California Institute of Technology
Physics 2a Recitation
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Breath of Fresh Air
21 October 2022

"A restaurant on the moon could not have had less atmosphere." —Geoff Dyer

Contents

1 Problem Statement

In this Problem, we will use a very simplified model of molecular oscillation modes in order to understand what frequencies of light will be resonant with certain molecules in our atmosphere.

(a) Before we proceed in constructing our models, we should first roughly estimate the "spring" constant which keeps the atoms in a molecule together.

The restorative force between atoms is dominated by the interactions of the electron clouds, with very little dependence on the nuclei. Table 1 gives the only possible constants which k can depend on.

Use dimensional analysis to construct something with the units of a spring constant k (which has dimensions of $\mathrm{M}^1\,\mathrm{T}^{-2}$). Make a numerical estimate of this spring constant.

For later parts, we will simply use the symbol k to denote this spring constant.

Constants	Description	Dimensions	Value
k_e	Coulomb constant	$\mathrm{M}^1\,\mathrm{L}^3\,\mathrm{T}^{-2}\,\mathrm{Q}^{-2}$	$8.99 \times 10^9\,\mathrm{kg\,m^3\,s^{-2}\,C^{-2}}$
e	electron charge	Q^1	$1.60 \times 10^{-19}\,\mathrm{C}$
m_e	electron mass	M^1	$9.11 \times 10^{-31}\,\mathrm{kg}$
$\hbar$	Planck's constant	$\mathrm{M}^1\,\mathrm{L}^2\,\mathrm{T}^{-1}$	$1.06 \times 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}$

Table 1: Fundamental physics constants which are important to electron clouds.

(b) First, consider a diatomic molecule with equal masses m (in one dimension), connected by a spring of spring constant k (Figure 1). Denote the positions of the two atoms (relative to their equilibrium positions) as x_1 and x_2.

Using Newton's second law, write down two (coupled) differential equations involving x_1 and x_2.

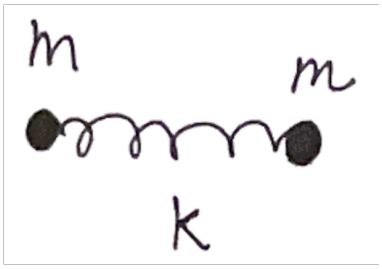

Figure 1: Diagram of a toy model of a diatomic molecule.

(c) Defining $v_1 = x_1 + x_2$ and $v_2 = x_1 - x_2$, derive two (now decoupled) differential equations involving v_1 and v_2.

What are the oscillation frequencies of v_1 and v_2, and to which kinds of atomic motions do they correspond?

(d) The proton mass is $u = 1.67 \times 10^{-27}\,\text{kg}$.

What are these frequencies for nitrogen gas N_2 ($m = 14u$) and oxygen gas O_2 ($m = 16u$), the most abundant gases in our atmosphere?

To what wavelengths of light do these frequencies correspond?

(e) Light only (effectively) scatters off of molecules when the corresponding oscillation mode has an effect on the electric dipole moment,

$$p = \sum_i q_i x_i = q_1 x_1 + q_2 x_2 \tag{1}$$

Do these equal-mass diatomic molecules actually scatter the light at the frequencies found in part (d)?

(f) Now consider a triatomic molecule (again in one dimension) with a central mass M connected to two equal masses m each with a spring with spring constant k (Figure 2). Denote the positions of the central mass as x_2, and the other two masses as x_1 and x_3.

Using Newton's second law, write down three (coupled) differential equations involving x_1, x_2, and x_3.

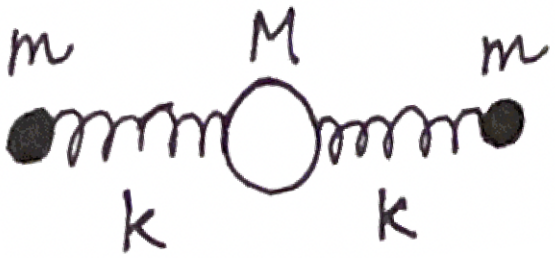

Figure 2: Diagram of a toy model of a triatomic molecule.

(g) Find the eigenvalues and eigenvectors of the resulting matrix equation.

What are the oscillation frequencies of each of the normal modes, and to what physical motions do they correspond?

(h) For carbon dioxide ($M = 12u$ and $m = 16u$), what are the numerical values of the oscillation frequencies, and to what wavelengths of light do they correspond?

(i) Do these modes actually couple to light?

2 Problem Solutions

2.1 Part (a): Spring constant

The only way to combine the given constants into a spring constant is

$$k = \frac{k_e^4 m_e^3 e^8}{\hbar^6} \approx 1.56 \times 10^3 \,\mathrm{kg\,s^2} \tag{2}$$

2.2 Part (b): Diatomic molecule equations

Newton's second law, when combined with Hooke's law, gives

$$m\ddot{x}_1 = -k(x_1 - x_2) = -kx_1 + kx_2 \tag{3a}$$
$$m\ddot{x}_2 = -k(x_2 - x_1) = +kx_1 - kx_2 \tag{3b}$$

2.3 Part (c): Diatomic molecular modes

We can add Equations 3a and 3b together to obtain

$$m\ddot{x}_1 + m\ddot{x}_2 = m\frac{\mathrm{d}^2}{\mathrm{d}t^2}(x_1 + x_2) = 0 \tag{4}$$

Defining $v_1 = x_1 + x_2$, this becomes

$$\ddot{v}_1 = 0 \tag{5}$$

This is a harmonic oscillator equation, but with a frequency of zero. The combination v_1 is the center of mass of the system (within a factor of two), and its change means that the entire center of mass of the system is changing. Therefore, this mode corresponds to motion of the entire molecule (which cannot be restored by any spring, since there are no external springs).

Similarly, we can subtract Equations 3a and 3b to obtain

$$m\ddot{x}_1 - m\ddot{x}_2 = m\frac{\mathrm{d}^2}{\mathrm{d}t^2}(x_1 - x_2) = -2k(x_1 - x_2) \tag{6}$$

Now, defining $v_2 = x_1 - x_2$, we obtain

$$\ddot{v}_2 + \frac{2k}{m}v_2 = 0 \tag{7}$$

We see that this is a harmonic oscillator equation with a frequency $\omega = \sqrt{2k/m}$. The combination v_2 is the difference of the positions of the atoms (i.e., it represents the distance between them). Therefore, this mode corresponds to motions where the two atoms oscillate apart and back together.

The displacements corresponding to v_1 and v_2 are shown in Figure 3.

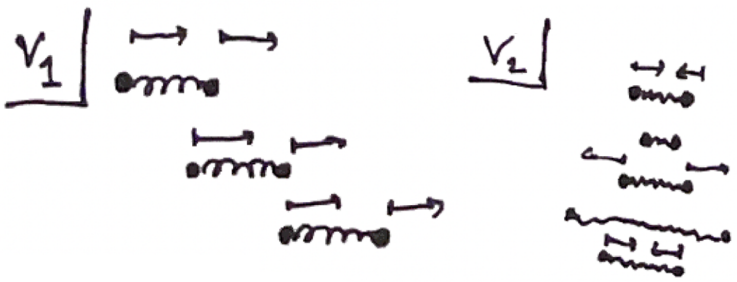

Figure 3: The normal modes of a one-dimensional diatomic molecule.

2.4 Part (d): Frequencies of N_2 and O_2

The center of mass mode for both N_2 and O_2 are zero.

The respective numerical values for the N_2 and O_2 "breathing" modes are

$$\omega_{N_2} = \sqrt{\frac{2k}{14u}} \approx 365\,\text{THz} \tag{8a}$$

$$\omega_{O_2} = \sqrt{\frac{2k}{16u}} \approx 341\,\text{THz} \tag{8b}$$

Both of these correspond to wavelengths $\approx 5\,\mu$m, which is in the infrared.

2.5 Part (e): Diatomic dipole moment

With respect to scattering light, scattering with respect to the breathing modes are "forbidden". They do not change the electric dipole moment $p = q_1x_1 + q_2x_2$, since x_1 and x_2 oscillate in opposite directions.

2.6 Part (f): Triatomic molecule equations

Once again, Newton's second law can be combined with Hooke's law to give

$$m\ddot{x}_1 = -k(x_1 - x_2) \tag{9a}$$

$$M\ddot{x}_2 = -k(x_2 - x_1) - k(x_2 - x_3) \tag{9b}$$

$$m\ddot{x}_3 = -k(x_3 - x_2) \tag{9c}$$

$$\tag{9d}$$

2.7 Part (g): Triatomic molecule modes

Equations 10 can be rewritten as

$$\ddot{x}_1 = \frac{k}{m}\left(-1x_1 + 1x_2 + 0x_3\right) \tag{10a}$$

$$\ddot{x}_2 = \frac{k}{m}\left(+1\mu^{-1}x_1 - 2\mu^{-1}x_2 + 1\mu^{-1}x_3\right) \tag{10b}$$

$$\ddot{x}_3 = \frac{k}{m}\left(0x_1 + 1x_2 + 1x_3\right) \tag{10c}$$

$$\tag{10d}$$

where we have defined $\mu = M/m$.

This yields the matrix equation

$$\ddot{\vec{x}} = \frac{k}{m}\mathbf{\Lambda}\vec{x} \tag{11}$$

where $\vec{x} = (x_1, x_2, x_3)$ and the matrix $\mathbf{\Lambda}$ is given by

$$\mathbf{\Lambda} = \begin{pmatrix} -1 & +1 & 0 \\ +1\mu^{-1} & -2\mu^{-1} & +1\mu^{-1} \\ 0 & +1 & -1 \end{pmatrix} \tag{12}$$

To find the normal modes, we seek the roots of the characteristic polynomial of $\mathbf{\Lambda}$:

$$\det(\mathbf{\Lambda} - \lambda\mathbf{I}) = 0 \tag{13}$$

where $\mathbf{I}$ is the identity matrix. This is

$$\begin{aligned}
\det(\mathbf{\Lambda} - \lambda\mathbf{I}) &= \begin{vmatrix} -1-\lambda & +1 & 0 \\ +1\mu^{-1} & -2\mu^{-1}-\lambda & +1\mu^{-1} \\ 0 & +1 & -1-\lambda \end{vmatrix} \\
&= (-1-\lambda)\begin{vmatrix} -2\mu^{-1}-\lambda & +1\mu^{-1} \\ +1 & -1-\lambda \end{vmatrix} - 1\begin{vmatrix} +1\mu^{-1} & +1\mu^{-1} \\ 0 & -1-\lambda \end{vmatrix} \\
&= (-1-\lambda)((-2\mu^{-1}-\lambda)(-1-\lambda) - (+1)(+1\mu^{-1})) - ((+1\mu^{-1})(-1-\lambda) - (0)(+1\mu^{-1})) \\
&= -\lambda^3 - (1+\mu^{-1})\lambda^2 - (1+2\mu^{-1})\lambda \\
&= -\lambda(\lambda+1)(\lambda+1+2\mu^{-1}) = 0
\end{aligned} \tag{14}$$

We see that the characteristic polynomial is solved by

$$\lambda_1 = 0 \tag{15a}$$

$$\lambda_2 = -1 \tag{15b}$$

$$\lambda_3 = -1 - 2\mu^{-1} \tag{15c}$$

For λ_1, we want to find the kernel of $\mathbf{\Lambda} - \lambda_1 \mathbf{I}$:

$$\mathbf{\Lambda} - \lambda_1 \mathbf{I} = \begin{pmatrix} -1 & +1 & 0 \\ +1\mu^{-1} & -2\mu^{-1} & +1\mu^{-1} \\ 0 & +1 & -1 \end{pmatrix} \tag{16}$$

This can be row-reduced ("$\to$") to

$$\mathbf{\Lambda} - \lambda_1 \mathbf{I} \to \begin{pmatrix} -1 & +1 & 0 \\ 0 & +1 & -1 \\ 0 & 0 & 0 \end{pmatrix} \tag{17}$$

This yields the equations $x_1 - x_2 = 0$ and $x_2 - x_3 = 0$, which is solved by $x_1 = x_2 = x_3$, e.g., the eigenvector

$$\vec{v}_1 = (1, 1, 1) \tag{18}$$

This eigenvector is the center-of-mass mode.

For $\lambda_2 = -1$, we want to find the kernel of $\mathbf{\Lambda} - \lambda_2 \mathbf{I}$:

$$\mathbf{\Lambda} - \lambda_2 \mathbf{I} = \begin{pmatrix} 0 & +1 & 0 \\ +1\mu^{-1} & -2\mu^{-1} - 1 & +1\mu^{-1} \\ 0 & +1 & 0 \end{pmatrix} \to \begin{pmatrix} 0 & +1 & 0 \\ +1 & 0 & +1 \\ 0 & 0 & 0 \end{pmatrix} \tag{19}$$

This yields the equations $x_2 = 0$ and $x_1 + x_3 = 0$, e.g.,

$$\vec{v}_2 = (1, 0, -1) \tag{20}$$

This eigenvector corresponds to the central mass M staying still and the masses m moving in opposite directions.

Finally, for λ_3, we want to find the kernel of $\mathbf{\Lambda} - \lambda_3 \mathbf{I}$:

$$\mathbf{\Lambda} - \lambda_3 \mathbf{I} = \begin{pmatrix} 2\mu^{-1} & +1 & 0 \\ +1\mu^{-1} & +1 & +1\mu^{-1} \\ 0 & +1 & 2\mu^{-1} \end{pmatrix} \to \begin{pmatrix} +1 & 0 & -1 \\ 0 & +1\mu & 2 \\ 0 & 0 & 0 \end{pmatrix} \tag{21}$$

This yields the equations $x_1 - x_3 = 0$ and $\mu x_2 + 2x_3 = 0$, e.g.,

$$\vec{v}_3 = (1, -2\mu^{-1}, 1) \tag{22}$$

This mode corresponds to the central mass M moving in one direction, and the other masses m moving together in the opposite direction.

In terms of these eigenvectors, Equations 11 become

$$\ddot{v}_1 = \frac{k}{m} \lambda_1 y_1 = 0 \tag{23a}$$

$$\ddot{v}_2 = \frac{k}{m} \lambda_2 y_2 = -\frac{k}{m} y_2 \tag{23b}$$

$$\ddot{v}_3 = \frac{k}{m} \lambda_3 y_2 = -k \left(\frac{2}{M} + \frac{1}{m} \right) y_3 \tag{23c}$$

These equations can be rewritten into

$$\ddot{v}_1 = 0 \tag{24a}$$

$$\ddot{v}_2 + \frac{k}{m} y_2 = 0 \tag{24b}$$

$$\ddot{v}_3 + k\left(\frac{2}{M} + \frac{1}{m}\right) y_3 = 0 \tag{24c}$$

We thus see that the eigenvectors all follow their own (decoupled) simple harmonic oscillator equations, with frequencies

$$\omega_1 = 0 \tag{25a}$$

$$\omega_2 = \sqrt{\frac{k}{m}} \tag{25b}$$

$$\omega_3 = \sqrt{k\left(\frac{2}{M} + \frac{1}{m}\right)} \tag{25c}$$

The normal modes $\vec{v}_1$, $\vec{v}_2$, and $\vec{v}_3$ are sketched in Figure 4.

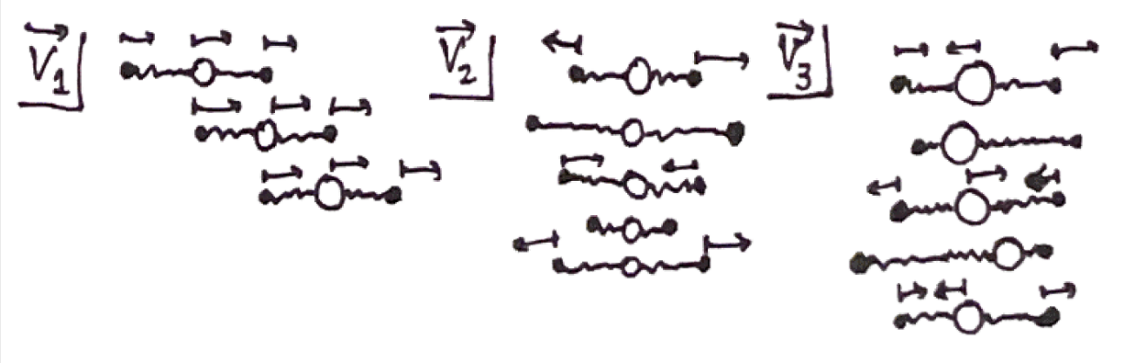

Figure 4: The normal modes of a one-dimensional triatomic molecule.

2.8 Part (h): Frequencies of CO_2

For $M = 12u$ and $m = 16u$,

$$\omega_1 = 0 \tag{26a}$$

$$\omega_2 = \sqrt{\frac{k}{16u}} \approx 241\,\text{THz} \tag{26b}$$

$$\omega_3 = \sqrt{k\left(\frac{2}{12u} + \frac{1}{16u}\right)} \approx 462\,\text{THz} \tag{26c}$$

The frequencies ω_2 and ω_3 correspond to wavelengths of $\approx 7.82\,\mu$m (near-infrared) and $4.08\,\mu$m (visible), respectively. These are also both in the infrared.

2.9 Part (i): Triatomic dipole moment

The breathing mode $\vec{v}_2$ does not change the dipole moment, since the two masses m oscillate in opposite directions.

However, in general, $\vec{v}_3$ *does*.

This discovery (arising from our simplified toy model) should make it plausible that carbon dioxide (CO_2) can preferentially scatter infrared blackbody radiation emitted by the Earth back towards it.