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[disclaimer]

# physics606 – Advanced Quantum Theory

## Problem Set 7

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## 1 Rate for (nP) to (n'S) transitions

### 1.1 Orthogonality

2.12

Given is the wave vector

$$\mathbf{k}_\gamma = k_\gamma \begin{pmatrix} \sin(\theta_\gamma) \sin(\phi_\gamma) \\ \sin(\theta_\gamma) \cos(\phi_\gamma) \\ \cos(\theta_\gamma) \end{pmatrix}$$

where we have used the notation where a vector in non-bold type is its absolute value, consistent with its look as a scalar. We hope this becomes apparent on this ink jet printout. Then there are also two polarization basis vectors given:

$$\epsilon_1 = \begin{pmatrix} \cos(\phi_\gamma) \\ -\sin(\phi_\gamma) \\ 0 \end{pmatrix}, \quad \epsilon_2 = \begin{pmatrix} \cos(\theta_\gamma) \sin(\phi_\gamma) \\ \cos(\theta_\gamma) \cos(\phi_\gamma) \\ -\cos(\theta_\gamma) \end{pmatrix}.$$

Checking for orthonormality among the  $\epsilon_i$  is  $X - X = 0$ . We done that, it checks out. It is also easy to see that  $\epsilon_1 \mathbf{k}_\gamma = 0$ . The last one requires application of the so called trigonometric identities. We present all the steps here in painstaking detail:

$$\epsilon_2 \mathbf{k}_\gamma = \cos(\theta_\gamma) \sin(\theta_\gamma) \sin(\phi_\gamma)^2 + \sin(\theta_\gamma) \cos(\theta_\gamma) \cos(\phi_\gamma)^2 - \sin(\theta_\gamma) \cos(\theta_\gamma)$$

The first two terms contain common factors. We factor those out to get a more compact expression.

$$= \cos(\theta_\gamma) \sin(\theta_\gamma) [\sin(\phi_\gamma)^2 + \cos(\phi_\gamma)^2] - \sin(\theta_\gamma) \cos(\theta_\gamma)$$

Here we use  $\sin(\phi_\gamma)^2 + \cos(\phi_\gamma)^2 = 1$ . This leaves us with

$$= \cos(\theta_\gamma) \sin(\theta_\gamma) - \sin(\theta_\gamma) \cos(\theta_\gamma).$$

After using commutation law of the product we have to equal terms. They cancel each other and just gives us

$$= 0.$$

The more interesting question, which was not asked in this problem, is “Why do the polarization vectors have to be perpendicular to the wave vector?”. This is because electromagnetic radiation is vector-polarized and a transverse wave. Therefore the polarization is perpendicular to the direction of propagation. This also means that the photon has spin 1. Gravitational waves are tensor-polarized and the graviton would have spin 2.

## 1.2 Angular part of integrands

2/2

We begin by copying the terms.

$$\begin{aligned} \mathbf{x}_e \epsilon_1 &= r_e \begin{pmatrix} \sin(\theta_e) \sin(\phi_e) \\ \sin(\theta_e) \cos(\phi_e) \\ \cos(\theta_e) \end{pmatrix} \begin{pmatrix} \cos(\phi_\gamma) \\ -\sin(\phi_\gamma) \\ 0 \end{pmatrix} \\ &= r_e [\sin(\theta_e) \sin(\phi_e) \cos(\phi_\gamma) - \sin(\theta_e) \sin(\phi_e) \sin(\phi_\gamma)] \\ &= r_e \sin(\theta_e) [\sin(\phi_e) \cos(\phi_\gamma) - \sin(\phi_e) \sin(\phi_\gamma)] \end{aligned}$$

Now we apply the addition theorem.

$$= r_e \sin(\theta_e) \sin(\phi_e - \phi_\gamma)$$

The second one is very similar.

$$\begin{aligned} \mathbf{x}_e \epsilon_2 &= r_e \begin{pmatrix} \sin(\theta_e) \sin(\phi_e) \\ \sin(\theta_e) \cos(\phi_e) \\ \cos(\theta_e) \end{pmatrix} \begin{pmatrix} \cos(\theta_\gamma) \sin(\phi_\gamma) \\ \cos(\theta_\gamma) \cos(\phi_\gamma) \\ -\cos(\theta_\gamma) \end{pmatrix} \\ &= r_e [\sin(\theta_e) \sin(\phi_e) \cos(\theta_\gamma) \sin(\phi_\gamma) + \sin(\theta_e) \cos(\phi_e) \cos(\theta_\gamma) \cos(\phi_\gamma) - \cos(\theta_e) \sin(\theta_\gamma)] \end{aligned}$$

We also apply the addition theorem here.

$$= r_e [\sin(\theta_e) \cos(\theta_\gamma) \cos(\phi_e - \phi_\gamma) - \cos(\theta_e) \sin(\theta_\gamma)]$$

## 1.3 Evaluation of the integrals

Now we got the middle of the bracket in terms of the angles. Next are initial and final states. Since there are a lot of combinations of  $m_i$  and  $\epsilon$ , we will do this in sections.

The final state is only trivial, because we are looking at the radial part of the wave function of  $l = 0$  states (the S-orbital)! That is spherically symmetric. ✓

The radial part,  $r_e$  will be set to 1 here. Since part five of this problem takes care of the radial part, we will only look at the angular part here. Luckily, radial and angular part are independent, so that the actual transition rates are the product of both: ✓

$$\Gamma_{fi} = \Gamma_{fi}^{\text{radial}} \Gamma_{fi}^{\text{angular}}, \quad \mathcal{M}_{fi} = \mathcal{M}_{fi}^{\text{radial}} \mathcal{M}_{fi}^{\text{angular}}.$$

In this part, we will take care of all the factors from the equation, such that in part five we only have to carry the factors that come from the Laguerre polynomials later on.

1.3.1 Case  $\epsilon = \epsilon_1$

Case  $m_i = 0$  We start by calculating the matrix element

$$\mathcal{M}_{fi}^{\text{angular}} = -\frac{\omega_{if}}{c} \langle f | \epsilon_1 \mathbf{x}_e | i \rangle.$$

In the first step, we insert the knowns.  $\langle f |$  just gives a factor. The scalar product is inserted,  $r_e$  is omitted since this belongs to the radial part.  $|i\rangle$  gives us a factor, the exponential function is 1 since  $m_i = 0$  is assumed. In  $f$ , we get another  $\cos(\theta_e)$  and a factor.

$$= -\frac{\sqrt{3}}{4\pi} \frac{\omega_{if}}{c} \int_{\Omega_e} d\Omega_e \sin(\theta_e) \sin(\phi_e - \phi_\gamma) \cos(\theta_e)$$

*if final state  $\langle f | \rightarrow 2$  but not  $\langle f | \rightarrow \frac{1}{\sqrt{4\pi}}$  &  $|i\rangle \rightarrow \sqrt{\frac{3}{8\pi}} \dots \Rightarrow$  how the denom. is  $4\pi$ ? it should be  $\sqrt{4\pi}$ !*

The volume element is  $d\Omega = d\theta d\phi \sin(\theta)$ .

$$= -\frac{\sqrt{3}}{4\pi} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \int_0^{2\pi} d\phi_e \sin(\theta_e)^2 \sin(\phi_e - \phi_\gamma) \cos(\theta_e)$$

We move the second integral as far back as possible.

$$= -\frac{\sqrt{3}}{4\pi} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e)^2 \cos(\theta_e) \int_0^{2\pi} d\phi_e \sin(\phi_e - \phi_\gamma)$$

The last integral will give zero.

$$= 0 \quad \checkmark$$

From this,  $\Gamma_{if}^{\text{radial}} = 0$  as well.

Case  $|m_i| = 1$  For this case, we start similarly.

$$\mathcal{M}_{fi}^{\text{angular}} = -m_i \frac{\omega_{if}}{c} \langle f | \epsilon_1 \mathbf{x}_e | i \rangle.$$

$|i\rangle$  gives us the exponential function. In  $f$ , we get another  $m_i \sin(\theta_e)$ . There are three  $\sin(\theta_e)$ , one from the integration measure, one from  $f$  and another from  $\epsilon_1 \mathbf{x}_e$ .

$$= m_i \frac{\sqrt{3}}{4\pi\sqrt{2}} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \int_0^{2\pi} d\phi_e \sin(\theta_e)^3 \sin(\phi_e - \phi_\gamma) \exp(-im_i \phi_e)$$

We do the same reordering.

$$= m_i \frac{\sqrt{3}}{4\pi\sqrt{2}} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e)^3 \int_0^{2\pi} d\phi_e \sin(\phi_e - \phi_\gamma) \exp(-im_i \phi_e)$$

The first and second integral are completely independent now. We just insert the result for the first one, 4/3, to get a bit more space on the line without loosing the chain of equalities.

$$= m_i \frac{1}{\pi\sqrt{6}} \frac{\omega_{if}}{c} \int_0^{2\pi} d\phi_e \sin(\phi_e - \phi_\gamma) \exp(-im_i\phi_e)$$

Now we expand the sine in terms of the exponential functions.

$$= m_i \frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \int_0^{2\pi} d\phi_e [\exp(i[\phi_e - \phi_\gamma]) - \exp(-i[\phi_e - \phi_\gamma])] \exp(-im_i\phi_e)$$

The last exponential can be moved into the first two.

$$= m_i \frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \int_0^{2\pi} d\phi_e [\exp(i[[1 - m_i]\phi_e - \phi_\gamma]) - \exp(-i[[1 + m_i]\phi_e - \phi_\gamma])] ]$$

From here, we have to discuss two cases. In either case, only one of the most inner square brackets will be nonzero.

**Sub case**  $m_i = 1$

$$\mathcal{M}_{fi}^{\text{angular}} = \frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \int_0^{2\pi} d\phi_e [\exp(-i\phi_\gamma) - \exp(-i[2\phi_e - \phi_\gamma])]$$

We use the linearity in the integration.

$$= \frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \left[ \int_0^{2\pi} d\phi_e \exp(-i\phi_\gamma) - \int_0^{2\pi} d\phi_e \exp(-i[2\phi_e - \phi_\gamma]) \right]$$

The first integrand does not depend on the integration variable, the integral is therefore trivial. In the second integral, we pull out the term that does not depend on the integration variable.

$$= \frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \left[ 2\pi \exp(-i\phi_\gamma) - \exp(i\phi_\gamma) \int_0^{2\pi} d\phi_e \exp(-2i\phi_e) \right]$$

The last integral will give zero, since the exponential will give 1 at 0 and  $2\pi$ . Only the first term will contribute.

$$= \frac{1}{i\sqrt{6}} \frac{\omega_{if}}{c} \exp(-i\phi_\gamma)$$

with  $\int_0^{2\pi} \sin(\phi_e - \phi_\gamma) e^{-i\phi_e} d\phi_e = -i\pi e^{-i\phi_\gamma}$   
 only an extra '2' factor difference (I did not get why)

**Sub case**  $m_i = -1$  Here, the terms are the other way around.

$$\mathcal{M}_{fi}^{\text{angular}} = -\frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \int_0^{2\pi} d\phi_e [\exp(i[2\phi_e - \phi_\gamma]) - \exp(i\phi_\gamma)]$$

We use the same linearity.

$$= -\frac{1}{2i\pi\sqrt{6}} \frac{\omega_{if}}{c} \left[ \int_0^{2\pi} d\phi_e \exp(i[2\phi_e - \phi_\gamma]) - \int_0^{2\pi} d\phi_e \exp(i\phi_\gamma) \right]$$

We do the same steps, the first integral will yield zero. The second gives an additional factor of  $2\pi$ .

$$= \frac{1}{i\sqrt{6}} \frac{\omega_{if}}{c} \exp(i\phi_\gamma) \quad \text{same here} \quad \int_0^{2\pi} \sin(\phi_e - \phi_\gamma) e^{+i\phi_e} d\phi_e = i\pi e^{i\phi_\gamma}$$

We can now see that the two results we have are almost complex conjugates. Their absolute value will be the same. We continue to compute the transition ratio.

$$\Gamma_{fi}^{\text{angular}} = \frac{\alpha}{2\pi} \omega_{if} \int d\Omega_\gamma \left| \mathcal{M}_{fi}^{\text{angular}} \right|^2.$$

The modulus squared of the matrix element does not have any angular dependence now. The angular integration will yield a factor of  $4\pi$ .

$$= \frac{\alpha}{3c^2} \omega_{if}^3 \quad \text{same with that extra factor of 2 difference}$$

### 1.3.2 Case $\epsilon = \epsilon_2$

**Case  $m_i = 0$**  We start by calculating the matrix element

$$\mathcal{M}_{fi}^{\text{angular}} = -\frac{\omega_{if}}{c} \langle f | \epsilon_2 \mathbf{x}_e | i \rangle.$$

In the first step, we insert the knowns.  $\langle f |$  just gives a factor. The scalar product is inserted.  $|i\rangle$  gives us a factor, the exponential function is 1 since  $m_i = 0$  is assumed. In  $f$ , we get another  $\cos(\theta_e)$  and a factor.

$$= -\frac{\sqrt{3}}{4\pi} \frac{\omega_{if}}{c} \int d\Omega_e \left[ \sin(\theta_e) \cos(\theta_\gamma) \cos(\phi_e - \phi_\gamma) - \cos(\theta_e) \sin(\theta_\gamma) \right] \cos(\theta_e)$$

The volume element is  $d\Omega = d\theta d\phi \sin(\theta)$ . We insert this.

$$= -\frac{\sqrt{3}}{4\pi} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e) \cdot \int_0^{2\pi} d\phi_e \left[ \sin(\theta_e) \cos(\theta_\gamma) \cos(\phi_e - \phi_\gamma) - \cos(\theta_e) \sin(\theta_\gamma) \right] \cos(\theta_e)$$

The integral over  $\phi_e$  will give zero for the first summand in the square bracket. For the second, it will just contribute a factor of  $2\pi$  since there is no dependence on  $\phi_e$ .

$$= \frac{\sqrt{3}}{2} \frac{\omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e) \cos(\theta_e)^2$$

This integral can be solved using the substitution  $z := \cos(\theta_e)$  and gives the value  $2/3$ . Our final result is

$$= \frac{1}{\sqrt{3}} \frac{\omega_{if}}{c}$$

From here, we compute the rate

$$\Gamma_{fi}^{\text{radial}} = \frac{\alpha}{2\pi} \omega_{if} \int d\Omega_\gamma \left| \mathcal{M}_{fi}^{\text{angular}} \right|^2.$$

We insert our previous result

$$= \frac{\alpha}{2\pi} \omega_{if} \int d\Omega_\gamma \left| \frac{1}{\sqrt{3}} \frac{\omega_{if}}{c} \sin(\theta_\gamma) \right|^2$$

and simplify

$$= \frac{\alpha}{6\pi} \frac{\omega_{if}^3}{c^2} \int d\Omega_\gamma \sin(\theta_\gamma)^2.$$

The integration has to be rewritten in terms of the chosen coordinates, the spherical polar coordinates. We already carry out the integration in  $\phi_\gamma$  which only gives a factor  $2\pi$ .

$$= \frac{\alpha}{3} \frac{\omega_{if}^3}{c^2} \int d\theta_\gamma \sin(\theta_\gamma)^3.$$

This integral can be solved with the power reduction formulas. Those can be derived using the binomial theorem and the exponential representation of the sine. All in all, the integral is  $4/3$ . That gives the final result for this choice of  $\epsilon$  and  $m_i$ .

$$= \frac{4\alpha}{9c^2} \omega_{if}^3$$

**Case**  $|m_i| = 1$

$$\begin{aligned} \mathcal{M}_{fi}^{\text{angular}} &= \frac{\sqrt{3}}{4\pi\sqrt{2}} \frac{m_i \omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e)^2 \int_0^{2\pi} d\phi_e \exp(im_i \phi_e) \\ &\quad \cdot [\sin(\theta_e) \cos(\theta_\gamma) \cos(\phi_e - \phi_\gamma) - \cos(\theta_e) \sin(\theta_\gamma)] \end{aligned}$$



The second summand in the square bracket will be integrated away because of the periodic exponential function. Only the first summand will contribute.

$$= \frac{\sqrt{3}}{4\pi\sqrt{2}} \frac{m_i \omega_{if}}{c} \int_0^\pi d\theta_e \sin(\theta_e)^2 \int_0^{2\pi} d\phi_e \exp(im_i \phi_e) \sin(\theta_e) \cos(\theta_\gamma) \cos(\phi_e - \phi_\gamma)$$

We reorder again,

$$= \frac{\sqrt{3}}{4\pi\sqrt{2}} \frac{m_i \omega_{if}}{c} \cos(\theta_\gamma) \int_0^\pi d\theta_e \sin(\theta_e)^3 \int_0^{2\pi} d\phi_e \exp(im_i \phi_e) \cos(\phi_e - \phi_\gamma)$$

From the previous integrals, we already know that the  $\theta_e$  integral will give  $4/3$ .

$$= \frac{m_i \omega_{if}}{\pi\sqrt{6}c} \cos(\theta_\gamma) \int_0^{2\pi} d\phi_e \exp(im_i \phi_e) \cos(\phi_e - \phi_\gamma)$$

Now we have enough space to combine the exponential function and the cosine.

$$= \frac{m_i \omega_{if}}{2\pi\sqrt{6}c} \cos(\theta_\gamma) \int_0^{2\pi} d\phi_e [\exp(i[[m_i + 1]\phi_e - \phi_\gamma]) + \exp(i[[m_i - 1]\phi_e - \phi_\gamma])]$$

We have to look at the cases again. They will only differ by a sign that does not make any difference later on in the transition rate. Without loss of generality, we will choose  $m_i = 1$ . The first term will again be integrated away due to the periodicity. Only the second term will give a contribution. That is constant, so it is just the term times  $2\pi$ , as in the other cases.

$$= \frac{m_i \omega_{if}}{\sqrt{6}c} \cos(\theta_\gamma) \exp(-i\phi_\gamma)$$

From here, we compute the transition rate.

$$\Gamma_{fi}^{\text{angular}} = \frac{\alpha \omega_{if}^3}{12\pi c^2} \int_{\Omega_\gamma} d\Omega_\gamma \cos(\theta_\gamma)^2$$

We insert the coordinates and perform the integration over  $\phi_e$  which gives us  $2\pi$ .

$$= \frac{\alpha \omega_{if}^3}{6c^2} \int_0^\pi d\theta_\gamma \sin(\theta_\gamma) \cos(\theta_\gamma)^2$$

We know this integral already as well, it is  $2/3$ .

$$= \frac{\alpha}{9c^2} \omega_{if}^3$$

**1.3.3 Summary**

Here we summarize the values that we have computed.

$\Gamma_{fi}^{\text{angular}} / \frac{\alpha\omega_{if}^3}{c^2}$	$m_i = 0$	$m_i = 1$	$m_i = -1$
$\epsilon_1$	0	$\frac{1}{3}$	$\frac{1}{3}$
$\epsilon_2$	$\frac{4}{9}$	$\frac{1}{9}$	$\frac{1}{9}$

We find it a little strange that only the cases  $|m_i| \leq 1$  were taken into account. The 3P orbital would allow for  $l = 2$  and therefore also  $|m_i| \leq 2$ . Later, we compute the transitions of (3P) to something else, where we would think that the  $|m_i| = 2$  cases would have to be included.

**1.4 Summation of contributions**

**Problem statement**

In order to compute the total decay rate, the contributions from both polarization states of the photon have to be added incoherently (why?).

The decays of different polarizations are independent of each other. The photons themselves might interfere if they are emitted at the same time from neighboring atoms, but that does not change the rates. ✓

**Problem statement**

Show that after this summation, which simply means adding the two contributions evaluated in the previous step, the decay rate is independent of  $m_i$ .

We just need to add the columns in the summary table that we have compiled earlier:

$\Gamma_{fi}^{\text{angular}} / \frac{\alpha\omega_{if}^3}{c^2}$	$m_i = 0$	$m_i = 1$	$m_i = -1$
$\epsilon_1$	0	$\frac{1}{3}$	$\frac{1}{3}$
$\epsilon_2$	$\frac{4}{9}$	$\frac{1}{9}$	$\frac{1}{9}$
Total	$\frac{4}{9}$	$\frac{4}{9}$	$\frac{4}{9}$

One can see that each column has the same total. ✓

**Problem statement**

Give a physical reason for this result.

When the atom is in a state that has a certain orientation as given by the  $m$ , which is  $L_z/\hbar$ , it has certain emission characteristics. It cannot emit light in any direction. However, when all values of  $\epsilon$ —and therefore all orientations in space—are accounted for, the emitted light has to go somewhere. Therefore it is independent of the orientation  $m_i$  of the emitting orbital. ✓

### 1.5 Radial part

As hinted in the third part of this problem, we took care of all the factors in equations (1) and (2) from the problem set already in the angular part. The radial part will then only have these equations:

$$\Gamma_{fi}^{\text{radial}} = \int_{\Omega_f} d\Omega_f \left| \mathcal{M}_{fi}^{\text{radial}} \right|^2, \quad \mathcal{M}_{fi}^{\text{radial}} = \langle f | r_e | i \rangle$$

#### Problem statement

Prove (by induction) and use the following result when evaluation the integrals:

$$\int_0^\infty dx x^n \exp\left(-\frac{x}{x_0}\right) = n! x_0^{n+1}.$$

*Proof.* We first show that this holds for  $n = 0$ .

$$\int_0^\infty dx \exp\left(-\frac{x}{x_0}\right) = \left[ -x_0 \exp\left(-\frac{x}{x_0}\right) \right]_0^\infty = x_0$$

Next is the induction step. We start with the left hand side at  $n + 1$  and try to recover the right hand side at  $n + 1$  by using the equation at  $n$ .

$$\text{LHS}(n + 1) = \int_0^\infty dx x^{n+1} \exp\left(-\frac{x}{x_0}\right)$$

Now we use partial integration.


$$= \left[ -x_0 n^{x+1} \exp\left(-\frac{x}{x_0}\right) \right]_0^\infty + [n + 1] x_0 \int_0^\infty dx x^n \exp\left(-\frac{x}{x_0}\right)$$

The surface term vanishes.

$$= [n + 1] x_0 \int_0^\infty dx x^n \exp\left(-\frac{x}{x_0}\right)$$

Now we use the theorem at  $n$ .

$$\begin{aligned} &= [n + 1] x_0 n! x_0^{n+1} \\ &= [n + 1]! x_0^{[n+1]+1} \\ &= \text{RHS}(n + 1) \end{aligned}$$

By the principle of induction, this equation holds for any  $n \geq 0$ . 

□

**1.5.1 Transition (2P) → (1S)**

The radial part of the matrix element is

$$\mathcal{M}_{fi}^{\text{radial}} = \int_0^{\infty} dr_e r_e^2 r_e R_{21}(r_e) R_{10}(r_e).$$

The first  $r_e^2$  comes from the integration measure, the second  $r_e$  comes from the bracket that we are supposed to compute. Another one will come from  $R_{21}$ . Then there are the radial wave functions according to the Hilbert  $L^2$  scalar product. Since they are completely real, the complex conjugation does not have any effect. We insert the wave functions.

$$= \frac{2}{a_0^{3/2}} \frac{1}{2\sqrt{6}a_0^{5/2}} \int_0^{\infty} dr_e r_e^4 \exp\left(-\frac{r_e}{a_0}\right) \exp\left(-\frac{r_e}{2a_0}\right)$$

Before we look at the integration, we simplify everything.

$$= \frac{1}{\sqrt{6}a_0^4} \int_0^{\infty} dr_e r_e^4 \exp\left(-\frac{3r_e}{2a_0}\right)$$

To apply the formula we just proved, we move the factor 3 into the denominator.

$$= \frac{1}{\sqrt{6}a_0^4} \int_0^{\infty} dr_e r_e^4 \exp\left(-\frac{r_e}{\frac{2}{3}a_0}\right)$$

Now we apply the theorem ...

$$= \frac{1}{\sqrt{6}a_0^4} 4! \left[\frac{2}{3}a_0\right]^5$$

... and simplify again.

$$= \frac{2^8}{3^4 \sqrt{6}} a_0$$

$$\approx 1.290 a_0$$

The transition rate is this squared:

$$\Gamma_{fi}^{\text{radial}} = \frac{2^{15}}{3^9} a_0^2 \approx 1.665 a_0^2$$

**1.5.2 Transition (3P) → (1S)**

This one works similarly.

$$\mathcal{M}_{fi}^{\text{radial}} = \int_0^\infty dr_e r_e^2 r_e R_{31}(r_e) R_{10}(r_e)$$

We insert the Laguerre polynomials.

$$= \frac{2}{a_0^{3/2}} \frac{4\sqrt{2}}{27\sqrt{3} a_0^{5/2}} \int_0^\infty dr_e r_e^4 \exp\left(-\frac{r_e}{a_0}\right) \left[1 - \frac{r_e}{6a_0}\right] \exp\left(-\frac{r_e}{3a_0}\right)$$

Then we simplify as much as possible, bringing it into a form that makes the application of the theorem easy.

$$= \frac{2^3 \sqrt{2}}{3^3 \sqrt{3} a_0^4} \int_0^\infty dr_e \left[ r_e^4 - \frac{r_e^5}{6a_0} \right] \exp\left(-\frac{r_e}{\frac{3}{4}a_0}\right)$$

Applying the theorem ...

$$= \frac{2^3 \sqrt{2}}{3^3 \sqrt{3} a_0^4} \left[ 4! \left[\frac{3}{4}a_0\right]^5 - \frac{5!}{6a_0} \left[\frac{3}{4}a_0\right]^6 \right]$$

The order of  $a_0$  is the same in both terms, we can pull this out.

$$= \frac{2^3 \sqrt{2}}{3^3 \sqrt{3}} \left[ 4! \left[\frac{3}{4}\right]^5 - \frac{5!}{6} \left[\frac{3}{4}\right]^6 \right] a_0$$

*For the amplitude, when you square this exp. there is an extra  $h^2$  suppression w.r.t.  $2P \rightarrow 1S$*   
 $\Downarrow$   
 $P_i \sim 0.267 a_0^2$

We used Maxima to simplify this.

$$\approx -\frac{1199}{27 \cdot 2 \cdot 3^{3/2}} a_0 \approx -20.395 a_0$$

*$\frac{27}{129} \sqrt{6} a_0$*

The transition rate is this squared:

$$\Gamma_{fi}^{\text{radial}} = \frac{1437601}{3456} a_0^2 \approx 415.973 a_0^2$$

**1.5.3 Transition (3P) → (2S)**

This one is the most convoluted one to compute.

$$\mathcal{M}_{fi}^{\text{radial}} = \int_0^\infty dr_e r_e^2 r_e R_{31}(r_e) R_{20}(r_e)$$

Inserting the Laguerre polynomials.

$$= \frac{1}{\sqrt{2} a_0^{5/2}} \frac{4\sqrt{2}}{27\sqrt{3} a_0^{5/2}} \int_0^\infty dr_e r_e^5 \left[1 - \frac{r_e}{2a_0}\right] \left[1 - \frac{r_e}{6a_0}\right] \exp\left(-\frac{r_e}{2a_0}\right) \exp\left(-\frac{r_e}{3a_0}\right)$$

We simplify a bit.

$$= \frac{4}{27\sqrt{3} a_0^5} \int_0^\infty dr_e r_e^5 \left[1 - \frac{r_e}{2a_0}\right] \left[1 - \frac{r_e}{6a_0}\right] \exp\left(-\frac{r_e}{6a_0}\right)$$

Now we factor out the square brackets.

$$= \frac{4}{27\sqrt{3} a_0^5} \int_0^\infty dr_e \left[ r_e^5 - \frac{r_e^6}{6a_0} - \frac{r_e^6}{2a_0} + \frac{r_e^7}{12a_0^2} \right] \exp\left(-\frac{r_e}{6a_0}\right)$$

We combine the middle summands.

$$= \frac{4}{27\sqrt{3} a_0^5} \int_0^\infty dr_e \left[ r_e^5 - \frac{2r_e^6}{3a_0} + \frac{r_e^7}{12a_0^2} \right] \exp\left(-\frac{r_e}{6a_0}\right)$$

$$= \frac{4}{27\sqrt{3} a_0^5} \left[ 5! [6a_0]^6 - \frac{6!}{6a_0} [6a_0]^7 + \frac{7!}{12a_0^2} [6a_0]^8 \right]$$

The order of  $a_0$  is the same in each term, we pull this out.

$$= \frac{4}{27\sqrt{3}} \left[ 5! 6^6 - \frac{6!}{6} 6^7 + \frac{7!}{12} 6^8 \right] a_0$$

We simplify with Maxima as well.

$$= 1\,239\,040 \cdot 3^{7/2} a_0$$

$$\approx 5.794 \times 10^7 a_0$$

The transition rate is this squared:

$$\Gamma_{fi}^{\text{radial}} = 3\,357\,526\,405\,939\,200 a_0^2 \approx 3.358 \times 10^{15} a_0^2$$

*seemed very huge to me*

### 1.5.4 Comparison

#### Problem statement

You should find that the matrix element for (2P) → (1S) transitions is significantly *larger* than that for (3P) → (1S) transitions. [...]. (3P) → (2S) transitions have the largest matrix element.

Just looking at this radial part, where we have taken out all the factors from the angular part, we do see that the last transition does have the largest matrix element. However, the first should be

larger than the second, and we got it the other way around. Since the factors from the angular parts are all the same, this must be wrong.

Here we collected all the transition rates that we have computed.

Transition	$\Gamma_{fi}^{\text{radial}}/a_0^2$
(2P) → (1S)	1.665
(3P) → (1S)	415.973
(3P) → (2S)	$3.358 \times 10^{15}$

### 1.6 Complete transition rate

The factors  $\omega_{if}$  can be computed like so:

$$\frac{E_i - E_f}{\hbar}$$

The energies of the hydrogen atom are

$$E_n = \frac{E_{\text{Ryd}}}{n^2}$$

Using all this, we can write the angular frequency as

$$\omega_{if} = \frac{E_{\text{Ryd}}}{\hbar} \left[ \frac{1}{i^2} - \frac{1}{f^2} \right]$$

The factor we are looking for is:

$$\frac{\omega_{13}}{\omega_{12}} = \frac{\frac{1}{1^2} - \frac{1}{3^2}}{\frac{1}{1^2} - \frac{1}{2^2}} = \frac{1 - \frac{1}{9}}{1 - \frac{1}{4}} = \frac{\frac{8}{9}}{\frac{3}{4}} = \frac{8 \cdot 4}{9 \cdot 3} = \frac{2^5}{3^3} = \frac{32}{27} \approx 1.185$$

$\frac{0.7}{2.6 \times 10^{-3}}$

The ratio between the angular frequency of (3P) → (1S) and (3P) → (2S) is this cubed,

$$\left[ \frac{\omega_{13}}{\omega_{12}} \right]^3 = \frac{2^{15}}{3^9} \approx 1.66$$

This factor does not change anything though, since it is too small or the transition rates that we have computed are wrong.