DOING PHYSICS WITH PYTHON

QUANTUM MECHANICS

TRANSITIONS BETWEEN STATES

FINITE SQUARE POTENTIAL WELL

SELECTION RULES

RADIATION LIFETIMES

ABSORPTION AND EMISSION OF EMR

Ian Cooper

matlabvisualphysics@gmail.com

DOWNLOAD DIRECTORY FOR PYTHON SCRIPTS

qm049.py **Transmission between states**
Electric dipole radiation

Solution of the [1D] Schrodinger equation by finding the eigenvalues and eigenvectors. Determination of selection rules for the transmission between eigenstates and the absorption and emission of electromagnetic radiation for a quantum system.

GitHub

Google Drive

RADIATION EMITTED BY A QUANTUM SYSTEM

In classical electromagnetism, an accelerated charge radiates electromagnetic radiation at a rate that increases with its acceleration. In quantum mechanics, the acceleration of a particle is not defined and an electron in a stationary state does not radiate electromagnetic radiation. But we can explain the radiation due to transitions between stationary states using a semi-classical approach by considering the expectation value $< x >$ instead of the classical well defined position coordinate x.

Classically a radiating electric dipole is made up of two equal and opposite charges moving back and forth in opposite directions, each one performing SMH (**Hertzian dipole**). Classically the electric dipole moment D is the product of the charge and the separation distance between the two charges ($D = q\,x$). But a confined electron behaves as a wave and not as a moving particles. Hence, in a quantum system, it is reasonable then to define the electric dipole moment D in terms of the wavefunction for an electron as

$$D = -e\int_{-\infty}^{\infty} \Psi^{*}\; x\; \Psi\, dx$$

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

Consider an electron in a stationary state (eigenstate). Then, both the probability density and the expectation value for position do not depend upon time

$$\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)\,dx = 1 \qquad \text{normalised eigenstate}$$

$$\int_{-\infty}^{\infty} \Psi_n^*(x,t)\; x\,\Psi_n(x,t)\,dx = \int_{-\infty}^{\infty} \psi_n^*(x)\;\; x\;\psi_n(x)\,dx = \text{constant}$$

Since $d^2 < x > / dt^2 = 0$ no energy is radiated since the "acceleration" is zero. For the eigenstate (**stationary state**), the exponential time factors in the wavefunction cancel and the electric dipole moment *D* is independent of time. Actually, the electric dipole on an atom is not merely constant, but is zero because of the symmetry of the quantum system. Therefore, an electron does not radiate so long as it remains in an eigenstate.

When the particle is in an eigenstate, it has a definite energy that does not change with time

$$\int_{-\infty}^{\infty} \Psi_n^*(x,t)\; E\,\Psi_n(x,t)\,dx = E\int_{-\infty}^{\infty} \psi_n^*(x)\;\; \psi_n(x)\,dx = E$$

So, **a stationary state does not radiate**. However, the bound particle is not alone in the universe, sooner or later the particle will interact

with its surroundings (photon, or some other particle, etc), perturbing the energy so that the particle is no longer in a stationary state. The particle will start in its initial stationary state, absorb a photon for example, and then exist in a compound state

$$\Psi(x,t) = \sum_n a_n \Psi_n(x,t)$$

where a_n are a set complex numbers where

$$\sum_n |a_n|^2 = 1$$

for a normalized wavefunction $\Psi(x,t)$.

When radiating, a system does not instantaneously change from its initial state to its final state with no time spent between states. If this was literally true, then the wavefunction would always describe a pure stationary state and never would be any radiation at all.

The coefficients a_n are time dependent. In the compound state, the system does not have a definite energy and the probability density function and the expectation value $< x >$ are both time dependent. Radiation can be emitted from the system when a compound state exists. This occurs when there is a transition from a higher energy level to a lower energy level. The energy (frequency) of the photon emitted depends on the spacing between the initial energy level and the final energy level for the transition

$$f = \frac{E_i - E_f}{h}$$

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

$$\Psi(x,t) = a_m \Psi_m(x,t) + a_n \Psi_n(x,t)$$
$$a_m{}^2 + a_n{}^2 = 1 \quad \omega_m = E_m / \hbar \quad \omega_n = E_n / \hbar$$
$$\Psi(x,t) = a_m \psi_m(x)\, e^{-i(E_m/\hbar)t} + a_n \psi_n(x)\, e^{-i(E_n/\hbar)t}$$
$$\Psi(x,t) = a_m \psi_m(x)\, e^{-i\omega_m t} + a_n \psi_n(x)\, e^{-i\omega_n t}$$

The expectation value of position for the compound wavefunction is

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

Before the transition the coefficient $a_m = 1$ (initial state) and $a_n = 0$ (final state). During the transition these coefficients change with time while maintaining the relationship $a_m{}^2 + a_n{}^2 = 1$. We assume that the time scale for the changes of a_m and a_n is very long compared to the period of oscillation of the emitted photon. After the transition, $a_m = 0$ and $a_n = 1$. The system ends in a stationary state and so no electric dipole radiation is possible.

Initial state $\quad \Psi_m = \psi_m\, e^{-i(E_m/\hbar)t} \quad a_m = 1 \quad a_n = 0$

Final state $\quad \Psi_n = \psi_n\, e^{-i(E_n/\hbar)t} \quad a_m = 0 \quad a_n = 1$

The expectation value $< x >$ is then

$$< x > = \left(\int_{-\infty}^{\infty} \psi_m \; x \, \psi_n \; dx \right) e^{-i\left(\frac{E_m - E_n}{\hbar} \right) t} = \left(\int_{-\infty}^{\infty} \psi_m \; x \, \psi_n \; dx \right) e^{-i \omega_{mn} t}$$

and the electric dipole moment is

$$D = -e < x >$$

where $\omega_{mn} = \left(E_m - E_n \right) / \hbar$.

The expectation value $< x >$ is no longer time independent because the probability density function depends on time. The time variation of $< x >$ may lead to the emission of a photon with energy

$$E_{photon} = E_m - E_n$$

and the frequency of the photon is $\omega_{mn} = \left(E_m - E_n \right) / \hbar = E_{photon} / \hbar$

The frequency of the emitted photon is the frequency of oscillation between the two states, that is, the frequency at which the probability density function (**charge density**) varies with time or charge distribution changes.

Even though the probability density changes with time, if there is no sloshing back and forward in the expectation value $< x >$ then no photon can be emitted. So, not all transitions from a higher energy state to lower energy states result in the emission of a photon as dipole radiation. This fact gives rise a set of **selection rules** which indicates which transitions are allowed and which are forbidden.

Selection rules

The overlap integral for the electric dipole moment is

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

Under certain circumstances this overlap integral between a particular pair of initial and final states is equal to zero. So, for this case, no radiation can be emitted for this transition via electric dipole radiation. From this, we can obtain a set of selection rules that govern the possibility of electric dipole transitions.

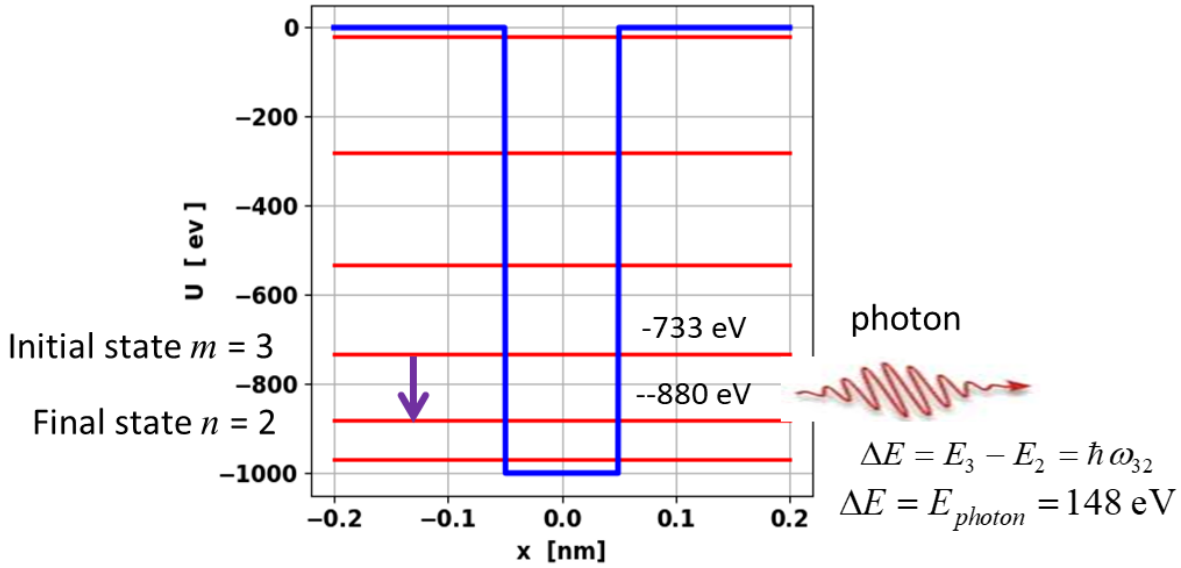

Fig. 1. An allowed transition from the eigenstate m = 3 to the eigenstate n = 2. A photon is emitted from the quantum system by electric dipole radiation with an energy equal spacing between the two energy levels E_3 and E_2. Well depth -1000 eV and width 0.100 nm. E_3 = -733 eV, E_2 = -881 eV, E_{photon} = 148 eV.

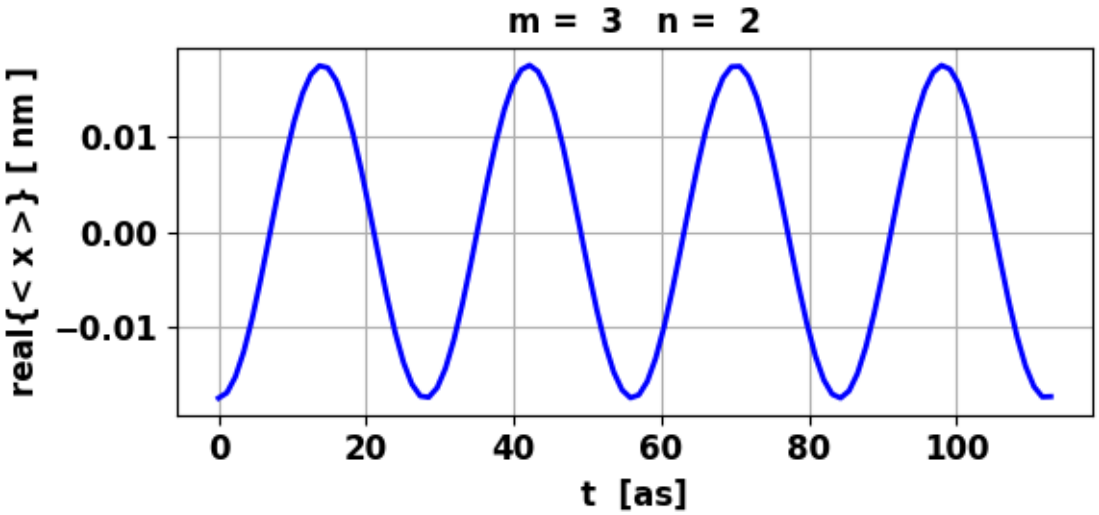

Fig.2. The time variation of the expectation value of position < x > is SHM with period T = 28 as (atto: 1 as = 1x10^{-18} s).

SIMULATION qm045.py

Finite square well parameters

```
N = 519              #  grid size
xMin = -0.2*sx       #  default = -0.2 nm   [m]
xMax =  0.2*sx       #  default = +0.2 nm   [m]
U0 = -1000*se        #  Depth of well:      [eV]
w = 0.1*sx           #  Width of well: default 0.1 nm  [m]
M = 30               # number of eigenvalues returned
# >>> Enter quantum states m and n (1,2,3,4,5,6) and coeff am
and an
m = 3; n = 2         # m > n
am = 1; an = 0.5     # Eigenfunction coefficients
```

Console output

```
Energy eigenvalues [ev]
  E1 = -970.048      E2 = -880.624      E3 = -733.192
  E4 = -530.987      E5 = -281.740      E6 = -19.645


Eigenstate n =  2
 Expectation values and Uncertainty Principle
   <x> = -0.00 m   deltax dX = 3.18e-11 m
   <p> = 0.00 N.s   deltax dP = 8.27e-24 m
   HUP = 4.99  > 1
```

Eigenstate energies

En = -733.19 eV

<E> = -733.19 <K> = 234.36 <U> = -967.55

<K> + <U> = -733.19

Compound state (mixed state) m = 3, n = 2

Eigenstates: m = 3 n = 2

Em = -733.19 eV En = -880.62 eV Ephoton = 147.43 eV

Frequency of emitted photon f = 3.56e+16 Hz

Period of emitted photon T = 28.05 as

Wavelength of emitted photon lambda = 8.42 nm

Execution time = 4 s ~ 60 s if save animation

Graphical output

Eigenfunctions

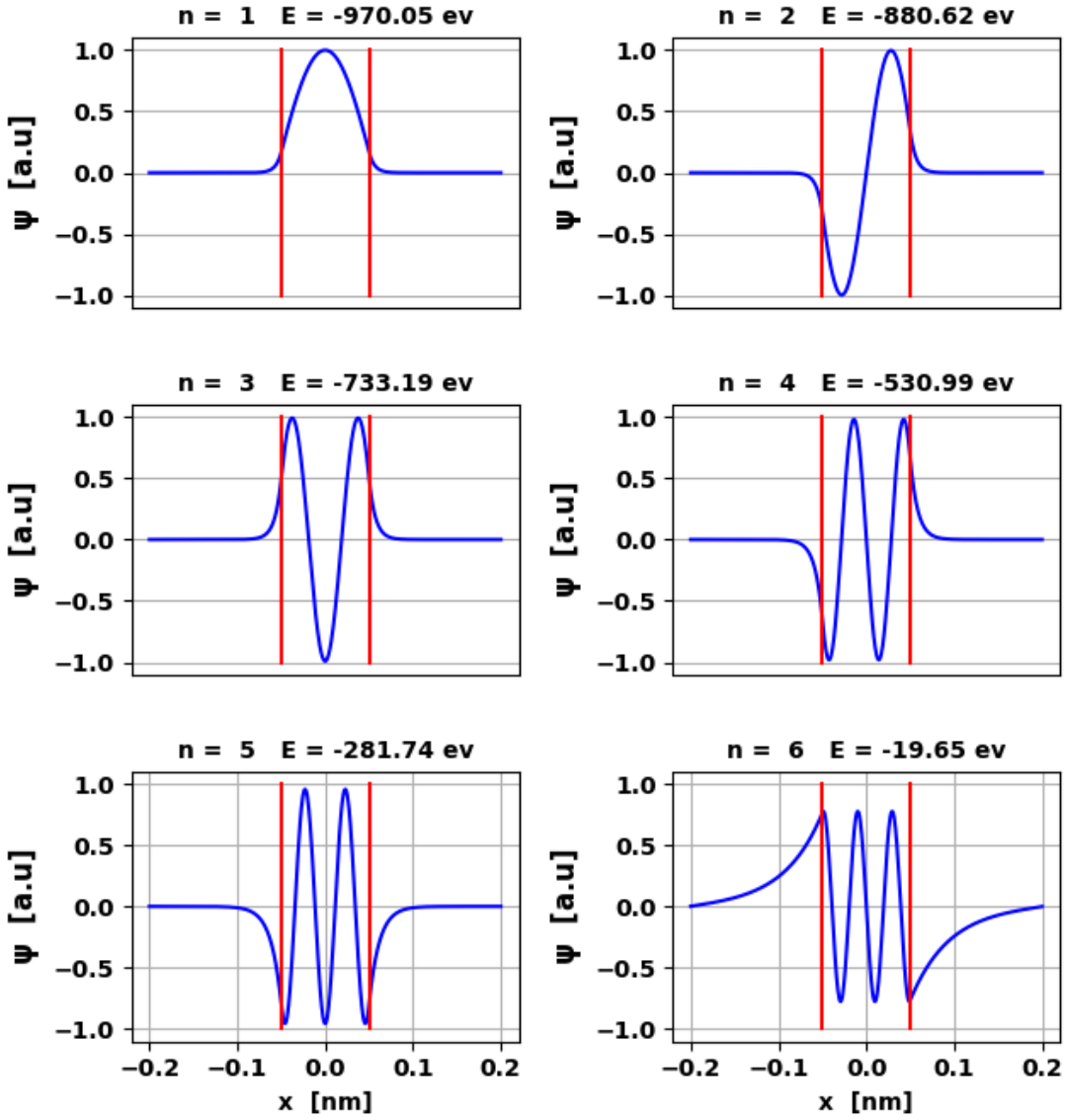

Fig. 3. The eigenfunctions for the 6 bound states.

Probability density functions

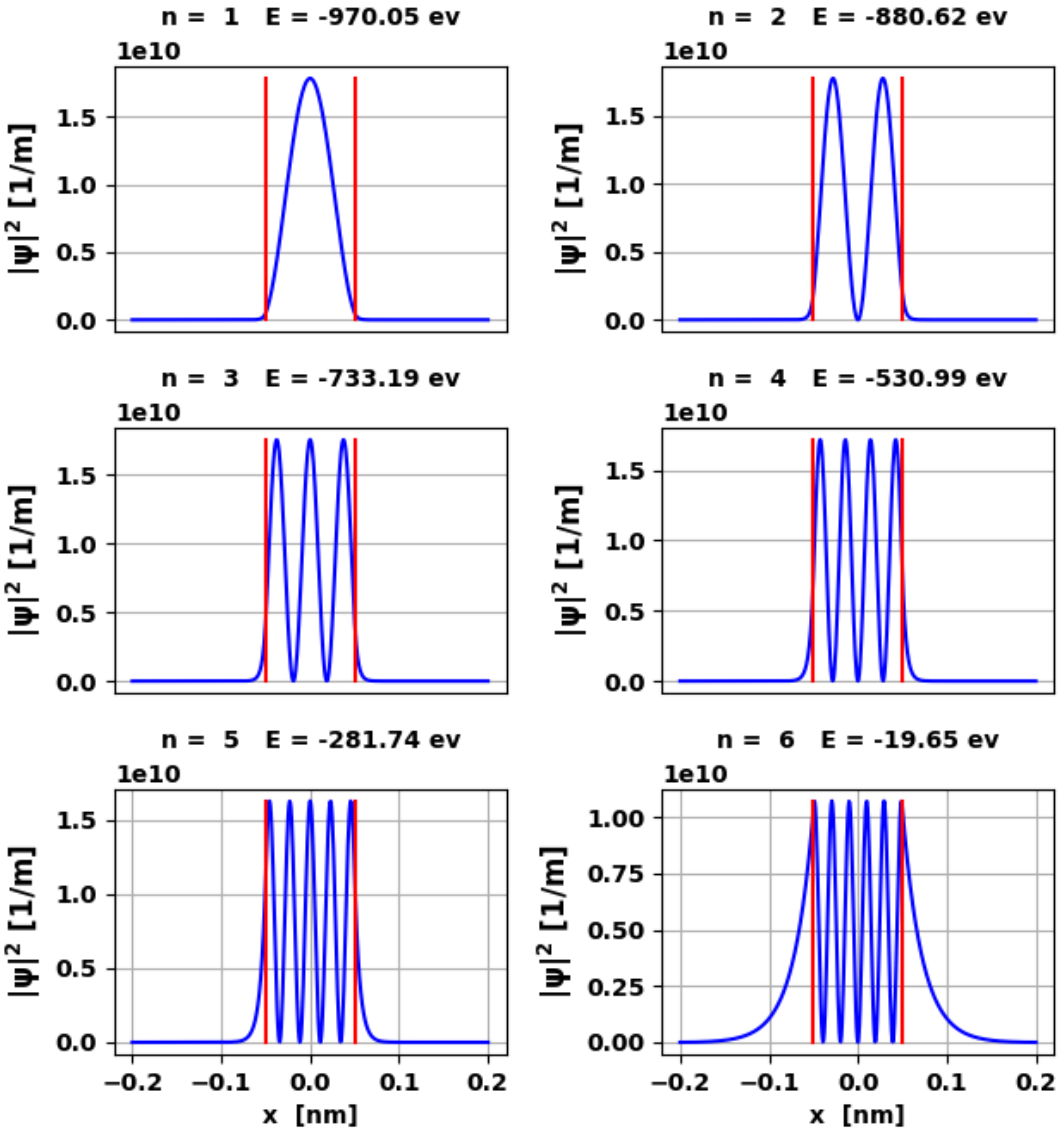

Fig. 4. Probability densities for the 6 bound states.

Compound (mixed) state $m = 3$, $n = 2$:

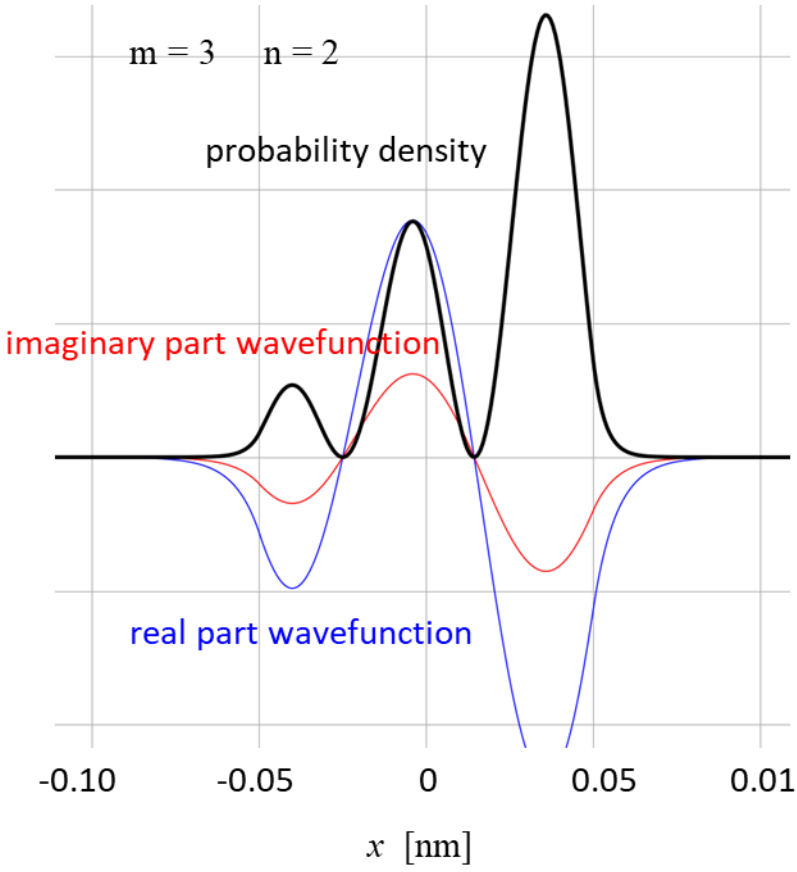

Fig. 5. Wavefunction (real and imaginary) and probability density (**black**) at time t = 56 as (2 periods). The probability density function (charge density) sloshes back and forth giving rise to an oscillating dipole moment and therefore, dipole radiation.

The photon emitted is in the ultraviolet region of the electromagnetic spectrum:

energy	E_{photon} = 147.43 eV
frequency	f = 3.56x1016 Hz
period	T = 28.05x10-18 s
wavelength	λ = 8.42 nm (UV)

Compound state (mixed state) m = 3, n = 1

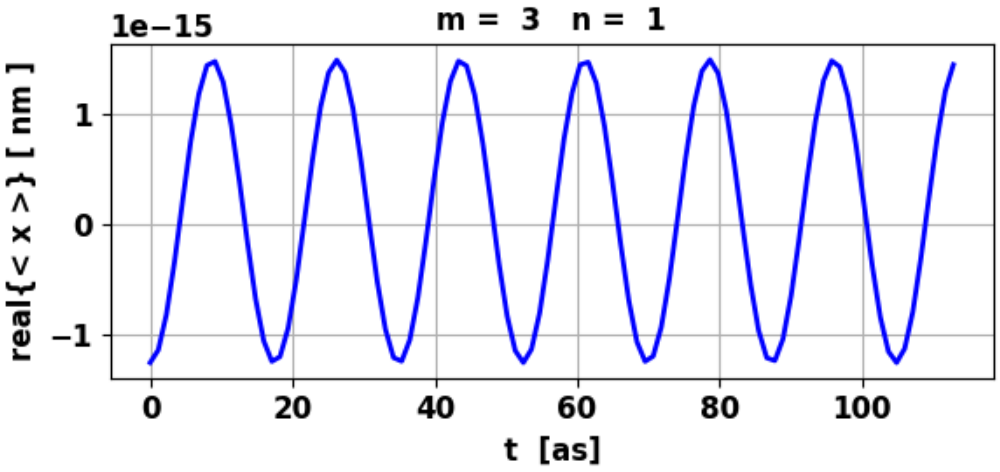

Fig. 6. The time variation of the expectation value of position < x >. ,$\langle x \rangle \approx 0$. So this transition is forbidden for electric dipole radiation.

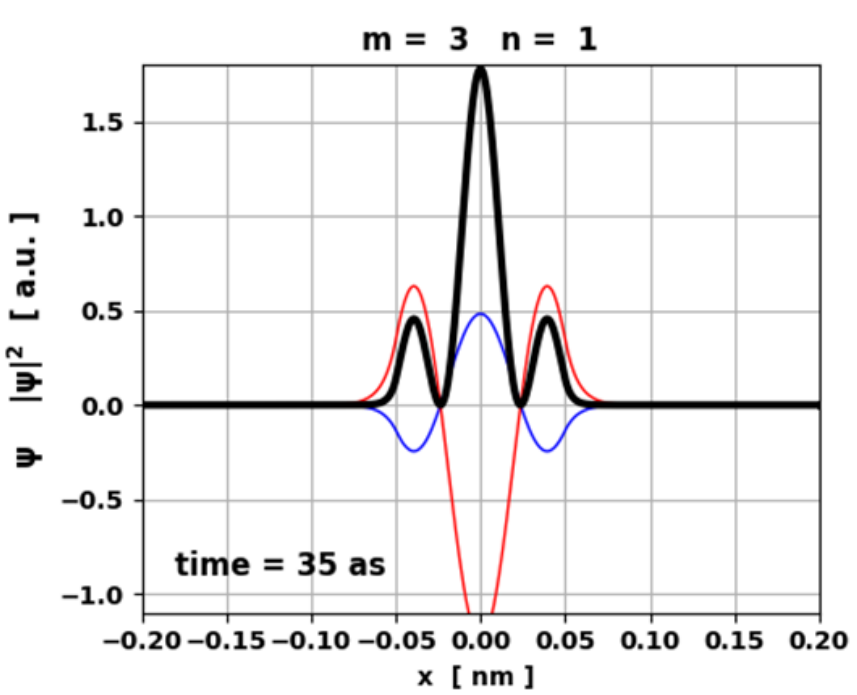

Fig. 7. Wavefunction (real and imaginary) and probability density (**black**) at time t = 35 as (2 periods). The probability density evolves symmetrical around x = 0 which results in < x > = 0. Hence, dipole radiation is forbidden for the transition m = 3 to n = 1.

Compound state (mixed state) m = 4, n = 1

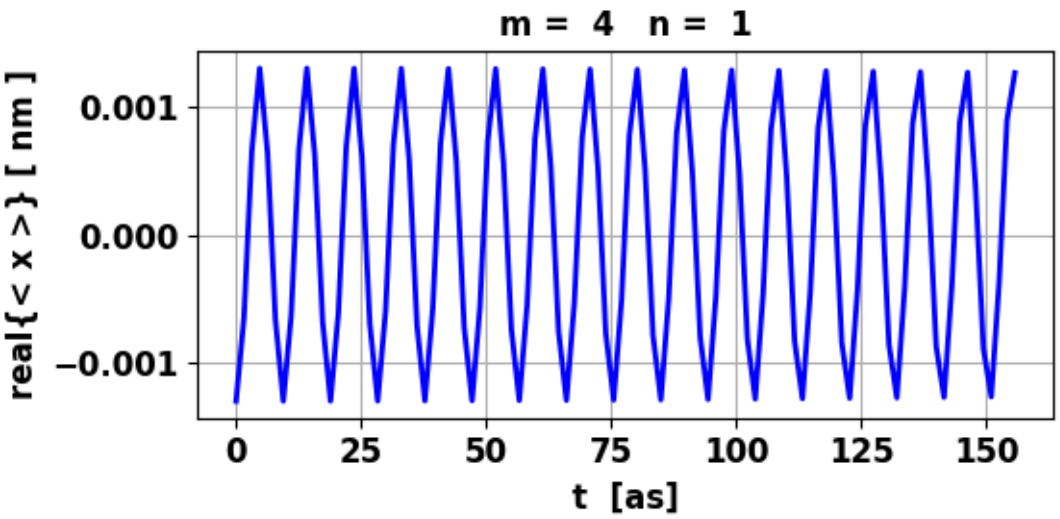

Fig. 8. The time variation of the expectation value of position < *x* >. The transition is allowed but the maximum in electric dipole moment for this transition 4→1 is an order of magnitude less than the transition 3→2.

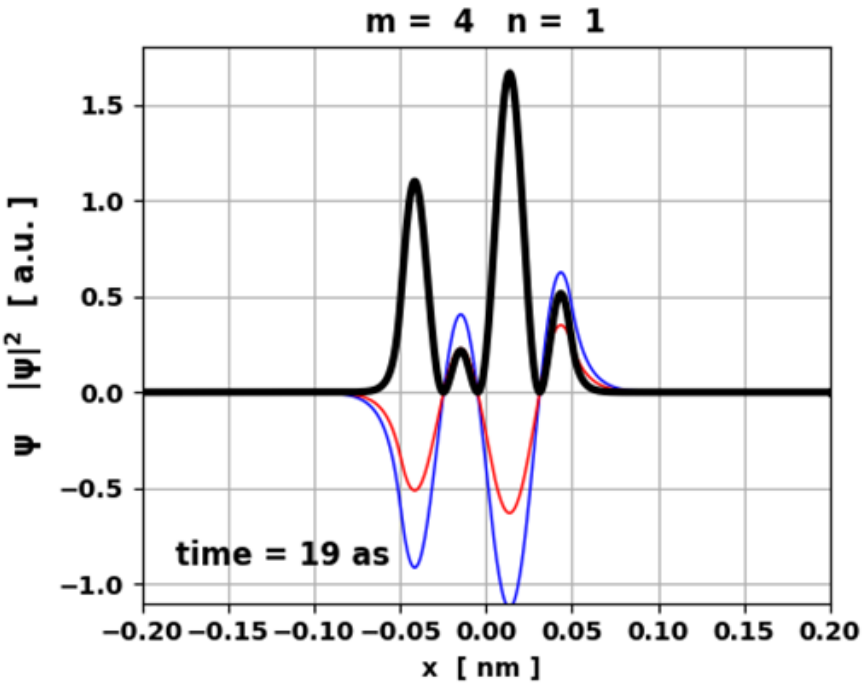

Fig. 9. Wavefunction (real and imaginary) and probability density (**black**) at time *t* = 19 as (2 periods).

If the two eigenstates have the **same symmetry** about $x = 0$ (even-even or odd-odd) then there is no dipole radiation emitted from the quantum system since the time evolution in the probability density function results in $\langle x \rangle \approx 0$ and electric dipole moment $D \approx 0$. If the two eigenstates do **not** have the same symmetry (even-odd) then electric dipole radiation is allowed. The computation of the overlap integral for the expectation value shows that the expectation value $< x >$ is greatest for the case when $|m - n| = 1$ and this means that this transition is most likely to occur.

RADIATION RATES AND LIFETIMES

How long on average, does it take for a set of quantum system in the same excited state m to drop directly to a lower state n?

We know that a quantum system can only emit electric dipole radiation during the time when a superposition of initial and final states exist. This time is determined by the wavefunction coefficients $a_m(t)$ and $a_n(t)$ where $a_m{}^2 + a_n{}^2 = 1$. Without any proof, based upon classical and quantum arguments, the rate of electric dipole radiation emission R from a set of identical quantum system initially in the excited state is

Rate of emission of emr $R = \dfrac{\omega_{mn}{}^4 D^2}{3c^3}$

A quantum jump involves the emission of a photon with energy $\hbar\omega$. Therefore, in classical terms, the radiation continues for the time τ which is called the **radiative lifetime** and is given by

$$\frac{\omega_{mn}{}^4 D^2}{3c^2}\tau = \hbar\omega_{mn}$$

Radiative lifetime $\tau = \dfrac{3\hbar c^3}{\omega_{mn}{}^3 D^2} = \dfrac{3\hbar\lambda_{mn}{}^3}{8\pi^3 D^2}$

Simulation results

$m \rightarrow n$	max(< x >) m	D C.m	R s^{-1}	τ s
3 → 2	$1.76\text{x}10^{-11}$	$2.83\text{x}10^{-30}$	$2.48\text{x}10^{-16}$	0.095
3 → 1	$3.74\text{x}10^{-24}$	$5.97\text{x}10^{-43}$	$7.39\text{x}10^{-41}$	$5.13\text{x}10^{23}$
4 → 1	$1.31\text{x}10^{-12}$	$2.10\text{x}10^{-31}$	$1.08\text{x}10^{-16}$	0.653

The transition from 3 → 1 is definitely forbidden. Transitions between adjacent levels have the shortest radiative lifetimes. The large the electric dipole moment D, the shorter the lifetime in the mor excited state.

VIEW ANIMATIONS