

DOING PHYSICS WITH MATLAB

QUANTUM PHYSICS

HYDROGEN ATOM

SELECTION RULES

TRANSITION RATES

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qp_rules.m

Calculates for a hydrogen atom, the transition rate and lifetime for a transition from an initial state $(n_1 l_1 m_{l1})$ to the final state $(n_2 l_2 m_{l2})$. The azimuthal wavefunction is given by an analytical expression, the angular wavefunction is found using the Matlab command **legendre** and the radial wavefunction is solved by the Matrix Method using the function **qp_fh.m**. Integrations use the function **simpson1d.m**. The mscript also can be used to create **animated gifs** for the oscillation of the probability of compound states. The states have to be changed within the mscript by editing the statement **state = [5 1 1 1 0 0]**; The first three numbers are n, l, m_l for State 2 (final State) and the second set of three numbers give the n, m, m_l values for State 1 (initial State).

qp_fh.m included within qp_rules.m

Function used to solve the radial Schrodinger Equation for the hydrogen atom

```
[ EB(1), R1, r ] = qp_fh(n(1), L(1), num, r_max);  
[ EB(2), R2, r ] = qp_fh(n(2), L(2), num, r_max);
```

Within this mscript you can change the maximum radial coordinate and the number of data pints for the calculations.

simpson1d.m (must have an odd number of grid points) included within qp_rules.m

Function for doing integrations using Simpson's rule, for example

```
% Normalize radial wavefunctions  
N(1) = simpson1d((R1 .* R1),0,max(r));  
N(2) = simpson1d((R2 .* R2),0,max(r));  
R1 = R1 ./ sqrt(N(1));  
R2 = R2 ./ sqrt(N(2));
```

In the input section of the script **qp_rules.m** you specify:

- The initial and final states.
- The saving of an animated gif of the probability cloud.
- The display of the animation of the probability cloud. Can select a contour plot or a surf plot.
- The maximum radial distance for the radial wavefunction r_{max} . This is an important variable for accurate predicts of the lifetime of the excited state. The value of r_{max} cannot be too small or too large when implementing the numerical procedure to solve the radial wave equation. Figure 1 shows the plot of the radial function functions for the initial and final states for one simulation with $r_{\text{max}} = 30 \times 10^{-9}$ m. The plots show that the wavefunctions approaches zero in an appropriate fashion. The calculated lifetime is 1168 ns. Figure 2 shows the wavefunction plots for $r_{\text{max}} = 10 \times 10^{-9}$ m. The tail is not a good representation of the wavefunction and the calculated of the lifetime is 246 ns and is not an accurate result.

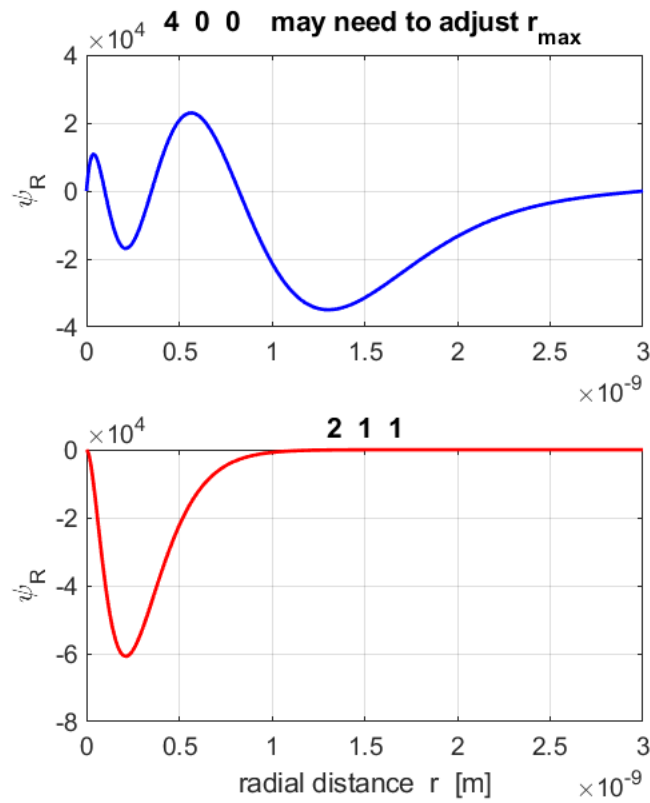


Fig. 1. Accurate plots of the wavefunctions when $r_{\max} = 30 \times 10^{-9}$ m.

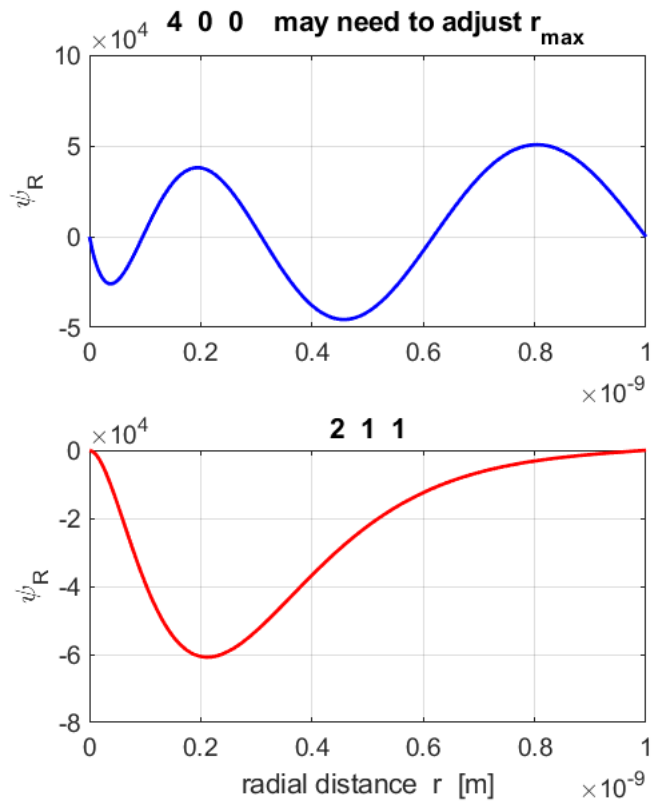


Fig. 2. Incorrect plots of the wavefunctions when $r_{\max} = 10 \times 10^{-9}$ m.

Excited states and transition rates in a hydrogen atom

If a hydrogen atom is excited to a higher energy level, it will at some later time spontaneously make transitions to successively lower energy levels. In a transition from a higher energy state (1) to a lower energy state (2), the frequency and wavelength of the emitted photon is

$$(1) \quad f = \left| \frac{E_2 - E_1}{h} \right| \quad \lambda = \frac{c}{f}$$

The discrete wavelengths emitted in all transitions that take place constitute the lines in the emission spectrum. But, **not** all possible transitions take place. Photons are observed only with frequencies corresponding to transitions between states whose quantum numbers satisfy the **selection rules**

$$(2) \quad \Delta l = \pm 1 \quad \Delta m_l = 0 \text{ or } \pm 1$$

These selection rules are found to apply to all one-electron atoms.

Why are some transitions forbidden?

We can answer this question by using a mix of classical and quantum physics.

A **transmission rate** R_t is the probability per second that an atom in a certain energy level will make a transition to some other lower energy level.

Typical allowed transition rates are $\sim 10^8 \text{ s}^{-1}$. This means that in about 10^{-8} s , the probability that the transition has occurred is about one. This time interval is called the **lifetime** t_L .

$$(3) \quad t_L = \frac{1}{R_i}$$

The eigenfunctions represent stationary states, that is, they do not vary with time. However, for compound states where the wavefunction is a combination of two stationary states of energies E_1 and E_2 , then, the probability density function contains a term that oscillates in time at frequency

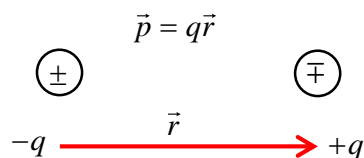
$$f_{12} = \left| \frac{E_2 - E_1}{h} \right|$$

Hence, the electron charge distribution must also oscillate at a frequency f_{12} and this is precisely the frequency of the emitted photon in the transition between the states.

View animations of compound states at

http://www.physics.usyd.edu.au/teach_res/mp/doc/qp_se_time.htm

The atom's evolving charge distribution can be modeled as an **oscillating electric dipole**.



The **electric dipole moment** \vec{p} for the oscillating charge distribution is the product of the electron charge e and the expectation value of its displacement $\langle \vec{r} \rangle$ value from the nucleus.

A charge distribution that is constant in time will not emit electromagnetic radiation, while a charge distribution with an oscillating electric dipole moment emits radiation at the frequency of the oscillator. The oscillating electric dipole is the most efficient radiator of electromagnetic radiation.

We can use a classical formula for the rate of emission of energy by an oscillating electric dipole

$$(4) \quad R_t = \frac{4\pi^3 f^3}{3\epsilon_0 h c^3} p^2$$

where p is the amplitude of its oscillating electric dipole moment and f is the frequency of the oscillation. R_t is the **atomic transition rate**, it gives the probability per second that a photon is emitted and thus it is equal to the probability per second that the atom has undergone the transition.

Relative to the Origin at the nucleus, the atomic electric dipole moment of a one electron atom is

$$(5) \quad \vec{p} = -e \vec{r}$$

where \vec{r} is the position vector from the nucleus at the Origin.

We can calculate the expectation value of \vec{p} to obtain an expression for the amplitude p of the oscillating electric dipole moment of the atom in a compound state as shown in the following arguments:

$$(6) \quad \Psi_1 = \psi_1 \exp(i E_1 t / \hbar) \quad \Psi_2 = \psi_2 \exp(i E_2 t / \hbar)$$

$$(7) \quad \Psi = \Psi_1 + \Psi_2$$

where Ψ_1 and Ψ_2 are both normalized wavefunctions.

The time independent parts of the wavefunctions are of the form

$$(8) \quad \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) = (g(r)/r) \Theta(\theta) \Phi(\phi) \quad g(r) = r R(r)$$

where $g(r)$ is the solution of the radial **Schrodinger Equation**

$$(9) \quad -\left(\frac{\hbar^2}{2m}\right) \frac{d^2 g(r)}{dr^2} + U_{\text{eff}}(r) g(r) = E g(r)$$

The solutions $\Theta(\theta)$ for the **angular equation** are polynomials in $\cos \theta$ known as the **associated Legendre polynomials** $P_l^{|m_l|}(\cos \theta)$

where $l = 0, 1, 2, \dots$ and $m_l = 0, \pm 1, \pm 2, \pm 3, \dots$. $|m_l| \leq l$

The normalized solution to equation (6) can be written as

$$(10) \quad \Theta(\theta) = N_{l m_l} P_l^{m_l}(\cos \theta)$$

where $N_{l m_l}$ is an appropriate normalization constant such that

$$(11) \quad \int_{\theta=0}^{\theta=\pi} N_{l m_l} P_l^{m_l}(\cos \theta) \sin \theta d\theta = 1$$

The normalized solution of the **azimuthal equation** is

$$(12) \quad \Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(-i m_l \phi)$$

The time independent part of the normalized wavefunctions that can be expressed as

$$(13) \quad \psi(r, \theta, \phi) = (g(r)/r) N_{l m_l} P_l^{m_l}(\cos \theta) \exp(-i m_l \phi) / \sqrt{2\pi}$$

where $g(r)$ is also normalized and both $g(r)$ and $P_l^{m_l}(\cos \theta)$ are real quantities.

Since the probability of finding the electron is 1, then

integrating over a volume element $dV = r^2 dr d\theta d\phi$

The electric dipole moment can be expressed as

$$(14) \quad \vec{p} = \int \psi_2^* (-e\vec{r}) \psi_1 dV = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_2^* (-e\vec{r}) \psi_1 r^2 \sin \theta d\phi d\theta dr$$

This is a vector quantity and has components (p_x, p_y, p_z) where

$$(15) \quad x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta$$

$$(16)$$

$$p_x = \left| e \int_0^\infty r g_2(r) g_1(r) dr \int_0^\pi P_{l_2}^{m_2}(\cos \theta) P_{l_1}^{m_1}(\cos \theta) \sin^2 \theta d\theta \int_0^{2\pi} \exp(i m_2 \phi) \exp(-i m_1 \phi) \cos \phi d\phi \right|$$

$$p_y = \left| e \int_0^\infty r g_2(r) g_1(r) dr \int_0^\pi P_{l_2}^{m_2}(\cos \theta) P_{l_1}^{m_1}(\cos \theta) \sin^2 \theta d\theta \int_0^{2\pi} \exp(i m_2 \phi) \exp(-i m_1 \phi) \sin \phi d\phi \right|$$

$$p_z = \left| e \int_0^\infty r g_2(r) g_1(r) dr \int_0^\pi P_{l_2}^{m_2}(\cos \theta) P_{l_1}^{m_1}(\cos \theta) \cos \theta \sin \theta d\theta \int_0^{2\pi} \exp(i m_2 \phi) \exp(-i m_1 \phi) \cos \phi d\phi \right|$$

Let

$$I_{Rx} = I_{Ry} = I_{Rz} = \int_0^\infty r g_2(r) g_1(r) dr$$

$$I_{Tx} = I_{Ty} = \int_0^\pi P_{l_2}^{m_2}(\cos \theta) P_{l_1}^{m_1}(\cos \theta) \sin^2 \theta d\theta$$

$$(17) \quad I_{Tz} = \int_0^\pi P_{l_2}^{m_2}(\cos \theta) P_{l_1}^{m_1}(\cos \theta) \cos \theta \sin \theta d\theta$$

$$I_{Px} = \int_0^{2\pi} \exp(i(m_2 - m_1)\phi) \cos \phi d\phi$$

$$I_{Py} = \int_0^{2\pi} \exp(i(m_2 - m_1)\phi) \sin \phi d\phi$$

$$I_{Pz} = \int_0^{2\pi} \exp(i(m_2 - m_1)\phi) d\phi$$

Therefore

$$(18) \quad \begin{aligned} p_x &= e \left| I_{Rx} I_{Tx} I_{Px} \right| \\ p_y &= e \left| I_{Ry} I_{Ty} I_{Py} \right| \\ p_z &= e \left| I_{Rz} I_{Tz} I_{Pz} \right| \end{aligned}$$

$$(19) \quad p^2 = p_x^2 + p_y^2 + p_z^2$$

$$(20) \quad p = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

The radial wavefunction $g(r)$ can be found numerically by solving the radial equation (equation 9) by the [Matrix Method](#) and the associated Legendre functions $P_l^m(\cos \theta)$ can be evaluated using the Matlab command **legendre**. The normalization constants can be found by numerical integration using Simpson's rule. The integrals in the set of equations (17) are computed numerically to find the numerical value of the amplitude of the oscillating electric dipole moment p . Then from equation (3) and equation (4) the transition rate R_t and t_L can be calculated respectively. A summary of the calculations is given in Table 1.

The msript **qp_rules.m** is used for the electric dipole calculations.

Table 1. Data for the transition from a higher energy level to a lower level. The initial and final states are given by the set of quantum numbers ($n l m_l$). The mscript **qp_rules.m** is used to calculate the binding energies of the two states ($E_B = -E$), the integrals given by equation (17), the lifetime t_L of the higher energy state and the wavelength λ of the photon emitted in the transition. Only the integral I_P components for the azimuthal coordinate are shown in the table. Published values are given for the lifetime so that the model results can be compared to accepted values. Reference*:

<http://www.nist.gov/srd/upload/jpcrd382009565p.pdf>

final state $n_2 l_2 m_{l2}$	initial state $n_1 l_1 m_{l1}$	lifetime t_L (ns) web*	lifetime t_L (ns) simulation	I_{Px}	I_{Py}	I_{Pz}	E_{B2} (eV)	E_{B1} (eV)	λ (nm)
Forbidden transitions $\Delta l \neq 1$									
1s (1 0 0)	2s (2 0 0)	$\sim \infty$	$\sim \infty$	0	0	0	13.58	3.40	
1s (1 0 0)	3s (3 0 0)	$\sim \infty$	$\sim \infty$	0	0	1	13.58	1.51	
1s (1 0 0)	3d (3 2 0)	$\sim \infty$	$\sim \infty$	0	0	0	13.58	1.51	
1s (1 0 0)	3d (3 2 1)	$\sim \infty$	$\sim \infty$	0.5	0	0	13.58	1.51	
1s (1 0 0)	3d (3 2 2)	$\sim \infty$	$\sim \infty$	0	0	0	13.58	1.51	
3p (3 1 1)	4f (4 3 0)	$\sim \infty$	$\sim \infty$	0.5	0	0	1.51	0.85	
Forbidden transitions $\Delta m_l \neq 0$ or 1									
3d (3 2 0)	4d (4 3 2)	$\sim \infty$	$\sim \infty$	0	0	0	1.51	0.85	1877
Allowed transitions $\Delta l = 1$ and $\Delta m_l = 0$ or 1									
1s (1 0 0)	2p (2 1 0)	1.60	1.60	0	0	1	13.58	3.40	122
1s (1 0 0)	2p (2 1 1)		1.60	0.5	0	0	13.58	3.40	122
1s (1 0 0)	3p (3 1 0)	5.98	6.00	0	0	1	13.58	1.51	102
1s (1 0 0)	3p (3 1 1)		6.00	0.5	0	0	13.58	1.51	102
1s (1 0 0)	4p (4 1 0)	14.5	12.1	0	0	1	13.58	0.85	97
2s (2 0 0)	3p (3 1 0)	44.5	44.6	0	0	1	3.40	1.51	658
2s (2 0 0)	3p (3 1 1)		44.6	0.5	0	0	3.40	1.51	658
2s (2 0 0)	4p (4 1 0)	103.4	103.5	0	0	1	3.40	0.85	487
2s (2 0 0)	4p (4 1 1)		103.5	0.5	0	0	3.40	0.85	487
2p (2 1 0)	3s (3 0 0)	475	478	0	0	1	3.40	1.51	657
2p (2 1 1)	3s (3 0 0)		478	0.5	0	0	3.40	1.51	657
2p (2 1 0)	3d (3 2 0)		23.3	0	0	1	3.40	1.51	657
2p (2 1 0)	3d (3 2 1)		31.0	0.5	0	0	3.40	1.51	657
2p (2 1 1)	3d (3 2 0)		93.1	0.5	0	0	3.40	1.51	657
2p (2 1 1)	3d (3 2 1)		31.0	0	0	1	3.40	1.51	657
2p (2 1 0)	4s (4 0 0)	1171	1168	0	0	1	3.40	0.85	487
2p (2 1 1)	4s (4 0 0)		1168	0.5	0	0	3.40	0.85	487

From Table 1, it is quite clear that not all transitions give rise to spectral emissions where spectral lines are not observed or very weak. For the case of dipole radiation, the transition rates are zero when the dipole matrix elements are zero. This gives rise to a set of **selection rules** which are conditions on the quantum numbers of the eigenfunctions of the initial state (state 1) and the final state (state 2) energy levels. For the dipole radiation, allowed transitions ($p \neq 0$) are given by the selection rules

$$\text{Allowed transitions} \quad (\Delta l = \pm 1) \quad \text{and} \quad (\Delta m_l = 0 \quad \text{or} \quad \Delta m_l = \pm 1)$$

Transitions rates of atom are typically $R_t \sim 10^8 \text{ s}^{-1}$.

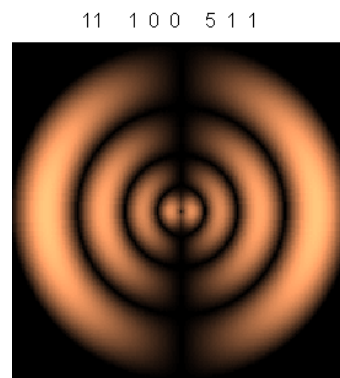
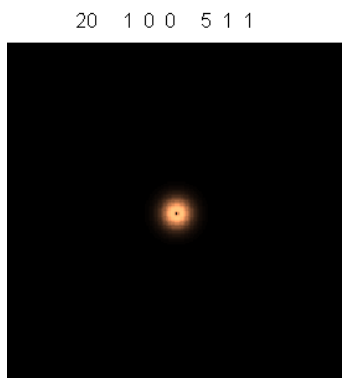
If these conditions are **not** satisfied, $p = 0$ and the transition is called **forbidden**.

Selection rules arise because of the symmetry properties of the oscillating charge distribution of the atom. The compound state formed by the superposition of two stationary states must have an oscillating charge distribution which oscillates at the same frequency of the emitted photon. Also, for the system of the atom and the emitted photon, angular momentum must be conserved. The angular momentum of the emitted photon in units of \hbar is one, hence the change in the angular momentum quantum number of the atom should be $\Delta l = \pm 1$.

Selection rules do not absolutely prohibit transitions that violate them, but only make such transitions very unlikely. The transition may occur through some other mechanism such as magnetic dipole moment radiation or electric quadrupole moment radiation.

From the links below, you can view schematic animations of compound states showing the variation in electron probability for the oscillations between two stationary states. The animations were created with the mscript **qp_rules.m**. Two frames of one of the animations are shown below

Transitions	Type of animated plot	
$(1\ 0\ 0) \Leftrightarrow (5\ 1\ 1)$	pcolor	surf
$(3\ 2\ 0) \Leftrightarrow (4\ 1\ 1)$	pcolor	surf
$(2\ 0\ 0) \Leftrightarrow (3\ 1\ 0)$	pcolor	surf



A summary of the numerical quantities is shown in a Figure Window

Initial State (n l m_l) 400

Binding Energy E_B = 0.817 eV

Final State (n l m_l) 211

Binding Energy E_B = 3.398 eV

Photon wavelength λ = 480.6 nm

Integral I_P = 0.5000 -0.0000 -0.0000

Integral I_T = -0.8165 -0.8165 0.0000

Integral I_R = 2.227e-11 2.227e-11 2.227e-11

Integral I_{xyz} = -9.092e-12 3.991e-30 -2.958e-45

Transition Rate T_R = 1.077e+06 s⁻¹

Lifetime t_L = 928.312 ns

Reference

<http://farside.ph.utexas.edu/teaching/qmech/Quantum/node122.html>

<https://www.nist.gov/sites/default/files/documents/srd/jpcrd382009565p.pdf>

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