

3_harmonic_oscillator

May 28, 2024

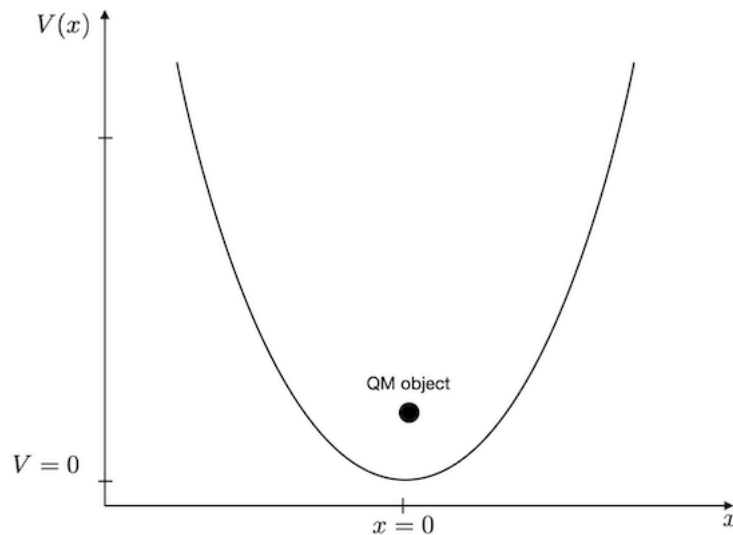
1 Harmonic Oscillator

The harmonic oscillator is certainly one of the working horses of physics. In quantum mechanics, it resembles to be a good model for the motion of two bound atoms, i.e. bond vibrations, which are of relevance for all types of molecules and solids.

As compared to the particle in a box, we have to change the potential in the Hamilton operator to solve the harmonic oscillator. The potential energy of the harmonic oscillator is given as

$$V(x) = \frac{k}{2}x^2 \quad (1)$$

where k is the spring constant and x is the deviation from its minimum potential energy position. For an atomic bond between carbon and oxygen, for example, the spring constant corresponds to $k = 396 \text{ N/m}$.



The C=O bond has a bond length of $x_0 = 1.229 \text{ \AA}$, so we do not have to look at a large domain. A region of $L = 1 \text{ \AA}$ provides already an energy change by 3 eV.

1.1 Definition of the problem

Before we start, we need to define some quantities:

- we will study a domain of $L=1$ Angström
- we will use $N=1001$ points for our x_i
- the spring constant shall be $k = 396$ N/m
- we will use the mass of the carbon atom

1.1.1 Potential energy

We first define the diagonal potential energy matrix.

1.1.2 Kinetic energy

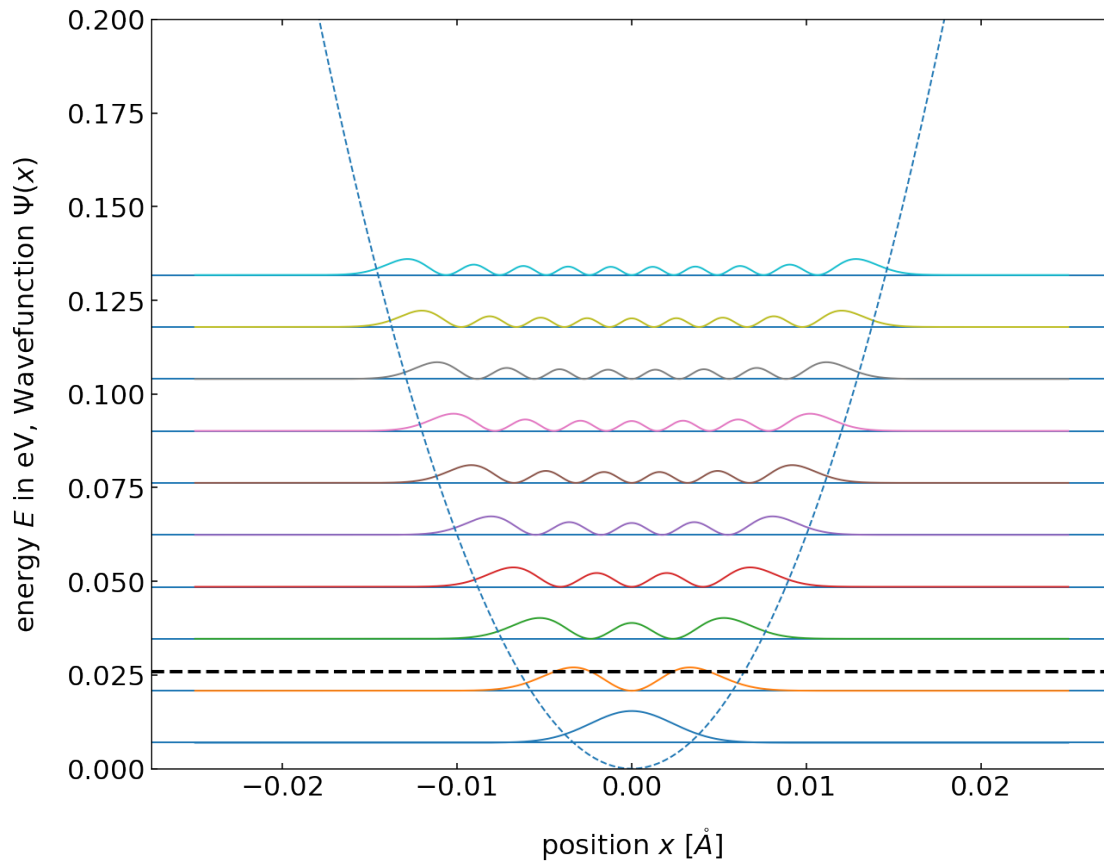
Next are the derivatives of the kinetic energy matrix.

And finally the total Hamilton operator matrix again.

1.1.3 Solution

The last step is to solve the system of coupled equations using the `eigsh` method of the `scipy` module again.

1.1.4 Plotting



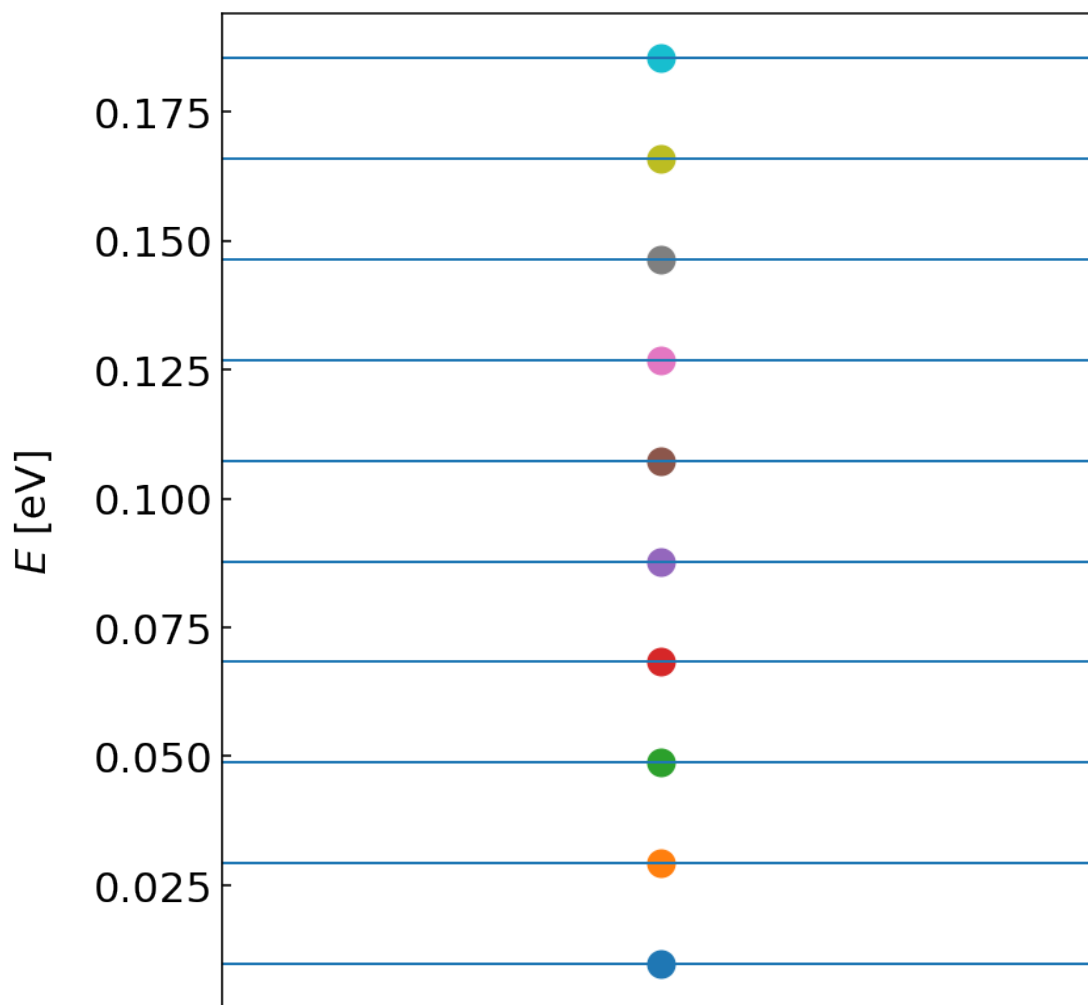
1.1.5 Energies of the states

The diagram above, shows that the energy values in the harmonic oscillator model are equally spaced. The horizontal dashed line corresponds to the thermal energy at 300 K temperature ($E_{th} = 0.026$ eV). The bond length changes x are pretty small as compared to the actual bond length.

The analytical solution of the harmonic oscillator shows energy states at

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (2)$$

where n is the quantum number running from $0, \dots$, and ω is the frequency of the bond vibration, i.e. $\omega = \sqrt{k/m}$. The graph below compares the

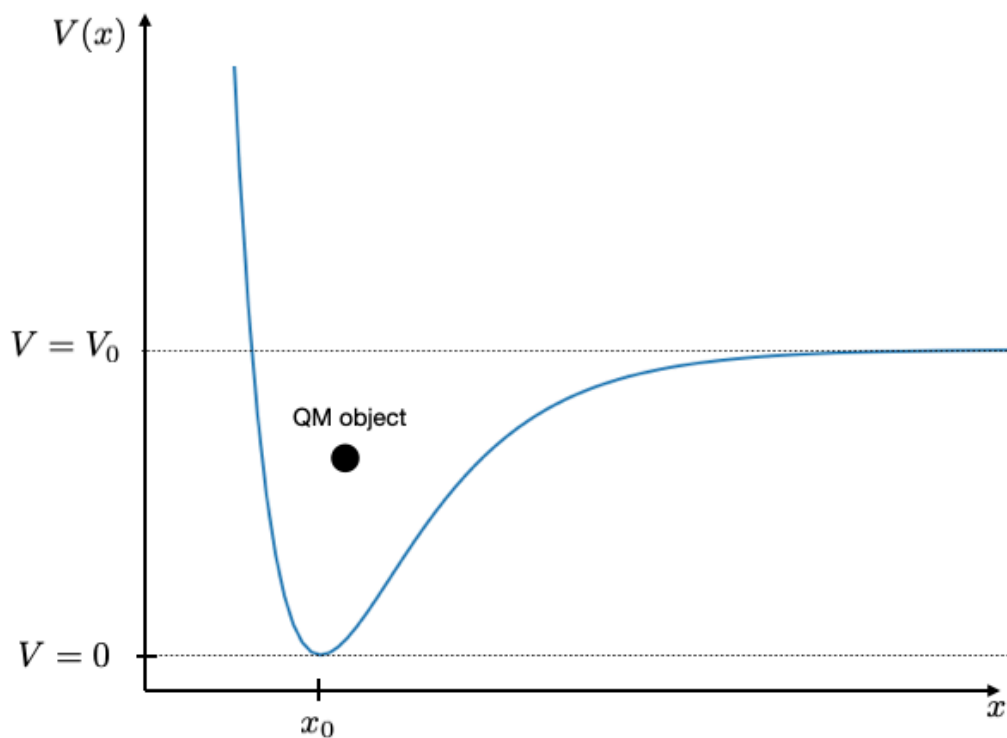


1.2 Where to go from here?

Bond potentials between atoms are typically not parabolic. They are anharmonic. You see that for example in the thermal expansion of materials. A more appropriate description of such bond potentials is the Morse potential

$$V(x) = V_0 (1 - e^{-\alpha(x-x_0)})^2 \quad (3)$$

The shape of this potential is shown below with a value of $x_0 = 3$, $\alpha = 1$ and $V_0 = 10$. When the energy in the bond is larger than the value V_0 , the molecule will dissociate.



If you are interested, try to find parameters for a real world example and the Morse potential and simulate the wavefunction and energy values and observe, for example, if the energy values are still equidistant or not.