DOING PHYSICS WITH PYTHON

QUANTUM MECHANICS

VIBRATIONAL MODES OF DIATOMIC MOLECULES

HARMONIC OSCILLATOR

ANHARMONIC OSCILLATOR (MORSE POTENTIAL)

HCl MOLECULE

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Please email any corrections, suggestions, improvements, etc

DOWNLOAD DIRECTORY FOR PYTHON SCRIPTS

qm050.py

Solution of the [1D] Schrodinger equation by finding the eigenvalues and eigenvectors for a parabolic potential well (harmonic oscillator) and a Morse potential well (anharmonic oscillator).

GitHub **Google Drive**

INTRODUCTION

The diatomic molecule HCl is used to illustrate the quantization of energy by solving the Schrodinger equation by finding the eigenvalues and eigenvectors for a parabolic potential well and a Morse potential well.

In the HCl molecule, the two atoms vibrate as the nuclear separation increases and decreases as the atoms move towards and away from each other. The HCl molecule has a permanent electric dipole moment even at the equilibrium separation of the atoms. Therefore, vibrational emission and absorption of electromagnetic radiation occurs due to the oscillation in the electric dipole moment arising from the oscillations in the nuclear separation. If we consider the reduced mass frame of reference, we only need to model the vibrations of the hydrogen atom with the mass of the system being the reduced mass of the chlorine and hydrogen atoms as shown in figure 1.

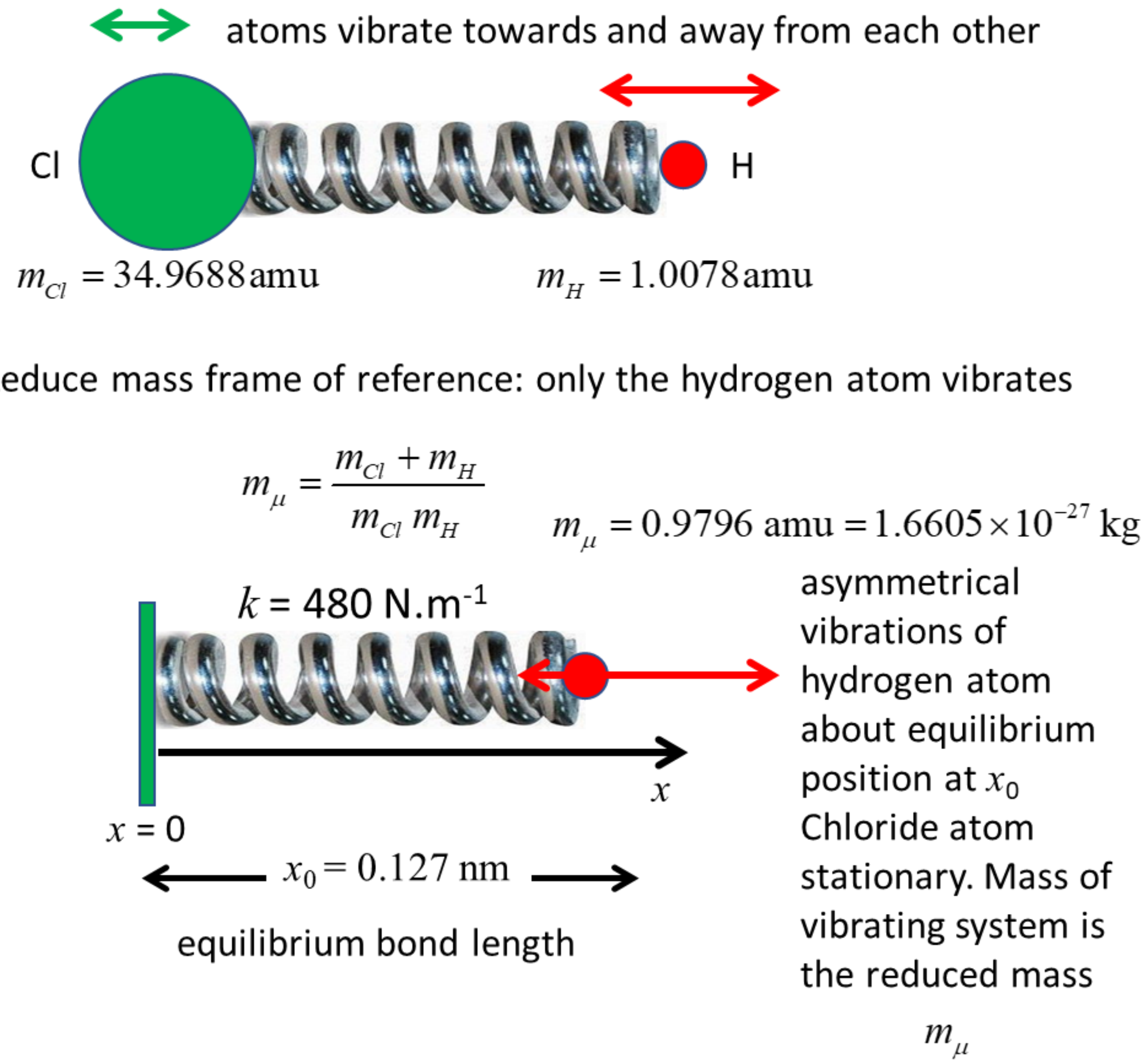


Fig. 1. Classical view: vibration of the chlorine and hydrogen atoms in the HCl molecule due to their motion. Quantum view: you don’t know anything about the trajectories of the two atoms. Using the reduced frame of reference, by solving the Schrodinger equation for the system, we can only predict the probability of a given separation between the two atoms.

The [1D] time independent Schrodinger equation for the single particle (lightest atom) that is solved by the matrix method is

$$\hat{H}\,\psi(x) = E\,\psi(x)$$

where the Hamiltonian operator is expressed as a matrix

$$\hat{H} = C_s \frac{d^2}{dx^2} + U(x) \qquad C_s = \frac{-\hbar^2}{2\,m_e}$$

In solving this Schrodinger equation, all distances are measured in metres and energies in joules, but for display purposes, distances are often in nanometres and energy in electron-volts.

Link for full details of the Matrix Method

The total energy E is due to the vibration of the atoms only, and does not relate to electronic or rotational total energies $\left(E \equiv E_{vibration}\right)$.

For small vibrations about the equilibrium bond length, we assume that the potential energy function is parabolic and use the harmonic oscillator model. The quantized total energy levels are

$$E = \left(n + \tfrac{1}{2}\right)\hbar\,\omega_0 \qquad n = 0, 1, 2, 3, \ldots$$

where ω_0 is the vibrational frequency of the ground eigenstate and n is the **vibrational quantum number**. The parabolic potential energy function $U(x)$ for the harmonic oscillations is

$$U(x) = \tfrac{1}{2}k\,(x - x_0)^2 + U_0$$

where k is the spring constant for the HCl molecule, k = 480 N.m^{-1}, x is the bond length, the separation distance between the Cl atom and the hydrogen atom, and x_0 is the equilibrium bond length, the position where $U(x)$ is a minimum, x_0 = 0.127 nm. U_0 is the well depth, U_0 = -4.57 eV .

The zero-point energy E_0 is

$$E_0 = \tfrac{1}{2}\hbar\,\omega_0$$

where the fundamental frequency of vibration (classical vibration frequency) is

$$\omega_0 = \sqrt{\frac{k}{m_\mu}} \qquad \text{reduced mass} \quad m_\mu = \frac{m_{Cl} + m_H}{m_{Cl}\, m_H}$$

For larger amplitude oscillations, the interaction between two atoms in a diatomic molecule can be represented by a potential well function known as the **Morse potential**. In the frame of reference of the reduced mass, the bond length x oscillates as the position of the hydrogen atom changes. Classical view: when the hydrogen atom moves closer to the chloride atom, a large repulsive force pushes them apart, and when they have a separation greater than the equilibrium separation the force between the two atoms is attractive.

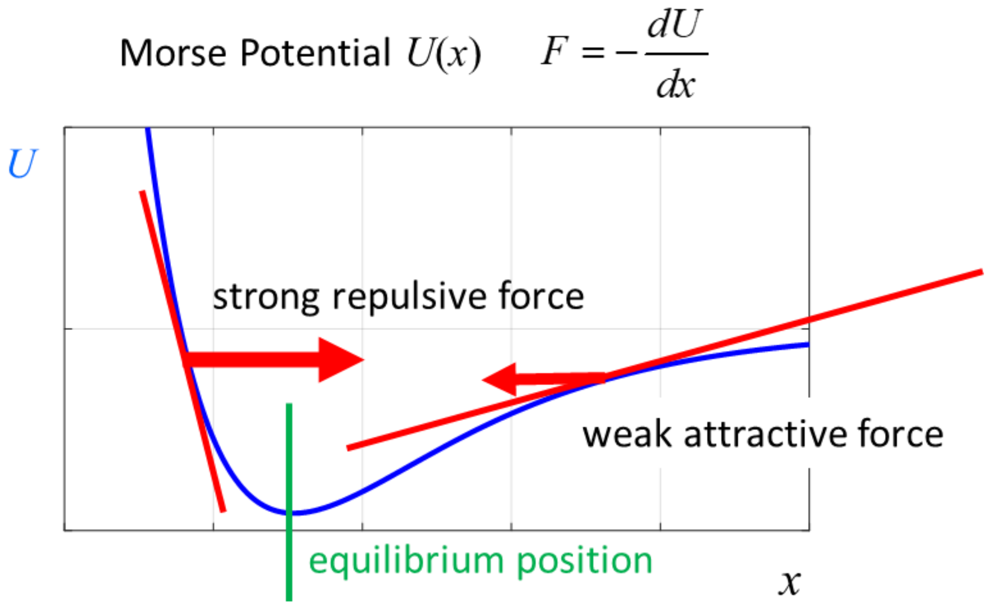


Fig. 2. Morse potential.

The potential energy function $U(x)$ for the **Morse potential** used in the Scripts **qm050.py** and **qm050morse.py** is given by the equation

$$U(x) = U_0 \left(1 - \left(\exp\left(\frac{x_0 - x}{S} \right) - 1 \right)^2 \right)$$

where U_0 is the maximum depth of the potential well at x_0 and S determines the width of the well. U_0 is the dissociation constant such $U \to 0$, as the separation distance increases $x \to \infty$.

Given the input values for k and U_0, the width parameter is

$$S = \sqrt{\frac{2U_0}{k}} \qquad S = 0.0552 \ \ \text{nm}$$

Figure 3 shows the plots for the parabolic potential well and the Morse Potential.

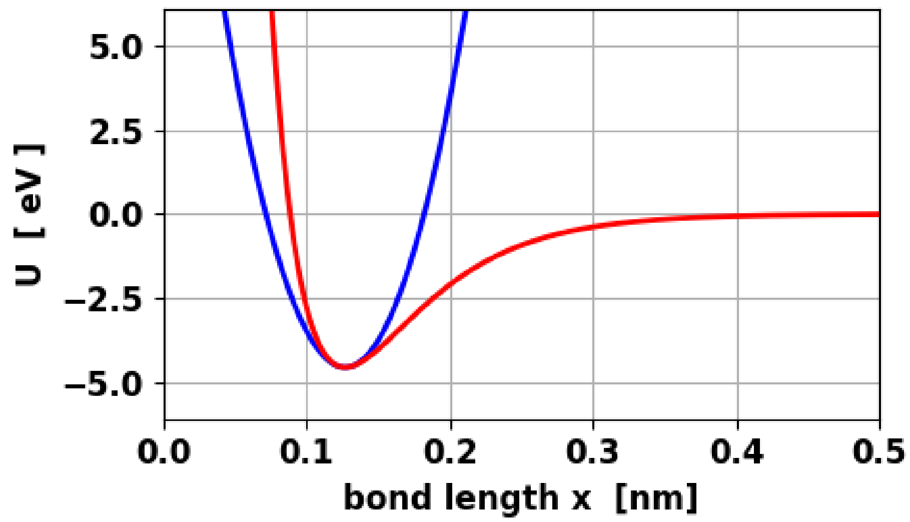


Fig. 3. Parabolic potential well and the Morse Potential.

U_0 = -4.57 eV, x_0 = 0.127 nm, S = 0.0552 nm.

A diatomic molecule acts essentially as a harmonic oscillator for low energy eigenstates and is analogous to a system which executes spring-like modes of oscillation. For higher energy states, the spacing between adjacent energy levels decrease with increasing energy and the validity of the harmonic oscillator is no longer valid for diatomic molecules.

PARABOLIC POTENTIAL WELL MODEL

qm050.py

There is excellent agreement between the theoretical predictions and the predictions of the numerical method of finding the eigenvalues and eigenfunctions of the Schrodinger equation.

Simulation parameters

grid point N = 801   eigenvalues returned M = 50

xMin = 0.00 nm   xMax = 0.30 nm

Equilibrium bond length x0 = 0.127 nm

well depth U0 = -4.570 ev

spring constant k = 480.000 N/m

Energy eigenvalues [eV]

State (vibrational quantum number), n

Total energy, E (simulation eigenvalue measured w.r.t. $U = 0$)

Total energy, E_w (simulation eigenvalue measured w.r.t. bottom of well $U = U_0$)

$$E_w = E - U_0 \,/\, se$$

U_0 well depth [J] $se = e$ [J ↔ eV]

Binding energy or **dissociation energy**, EB (the amount of energy required to separate the two particles)

$$EB = - E$$

Theoretical value for binding energy, ET

$$ET = E_n = \left(n + \tfrac{1}{2}\right)\hbar\,\omega_n \qquad n = 0, 1, 2, \; 3, \ldots$$

Spacing between adjacent energy levels, dE

State n	Ew	ET	dE	E	EB
0	0.179	0.179	0.000	-4.391	4.391
1	0.536	0.536	0.357	-4.034	4.034
2	0.893	0.894	0.357	-3.677	3.677
3	1.251	1.251	0.357	-3.319	3.319
4	1.608	1.609	0.357	-2.962	2.962
5	1.965	1.966	0.357	-2.605	2.605
6	2.322	2.324	0.357	-2.248	2.248
7	2.679	2.681	0.357	-1.891	1.891
8	3.037	3.038	0.357	-1.533	1.533
9	3.394	3.396	0.357	-1.176	1.176
10	3.750	3.753	0.357	-0.820	0.820
11	4.107	4.111	0.357	-0.463	0.463
12	4.464	4.468	0.357	-0.106	0.106

Zero-point energy E_0 is the lowest possible energy that a quantum mechanical system may have.

E_0 = 0.179 eV ground state n = 0

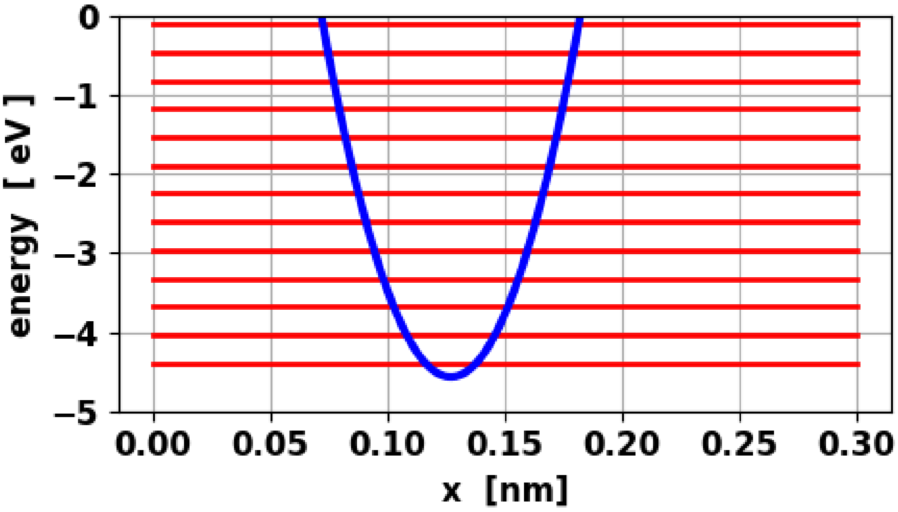


Fig. 4. Parabolic potential well and energy level spectrum. Note: the even spacings between adjacent energy levels. Zero-point energy, E_0 = 0.179 eV ground state n = 0, n > 0 are the excited states.

Eigenfunctions for the first six states

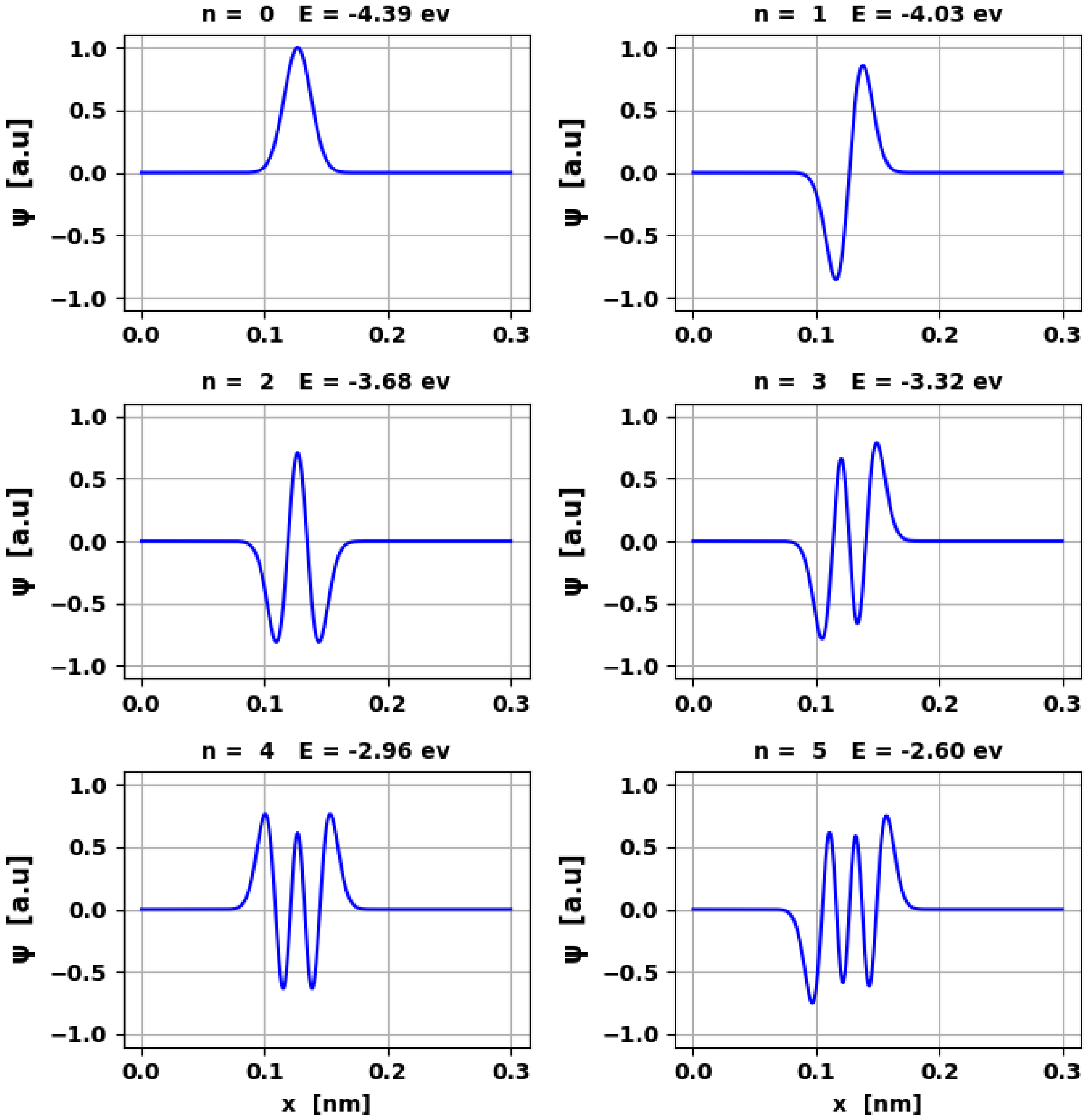


Fig. 5. Eigenfunctions for the first six eigenstates. The amplitudes of the eigenfunctions have been scaled so that the maximum amplitude of the ground state n = 0 is 1.00.

Probability densities for the first six states

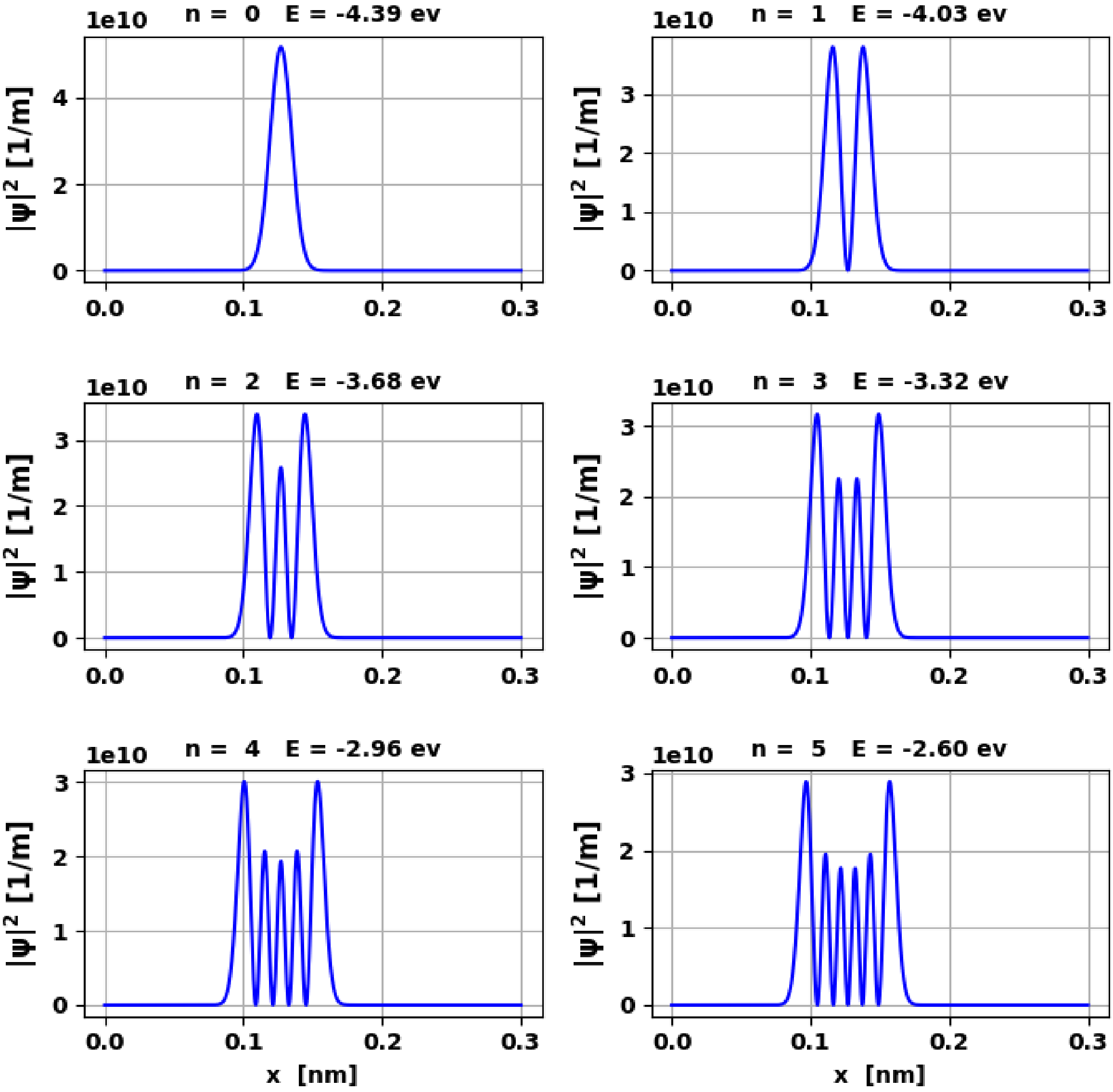


Fig. 6. Probability density functions for the first six eigenstates. The eigenfunctions are normalized so that the each under each curve is one. The number of humps in each plot is equal to $n+1$.

COMPOUND (MIXED STATES)

Consider a normalized compound state which is the summation of two eigenstates m and n with wavefunction

$$\Psi(x,t) = a_m \Psi_m(x,t) + a_n \Psi_n(x,t)$$

$$a_m{}^2 + a_n{}^2 = 1 \quad \omega_m = E_m / \hbar \quad \omega_n = E_n / \hbar$$

$$\Psi(x,t) = a_m \psi_m(x)\, e^{-i\left(E_m/\hbar\right)t} + a_n \psi_n(x)\, e^{-i\left(E_n/\hbar\right)t}$$

$$\Psi(x,t) = a_m \psi_m(x)\, e^{-i\,\omega_m t} + a_n \psi_n(x)\, e^{-i\,\omega_n t}$$

The expectation value of the separation distance $\langle x(t) \rangle$ between the Cl and H nuclei for the compound wavefunction is

$$< x(t) > = \int_{-\infty}^{\infty} \Psi^*(x,t)\; x\; \Psi(x,t)\; dx$$

In a quantum system, it is reasonable then to define the electric dipole moment $D(t)$ in terms of the wavefunction for the system (charge q) as

$$D(t) = -q \int_{-\infty}^{\infty} \Psi^*(x,t)\; x\; \Psi(x,t)\, dx = -q \langle x(t) \rangle$$

The most common form of radiation from a quantum system is due to an oscillating **electric dipole** (**dipole radiation**).

The expectation value for the separation distance $< x(t) >$ varies sinusoidally with time

$$\langle x(t) \rangle = A\cos\left(\omega_{mn}\, t\right) \qquad \omega_{mn} = \frac{\left|E_m - E_n\right|}{\hbar}$$

If the amplitude of the variation of the separation distance between the two nuclei is very small such that $A \approx 0$ then the electric dipole moment will also be $D(t) \approx 0$. In this case, electric dipole radiation from the system can be consider as forbidden.

If the amplitude of the variation of the separation distance between the two nuclei is large such that $A \gg 0$ then the electric dipole moment will also be $D(t) \gg 0$. In this case, via electric dipole radiation a photon will be emitted in the transition from the higher energy state m to the lower energy state n $\left(m \to n\right)$. For this transition, the energy, frequency and wavelength of the photon are given by

$$E_{photon} = \hbar\,\omega_{mn} \qquad f_{mn} = \frac{\omega_{mn}}{2\pi} \qquad \lambda_{mn} = \frac{c}{f_{mn}}$$

Compound state m = 3, am = 0. 89443 / n = 2, an = 0.44721

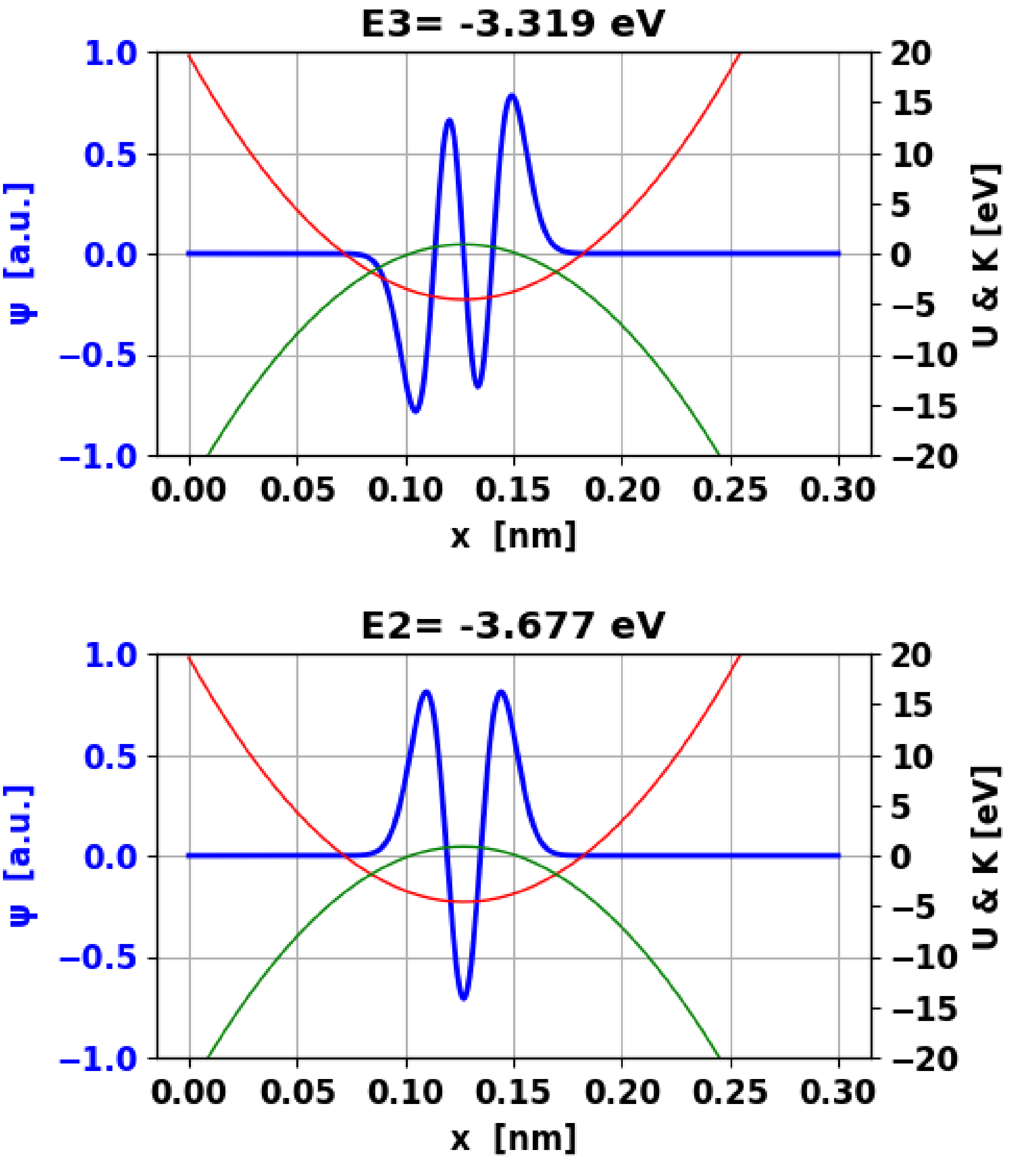


Fig. 7. Scaled eigenfunction for the states m = 3 and n = 2 and the potential energy and kinetic energy functions.

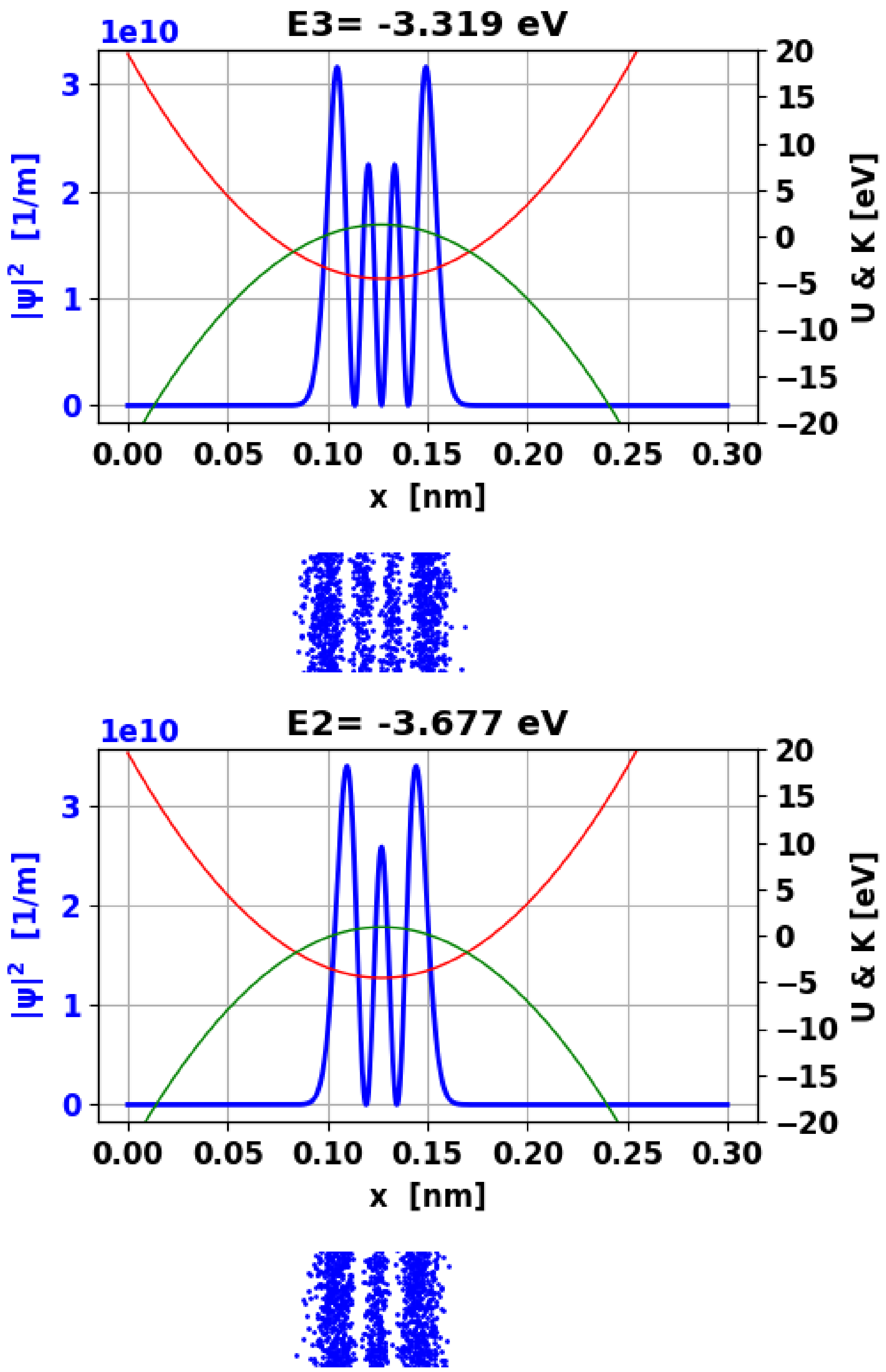


Fig. 8. Probability density for the states m = 3 and n = 2 and the potential energy and kinetic energy functions. The blue scatter plot shows the results of the separation distance measurements between Cl and H nuclei for a set of identical systems. The separation distance is also quantized, since there are separation distances that will never be measured.

The Compound state

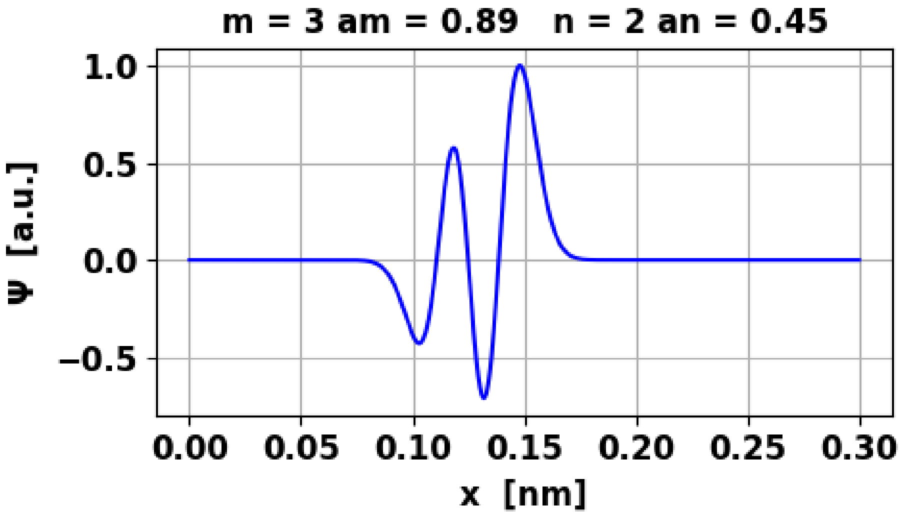


Fig. 9. The wavefunction at time t = 0 for the compound state.

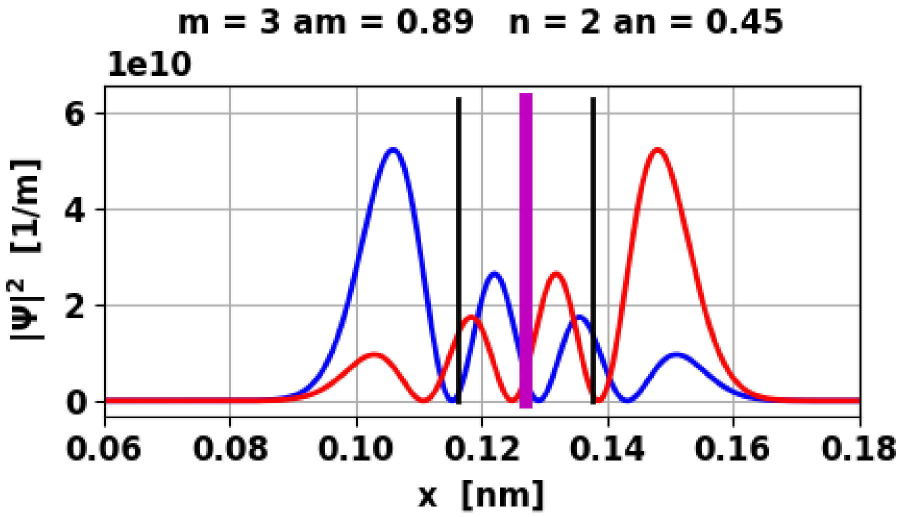


Fig. 10. The probability distribution for the compound is time dependent. The period of oscillation is $T_{mn} = 2\pi / \omega_{mn}$.

Blue curve $t = 0$. Red curve $t = T_{mn} / 2$ (half-period later). The magenta line shows the equilibrium separation x_0 = 0.127 nm. The **black** lines show the expectation value of the separation distance $< x >$ at $t = 0$ and $t = T_{mn} /2$.

The large amplitude oscillation in the separation distance about the equilibrium separation gives a fluctuating charge distribution producing an electric dipole moment. So, a photon can be emitted from the system with an energy equal the energy spacing between the two energy levels and at the frequency of oscillation in the compound wavefunction

$$E_{photon} = \left| E_m - E_n \right| = \hbar \, \omega_{mn}$$

```
COMPOUND STATE
m = 3 am = 0.894   n = 2 an = 0.447
dE = 0.357  eV
osc. frequency omega = 7.486e+15  rad/s
osc. frequency f = 1.191e+15  Hz
osc. period T = 8.393e-16  s
photon wavelength lambda = 251.627  nm
equilibrium bond length = 0.127  nm
el. dipole separation = 0.0214003  nm
```

The photon has a wavelength of 252 nm which is in the infrared part of the electromagnetic spectrum. For this transition, 3 → 2, the radiation lifetime is relatively short.

Compound state *m* = 4, *am* = 0. 89443 / *n* = 2, *an* = 0.44721

The results for this transition 4 → 2 are very different to the transition 3 → 2. The probability density for the transition 4 → 2 is symmetrical about the equilibrium separation resulting approximately zero fluctuations in the charge density and the dipole moment can be considered zero $D = 0$. The radiative lifetime can be considered to be infinite and no photon is emitted from the system. We can conclude that the transition is **forbidden** for electric dipole radiation.

```
COMPOUND STATE
m = 4 am = 0.894   n = 2 an = 0.447
dE = 0.715  eV
osc. frequency omega = 8.029e+15  rad/s
osc. frequency f = 1.278e+15  Hz
osc. period T = 7.826e-16  s
photon wavelength lambda = 234.616  nm
equilibrium bond length = 0.127  nm
el. dipole separation = 0.0000000  nm
```

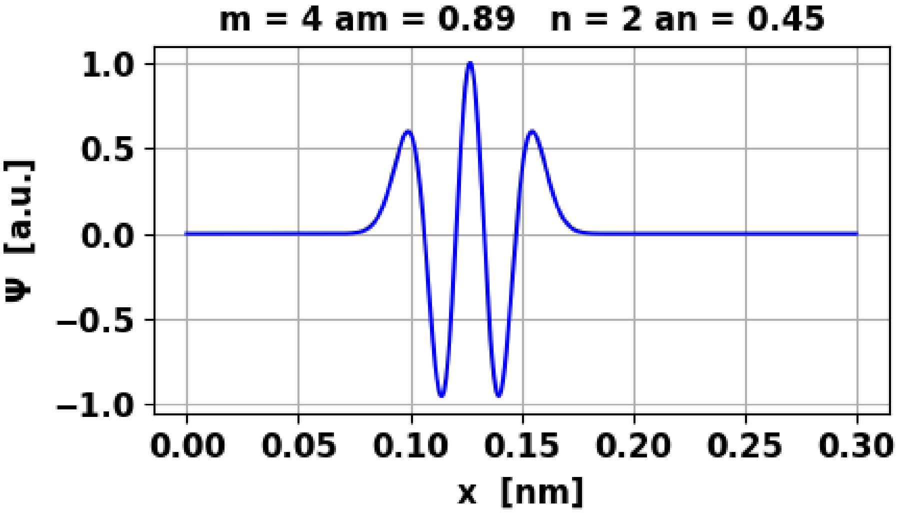


Fig. 11. Scaled compound wavefunction. The wavefunction is symmetrical about the equilibrium separation at all times.

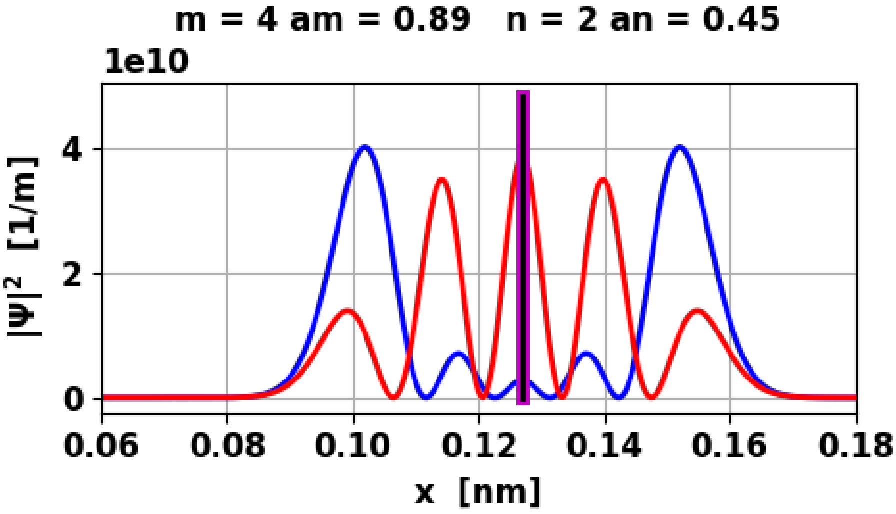


Fig. 12. Probability density at times $t = 0$ and $t = T_{mn} / 2$. The deviation of $< x(t) >$ from the equilibrium separation is essentially zero. Because of the symmetry of the wavefunction, there is ~zero fluctuation in the charge distribution.

Compound state *m* = 4, *am* = 0. 89443 / *n* = 1, *an* = 0.44721

The transition 4 → 1 is also forbidden as

$$\langle x(t) \rangle \approx x_0 \quad \Rightarrow \quad D \approx 0$$

COMPOUND STATE

m = 4 am = 0.894   n = 1 an = 0.447

dE = 1.072 eV

osc. frequency omega = 8.572e+15 rad/s

osc. frequency f = 1.364e+15 Hz

osc. period T = 7.330e-16 s

equilibrium bond length = 0.127 nm

el. dipole separation = 0.0000022 nm

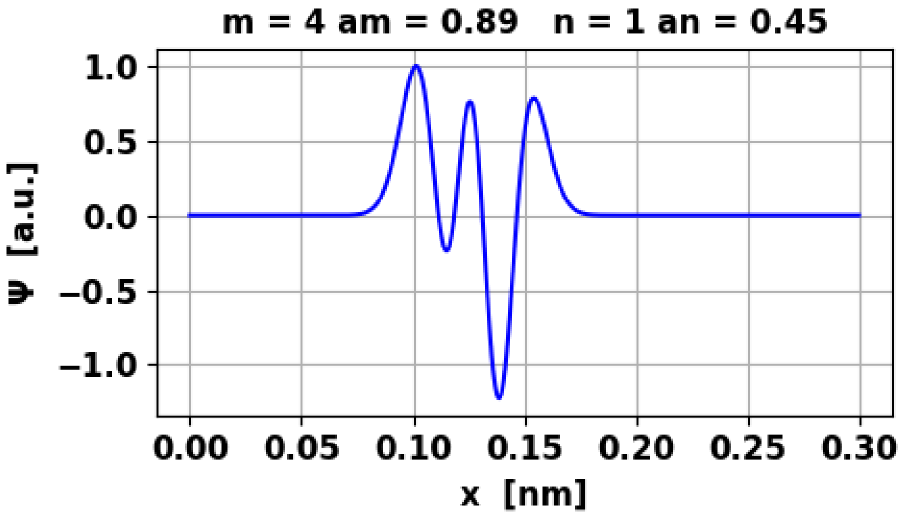


Fig. 13. Scaled compound wavefunction.

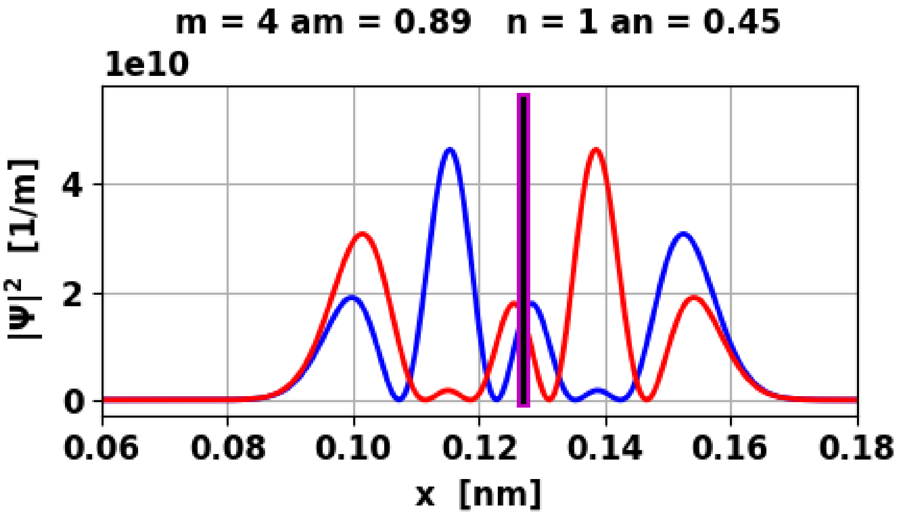


Fig. 14. Probability distribution. No fluctuations in the charge distribution and so no photon is emitted for the transition 4 → 1.

Compound state *m* = 4, *am* = 0. 89443 / *n* = 3, *an* = 0.44721

The transition 4 → 3 is allowed since there is a non-zero electric dipole moment produced by fluctuations in the charge density of the system.

```
COMPOUND STATE
m = 4 am = 0.894   n = 3 an = 0.447
dE = 0.357  eV
osc. frequency omega = 7.486e+15  rad/s
osc. frequency f = 1.191e+15  Hz
osc. period T = 8.393e-16  s
photon wavelength lambda = 251.630  nm
equilibrium bond length = 0.127  nm
el. dipole separation = 0.0247091  nm
```

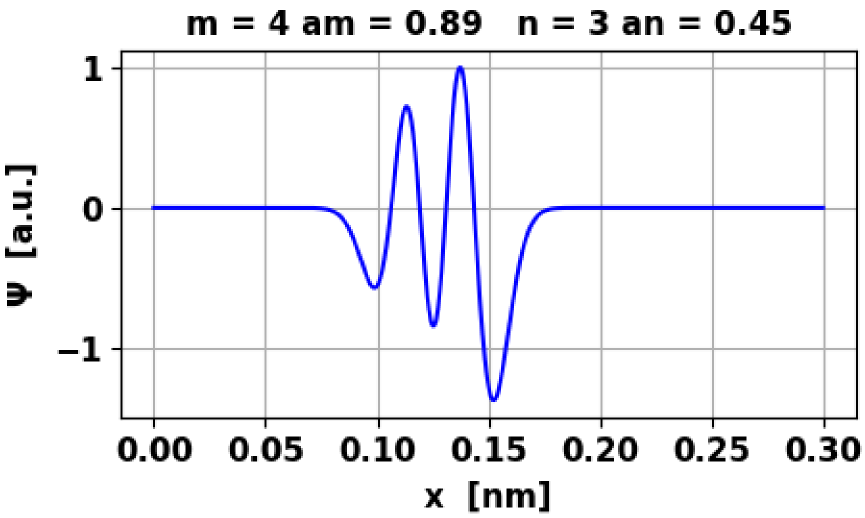


Fig. 13. Scaled compound wavefunction.

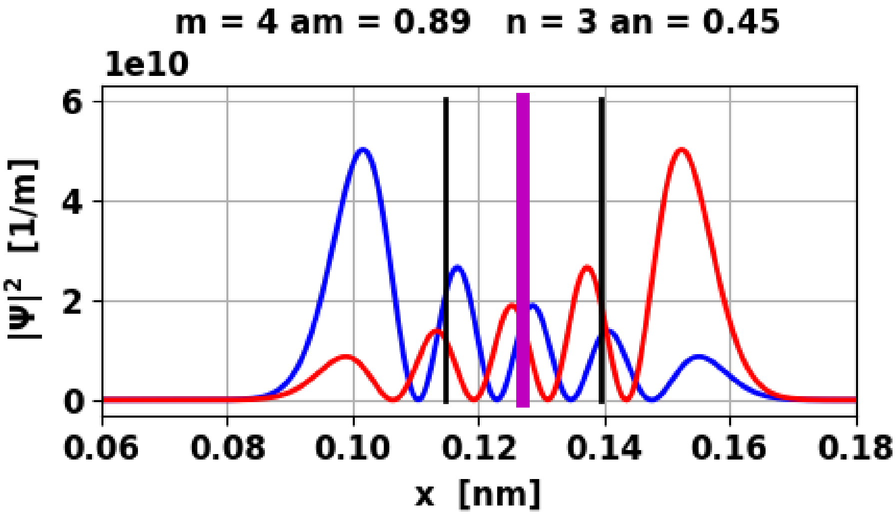


Fig. 14. Probability distribution. The non-zero fluctuations in the charge distribution means that the transition is not forbidden and a photon in the infrared is emitted in 4 → 2.

In our model with a parabolic potential well, the only allowed transitions are when the vibration quantum number changes only by 1 $(\Delta n = \pm 1)$, all other transitions are forbidden for electric dipole radiation.

Selection rule for parabolic potential well (harmonic oscillator) is

allowed transitions $\Delta n = \pm 1$

MORSE POTENTIAL

qm050morse.py

The Morse potential is a convenient interatomic interaction model for the potential energy function of a diatomic molecule. It is a better approximation for the vibrational structure of the molecule than the quantum harmonic oscillator (parabolic potential well). It takes into consideration for the anharmonicity of real bonds (figure 2).

Simulation parameters

grid point N = 801   eigenvalues returned M = 100

xMin = 0.00 nm   xMax = 0.50 nm

Equilibrium bond length x0 = 0.127 nm

well depth U0 = -4.570 ev

spring constant k = 480.000 N/m

Energy eigenvalues [eV]

n	State (vibrational quantum number)
Ew	Eigenvalue measured w.r.t to bottom of well, $U = U_0$

$Ew = E - U0 / se$

$U0$ well depth [J] *se* = *e* [J ↔ eV]

ET	Theoretical value for binding energy, $ET = E_n = \left(n + \frac{1}{2}\right)\hbar\,\omega_n$
dE	Spacing between adjacent energy levels
E	Total energy measured w.r.t $U = 0$
EB	Binding energy or dissociation energy, $EB = -E$

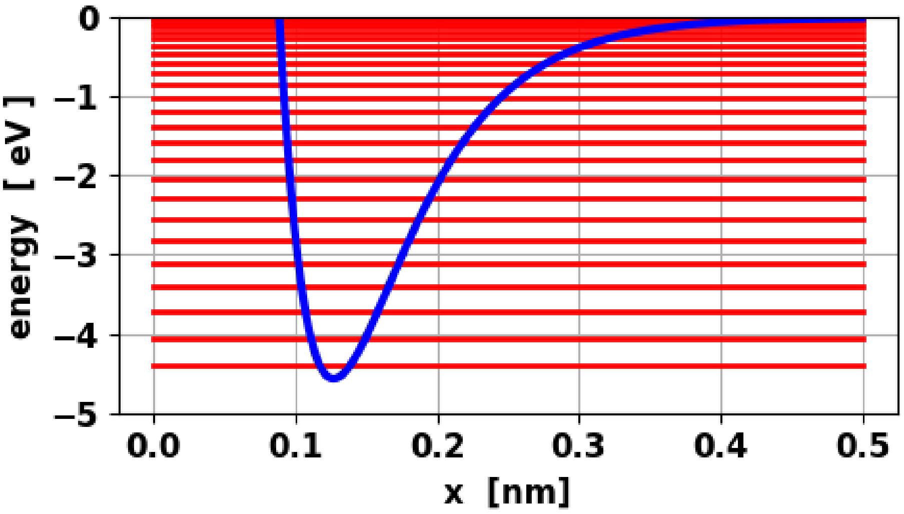


Fig. 15. Morse potential well and energy level spectrum. Note: the reduction in spacings between adjacent energy levels as the vibrational quantum number increases. Ground state $n = 0$, $n > 0$ are the excited sates. Zero-point energy, $E_0 = 0.179$ eV

State n	Ew	ET	dE	E	EB
0	0.177	0.179	0.000	-4.393	4.393
1	0.520	0.536	0.343	-4.050	4.050
2	0.850	0.894	0.329	-3.720	3.720
3	1.165	1.251	0.315	-3.405	3.405
4	1.466	1.609	0.301	-3.104	3.104
5	1.753	1.966	0.287	-2.817	2.817
6	2.026	2.324	0.273	-2.544	2.544
7	2.285	2.681	0.259	-2.285	2.285
8	2.531	3.038	0.245	-2.039	2.039
9	2.762	3.396	0.231	-1.808	1.808
10	2.979	3.753	0.217	-1.591	1.591
11	3.183	4.111	0.203	-1.387	1.387
12	3.372	4.468	0.189	-1.198	1.198
13	3.548	4.826	0.176	-1.022	1.022
14	3.709	5.183	0.162	-0.861	0.861
15	3.857	5.541	0.148	-0.713	0.713
16	3.991	5.898	0.134	-0.579	0.579
17	4.111	6.256	0.120	-0.459	0.459
18	4.217	6.613	0.106	-0.353	0.353
19	4.309	6.971	0.092	-0.261	0.261
20	4.388	7.328	0.078	-0.182	0.182
21	4.452	7.685	0.064	-0.118	0.118
22	4.502	8.043	0.050	-0.068	0.068
23	4.539	8.400	0.037	-0.031	0.031
24	4.567	8.758	0.028	-0.003	0.003

Note: **The decreasing spacing between adjacent energy levels as the vibrational quantum number increases**. ET are the theoretical values for the parabolic potential well.

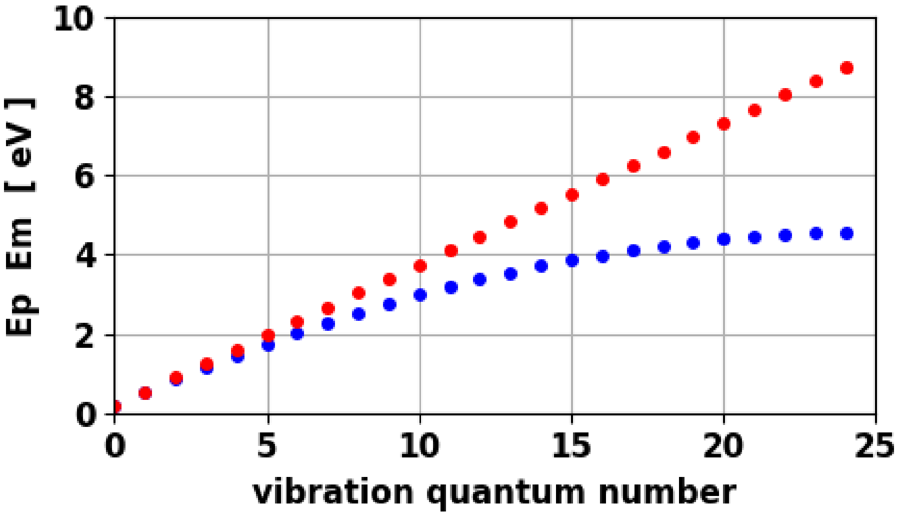


Fig. 15. Energy eigenvalues for the harmonic (parabolic) potential well and the Morse potential well. The eigenvalues are measured w.r.t. the bottom of the well $\left(U = U_0\right)$.

As the vibrational quantum number increases, the Morse potential energy function becomes wider, which results in a reduction in the magnitude of the energy eigenvalues. Thus, the spacing between energy levels decreases as the vibrational number increases.

Eigenfunctions for the first six states

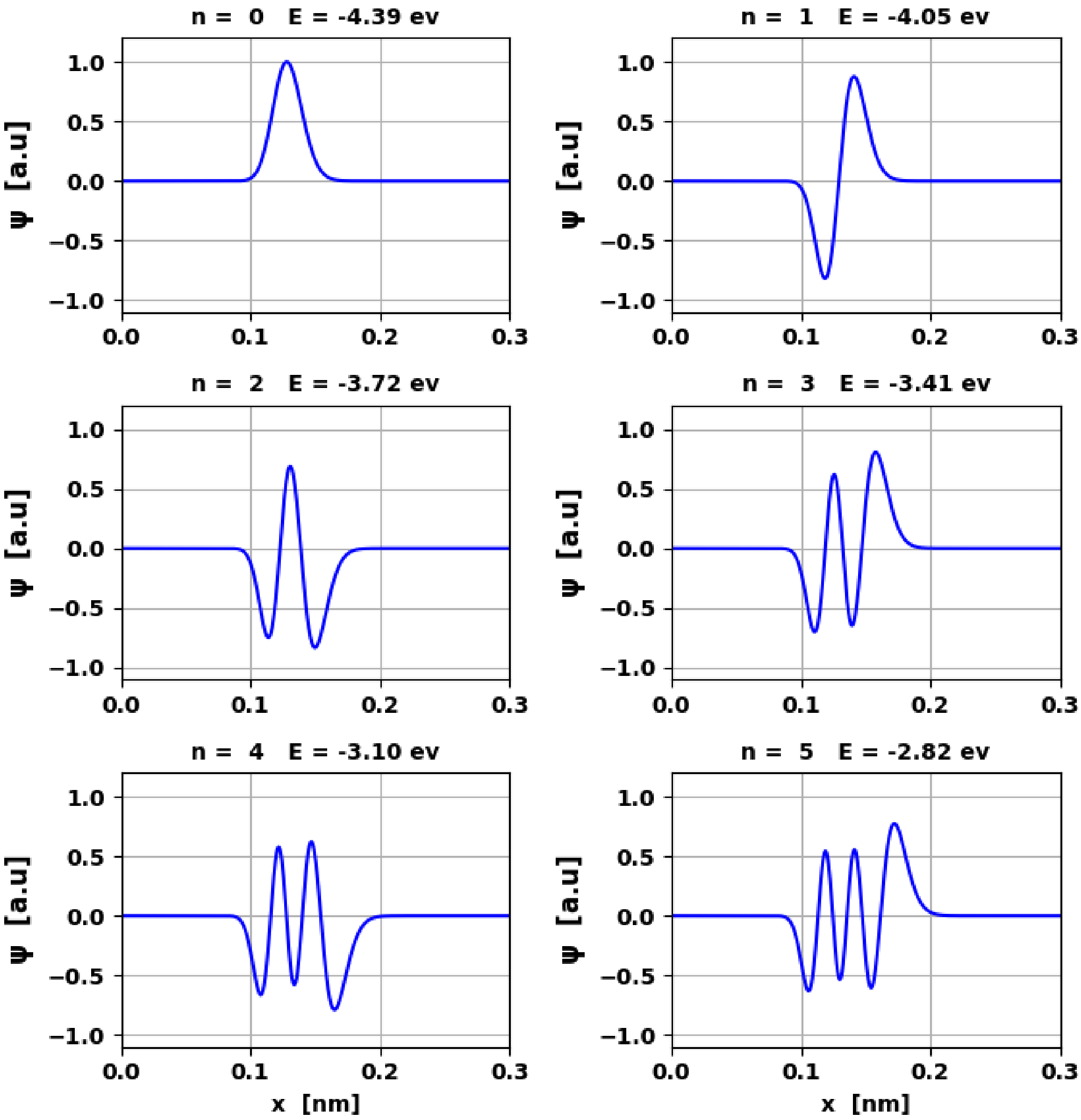


Fig. 16. Eigenfunctions for the first six eigenstates. The amplitudes of the eigenfunctions have been scaled so that the maximum amplitude of the ground state *n* = 0 is 1.00.

Probability densities for the first six states

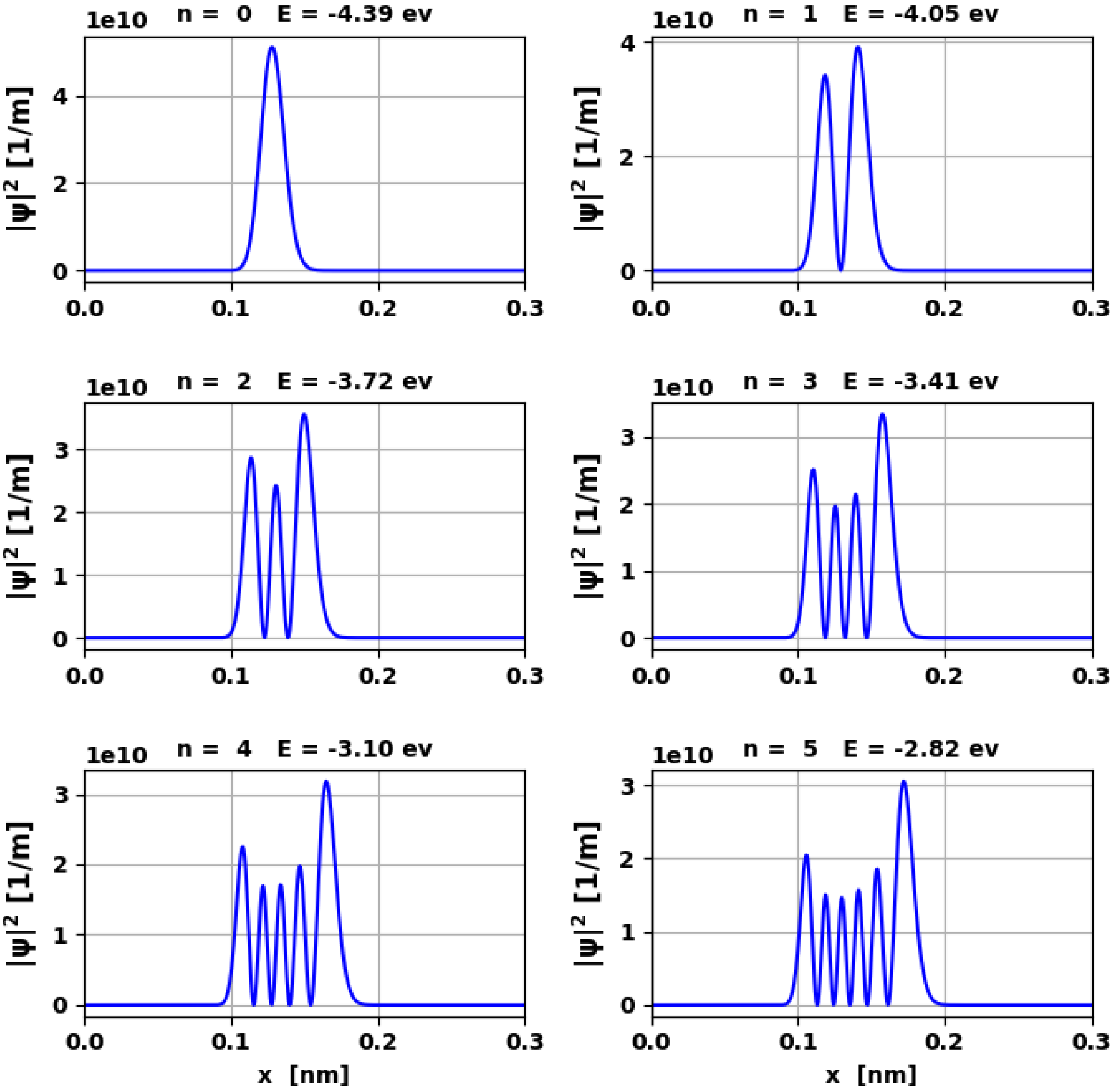


Fig. 17. Probability density functions for the first six eigenstates. The eigenfunctions are normalized so that the each under each curve is one. The number of humps is equal to $n+1$.

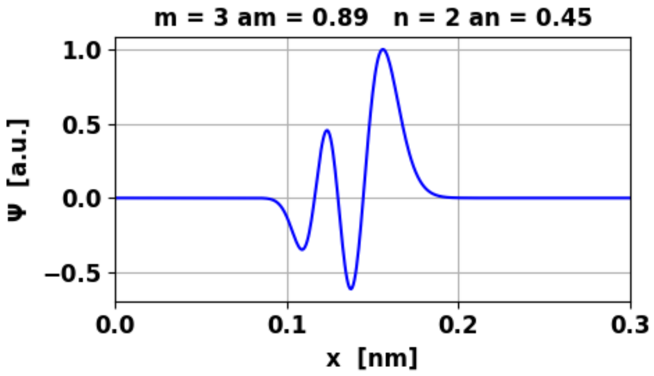
Compound states

The same selections rules apply for the Morse potential as the harmonic oscillator potential (parabolic).

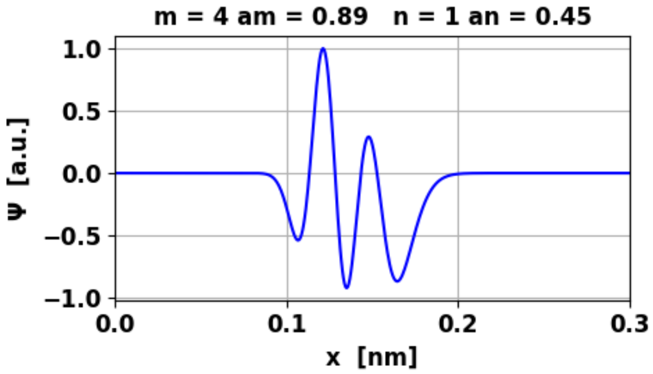
Allowed transitions $m - n = \Delta n = \pm 1$

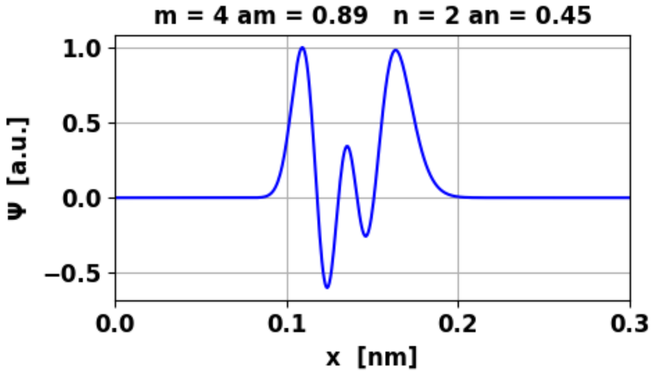
m → n	**3 → 2**	**4 → 1**	**4 → 2**	**4 → 3**
dE [eV]	0.315	0.894	0.616	0.301
f [Hz]	1.181×10^{15}	1.334×10^{15}	1.254×10^{15}	1.178×10^{15}
T [fs]	0.847	0.750	0.797	0.849
λ [nm]	254	225	239	255
xD [nm]	**0.0220458**	**0.0004336**	**0.0031979**	**0.0257214**

Blue: allowed transitions   Red: Forbidden transitions



Wavefunctions





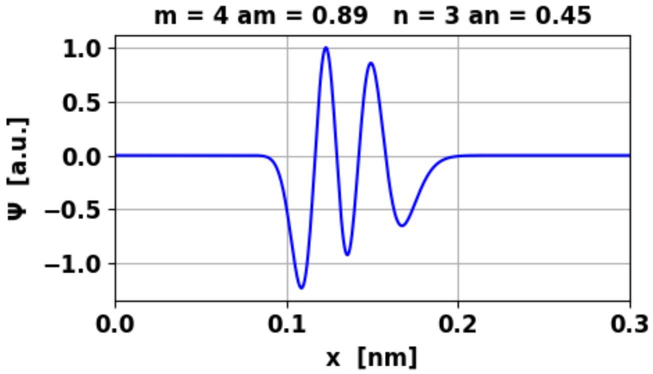
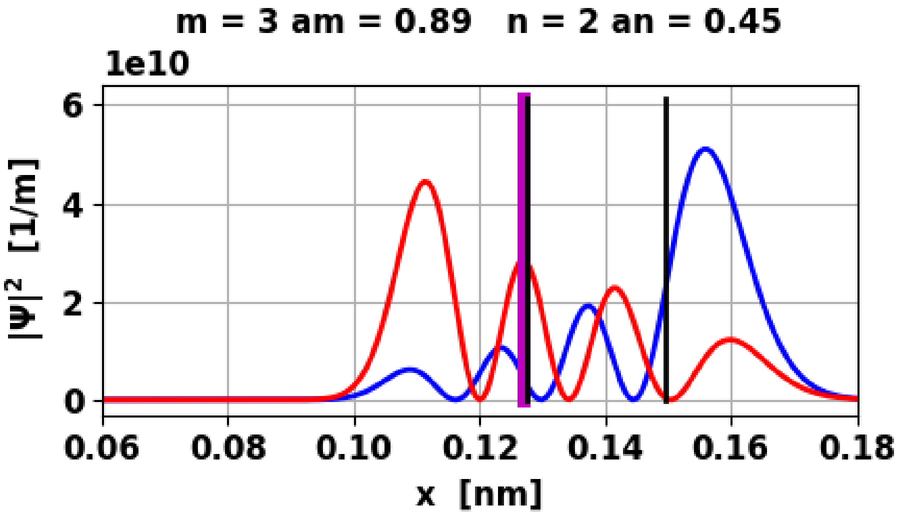


Fig. 18. Compound wavefunctions.

Probability densities



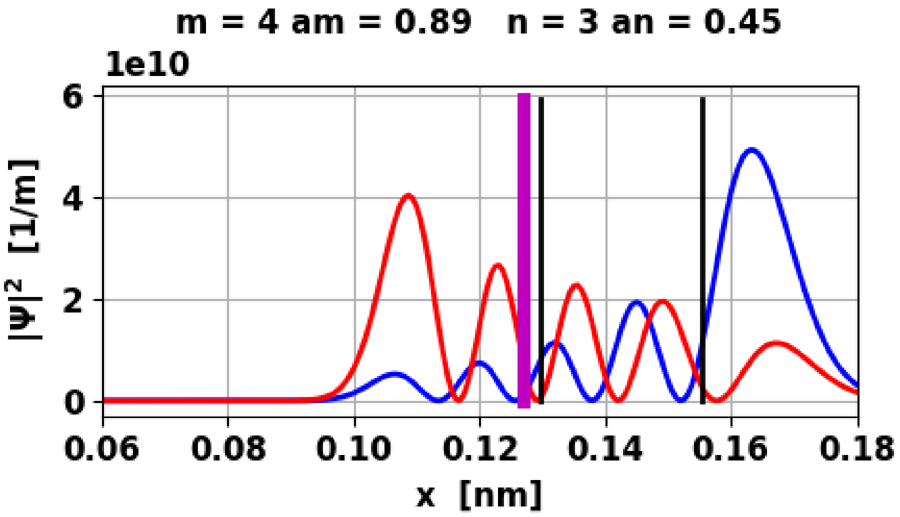
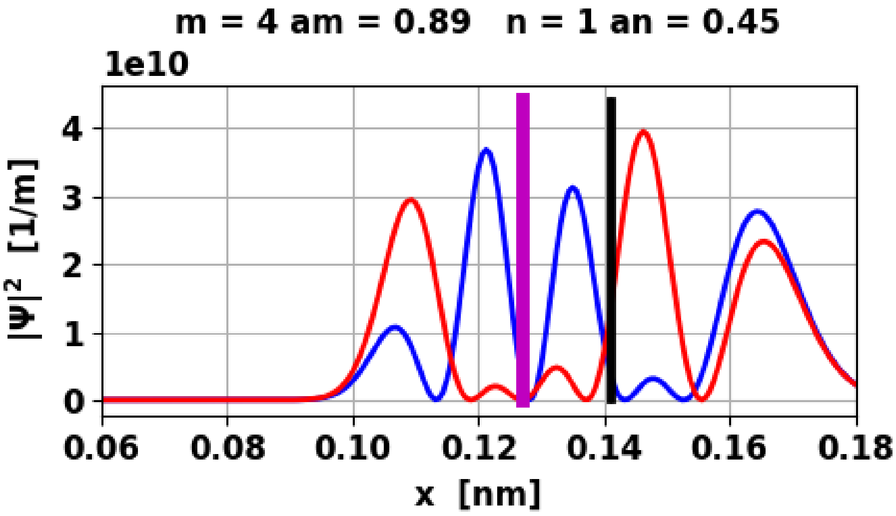


Fig. 19. Probability density functions at time $t = 0$ and time $t = T_{mn} / 2$ (half period later). Vertical **black** lines correspond to $< x(t = 0) >$ and $< x(t = T_{mn} / 2) >$. The charge distribution has a large oscillation producing an electric dipole moment $D >> 0$. Therefore, the two transitions 3 → 2 and 4 → 3 are allowed for the emission of a photon due to electric dipole radiation.



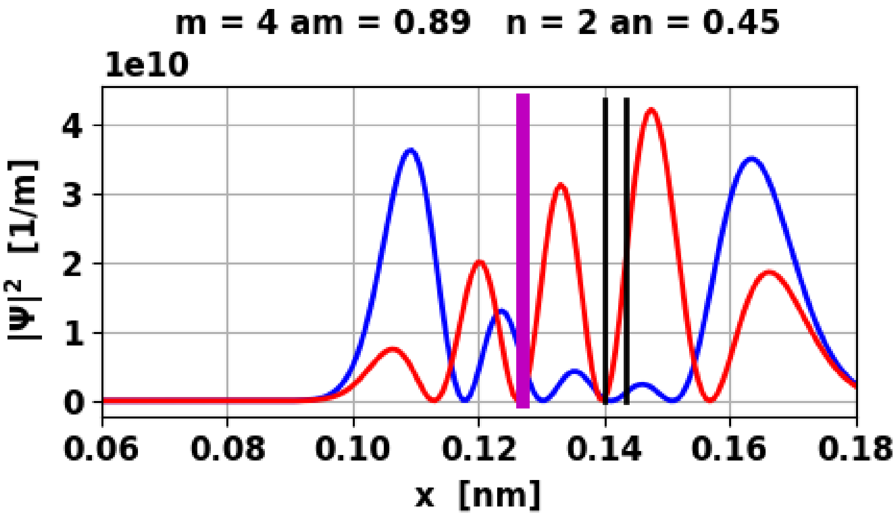


Fig. 20. Probability density functions at time ***t* = 0** and time **$t = T_{mn} / 2$** (half period later). Vertical **black** lines correspond to $< x(t = 0) >$ and $< x(t = T_{mn} / 2) >$. The oscillation in the charge distribution is very small, hence the electric dipole moment is $D \approx 0$. Therefore, the two transitions 4 → 1 and 4 → 2 are forbidden for the emission of a photon due to electric dipole radiation.

The atoms of a molecule exert complicated forces on one another. These forces are harmonic only when the atoms are close to their equilibrium separation positions. More vibrational energy means larger amplitude vibrations and the harmonic approximation breaks down. A better approximation is to use the Morse potential. Near the equilibrium separation, the Morse potential is harmonic. As the separation distance between the atoms increases, the potential energy approaches zero. But the Morse potential rises very sharply as the atoms come close together. Thus, the average separation distance $< x >$ between the atoms increases with increasing vibrational energy. This is the origin of thermal expansion. When the temperature of a sample increases, there is an increase in the asymmetrical vibrations, $< x >$ is greater and the sample expands.