I. Classical dynamics of atoms and vibrational modes

In chemistry and condensed matter physics the description of the motion of atoms in molecules and in solids is of great importance. The atoms first of all vibrate about well defined average configurations. Occasionally, a rearrangement occurs from one such configuration to another. Such a rearrangement can, for example, represent a chemical reaction or a diffusion event. In principle one would need to deal with both the electronic and nuclear degrees of freedom simultaneously to describe such motion. But, the Born-Oppenheimer approximation simplifies the problem greatly. There, it is assumed that the electrons can adjust to new positions of the nuclei so fast that that the problem can be broken up into two parts: First, the nuclei are fixed while the wavefunction for the electrons and corresponding energy is found. By repeating this procedure for various positions of the nuclei, a function $E_e(\vec{x})$ can, in principle, be found (here E_e is the energy appearing in the time-independent Schroedinger equation for the electrons and $\vec{x}$ is the vector giving the location of the nuclei). Secondly, the motion of the nuclei is treated. The function $E_e(\vec{x})$ obtained in the first step represents a potential energy function for the motion of the nuclei in the second step. Because of the small mass of the electrons it is essential to use quantum mechanics in the first step. While quantum mechanics should again be used in the second step to describe the dynamics of the nuclei, it is often a good approximation to use classical mechanics possibly with corrections due to quantum behaviour added afterwards. The heavier the atoms are and the higher the temperature is, the better the classical approximation is. In the case of light atoms, such as hydrogen atoms, the classical approximation may fail especially when tunneling is important, but these cases are rather exceptional. It is a lot simpler to use classical mechanical description of the atomic motion than the quantum mechanical one. At present, only the classical mechanical method for estimating rates of rearrangements has been well established - the quantum mechanical extension is still a topic of active research. The discussion here will, therefore, focus on a classical description of the motion of the atoms.

The calculation of the time evolution of a particular system is often approached in such a way that a good representation of the potential energy as a function, $E_e(\vec{x})$, is first found and then the equation of motion for the atoms is solved to get the classical trajectories. The reason for constructing a convenient representation of the energy function rather than just doing a quantum mechanical calculation for each position of the nuclei that comes up in the classical trajectories is the large amount of effort in solving the Schroedinger equation for the electrons. A few such calculations can sometimes be used to parametrize a reasonable functional form for, $E_e(\vec{x})$, thereby

making it possible to calculate classical trajectories for a much longer time interval than otherwise would be possible. In the following subsections, we will first of all examine a few potential functions which are commonly used to represent the interaction between atoms of various types. Then, a brief review of classical dynamics will be given as well as a numerical algorithm for calculating classical trajectories for an arbitrary potential energy function will be presented. The discussion will then focus on harmonic systems, i.e. systems where the potential energy function can be represented with a quadratic form, first in one dimension and then many dimensions.

Ia. Potential energy functions

In calculating the dynamics of atoms and molecules, it is very important to choose a potential function that accurately mimics the system of interest. The potential energy function describes how the potential energy of a system of atoms depends on the coordinates of the atomic nuclei. Most often, a simple functional form is assumed for the potential function and the parameters adjusted to reproduce energy values obtained by solving the Schroedinger equation for few positions of the nuclei. Alternatively, one can use experimental data for example on vibrational frequencies and stable structures (coming from IR and X-ray measurements, in particular) to determine appropriate values of the parameters. Such potential functions are referred to as *empirical* potentials (based on experimental measurements). One can also use a combination of the the two procedures, both theoretical calculations and experimental measurements in which case the potential functions are classified as *semi-empirical*. Although the potential functions are discussed here in the context of classical simulations, the same considerations and functional forms apply when the motion of the atoms and molecules is treated quantum mechanically.

In principle, the interaction potential of N atoms can be expanded in a many-body expansion

$$E_e(r_1, r_2, \ldots, r_N) = \sum_i v_i(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \ldots$$

where the first sum is over one-body terms, the second sum over pairwise interactions, the third one over three-body contributions, etc. The one-body terms arise if an external field is applied (for example, the interaction with an external electrical field, or the potential describing the wall of a container). The pairwise interactions are usually most important and are at short range repulsive due to repulsion of the two electron clouds and at long range attractive due to the induced-dipole/induced-dipole interactions. The three-body terms arise because the interaction of a pair of atoms is modified by the presence of a third atom. For rare gases, the pairwise potentials alone describe quite well the potential energy function, but even there the three-body corrections are significant

(amounting to ca. 10% in the binding energy of the crystals of heavier rare gases). For atoms that interact strongly, the many-body expansion converges slowly and can be very difficult to carry out to convergence. More often, an implicit many-body interaction is used. One example of that is the LEPS potential described below.

The most commonly used pair potential is the Lennard-Jones potential

$$E_e(r) \; = \; 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

where the first term describes the repulsion at short range as the electron clouds overlap more than is optimal and the second term represents the long range attraction. The form of the second term r^{-6} has the correct behaviour for the induced-dipole/induced-dipole interaction. The form of the repulsive term is, however, not supported by theoretical calculations and is simply chosen for convenience. The repulsion arises because of the Pauli exclusion principle, the electron wavefunctions must be orthogonal. There is no reason why the Pauli exclusion repulsion would vary as the inverse 12th power of the distance.

A more accurate pair potential form for describing the interaction of rare gas atoms is

$$E_e(r) \; = \; A e^{-\alpha r} - f_\alpha(r) \frac{C}{r^6} \; .$$

The overlap of the closed shell electron clouds is usually well described with an exponential form. The function $f_\alpha(r)$ is a switching function, which is 1 at long range but goes to zero at short range and prevents the attractive energy term from diverging.

Bonded interactions, where the attractive interaction comes from the formation of a chemical bond, is better described with a Morse potential.

$$E_e(r) \; = \; D \left(e^{-2\alpha(r-r_0)} - 2 e^{-\alpha(r-r_0)} \right) \; .$$

The attraction decays exponentially as the overlap of the electron clouds decreases. In addition to this exponential attraction, a longer range van der Waals attraction should be added, but in comparison to chemical bond energies, this can often be neglected.

When bonding constraints need to be taken into account, for example, when the number of bonded neighbors is small and the angle between bonds has a prefered value, the many-body terms are very important and the potential function becomes quite complicated. One good example is carbon, which only bonds to at most 4 other atoms if sp^3 hybridized (as opposed to rare gas atoms that can surround themselves with up to 12 near neighbors), but in different hybridization states will prefer 2 or 3 neighbors. A great deal of effort in theoretical chemistry goes into the development of accurate and yet convenient functional forms that take into account many-body effects.

One functional form that has been used extensively in modeling chemical reactions involving formation and rupture of chemical bonds is the LEPS form. As an example,

the 'extended LEPS' potential for a three atom system A, B and C, capable of describing a substitution reaction

$$A \ + \ BC \ \rightarrow \ AB \ + \ C$$
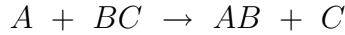
is of the form

$$E_e(r_{ab}, r_{bc}, r_{ac}) \ = \ \frac{Q_{ab}}{1+a} \ + \ \frac{Q_{bc}}{1+b} \ + \ \frac{Q_{ac}}{1+c} \ -$$

$$\left[\frac{J_{ab}^2}{(1+a)^2} \ + \ \frac{J_{bc}^2}{(1+b)^2} \ + \ \frac{J_{ac}^2}{(1+c)^2} \ - \ \frac{J_{ab}J_{bc}}{(1+a)(1+b)} \ - \ \frac{J_{bc}J_{ac}}{(1+b)(1+c)} \ - \ \frac{J_{ab}J_{ac}}{(1+a)(1+c)} \right]^{\frac{1}{2}}$$

The parameters can be chosen in such a way that the energy is large when all three atoms are close to each other, i.e. when only one bond is allowed at a time. The parameters a, b and c can be adjusted to change the height and location of the potential barrier for the reaction. The functional form is inspired by approximate calculations of the interaction of three H atoms. The Qs stand for Coulomb interactions between the electron clouds and the nuclei and the Js stand for exchange interactions (terms that arise because of the indistinguishability of the quantum mechanical electrons). A typical form for the distance dependence of the Q and J terms is similar to the Morse potential

$$Q(r) \ = \ \frac{D}{2} \left(\frac{3}{2} e^{-2\alpha(r-r_0)} \ - \ e^{-\alpha(r-r_0)} \right)$$

and

$$J(r) \ = \ \frac{D}{4} \left(e^{-2\alpha(r-r_0)} \ - \ 6e^{-\alpha(r-r_0)} \right) \ .$$

The bonded interaction of two atoms is $Q + J$ (in the singlet state, where unpaired electrons on each atom have opposite spin and can pair up as the atoms approach each other) and the non-bonded interaction is $Q - J$ (purely repulsive as would be the case if the unpaired electrons have the same spin, a triplet).

1b. Numerical calculations of classical trajectories

The classical mechanical description of the state of a system that consists of N atoms is in terms of the 3N coordinates and 3N momenta. By specifying the coordinates and momenta of all the atoms, the state of the system has been completely described. Recall that in quantum mechanics such a detailed description is not possible, we cannot simultaneously know the position and momentum of a quantum particle. The classical equation of motion, Newton's second law, $\vec{F} = \frac{d\vec{P}}{dt}$ can then be used to calculate the time evolution of the system if the force, $\vec{F}$, acting on the atoms is known. Here $\vec{P}$ is the momentum given by $\vec{P} = m\vec{v}$, where m is the mass and $\vec{v}$ is the velocity. Since the velocity is the first derivative of position with respect to time, the equation of motion is

a second order differential equation for the position of the particle as a function of time (the second derivative being the acceleration)

$$\frac{d^2\vec{x}(t)}{dt^2} = \vec{F}/m \ .$$

In most cases of interest in chemistry, the force is *conservative*, i.e. it can be written as the negative derivative the potential energy function, $E_e(\vec{x})$. For each coordinate of each atom, $F_i = -\partial E_e/\partial x_i$ where i indicates a Cartesian coordinate (x, y or z) of one of the atoms. The force is only a function of the coordinates of the atoms, $\vec{x}$, and not, for example, dependent on their velocity. Given a position and velocity of all the atoms (two conditions are needed to specify a unique solution to a second order differential equation), the equation of motion can, in principle, be solved to give the coordinates of all the atoms as a function of time, $\vec{x}(t)$, both forward as well as backward in time. The solution is often referred to as a classical trajectory. By taking the first derivative of position with respect to time, one can obtain the velocity of each of the atoms, $\vec{v}_i = d\vec{x}_i/dt$, and by taking the second derivative with respect to time, one obtains the acceleration, $d^2\vec{x}_i/dt^2$.

The classical trajectory of systems with several thousands and up to millions of atoms are routinely calculated on modern personal computers. The method for numerically solving the equation of motion is remarkably simple. First of all, the time is discretized, i.e. time evolves in discrete steps $\Delta t = h$. The spacial coordinates of the atoms are, however, not be discretized. We will focus on a one-dimensional problem for simplicity, but the generalization of the algorithm to three-dimensional space and multiple atoms is straightforward.

Let x_k be the position of the atom after k timesteps, i.e. $x_k = x(t = kh)$. The standard central finite difference approximation for the second derivative is

$$\ddot{x}_k = \frac{x_{k+1} + x_{k-1} - 2x_k}{h^2} \ .$$

Inserting this into the left hand side of the equation of motion above gives the most commonly used algorithm in classical dynamics simulations, the Verlet algorithm

$$x_{k+1} = 2x_k - x_{k-1} + h^2 F(x_k)/m \ .$$

Since the differential equation is second order, we need to know two initial conditions to get the calculation started. As written here, one would need to know the coordinates of the atoms at a given time step as well as the previous time step in order to calculate the coordinates at a later time step. More typically, one knows the coordinate and velocity at the initial time. The coordinates at a previous time step can then be estimate from the velocity (assuming constant velocity) in order to get the calculation going. For each iteration in the Verlet algorithm, time evolves by one time step. In principle, one can

calculate the trajectory of the atoms for as long time as one desires. By using a negative time step, one can also calculate the previous history of the system. As we will see later, there is however a serious time constraint on the length of time that can be simulated because of limitations in the computational power of present day computers.

A simple example of a classical mechanical calculation of a chemical reaction is the collision of an atom, A, with a diatomic molecule, B-C. For simplicity the motion of all the atoms is assumed to be only along a line. It is possible that an exchange reaction takes place, an A-B molecule gets formed and a C atom leaves. There are only two relevant variables in this case, the distance between the A and B atoms, and the distance between the B and C atoms. Let r_{AB} denote the former and r_{BC} the latter. The overall translation of the molecules center of mass is not relevant for the purpose of analysing the reaction probability. When there are only two degrees of freedom, it is possible to plot the potential energy for all possible configurations of the atoms (r_{AB}, r_{BC}). The function $E_e(r_{AB}, r_{BC})$ is often referred to as a potential energy surface, and is commonly presented as a contour plot or a three-dimensional plot where $z=E_e(x, y)$ where $x = r_{AB}$ and $y = r_{BC}$. The figure corresponds to a three atom system where only one bond can be formed. The atoms could, for example, be hydrogen or halogen atoms and the potential energy function could be represented by the LEPS form.
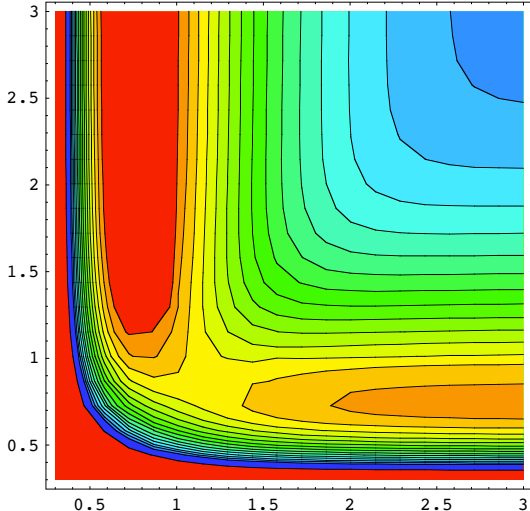

Figure 1: *A potential energy surface for a triatomic molecule where the atoms are confined to move along a line and the interaction is described by the LEPS potential function.*

A calculation of the dynamics can be carried out by starting the A atom a few Angstrom away from the B-C molecule with a velocity towards the B-C molecule, and

the B-C molecule can be given some vibrational energy. The probability of an exchange reaction depends on the system having enough kinetic energy to overcome the rise in the potential energy as the three atoms get close together. A reaction can only occur if the sum of the translational kinetic energy of the A atom approaching the B-C molecule and the kinetic energy of the vibration of the B-C molecule is enough to overcome the potential energy barrier, represented by the saddle point on the potential energy surface. Depending on the shape of the potential energy surface, sometimes the translation may be more effective in increasing the reaction probability, but sometimes the vibration is more effective.

If we are dealing with a situation where the reactants have thermalized to a certain bath temperature, then the translational kinetic energy is on average kT/2 per translational degree of freedom and the vibrational kinetic energy is kT/2 per vibrational degree of freedom. A statistical theory of transition rates, the so-called transition state theory, can then be used to estimate the rate of transitions. This will be the topic of section II.

1c. The harmonic approximation

The atoms in molecules are constantly moving. The distance between any pair of atoms and bond angles is constantly changing with time, although the average bond length and bond angles are well defined and remain the same for long periods of time. At room temperature, this motion is mostly small amplitude oscillations, so called molecular vibration. Chemical reactions occur on a much longer time scale than vibration (many orders of magnitude). Each degree of freedom of the molecule has on average an energy of $k_B T$ where k_B is the Boltsmann constant and T is the temperature. It is important to understand vibrational motion of molecules for many reasons. Vibrational motion is an important source and sink of kinetic energy in chemical reactions. Also, by using infrared spectroscopy which probes the vibrational motion, one can learn about molecular structure and the chemical composition of unknown samples. Sharp peaks in the IR absorption can be associated with particular molecules, or fragments of molecules. Each peak corresponds to a 'vibrational mode' of the molecule. In most cases the vibrational modes can be well approximated by so-called 'normal modes' of vibration.

1c.1 Vibration of a diatomic molecule

In a diatomic molecule, the vibrational motion corresponds to oscillations in the bond length. The interaction potential function may, for example, be approximated by a Morse potential

$$E_e(r) = D\left(e^{-2\alpha(r-r_b)} - 2e^{-\alpha(r-r_b)}\right)$$

This form of the potential function often gives a good representation of the potential energy of covalently bonded atoms. Under typical conditions - for reasonably strong bonds and temperature near room temperature - the deviations of the bond length from its optimal value is small, on the order of 0.1 or less. For such small displacements of the atoms, the potential energy can often be well described by a harmonic oscillator approximation. The appropriate harmonic approximation can be found by Taylor expansion the potential function about the minimum energy. Let x denote the deviation, $x = r - r_0$, from the optimal distance between the atoms. The Taylor expansion about $x = 0$ is

$$E_e(x) \;=\; E_e(0) \;+\; xE_e'(0) \;+\; \frac{x^2}{2}E_e''(0) \;+\; h.o.t.$$

Since $E_e(x)$ has a minimum at $x = 0$, $E_e'(0) = 0$. Neglecting the higher order terms, we have

$$E_e(x) - E_e(0) \;=\; \frac{1}{2}\,E_e''(0)\,x^2 \;=\; \frac{1}{2}\,k\,x^2$$

Here, k denotes the so called spring constant (the harmonic oscillator potential function is applicable to a spring with stiffness given by the spring constant). The force acting on the harmonic oscillator is

$$F(x) \;=\; -\frac{d}{dx}E_e(x) \;=\; -kx$$

The classical trajectory of a harmonic oscillator can be obtained from the equation of motion (Newton's second law)

$$F(x) \;=\; m\ddot{x}(t)$$

$$-kx(t) \;=\; m\ddot{x}(t)$$

$$\ddot{x}(t) \;=\; -(k/m)\,x(t)$$

The notation $\ddot{x}(t)$ means second derivative of x with respect to t. This differential equation has the general solution

$$x(t) \;=\; A sin(\omega t) \;+\; B cos(\omega t)$$

where $\omega = \sqrt{k/m}$. A and B are constants that need to be evaluated from the initial conditions. Another way to write the general solution is

$$x(t) \;=\; C sin(\omega t + \phi)$$

The deviation of the bond length from the optimal value varies in a sinusoidal way in time with frequency, ω.

Quantum mechanically, the harmonic oscillator has bound state energy levels spaced apart by $\Delta E = \hbar\omega$. The vibrational motion can be excited by the absorption of a quantum of light, a photon, with energy $\Delta E = h\nu = \hbar\omega$. The selection rule for vibrational

excitations in the harmonic approximation is $\Delta\nu = \pm 1$, i.e. the system can only be excited by absorption of a photon to the next higher level, or de-excited by emission of a photon to the next lower level. Within the harmonic approximation, the absorption spectrum therefore has just one peak This frequency typically corresponds to the infrared radiation.

1c.2 Vibration of polyatomic molecules, the normal modes

For larger molecules, the trajectory of an atom is in general not a simple sinusoidal function corresponding to just one frequency. Also, even if the molecule is initially distorted in such a way that only one of the bonds is stretched, all the bond lengths will eventually be changing with time. Special modes, so-called normal modes, can under some circumstances be defined so that if only one mode is excited initially, then the other modes will not be excited. In that sense the simplicity of a diatomic molecule is recovered in molecules with many atoms when normal mode coordinates are used. One can think about this as a coordinate transformation, going from the coordinates of individual atoms, $(x_1, y_1, z_1, x_2, ..., z_N)$, to the normal mode coordinates for vibration plus rotation and translation, $(q_1, .., q_M, R, ..., T)$. The normal mode coordinates are special linear combinations of the displacements of the individual atoms For a molecule consisting of N atoms in three-dimensional space, there will be M = 3N-5 vibrational modes if the molecule is linear and M = 3N-6 modes if it is non-linear.

A simple system can be used to illustrate how the normal modes are found. Consider a linear triatomic molecule where the atoms can only move along a line (one-dimensional motion). Even if only atom A is displaced initially, the motion of atom A, $x_A(t)$, is not just a sinusoidal function corresponding to a single frequency. After a while, the B-C bond starts vibrating also. The vibrational motion of the three atoms is coupled together. The normal modes are a set of linear combinations which have the property that the motion in one normal mode is independent, i.e. decoupled, from the other normal modes. This leads to a great simplification when describing the dynamics.
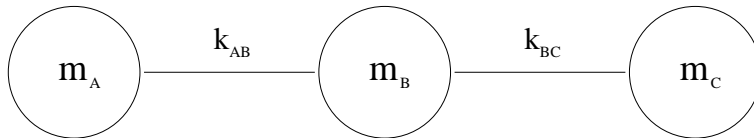

Figure 2: *A simple model of a molecule. The three atoms A, B, and C, with mass m_A, m_B og m_C, are confined to move along a line. The chemical bonds can be approximated by springs with spring constants k_{AB} and k_{BC}.*

The classical equation of motion (Newton's second law) can be solved exactly for polyatomic molecules if the interaction potential is approximated as a quadratic func-

tion (a multidimensional harmonic oscillator). The solutions are called 'normal modes' and they give the characteristic frequencies which are the dominant features in typical absorption spectra of polyatomic molecules. Let $x_A(t)$ be the displacement of atom A at time t from the optimal, lowest potential energy position of the atom, and similarly for $x_B(t)$ and $x_C(t)$. Analogous to the case of a diatomic molecule, a Taylor expansion of the potential energy about the optimal configuration of the atoms gives

$$E_e(x_A, x_B, x_C) = \frac{k_{AB}}{2}(x_B - x_A)^2 + \frac{k_{BC}}{2}(x_C - x_B)^2 \tag{1}$$

if third order and higher terms are neglected. This is the harmonic approximation to the full potential energy surface. The spring constants k_{AB} and k_{BC} are directly related to the second derivative of the potential energy with respect to the distance between atoms.

The equation of motion for each one of the atoms is

$$F_i = m_i \ddot{x}_i \tag{2}$$

where i is A, B or C. Using the fact that the force is the negative derivative of the potential energy, the three equations can be written as

$$-\frac{\partial V}{\partial x_i} = m_i \ddot{x}_i \tag{3}$$

where the partial derivative, $\frac{\partial V}{\partial x_i}$, denotes differentiation with respect to x_i while the other variables are kept fixed. In the case of the linear, triatomic molecule the force on each atom is

$$\begin{cases} \frac{\partial V}{\partial x_A} &=& -k_{AB}(x_B - x_A) \\\\ \frac{\partial V}{\partial x_B} &=& k_{AB}(x_B - x_A) - k_{BC}(x_C - x_B) \\\\ \frac{\partial V}{\partial x_C} &=& k_{BC}(x_C - x_B). \end{cases} \tag{4}$$

Inserting this form of the force into the equations of motion, and dividing by the mass of the atom gives

$$\begin{cases} \frac{k_{AB}}{m_A}(x_B - x_A) &=& \ddot{x}_A \\\\ -\frac{k_{AB}}{m_B}(x_B - x_A) +\frac{k_{BC}}{m_B}(x_C - x_B) &=& \ddot{x}_B \\\\ -\frac{k_{BC}}{m_C}(x_C - x_B) &=& \ddot{x}_C. \end{cases} \tag{5}$$

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The problem is to solve this set of three, coupled differential equations. One can attempt to find a solution where all the atoms oscillate with the same frequency, i.e.

$$
\begin{cases}
\ddot{x}_A &= -\omega^2 x_A \\
\ddot{x}_B &= -\omega^2 x_B \\
\ddot{x}_C &= -\omega^2 x_C.
\end{cases}
\tag{6}
$$

Here, ω is some frequency which has the same value in all three equations. To test if this will work, this form for $\Delta \ddot{x}_A$ can be inserted into the equation of motion to give (after switching left and right hand sides of each equation)

$$
\begin{cases}
-\frac{k_{AB}}{m_A} x_A & +\frac{k_{AB}}{m_A} x_B & & = -\omega^2 x_A \\
\frac{k_{AB}}{m_B} x_A & -\left(\frac{k_{AB}}{m_B} + \frac{k_{BC}}{m_B}\right) x_B & +\frac{k_{BC}}{m_B} x_C & = -\omega^2 x_B \\
& \frac{k_{BC}}{m_C} x_B & -\frac{k_{BC}}{m_C} x_C & = -\omega^2 x_C.
\end{cases}
\tag{7}
$$

This set of linear equations can be written in a matrix form as

$$
\begin{bmatrix}
-\frac{k_{AB}}{m_A} & \frac{k_{AB}}{m_A} & 0 \\
\frac{k_{AB}}{m_B} & -\frac{k_{AB}}{m_B} - \frac{k_{BC}}{m_B} & \frac{k_{BC}}{m_B} \\
0 & \frac{k_{BC}}{m_C} & -\frac{k_{BC}}{m_C}
\end{bmatrix}
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
= -\omega^2
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
\tag{8}
$$

This is a matrix eigenvalue problem. The task is to determine the eigenvalue $-\omega^2$ and corresponding eigenvector. As will be discussed below, three different eigenvalues $-\omega_i^2$ and eigenvectors $\mathbf{v}_i$ can be found in this case. A non-trivial solution exists only when the determinant of the matrix

$$
\begin{bmatrix}
-\frac{k_{AB}}{m_A} + \omega^2 & \frac{k_{AB}}{m_A} & 0 \\
\frac{k_{AB}}{m_B} & -\frac{k_{AB}}{m_B} - \frac{k_{BC}}{m_B} + \omega^2 & \frac{k_{BC}}{m_B} \\
0 & \frac{k_{BC}}{m_C} & -\frac{k_{BC}}{m_C} + \omega^2
\end{bmatrix}
\tag{9}
$$

is zero. This gives a third order polynomial equation for ω^2 which has three roots.

A special case: A molecule of the type $A - A - A$

The calculation is simplified greatly if the mass of all three atoms is taken to be the same, i.e. $m_A = m_B = m_C \equiv m$, and the two spring constants are taken to be the same, i.e. $k_{AB} = k_{BC} \equiv k$. Then the eigenvalue problem becomes

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$$
\begin{bmatrix} -\frac{k}{m} & \frac{k}{m} & 0 \\ \frac{k}{m} & -\frac{k}{m}-\frac{k}{m} & \frac{k}{m} \\ 0 & \frac{k}{m} & -\frac{k}{m} \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} = -\omega^2 \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}. \tag{10}
$$

After dividing through by $\frac{k}{m}$ and defining $\lambda \equiv -m\omega^2/k$ this becomes

$$
\begin{bmatrix} -1 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} = \lambda \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} \tag{11}
$$

which has a non-trivial solution only when the determinant is zero. The determinant is the third order polynomial

$$
\begin{aligned}
p(\lambda) &= (-1-\lambda)(-2-\lambda)(-1-\lambda) - (-1-\lambda) - (-1-\lambda) \\
&= -\lambda(\lambda+1)(\lambda+3)
\end{aligned} \tag{12}
$$

which has roots at $\lambda_1 = 0, \lambda_2 = -1$, and $\lambda_3 = -3$. By inserting the eigenvalues into the eigenvalue equation one can find the corresponding eigenvectors. The normalized eigenvectors are

$$
q_1 = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}, \quad q_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \quad q_3 = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ -2 \\ 1 \end{bmatrix}.
$$

These are the normal mode coordinates. The interpretation of the three solutions are as follows:

- The first solution corresponds to zero frequency and all three atoms are displaced in the same way $x_A = x_B = x_C$. This is simply uniform translation.
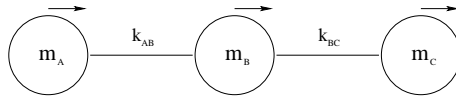
- The second solution corresponds to frequency $\omega_2 = \sqrt{k/m}$. The eigenvector shows that atom B does not move at all, while A and C move equally much but in opposite direction. This is the so-called symmetric stretch.
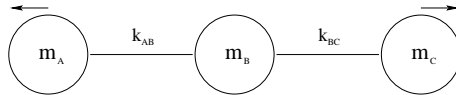
- The third solution corresponds to $\omega_3 = \sqrt{3k/m}$ a higher frequency than the symmetric stretch. The eigenvector shows that while atoms A and B are displaced equally much in the same direction, atom B is displaced twice as much in the opposite direction. This is the so-called asymmetric stretch.
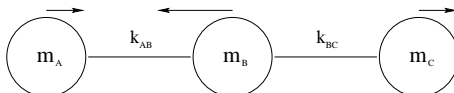
A general solution for the dynamics of the three atoms is some linear combination of these three normal mode solutions. In a sense, going from the original coordinates, (x_A, x_B, x_C), to a linear combination of the normal mode vectors is just a coordinate transformation. The advantage of the normal modes is that they are independent, i.e. there is no energy flow from one mode to another. If the molecule is vibrating in such a way that only one mode is active, then the molecule will continue to move according to that one normal mode forever. The others never come into play. Recall, that the central approximation here is that the interaction potential is harmonic. For more realistic anharmonic interaction potentials, such as the Morse potential, the independent normal modes are only approximate solutions. Energy will then flow between these modes, but only slowly if the anharmonic corrections are small.

When the mass of the atoms is not the same, for example CO_2, the solution of the eigenvalue problem is a little more complicated, but the normal modes are still a symmetric stretch and an aymmetric stretch. Also, when the spring constant for the two bonds is not the same, as a OCS molecule for example, the calculation is much more tedious and the solutions do not have any symmetry (or antisymmetry). These problems can, however, easily be solved using Matlab or similar tools.

Quantum mechanical treatment

Quantum mechanical treatment of a polyatomic molecule within the harmonic approximation can also make use of the simplification that occurs when one uses normal mode coordinates. The Schroedinger equation separates just as Newton's equation does when the normal coordinates are used and one obtains separate, uncoupled harmonic oscillator equations for each normal mode. The total wavefunction describing the vibration of the molecule is then the product of the normal mode wavefunctions, and the total vibrational energy is the sum of the energy associated with each normal mode. For example, the ground state energy is

$$E = \sum_i \frac{\hbar \omega_i}{2} = \sum_i \frac{\hbar}{2} \sqrt{\frac{k}{m}} \tag{13}$$

In absorption spectroscopy, the molecule absorbs energy from the oscillating electric and magnetic field in the electromagnetic wave only if the frequency matches one of the vibrational oscillations (such matching of frequencies is called resonance). In order to excite mode i, the energy of the absorbed photon needs to be

$$E_i = h\nu_i = \hbar \omega_i = \hbar \sqrt{\frac{k_i}{m_i}}. \tag{14}$$

13

where h is Planck's constant and $\nu_i = \omega_i/2\pi$ is the vibrational frequency of mode i. Each normal mode has a different frequency and there is, in principle, an absorption peak for each one of the modes. A peak is only observed, however, if the displacement of the atoms corresponding to the normal mode eigenvector leads to a change in the dipole moment of the molecule (recall the derivation of the selection rules for the harmonic oscillator).