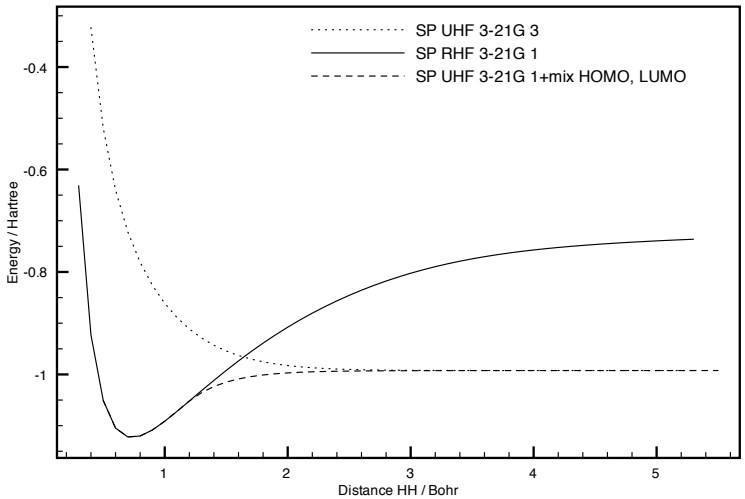
Vibrational modes

Recall Born Oppenheimer approximation:

Since nuclei are much heavier than electrons (more than a thousand times)
the spacing between electronic levels is in general much larger than that of vibrational levels.

1. Fix the position of the nuclei and solve for the distribution of the electrons
   using for example Hartree-Fock, CI, MP2 or DFT.
   Gives energy surface $E(R_1,R_2, \ldots)$ where R_1 is location of nucleus 1, etc.

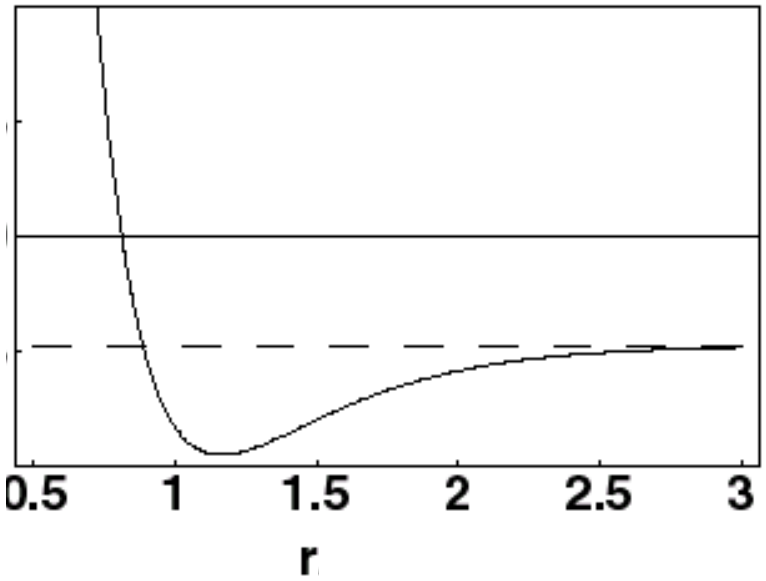


2. Let nuclei move (classically or quantum mechanically) on the energy surface
   $E(R_1,R_2, \ldots)$.

Potential energy function describing the stretching of a covalent bond

Commonly used functional form: The Morse potential

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



D is the well depth

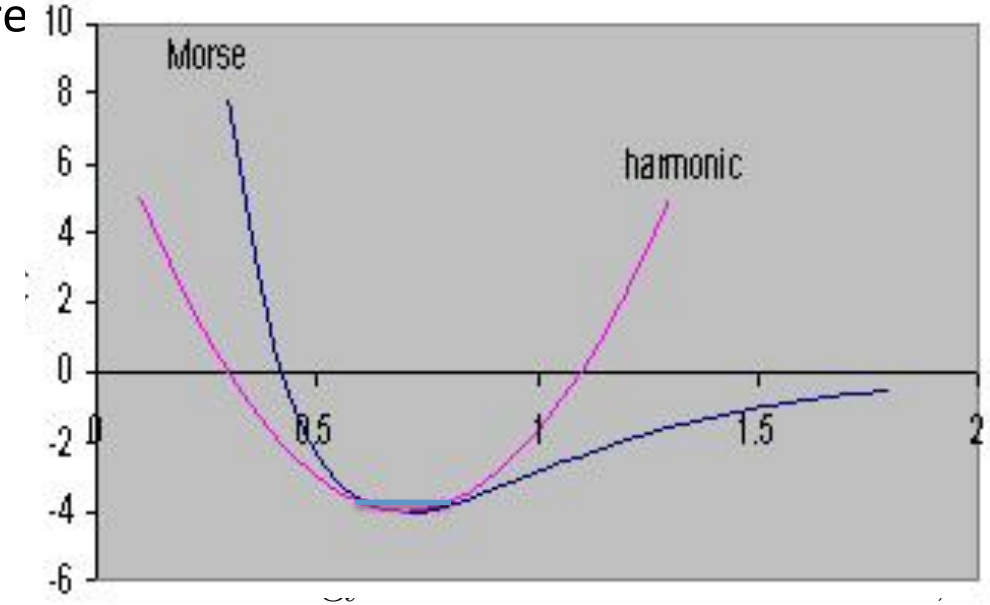
r_b is the position of the minimum (bond length, here 1.2)

alpha determines the curvature, i.e. the stiffness of the bond

Harmonic approximation:

Thermal energy at room temperature is only , kT=0.025 eV.

So, a second order Taylor approximation to the potential energy curve (or energy surface) is good enough in the region that has appreciable statistical weight.



$x = r - r_0$, from the optimal distance between the atoms. The Taylor expansion about $x = 0$ is

$$E_e(x) = E_e(0) + xE'_e(0) + \frac{x^2}{2}E''_e(0) + h.o.t.$$

$E_e(x)$ has a minimum at $x = 0$, $E'_e(0) = 0$. Neglecting the higher order terms

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

Vibrational motion within the harmonic approximation

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

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

$$x(t) \;=\; Asin(\omega t) \;+\; Bcos(\omega t)$$

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

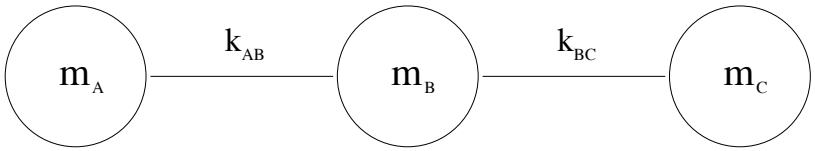
$$x(t) \;=\; Csin(\omega t + \phi)$$

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 $\Delta E = h\nu = \hbar\omega$.

Extend to polyatomic molecules

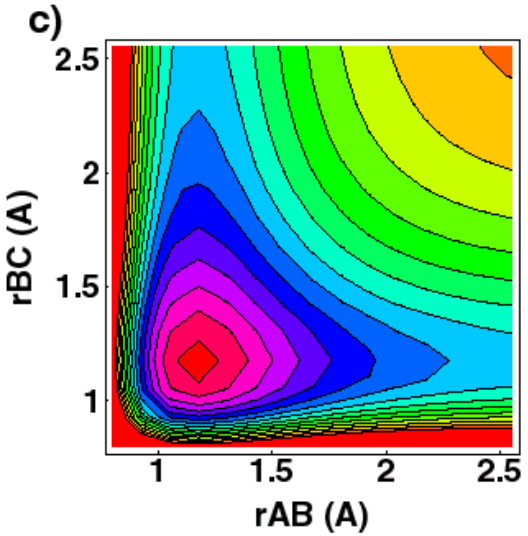
Simplest case, a linear tri-atomic molecule
with atomic motion confined to a line (i.e. no bends)

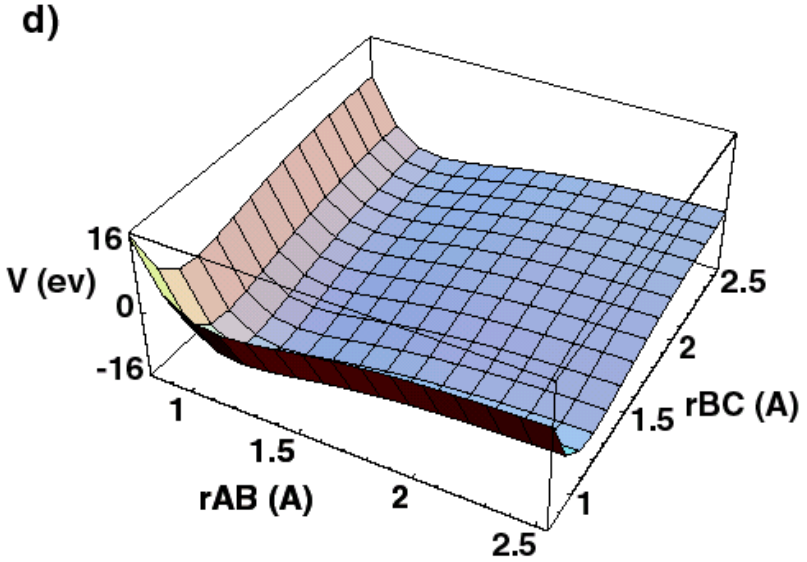


Just two degrees of freedom, distance A-B and distance B-C, (r_{AB} and r_{BC})

Potential energy surface formed by summing up two Morse potentials, one for each bond

$$V(r_{AB}, r_{BC}) = V_{AB}(r_{AB}) + V_{BC}(r_{BC})$$





Calculate classical dynamics of the atoms

The equation of motion for each one of the atoms is

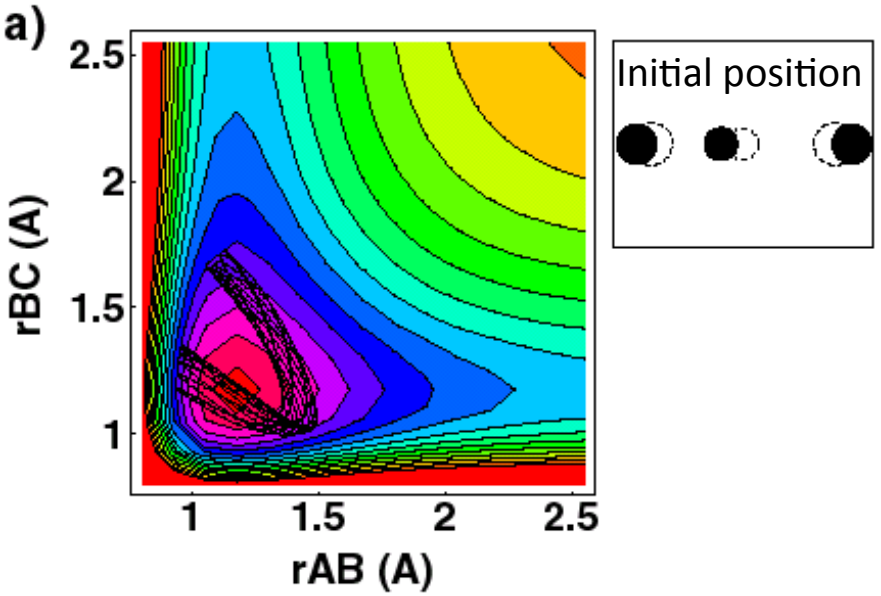
$$F_i = m_i \ddot{x}_i \tag{2}$$

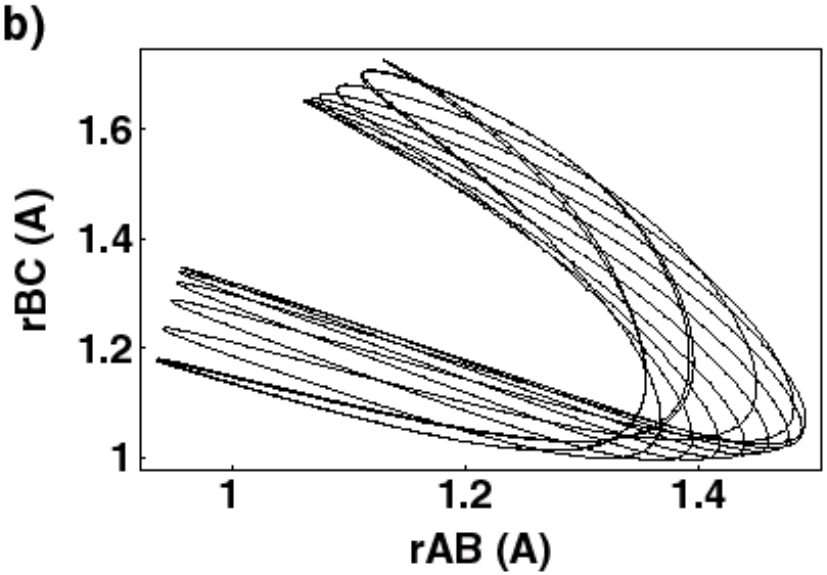
where i is A, B or C. Using the fact that the force is the negative derivative of the potential energy, the three equations can be written as

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

where the partial derivative, $\frac{\partial V}{\partial x_i}$, denotes differentiation with respect to x_i while the other variables are kept fixed.

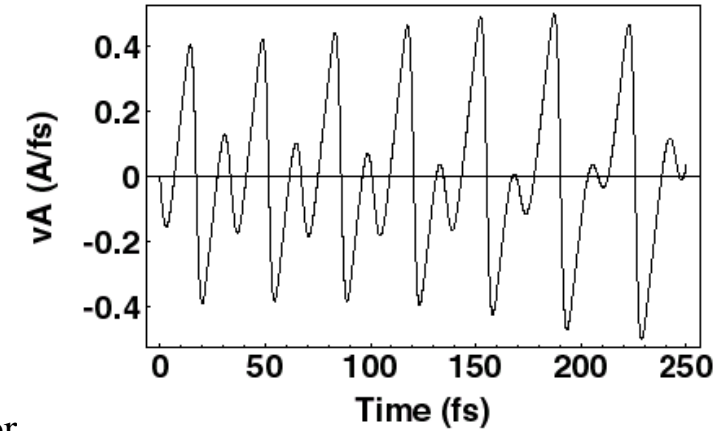
Example trajectory (very large amplitude!)





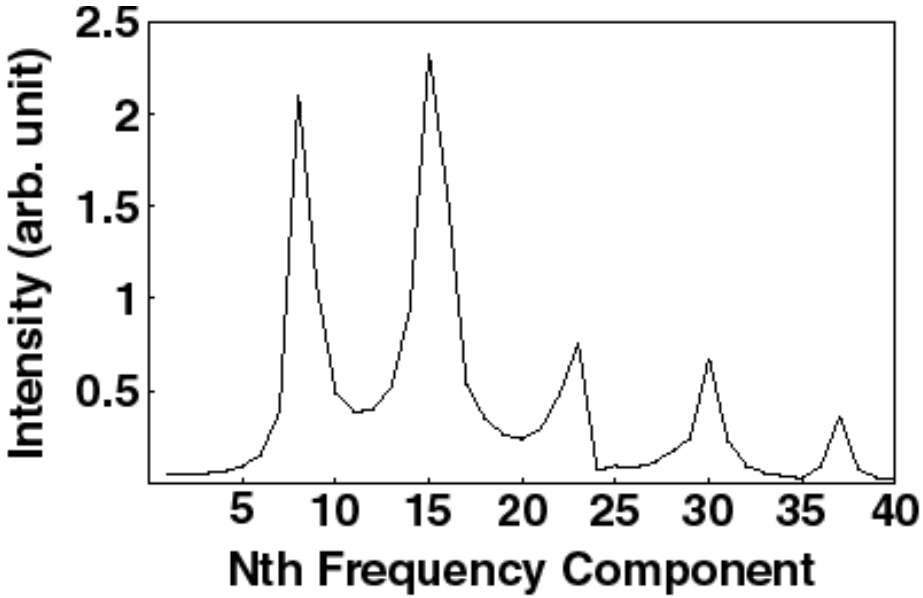
Fourier expansion of the velocity or position of the atoms

The velocity of atom A in the trajectory on the previous slide as a function of time



or

Fourier expansion of the velocity of atom A gives



Two main peaks (fundamentals).
Also smaller peaks that
disappear as the amplitude
is decreased (overtones).

Harmonic approximation

$$\mathsf{V}\,(x_A, x_B, x_C) = \frac{k_{AB}}{2}(x_B - x_A)^2 + \frac{k_{BC}}{2}(x_C - x_B)^2$$

The force on each atom within the harmonic approximation 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

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

Find vibrational normal modes

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)

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

Find vibrational normal modes

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.

Find vibrational normal modes (cont.)

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

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

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

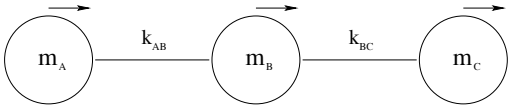
Find vibrational normal modes (cont.)

the eigenvalue equation one can find the corresponding eigenvectors. The normalized eigenvectors are

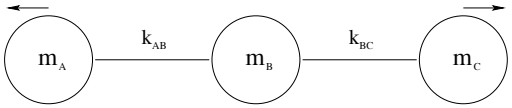
$$q_1 = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}, \; q_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \; q_3 = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ -2 \\ 1 \end{bmatrix}.$$

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

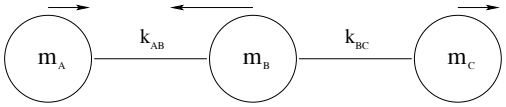
- The first solution corresponds to zero frequency and all three atoms are displaced in the same way $x_A = x_B = x_C$. This is simply uniform translation.



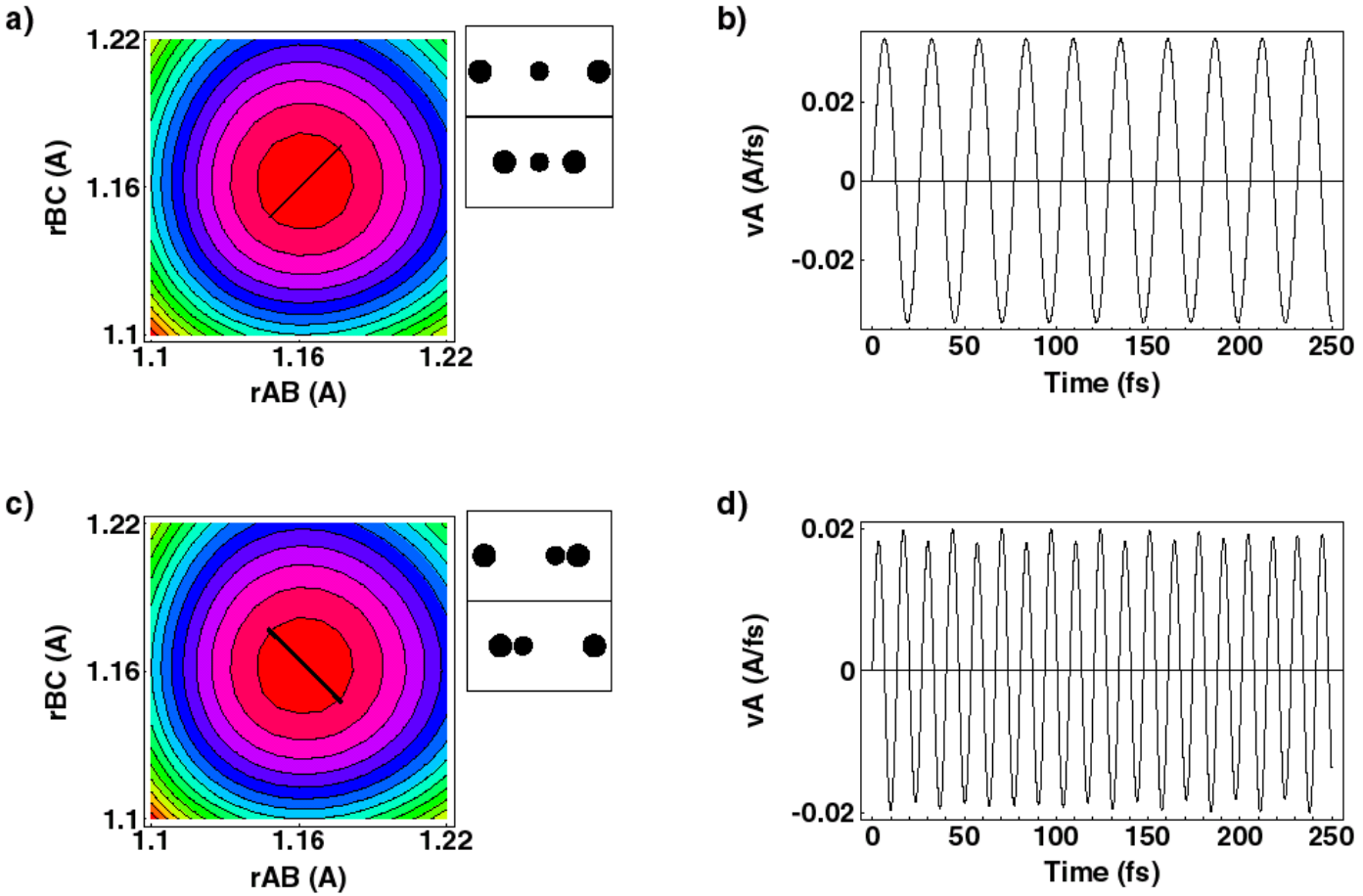
- The second solution corresponds to frequency $\omega_2 = \sqrt{k/m}$. The eigenvector shows that atom B does not move at all, while A and C move equally much but in opposite direction. This is the so-called symmetric stretch.



- 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.



The vibrational normal modes do not couple as long as harmonic approximation is valid



If the motion of the molecule is started by exciting the symmetric stretch, then the molecule will continue to vibrate in the symmetric stretch only, no energy flow to asymmetric stretch, and vice versa. This makes normal modes *convenient coordinates*.

A general vibrational motion is a combination of normal modes

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.

A general vibrational motion is a combination of normal modes

Arbitrary motion of the atoms can be described in terms of normal mode coordinates,
simply a coordinate transformation from Cartesian coordinates or spherical polar coords.

Normal modes can be a good choice because energy does not flow between normal modes
if the harmonic approximation is valid.
More generally, anharmonicity will couple the normal modes. If anharmonicity is large,
then other descriptions, such as *local modes* may be better.