

Serial: Vibrating quanta

In today's episode, we will finally take a look at what happens if we move the nuclei in the molecules.

That needs to have potential!

You may remember that in the last episode, we simplified the Schrödinger equation for a molecule by finding the effective potential in which each electron moves, so we did not have to solve the Schrödinger equation for all the electrons at once and neglected the nuclear motion altogether. Instead, we only needed to solve a set of nearly independent equations for the individual electrons. At this point, we would like to find the potential for the motion of the nuclei in a similar way.

In the previous episode, we fixed the nuclei in our calculations on the assumption that electrons move much faster than nuclei because of the difference in mass, so to describe the motion of electrons we can assume that the nuclei are stationary. But now we are dealing with the opposite problem. We need to solve the problem for the motion of the nuclei, while the electrons serve only as a kind of glue that holds the nuclei together. This time, the tricks from the last episode will not help us. Furthermore, it would not work even if we took an average charge density of electrons that we had calculated in advance, and then used that to form the potential of nuclear motion. The problem in this case is that the electron orbitals are centered on the nuclei, and therefore move with them. Moreover, as the geometry of the molecule changes, the shapes of the orbitals change as well. What can we do about it?

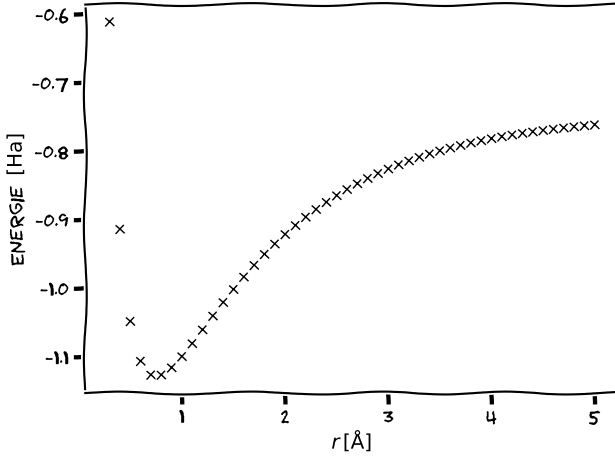
Let's imagine that we have a diatomic molecule, e.g. H_2 . We take this molecule, and for some particular internuclear distance, for example, 0.3 \AA , and calculate its electron energy. In this case, we get a value of -0.61 Ha . Now we move the nuclei a little bit further from each other, so the distance is 0.4 \AA . We get slightly lower energy, -0.91 Ha . We can calculate the energy for every relevant distance and plot the energies on the graph. We get a picture that is also called the dissociation curve of the molecule.

But that almost looks like a potential for nuclear motion.

There is a small problem that we do not have just one particle moving in this potential, but two particles moving towards and away from each other. This shortcoming, however, is easily solved by a trick that is much older than quantum mechanics itself and has been used for over a century to describe the motion of astronomical bodies. It turns out that if we describe the motion of two bodies whose mutual interaction depends on the distance separating them, we can instead take the corresponding potential, and let a body of so-called reduced mass move in it. This reduced mass for two bodies of masses m_1 and m_2 is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

In a special case where the two bodies have the same mass (i.e. $m_1 = m_2$), the reduced mass will be exactly equal to half the mass of the bodies $\mu = m_1/2$. Conversely, in the limiting case that one of the bodies is about an order of magnitude heavier than the other $m_2 \gg m_1$, the reduced mass will be nearly equal to the mass of the lighter body $\mu \approx m_1$.

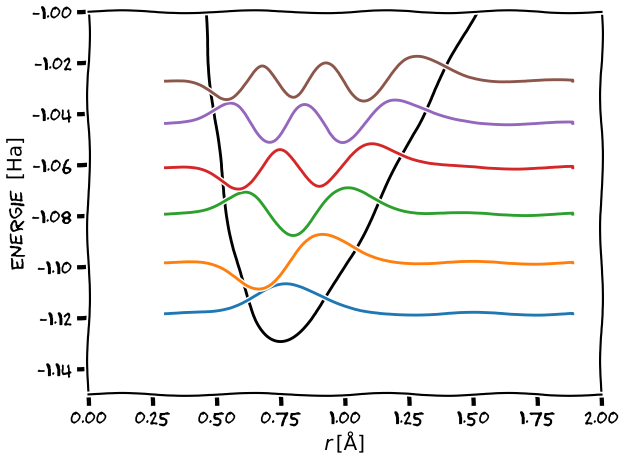


At this point, nothing prevents us from numerically solving the Schrödinger equation for the motion of nuclei in this potential

$$-\frac{\hbar^2}{2\mu} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x),$$

where $V(x)$ is the potential given by the dissociation curve of the molecule.

This gives us the following states, which we will plot similarly as in the second part of this series. That is, we will plot the wave function of several states with the lowest energy, which we shift vertically by the energy of that state.



The resulting wave functions $\Psi(x)$ have a probability amplitude interpretation in this case as well. There is a slight difference, the probability density in this case $|\Psi(x)|^2$ does not directly correspond to the probability of a particle occurring at a particular location, but instead gives the probability of their given mutual distance. Thus, in the ground state, we can expect that the internuclear distance of the molecule is most likely to be in the vicinity of the minimum of the potential. On the contrary, for the first excited state, we can expect the molecule to have either a larger or, conversely, a smaller nuclear distance than the equilibrium distance, since the probability density is zero around the minimum.

It may seem that this was just a sort of textbook exercise on the applications of quantum mechanics, but the opposite is true. We have essentially converted the vibrations of molecules into quantum form. It is not surprising that these vibrations can often occur in nature.

Vibrations of molecules in nature and in the laboratory

Just as a molecule can go into an excited state by the action of electromagnetic radiation, which actually means jumping to a higher electronic quantum state, it can just as well jump to a higher vibrational state. The difference is that electron jumps have energies that correspond to photons in the ultraviolet and visible regions of the spectrum, so they can often be directly observed as the colors of individual chemical compounds. In contrast, the vibrational transitions of molecules lie in the infrared region, so we need special instruments to observe them. Yet they are essential to us. For example, the vibrational transitions of water, carbon dioxide, and other molecules in the atmosphere absorb infrared radiation that would otherwise be radiated into space. This is the essence of the much-discussed greenhouse effect.

At the same time, the vibrations of more complex molecules can be used to quickly and accurately identify a substance in an unknown sample. While it is possible to measure the infrared spectrum directly, it is considerably complicated. One of the most essential problems is that substances we consider transparent, such as glass or water, are not transparent to infrared radiation at all. Thus we lose the ability to observe samples in a solution. For this reason, a trick has been adopted that allows it to work with visible radiation all the time, using a phenomenon called Raman scattering. If there is light passing through a substance at a wavelength that is not absorbed, it can still occasionally scatter and reflect in a direction other than the original direction when it collides randomly with molecules. This effect is called Rayleigh scattering, and among other things, it causes the sky to be blue. (And that shadows are not completely dark.) However, in a small fraction of cases (cited as one in a million), the scattering of the photon simultaneously excites the molecule to a higher vibrational state. This is the essence of the aforementioned Raman scattering. Consequently, because of the law of conservation of energy, the wavelength of the scattered photon must slightly change.

Raman spectroscopy is based on this principle, where we illuminate a sample with a laser of a specific wavelength and detect only the scattered radiation that differs in wavelength from the original radiation. We then plot only the value of this shift on the graph. From how much the wavelength shifts, we can then determine the energies of the individual vibrational levels. This method is now used in many areas of day-to-day life. For example, it proved useful in the methanol affair in the Czech Republic a few years ago. The fact that we can detect methanol through glass without having to open the bottle, was used in this case. It is also commonly used at airports to detect explosives and drugs. Even the newest rover on Mars, Perseverance, has one Raman spectroscope built in. The success of Raman spectroscopy is that, especially in

organic molecules, each functional group has specific frequencies at which it vibrates. We can then easily identify these in the spectrum and see what the molecule looks like.

Practical aspects of vibration spectra calculation.

To find the potential for the nuclei, we had to repeat the quantum chemical calculation for many different internuclear distances. However, this means that for one calculation of the vibration of the nuclei we have to perform a large number of individual calculations for the electrons. This very quickly becomes computationally prohibitive for larger molecules. Fortunately, we have one more trick up our sleeve. If we look at the dissociation curve in the vicinity of the minimum, which we are interested in, it could be fitted with a parabola. The general form of a parabolic function is $f(x) = ax^2 + bx + c$, but we can modify it and write the expression for our parabolic potential as $V(x) = k(x - x_{\min})^2/2 + E_{\min}$. But we already know most of the parameters! x_{\min} is the equilibrium distance and E_{\min} is the energy at minimum potential. In addition, the parameter E_{\min} just shifts the energies of all states, and therefore we can set it to zero, and all energies that emerge will then be defined as the difference with respect to that value.

Thus, the only unknown quantity is the stiffness k . We do not have to determine it via fitting, but we can determine it directly from the second derivative of the energy with respect to the position of the nuclei. This second derivative can be analytically obtained directly from the wave function in the field of geometry optimization, and all we need is a single quantum chemical calculation. For calculating the second derivative from definition we would need at least three energy calculations.

But this is not the end of the simplifications. If you recall the beginning of the third episode of the series, we showed a linear harmonic oscillator, which had a parabolic potential. Thus, we do not have to worry about solving the Schrödinger equation numerically, as we can find the energies of the individual levels analytically. The Schrödinger equation of a harmonic oscillator comes in the form

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + \frac{k}{2}x^2\psi(x) = E\psi(x),$$

where we also used the reduced mass μ which was introduced above.

We will not show the procedure by which the equation is solved, as it would disproportionately stretch this episode. To calculate the positions of the vibrational lines in the spectra, we only need to know the energies of individual levels. These levels are equidistant and the energy of the n -th level is given by

$$E_n = \sqrt{\frac{k}{\mu}} \hbar \left(n + \frac{1}{2} \right),$$

where n has integer values from 0 to ∞ . Note that the energy difference between neighboring levels is $\hbar\sqrt{k/\mu}$, which corresponds to a photon of the same frequency as an oscillator with stiffness k in classical mechanics. This is one of many examples of the correspondence between classical and quantum mechanics. Jumps between adjacent levels will therefore cause absorption at this energy $\hbar\sqrt{k/\mu}$. Moreover, it turns out that jumps of more than one level are forbidden, and they hardly take place in nature.

But, what if we have more atoms?

If we have more than a two-atom molecule, the situation gets a bit more complicated. A system of N atoms has $3N$ degrees of freedom in total because the position of each nucleus can be described by three coordinates. However, three of those degrees of freedom correspond to translation, i.e. the motion of the molecule as a whole. Additionally, three degrees of freedom match the rotation of the molecule. (Only two for a linear molecule). If we neglect these as they are not interesting to us, we are left with $3N - 6$ ($3N - 5$ for a linear molecule) degrees of freedom, which correspond to different vibrations.

The solving procedure is similar to that shown in the previous section for a single vibration, except that we are solving the problem in many dimensions. We shall find the optimal geometry, calculate the wave function, and calculate the second derivative of the energy in all directions. Then we finally obtain the energies of the individual vibrations. The advantage is that the programs perform this whole sequence of steps automatically, so we just need to optimize the geometry and the program takes care of the rest.

The results of the calculation in this case are eigenmodes, i.e. standing waves that have a precisely defined frequency. This is, again, an analogy to classical mechanics, where we can also observe such modes in the vibration of macroscopic bodies. We are, however, primarily interested in the frequencies of these modes, which we can compare with the experimental Raman spectrum. It may also happen that the program will output some frequencies as negative –this indicates that we do not have the optimal geometry, because the energy will decrease in the direction of the vibrational mode.

As an example, we will show a calculation in the Psi4 program on a water molecule. We prepare an input similar to the last episode, but add the line `frequency("HF")`. The input for Psi4 will look like this:

```
set basis cc-pvdz
molecule {
0 1
O -1.818556 -0.320567 1.225399
H -0.898992 -0.062457 1.771117
H -2.278145 -1.054597 1.903623
}
optimize("HF")
frequency("HF")
```

After running the program, just before the end of the output, we shall find the section `==> Harmonic Vibrational Analysis <==`, where we can find the resulting frequencies. At the end of this section, there is

...

```
Vibration 7 8 9
Freq [cm-1] 1776.1024 4113.4307 4211.9124
Irrep Ap Ap Ap
Reduced mass [u] 1.0817 1.0461 1.0820
Force const [mDyne/A] 2.0105 10.4283 11.3092
Turning point v=0 [a0] 0.2503 0.1673 0.1625
```

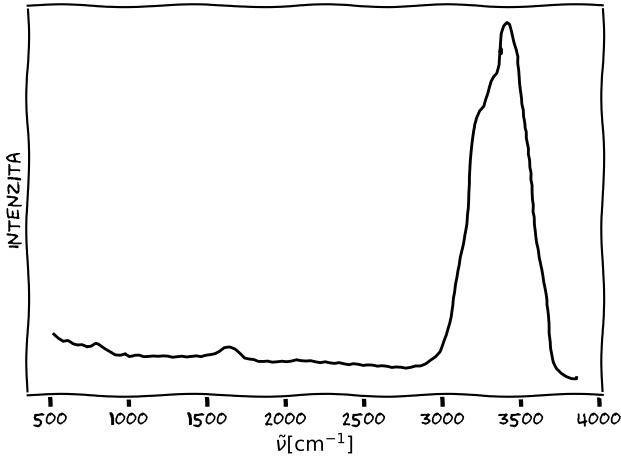
RMS dev $v=0$ [a0 $u^{1/2}$] 0.1841 0.1210 0.1196
 IR activ [km/mol] 80.8468 21.1727 60.6078
 Char temp [K] 2555.4159 5918.3109 6060.0042

 1 0-0.01 -0.07 0.00 -0.00 0.05 -0.00 -0.07 -0.01 0.00
 2 H 0.38 0.59 -0.00 0.61 -0.35 0.00 0.59 -0.38 -0.00
 3 H -0.48 0.52 0.00 -0.54 -0.45 -0.00 0.52 0.48 0.00

...

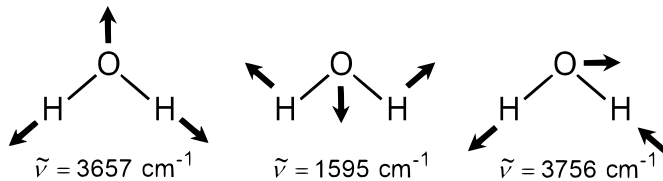
This is per the above rule, which predicts exactly three vibrational modes. Thus, the water molecule should vibrate at energies 1776 cm^{-1} , 4113 cm^{-1} and 4211 cm^{-1} . The energies of vibration in spectroscopy are standardly given by the wave number in reciprocal centimeters (cm^{-1}). The advantage is that the wavenumber $\tilde{\nu} = 1/\lambda = E/(hc)$ is, in contrast to the wavelength, directly proportional to the energy of the radiation.

We can now look at the experimental Raman spectrum of water.



We can find all three modes in it, although their frequencies are a bit different from those that we have calculated. The two lines in our calculations have energies 4113 cm^{-1} and 4211 cm^{-1} and they merge into one broad peak, which lies between 3000 cm^{-1} and 3500 cm^{-1} . The third line, predicted at 1776 cm^{-1} is barely visible on the graph, but it lies almost exactly where we anticipated it, at approximately 1600 cm^{-1} . That is yet another problem with vibrational spectrum calculations, not all vibrational transitions are visible in Raman spectroscopy. Some of the transitions may be prohibited by quantum mechanics, so they will be weak in the spectrum or they will not occur at all. Of course, it is possible to determine also the intensities of individual transitions by quantum chemical calculations, but that is beyond the reach of our text.

Finally, we should add that the three modes mentioned above look like this. Their experi-



mental energies are given below the figures.

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