

14.9: Molecular coupled oscillator systems

There are many examples of coupled oscillations in atomic and molecular physics most of which involve nearest-neighbor coupling. The following two examples are for molecular coupled oscillators. The triatomic molecule is a typical linearly-coupled molecular oscillator. The benzene molecule is an elementary example of a ring structure coupled oscillator.

Example 14.9.1: Linear triatomic molecular CO₂

Molecules provide excellent examples of vibrational modes involving nearest neighbor coupling. Depending on the atomic structure, triatomic molecules can be either linear, like CO₂, or bent like water, H₂O which has a bend angle of $\theta = 109^\circ$. A molecule with n atoms has $3n$ degrees of freedom. There are three degrees of freedom for translation and three degrees of freedom for rotation leaving $3n - 6$ degrees of freedom for vibrations. A triatomic molecule has three vibrational modes, two longitudinal and one transverse. Consider the normal modes for vibration of the linear molecule CO₂

Longitudinal modes

The coordinate system used is illustrated in the adjacent figure.

The Lagrangian for this system is

$$L = \left(\frac{m}{2} \dot{x}_1^2 + \frac{M}{2} \dot{x}_2^2 + \frac{m}{2} \dot{x}_3^2 \right) - \frac{\kappa}{2} [(x_2 - x_1)^2 + (x_3 - x_2)^2]$$

Evaluating the kinetic energy tensor gives

$$\mathbf{T} = \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}$$

while the potential energy tensor gives

$$\mathbf{V} = \kappa \begin{pmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix}$$

The secular equation becomes

$$\begin{vmatrix} (-m\omega^2 + \kappa) & -\kappa & 0 \\ -\kappa & (-M\omega^2 + 2\kappa) & -\kappa \\ 0 & -\kappa & (-m\omega^2 + \kappa) \end{vmatrix} = 0$$

Note that the same answer is obtained using Newtonian mechanics. That is, the force equation gives

$$\begin{aligned} m\ddot{x}_1 - \kappa(x_2 - x_1) &= 0 \\ M\ddot{x}_2 + \kappa(x_2 - x_1) - \kappa(x_3 - x_2) &= 0 \\ m\ddot{x}_3 - \kappa(x_3 - x_2) &= 0 \end{aligned}$$

Let the solution be of the form

$$x_j = a_j e^{i\omega t} \quad j = 1, 2, 3$$

Substitute this solution gives

$$\begin{aligned} (-m\omega^2 + \kappa)a_1 - \kappa a_2 &= 0 \\ -\kappa a_1 + (-M\omega^2 + 2\kappa)a_2 - \kappa a_3 &= 0 \\ -\kappa a_2 + (m\omega^2 + \kappa)a_3 &= 0 \end{aligned}$$

This leads to the same secular determinant as given above with the matrix elements clustered along the diagonal for nearest-neighbor problems.

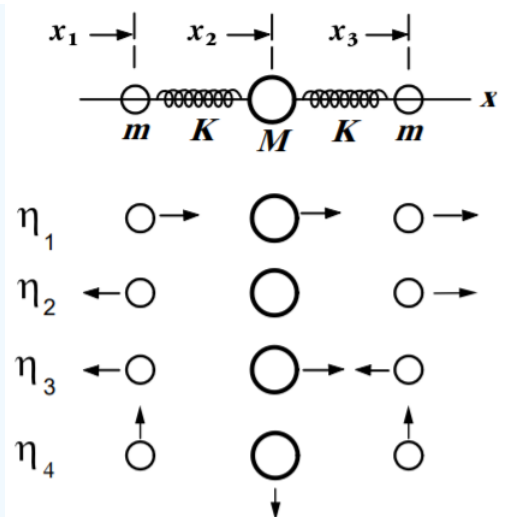


Figure 14.9.1: Normal modes of a linear triatomic molecule

Expanding the determinant and collecting terms yields

$$\omega^2(-m\omega^2 + \kappa)(-mM\omega^2 + \kappa M + 2\kappa m) = 0$$

Equating either of the three factors to zero gives

$$\begin{aligned}\omega_1 &= 0 \\ \omega_2 &= \sqrt{\frac{\kappa}{m}} \\ \omega_3 &= \sqrt{\left(\frac{\kappa}{m} + \frac{2\kappa}{M}\right)}\end{aligned}$$

The solutions are:

1) $\omega_1 = 0$; This solution gives $\eta_1 = a\{1, 1, 1\}$. This mode is not an oscillation at all, but is a pure translation of the system as a whole as shown in the adjacent figure. There is no change in the restoring forces since the system moves such as not to change the length of the springs, that is, they stay in their equilibrium positions. This motion corresponds to a spurious oscillation of the center of mass that results from referencing the three atom locations with respect to some fixed reference point. This reference point should have been chosen as the center of mass since the motion of the center-of-mass already has been taken into account separately. Spurious center of mass oscillations occur any time that the reference point is not at the center of mass for an isolated system with no external forces acting.

2) $\omega^2 = \sqrt{\frac{\kappa}{m}}$: This solution corresponds to $\eta_2 = a\{1, 0, -1\}$ and is shown in the adjacent figure. The central mass M remains stationary while the two end masses vibrate longitudinally in opposite directions with the same amplitude. This mode has a stationary center of mass. For CO_2 the electrical geometry is $\text{O}^-\text{C}^{++}\text{O}^-$. Mode 2 for CO_2 does not radiate electromagnetically because the center of charge is stationary with respect to the center of mass, that is, the electric dipole moment is constant.

3) $\omega_3 = \sqrt{\left(\frac{\kappa}{m} + \frac{2\kappa}{M}\right)}$: This solution corresponds to $\eta_3 = a\{1, -2(\frac{m}{M}), 1\}$. As shown in the adjacent figure, this motion corresponds to the two end masses vibrating in unison while the central mass vibrates oppositely with a different amplitude such that the center-of-mass is stationary. This CO_2 mode does radiate electromagnetically since it corresponds to an oscillating electric dipole.

It is interesting to note that the ratio $\frac{\omega_3}{\omega_2} = 1.915$ for CO_2 and the ratio of the two modes is independent of the potential energy tensor V . That is

$$\frac{\omega_3}{\omega_2} = \sqrt{\left(1 + 2\frac{m}{M}\right)}$$

Transverse modes

The solutions are:

4) $\omega_4 = \sqrt{2 \left(\frac{2m+M}{M} \right) \frac{\kappa}{m}}$. This is the only non-spurious transverse mode η_4 which corresponds to the two outside masses vibrating in unison transverse to the symmetry axis while the central mass vibrates oppositely. This mode radiates electric dipole radiation since the electric dipole is oscillating.

5) $\omega_5 = 0$. This transverse solution η_5 has all three nuclei vibrating in unison transverse to the symmetry axis and corresponds to a spurious center of mass oscillation.

6) $\omega_6 = 0$. This transverse solution η_6 corresponds to a stationary central mass with the two outside masses vibrating oppositely. This corresponds to a rotational oscillation of the molecule which is spurious since there are no torques acting on the molecule for a central force. Rotational motion usually is taken into account separately.

The normal modes for the bent triatomic molecule are similar except that the oscillator coupling strength is reduced by the factor $\cos \theta$ where θ is the bend angle.

Example 14.9.2: Benzene ring

The benzene ring comprises six carbon atoms bound in a plane hexagonal ring. A classical analog of the benzene ring comprises 6 identical masses m on a frictionless ring bound by 6 identical springs with linear spring constant K , as illustrated in the adjacent figure. Consider only the in-plane motion, then the kinetic energy is given by

$$T = \frac{1}{2} m r^2 \sum_{i=1}^6 \dot{\theta}_i^2$$

The potential energy equals

$$U = \frac{1}{2} K r^2 \sum_{i=1}^6 (\theta_{i+1} - \theta_i)^2 = K r^2 \left[\sum_{i=1}^6 \theta_i^2 - \theta_1 \theta_2 - \theta_2 \theta_3 - \theta_3 \theta_4 - \theta_4 \theta_5 - \theta_5 \theta_6 - \theta_6 \theta_1 \right]$$

where $i = 7 \equiv 1$. Thus the kinetic energy and potential energy tensors are given by

$$T = m r^2 \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad U = K r^2 \begin{pmatrix} 2 & -1 & 0 & 0 & 0 & -1 \\ -1 & 2 & -1 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & 0 & -1 & 2 \end{pmatrix}$$

This nearest-neighbor system includes non-zero $(n, 1)$ and $(1, n)$ elements due to the ring structure. Define $x = \frac{m \omega^2}{K} - 2$ then the solution of the set of linear homogeneous equations requires that

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

that is

$$(x-2)(x-1)^2(x+1)^2(x+2) = 0$$

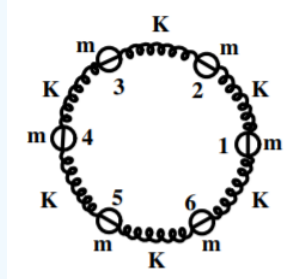


Figure 14.9.2

The eigenvalues and eigenfunctions are given in the table

Table 14.9.1: Classical analog of a benzene molecular ring.

n	x_n	ω_n^2	Normal modes
1	2	$\frac{4K}{m}$	$\theta_1 - \theta_2 + \theta_3 - \theta_4 + \theta_5 - \theta_6$
2	1	$\frac{3K}{m}$	$-\theta_1 + \theta_3 - \theta_4 + \theta_6$
3	1	$\frac{3K}{m}$	$-\theta_1 + \theta_2 - \theta_4 + \theta_5$
4	-1	$\frac{K}{m}$	$\theta_1 - \theta_3 - \theta_4 + \theta_6$
5	-1	$\frac{K}{m}$	$-\theta_1 - \theta_2 + \theta_4 + \theta_5$
6	-2	0	$\theta_1 + \theta_2 + \theta_3 + \theta_4 + \theta_5 + \theta_6$

Note the following properties of the normal modes and their frequencies.

$n = 1$: Adjacent masses vibrate 180° out of phase, thus each spring has maximal compression or extension, leading to the energy of this normal mode being the highest.

$n = 2, 3$: These two solutions are degenerate and correspond to two pairs of masses vibrating out of phase while the third pair of masses are stationary. Thus the energy of this normal mode is slightly lower than the $n = 1$ normal mode. Any combination of these degenerate normal modes are equally good solutions.

$n = 4, 5$: From the figure it can be seen that both of these solutions correspond to a center of mass oscillation and thus these modes are spurious.

$n = 6$: This vibrational mode has zero energy corresponding to zero restoring force and all six masses moving uniformly in the same direction. This mode corresponds to the rotation of the benzene molecule about the symmetry axis of the ring which usually is taken into account assuming a separate rotational component.

This classical analog of the benzene molecule is interesting because it simultaneously exhibits degenerate normal modes, spurious center of mass oscillation, and a rotational mode.

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