue $\lambda = 0$ occurs for every linear molecule, regardless of the number of atoms. There is *no* vibration in the $\lambda = 0$ mode, because the relative distance of the atoms remains fixed. The $\lambda = 0$ mode always corresponds to the linear movement of the entire molecule–or its center of mass–while the negative eigenvalues of A always correspond to vibrational modes of different frequencies in which the center of mass is at rest.

Notice that the angular frequency of a vibrational normal mode is always just the number $\sqrt{|\lambda|}$. You can find this frequency without solving for the eigenvectors. However, without knowing the eigenvectors you cannot describe what the relative motion of the atoms is like in the given mode. If you do not find the eigenvectors, then you only know the frequency with which the atoms vibrate, but not the relative amplitudes or phases of their oscillations.