Quantum Physics 2011/12

Solutions to Tutorial Sheet 6: Time-Dependence and Pseudopotentials

For the first two problems, you may assume that the hydrogen eigenfunctions are:

$$\begin{aligned} u_{100} &= (\pi a_0^3)^{-1/2} \exp(-r/a_0) \\ u_{211} &= -\left(\pi a_0^3\right)^{-1/2} \frac{r}{8a_0} \sin\theta \exp(i\phi) \exp(-r/2a_0) \\ u_{210} &= \left(8\pi a_0^3\right)^{-1/2} \frac{r}{2a_0} \cos\theta \exp(-r/2a_0) \\ u_{21-1} &= \left(\pi a_0^3\right)^{-1/2} \frac{r}{8a_0} \sin\theta \exp(-i\phi) \exp(-r/2a_0) \end{aligned}$$

and

$$\int_0^\infty \exp(-br)\, r^n \,\mathrm{d}r = n!/b^{n+1}, \quad n > -1$$

1. *A hydrogen atom is placed in a uniform but time-dependent electric field of magnitude*

$$\mathcal{E} = 0 \quad \text{for } t < 0, \qquad \mathcal{E} = \mathcal{E}_0 \exp(-t/\tau) \quad \text{for } t \geq 0 \quad (\tau > 0)$$

where $\mathcal{E}_0$ is a constant. At time $t = 0$, the atom is in the ground ($1s$) state. Show that the probability, to lowest order in perturbation theory, that as $t \to \infty$, the atom is in the $2p$ state in which the component of the orbital angular momentum in the direction of the field is zero, is given by

$$p_{1s\to 2p} = |c(\infty)|^2 = \frac{2^{15}}{3^{10}} \frac{(e\mathcal{E}_0 a_0)^2}{(E_{2p} - E_{1s})^2 + (\hbar/\tau)^2}$$

[**Hint:** *take the field direction to be the z-direction. Write down the potential energy of the electron in the given field and treat as a time-dependent perturbation].*

We will use time-dependent perturbation theory. Since the field decays away exponentially there is only a finite probability that the transition will occur. The approximation from TDPT is that there is no probablity of transition to 2p and back again.

We take the direction of the electric field to be the z-direction, as suggested. Then the perturbation for $t \geq 0$ is

$$\hat{H}'(t) = -e\left(-\mathcal{E}_0 z \exp(-t/\tau)\right)$$

and the transition probability amplitude is

$$c_{1s\to 2p}(t) = (i\hbar)^{-1} \int_0^t \langle 210|\hat{H}'(t')|100\rangle \exp(i\omega t')\,\mathrm{d}t'$$

where $\omega = (E_{2p} - E_{1s})/\hbar$.

Using the given eigenfunctions, the required matrix element is

$$\begin{aligned} \langle 210|\hat{H}'|100\rangle &= e\mathcal{E}_0 \exp(-t/\tau) \langle 210|r\cos\theta|100\rangle \\ &= \frac{e\mathcal{E}_0 \exp(-t/\tau)}{\pi a_0^4 4\sqrt{2}} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r^4 \exp(-3r/2a_0)\,\mathrm{d}r\, \cos^2\theta \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi \end{aligned}$$

The ϕ integration just gives 2π, whilst the θ integration yields

$$\int_{-1}^{+1} \cos^2\theta \, \mathrm{d}(\cos\theta) = \left[\frac{\cos^3\theta}{3}\right]_{-1}^{+1} = \frac{2}{3}$$

The radial integral is

$$\int_0^\infty r^4 \exp(-3r/2a_0)\, \mathrm{d}r = \left(\frac{2a_0}{3}\right)^5 4!$$

from the given integral. Putting it all together

$$\langle 210|\hat{H}'(t)|100\rangle = A\exp(-t/\tau) \quad \text{where} \quad A = \frac{2^{15/2}}{3^5}\, e\mathcal{E}_0 a_0$$

Thus

$$c_{1s\to 2p}(t) = \frac{A}{i\hbar}\int_0^t \exp(-t'/\tau + i\omega t')\, \mathrm{d}t' = \frac{A}{i\hbar}\left[\frac{\exp(i\omega t - t/\tau) - 1}{i\omega - 1/\tau}\right]$$

Thus the desired probability is

$$\boxed{p_{1s\to 2p} = |c(\infty)|^2 = \frac{2^{15}}{3^{10}}\,\frac{(e\mathcal{E}_0 a_0)^2}{(E_{2p} - E_{1s})^2 + (\hbar/\tau)^2}}$$

If we had numbers, for we should now check that this probability is indeed small - if so then we justify our use of TDPT, if not then we know we should solve the problem exactly.

What is the probability that it is in the $2s$-state?

We can write:

$$c_{1s\to 2s}(t) = (i\hbar)^{-1}\int_0^t \langle 200|\hat{H}'(t')|100\rangle \exp(i\omega t')\, \mathrm{d}t'$$

However, we note that the integral over space has an odd function as its integrand: $\langle 200|z|100\rangle$. It is therefore zero, and there is no probability of a $1s \to 2s$ transition to first order.

Remark: As we saw in the Stark effect, a constant field induces a dipole on the atom. This permits *dipole radiation*, i.e. the emission of a single photon. Since a photon has angular momentum $\ell = 1$, conservation of angular momentum tell us it cannot be involved in a transition from an $\ell = 0$ state to another $\ell = 1$. The $1s \to 2s$ transition is allowed at second order, corresponding to the emission of *two* photons of opposite $\ell = \pm 1$.

2. *The neutral kaon states produced by pion decay via the strong interaction are $|K^0\rangle$ and $|\overline{K}^0\rangle$, eigenvalues of strangeness $\hat{S}$ such that $\hat{S}|K^0\rangle = |K^0\rangle$ and $\hat{S}|\overline{K}^0\rangle = -|\overline{K}^0\rangle$. Acting on these states with a weak force-related operator $\hat{CP}$ gives:*

$$CP|K^0\rangle = |\overline{K}^0\rangle; \qquad\qquad CP|\overline{K}^0\rangle = |K^0\rangle$$

Evaluate the CP eigenstates for neutral kaons $|K_1\rangle$ and $|K_2\rangle$ with eigenvalues CP=+1 and CP=-1 respectively.

In the basis of K^0, $\overline{K}^0$ the CP matrix becomes:

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

with eigenvectors $(\sqrt{\frac{1}{2}}, \pm\sqrt{\frac{1}{2}})$, eigenvalues ± 1 corresponding to CP eigenstates:

$$|K_1\rangle = (|K^0\rangle + |\overline{K}^0\rangle)/\sqrt{2}; \qquad |K_2\rangle = (|K^0\rangle - |\overline{K}^0\rangle)/\sqrt{2}$$

Show that the wavefunction $a_1(t) = a_1(0)e^{-t/2\tau}e^{-iEt/\hbar}|\Phi(\mathbf{r})\rangle$, where E is the energy, represents decay with lifetime τ, and that the amplitudes of the $|K_1\rangle$ and the $|K_2\rangle$ states at rest (i.e. with $E = mc^2$) are:

$$a_1(t) = a_1(0)e^{-t/2\tau_1}e^{-im_1c^2t/\hbar} \qquad \text{and} \qquad a_2(t) = a_2(0)e^{-t/2\tau_2}e^{-im_2c^2t/\hbar}$$

The number of particles described by the wavefunction (Intensity) is given by

$$|a_1(t)|^2| = \int d^3\mathbf{r} a_1^*(0)e^{-t/2\tau}e^{iEt/\hbar}\Phi^*(\mathbf{r})a_1(0)e^{-t/2\tau}e^{-iEt/\hbar}\Phi(\mathbf{r}) = |a_1(0)|^2e^{-t/\tau}$$

and the expressions for $a_1(t)$, $a_2(t)$ are obtained by substitution of $E = mc^2$ and the appropriate decay constants.

Show that the intensity of $|K^0\rangle$ is measured by the operator $\frac{1}{2}(\hat{S}+1)$. What is the operator for the intensity of $|\overline{K}^0\rangle$?

Consider a general state $|\phi\rangle = a_0|K^0\rangle + b_0|\overline{K}^0\rangle$

$$\langle\phi|\frac{1}{2}(\hat{S}+1)|\phi\rangle = \frac{1}{2}(1+1)|a_0|^2\langle K^0|K^0\rangle + \frac{1}{2}(-1+1)|b_0|^2\langle\overline{K}^0|\overline{K}^0\rangle + a_0^*b_0\langle K^0|\overline{K}^0\rangle + a_0b_0^*\langle\overline{K}^0|K^0\rangle = |a_0|^2+0+0$$

using the orthogonality relation $\langle K^0|\overline{K}^0\rangle = 0$ The total intensity is proportional to $\langle\phi|\phi\rangle = |a_0|^2 + |b_0|^2$, of which $|a_0|^2$ represents the K^0s.

Similarly, the intensity of $\overline{K}^0$ is $|b_0|^2$. This comes from switching the minus sign in the first two terms, i.e. it is the expectation value of $\frac{1}{2}(1-\hat{S})$

At t=0 a kaon beam is in a pure $|K^0\rangle$ state, with intensity proportional to $|a_0(0)|^2 = 1$ show that at time t

$$|a_0(t)|^2 = \langle\frac{1}{2}(\hat{S}+1)\rangle = \frac{1}{4}\left[e^{-t/\tau_1} + e^{-t/\tau_2} + 2e^{-t/2\tau_1}e^{-t/2\tau_2}\cos(m_{12}t)\right]$$

$$\text{and} \quad I(\overline{K}^0) = \frac{1}{4}\left[e^{-t/\tau_1} + e^{-t/\tau_2} - 2e^{-t/2\tau_1}e^{-t/2\tau_2}\cos(m_{12}t)\right]$$

where $m_{12} = (m_2 - m_1)c^2/\hbar$.

Consider a general state in the K_1, K_2 basis, and the same state in $\overline{K}^0$, K^0 we have:

$$\Phi = a_1|K_1\rangle + a_2|K_2\rangle = a_0|K^0\rangle + b_0|\overline{K}^0\rangle$$

These are two equivalent descriptions of the same system. From above, we have $|a_0|^2 = \frac{1}{2}|a_1 + a_2|^2$ $|b_0|^2 = \frac{1}{2}|a_1 - a_2|^2$

If we assume an initial state pure K^0, unit intensity $1 = |a_0(0)|^2$, $0 = |b_0(0)|^2$ then solving the above gives $a_1(0) = b_1(0) = \sqrt{\frac{1}{2}}$. For the time dependence, we must consider decays of $|K_1\rangle$ and $|K_2\rangle$, thus

$$|a_0(t)|^2 = \frac{1}{2}|a_1(t) + a_2(t)|^2$$

Substituting the time dependent expressions for a_1, a_2

$$\begin{aligned}
|a_0(t)|^2 &= \frac{1}{4}(a_1(0)e^{-t/2\tau_1}e^{im_1c^2t/\hbar} + a_2(0)e^{-t/2\tau_2}e^{im_2c^2t/\hbar}) \times & (1)\\
&\quad (a_1(0)e^{-t/2\tau_1}e^{-im_1c^2t/\hbar} + a_2(0)e^{-t/2\tau_2}e^{-im_2c^2t/\hbar}) & (2)\\
&= \frac{1}{4}\left[e^{-t/\tau_1} + e^{-t/\tau_2} + 2e^{-t/2\tau_1}e^{-t/2\tau_2}(e^{im_{12}t} + e^{-im_{12}t})\right] & (3)\\
&= \frac{1}{4}\left[e^{-t/\tau_1} + e^{-t/\tau_2} + 2e^{-t/2\tau_1}e^{-t/2\tau_2}\cos m_{12}t\right] & (4)
\end{aligned}$$

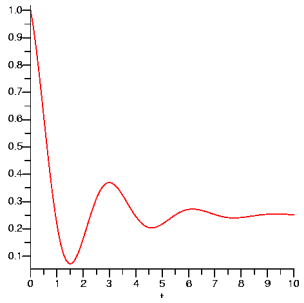
as required. Similarly we obtain:

$$|b_0(t)|^2 = \frac{1}{2}|a_1(t) - a_2(t)|^2$$

$$|b_0(t)|^2 = \langle\frac{1}{2}(\hat{S}+1)\rangle = \frac{1}{4}|a_0(0)|^2\left[e^{-t/\tau_1} + e^{-t/\tau_2} - 2e^{-t/2\tau_1}e^{-t/2\tau_2}\cos(m_{12}t)\right]$$

Sketch, as a function of time, the expectation values of: $\frac{1}{2}(\hat{S}+1)$, $\hat{S}$, $\hat{S}^2$, $\hat{CP}$, $\frac{1}{2}(\hat{CP}+1)$ *in a system which began in state* $|K^0\rangle$. For the sake of the plots, we take units where $1/2\tau_1 = m_{12} = 1$, $|a_0(t)|^2 = 1$

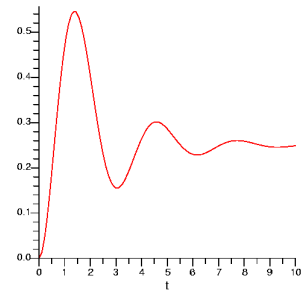
the expectation value for number of $|K^0\rangle$ particles is then $\langle\frac{1}{2}(1+\hat{S})\rangle = |a_0(t)|^2$

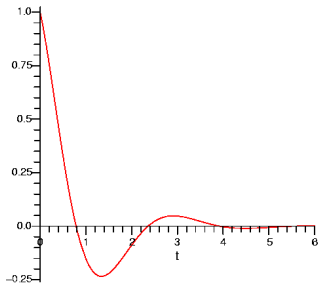


while the expectation value for number of $|\overline{K^0}\rangle$ particles $\langle\frac{1}{2}(1+\hat{S})\rangle$ increases from zero, then oscillates.

The strangeness decays towards zero over time.

and the expectation value of CP, $|a_1(t)|^2 - |a_2(t)|^2|$ also drops as the system becomes pure $|K_2\rangle$





$$\langle \hat{CP} \rangle = \frac{1}{2}|a_0(0)|^2 \left(e^{-t/\tau_1} - e^{-t/\tau_2}\right)$$

While $\frac{1}{2}(1 + CP)$, the number of K_1 particles, drops to zero.

Figure 1 shows an experiment where kaons are generated in state $|K^0\rangle$*. After* 10^{-9} *seconds the kaons pass through a small region of matter, where they interact via the strong interaction (assume that after* 10^{-9} *seconds all the* $|K_1\rangle$ *particles have decayed). Very soon after, the kaons leave the matter and move into a region of vacuum where they begin to decay via the weak interaction (*$\hat{CP}$*). Assume that all coherence between this region and the previous region is lost i.e. the wavefunction is completely collapsed onto its strong interaction eigenstates. Evaluate the appropriate eigenstates and intensities just before the beam enters the matter and just after it leaves the matter. What is the total intensity of kaons and antikaons which survive a further* 10^{-9} *seconds?*

When formed, the beam is in a pure state $|K^0\rangle$,

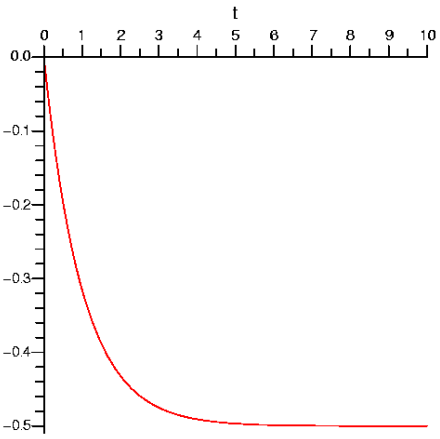
$$\Phi(0) = |K^0\rangle; \quad a_1(0) = \sqrt{\frac{1}{2}}; \;\; a_2(0) = \sqrt{\frac{1}{2}}$$

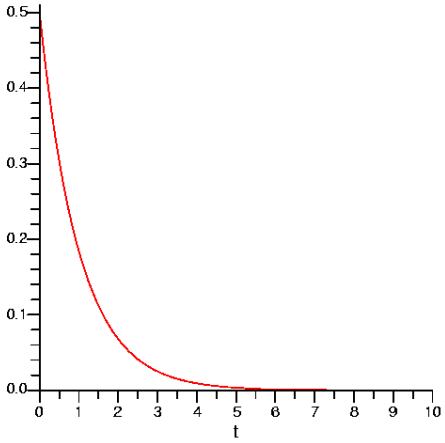
at $t = 10^{-9}$ we have

$$a_1(t) = \sqrt{\frac{1}{2}} e^{-5.5} e^{-im_1 c^2 t/\hbar} \approx 0 \;\; a_2(t) = \sqrt{\frac{1}{2}} e^{-0.01} e^{-im_1 c^2 t/\hbar}$$

i.e. pure K_2 $|a_2(0)|^2 \approx \frac{1}{2}$

$$\Phi(t) = \sqrt{\frac{1}{2}}|K_2\rangle = \frac{1}{2}(|K_0\rangle - |\overline{K_0}\rangle)$$





Passing through the matter, the kaons are returned to eigenstates of $\hat{S}$ by wavefunction collapse. The interference disappears and we have to treat the subsequent evolution of $K_0\rangle$ and $|\overline{K_0}\rangle)$ independently.

Leaving the matter, the appropriate collapsed eigenstates are $|K^0\rangle$ and $|\overline{K}^0\rangle$. Consider the intensities at time t.

$$I(K^0)(t) = |\langle\Phi(t)|K^0\rangle|^2 = \frac{1}{4}.$$

similarly

$$I(\overline{K^0})(t) = |\langle\Phi(t)|\overline{K^0}\rangle|^2 = \frac{1}{4}.$$

These now evolve as above, until after another 10^{-9} both the K^0 and the $\overline{K^0}$ decay, half the kaons remaining as K_2, and half the kaons decaying as K_1. Thus the final intensity of kaons is

$$I(2t) = \frac{1}{2}[I(\overline{K^0})(t) + I(K^0)(t) = frac14$$

The final kaon intensity is a quarter of the initial intensity.

Had it not been for the matter, what would have been the total intensity of kaons and antikaons after 2×10^{-9}*?*

Had the matter not intervened, the final kaon intensity would have been half of the initial intensity (strictly $\frac{1}{2}(e^{-0.02} + e^{-11.1})$

The effect of the matter on the beam is known as regeneration - it regenerates the $|K_1\rangle$ eigenstate which then decays away.

n.b. The regeneration here is known as incoherent regeneration, because the wavefunction is collapsed in the matter and all 'memory' of the previous state is lost. In practice there is also an effect known as coherent regeneration, in which a difference between the amount of scattering of $|K^0\rangle$ and $|\overline{K}^0\rangle$ leads to a component of $|K_1\rangle$ being reintroduced. There are also other decay modes, corresponding to slightly different basis sets for the kaons.

3. *Compare question 3 to a system of polarisers and light beams.*

   An initially unpolarised beam of light moving in the z direction has equal amounts of all polarisations. It can be polarised by passing through a polariser to form a plane-polarised beam e_x, with half the initial intensity. If this e_x beam (analogous to pure K^0) now passes through a polariser oriented at 45 degrees to the first we halve the intensity and create another plane-polarised beam $(e_x + e_y)/2$. It appears that some of the e_y has been regenerated.

4. *This question illustrates the principle of the pseudopotential.*

   A particle is bound in 1D by a potential which has a complicated form for $|x| < x_c$ *but is zero outside this "cut-off" radius. It is known to have a bound eigenstate with energy* $-E_0$*. Show that in this region of space, the wavefunction can be written as*

$$\Phi(x > x_c) = a \exp(-k|x|)$$

   and determine k*.*

   Outside the cutoff, the Schroedinger equation is:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Phi(x) = -E_0\Phi(x)$$

   Which with the given wavefunction gives

$$\frac{-\hbar^2 k^2}{2m} a \exp(-kx) = -E_0 a \exp(-kx).$$

   From which it follows that $k = \sqrt{2mE_0}/\hbar$.

   What can you say about a*?*

   Only part of the wavefunction lies outside x_c, and we do not know how much. So the normalisation a remains undetermined.

   Now suppose that we know that the normalisation constant $a = a_0$*. Show that the ground state of a finite square well pseudopotential can be used to give exactly the same wavefunction i.e.* $\Phi_{PS}(x) = \Phi(x)$*, for* $x > x_c$*.*

For a bound state in the finite square well, we have exactly the same Schroedinger equation outside x_c, so the eigenfunction must also be a decaying exponential, and provided we match the energy and a_0 it will be identical $\Phi_{PS}(x > x_c) = \Phi(x > x_c)$.

Writing the ground state wavefunction of the square well as:

$$\Phi_{PS}(x) = b\cos(k_1 x) \qquad |x| < x_c$$

$$\Phi_{PS}(x) = \Phi(x) = a\exp(-k|x|) \qquad |x| > x_c$$

where $k_1 = \sqrt{2m(V - E_0)}/\hbar$*, determine three simultaneous equations for the values of the finite well depth* V *and range* x_c*, and the normalization constant* b*.*

At the boundary, we have that the actual and pseudowavefunctions and their slopes must match.

$$a_0 \exp -kx_c = b\cos(k_1 x_c)$$

$$-ka_0 \exp -kx_c = -k_1 b\sin(k_1 x_c)$$

You may think that there should be two other equations here from continuity of $\Phi(x)$, however we are assuming that $\Phi(x < x_c)$ is unknown (i.e. too complicated to calculate).

The third equation comes from the normalisation of the pseudowavefunction:

$$2\int_0^{x_c} b\cos(k_1 x)dx + 2\int_{x_c}^{\infty} a_0 \exp(-kx)dx = 1$$

This gives three equations in three unknowns (k_1, b and x_c), which in principle can be solved. In practice, we have the same problem as with the finite square well: one of the equations is transcendental so it cannot be solved analytically.

When are pseudopotentials useful?

We notice that $\Phi(x)$ is not necessarily the ground state of the potential, although $\Phi_{PS}(x)$ is the ground state of the square well. This means that a very complicated $\Phi(x)$ wavefunction can be replaced by a smooth, nodeless $\Phi_{PS}(x)$. If $V(x)$ is the potential of an atom, and we are interested in combining many such atoms which do not overlap (i.e. are more than $2x_c$ apart) then the pseudowavefunctions give the correct behaviour in the space between atoms. Any error inside x_c will be the same in the free atom and the many-atom problems: so it will cancel. It is especially useful if we wish to describe valence electrons, assuming that high energy "core" electrons do not contribute to the bonding. The problem of keeping wavefunctions orthogonal is removed because the pseudowavefunction is a ground state.

In practice, pseudopotentials are slightly more complicated than square wells, having extra degrees of freedom. These are used to match the energies of wavefunction and pseudowavefunction, their values and slopes at the cutoff, and to satisfy "norm conservation" (i.e. the probability of the electron being inside x_c is the same in each case). Often one degree of freedom is left "spare", so that the cut-off can be chosen freely to suit the problem at hand.

5. * **Online bonus question**

The electric dipole moment operator is $\underline{D} \equiv -e\underline{r}$. *The position vector can be written*

$$\underline{r} = r\,\{\underline{e}_1 \sin\theta\cos\phi + \underline{e}_2 \sin\theta\sin\phi + \underline{e}_3\cos\theta\}$$

where $\underline{e}_i$, $i = 1, 2, 3$, *are the usual Cartesian unit vectors in the* x, y, z *directions and* θ, ϕ *are the polar and azimuthal angles in spherical polar coordinates.*

Calculate the dipole matrix elements for the radiative transition from the $n = 2$ *states to the* $1s$ *state of atomic hydrogen.*

We need to evaluate matrix elements of the position operator, $\underline{r}$,

$$\underline{r} = r\,\{\underline{e}_1 \sin\theta\cos\phi + \underline{e}_2 \sin\theta\sin\phi + \underline{e}_3\cos\theta\}$$

for initial states $|2lm\rangle$, $m = 1, 0, -1$, $l = 1, 0$ and a final state $|100\rangle$. We consider each case in turn.

The first one is easy.

$$\langle 100|\underline{r}|200\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} u^*_{100}(\underline{r})\,\underline{r}\,u_{200}(\underline{r})\,r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

Considering each component in turn, for $\underline{e}_1$ the ϕ integral is:

$$\int_0^{2\pi}\cos\phi\,\mathrm{d}\phi = 0$$

for $\underline{e}_2$ the ϕ integral is:

$$\int_0^{2\pi}\sin\phi\,\mathrm{d}\phi = 0$$

and for $\underline{e}_3$ the θ integral is:

$$\int_0^{\pi}\sin\theta\cos\theta\mathrm{d}\theta = 0$$

Hence regardless of the direction of the dipole moment, $\langle 100|\underline{r}|200\rangle = 0$: the transition rate is zero, and dipole transitions from u_{2s} to u_{1s} are forbidden. Physically, this is because the dipole radiation emits a single photon with angular momentum $l = 1$. The angular momentum of the atom doesn't change, so transition cannot conserve angular momentum.

$$\langle 100|\underline{r}|211\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} u^*_{100}(\underline{r})\,\underline{r}\,u_{211}(\underline{r})\,r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

The radial integral is

$$\int_0^{\infty} r^4\,\exp(-3r/2a_0)\,\mathrm{d}r = \left(\frac{2a_0}{3}\right)^5 4!$$

using the given integral.

Noting that $\exp(i\phi) = \cos\phi + i\sin\phi$, the angular integration is

$$\int_0^{2\pi}\int_0^{\pi} \Big[\underline{e}_1 \sin^3\theta \left(\cos^2\phi + i\cos\phi\sin\phi\right) \quad + \quad \underline{e}_2 \sin^3\theta \left(\cos\phi\sin\phi + i\sin^2\phi\right) \\ + \quad \underline{e}_3 \cos\theta\sin^2\theta\left(\cos\phi + i\sin\phi\right)\Big]\,\mathrm{d}\theta\mathrm{d}\phi$$

We use the following simple integrals

$$\int_0^{2\pi}\cos\phi\,\mathrm{d}\phi = \int_0^{2\pi}\sin\phi\,\mathrm{d}\phi = \int_0^{2\pi}\cos\phi\sin\phi\,\mathrm{d}\phi = 0, \quad \int_0^{2\pi}\sin^2\phi\,\mathrm{d}\phi = \int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi = \pi$$

and

$$\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta = \int_0^{\pi}\sin^2\theta\,\sin\theta\mathrm{d}\theta = \int_{-1}^{+1}(1-\cos^2\theta)\,\mathrm{d}(\cos\theta) = \left[\cos\theta - \frac{1}{3}\cos^3\theta\right]_{-1}^{+1} = \frac{4}{3}$$

to give for the angular integral

$$\frac{4\pi}{3}\left[\underline{e}_1 + i\underline{e}_2\right]$$

Including the normalisation factors thus gives

$$\langle 100|\underline{r}|211\rangle = -\frac{1}{8\pi a_0^4}\cdot\left(\frac{2a_0}{3}\right)^5 4!\cdot\frac{4\pi}{3}\left[\underline{e}_1 + i\underline{e}_2\right] = -\frac{2^7}{3^5}\left[\underline{e}_1 + i\underline{e}_2\right]\,a_0$$

Thus

$$|\langle 100|\underline{r}|211\rangle|^2 = (\langle 100|\underline{r}|211\rangle)^*\cdot\langle 100|\underline{r}|211\rangle = \frac{2^{15}}{3^{10}}\,a_0^2$$

In the calculation of $\langle 100|\underline{r}|21-1\rangle$ the only difference is that $\cos\phi + i\sin\phi$ is replaced by $\cos\phi - i\sin\phi$ and the overall sign of the matrix element is $+$ instead of $-$. Thus

$$\langle 100|\underline{r}|21-1\rangle = \frac{2^7}{3^5}\left[\underline{e}_1 - i\underline{e}_2\right]\,a_0$$

giving

$$|\langle 100|\underline{r}|21-1\rangle|^2 = \frac{2^{15}}{3^{10}}\,a_0^2$$

Lastly, we consider the case where $m = 0$ and the angular integral is

$$\int_0^{2\pi}\int_0^{\pi}\left[\underline{e}_1\left(\sin^2\theta\cos\theta\cos\phi\right) + \underline{e}_2\left(\sin^2\theta\cos\theta\sin\phi\right) + \underline{e}_3\cos^2\theta\sin\theta\right]\,\mathrm{d}\theta\mathrm{d}\phi$$

The ϕ integrals in the first two terms vanish and

$$\int_0^{\pi}\cos^2\theta\sin\theta\,\mathrm{d}\theta = \int_{-1}^{+1}\cos^2\theta\,\mathrm{d}(\cos\theta) = \frac{2}{3}$$

so that

$$\langle 100|\underline{r}|210\rangle = \frac{1}{4\sqrt{2}\,\pi a_0^4}\cdot\left(\frac{2a_0}{3}\right)^5 4!\cdot\frac{4\pi}{3}\underline{e}_3 = \frac{2^{15/2}}{3^5}\,a_0\,\underline{e}_3$$

and hence

$$|\langle 100|\underline{r}|210\rangle|^2 = \frac{2^{15}}{3^{10}}\, a_0^2$$

All three elements from $2p \to 1s$ are the same. This should be expected, because the dipole is symmetric with respect to interchanging x, y and z, and the final state $1s$ is spherically symmetric.

The spontaneous transition rate for the $2p \to 1s$ transition is given by

$$R_{mk} = \frac{\omega_{mk}^3}{3\pi c^3 \hbar \epsilon_0} |D_{mk}|^2 = \frac{e^2 \omega_{mk}^3}{3\pi c^3 \hbar \epsilon_0} |r_{mk}|^2$$

where k and m label initial (2p) and final (1s) states and $\alpha \equiv e^2/(4\pi\epsilon_0)\hbar c$ is the fine structure constant.

Explain in words how this relates to the Fermi Golden Rule.

Like the Fermi Golden Rule,

$$R = \frac{2\pi}{\hbar} \left[|V_{mk}|^2 \, g(E_m) \right]_{E_m = E_k}$$

Einstein's spontaneous emission rate describes how quickly transitions take place between states. The Dipole operator plays the role of the perturbing matrix element, while the density of final states has only one final state for the atom (1s), but many states for the different directions of emitting the photon encapsulated in the geometric term. The degeneracy of the initial $2p$ state does not affect the transition rate, because each atom can be in only one of those states. When the matrix element is zero (as for $2s \to 1s$ the transition is forbidden.

Assuming that an initial $2p$ state is unpolarised; that is, each of the three possible values of m_ℓ is equally likely, show that this is equal to.

$$R_{2p\to 1s} = \left(\frac{2}{3}\right)^8 \frac{mc^2}{\hbar}\, \alpha^5$$

since $\underline{D} = -e\underline{r}$. We can express R_{mk}^{spon} in terms of the fine structure constant $\alpha = e^2/(4\pi\epsilon_0)\hbar c$:

$$R_{mk}^{\text{spon}} = \frac{4}{3}\alpha \frac{\omega_{mk}^3}{c^2} |r_{mk}|^2$$

We have calculated $|r_{mk}|^2$ for the cases where the initial state is $2P$ with $m = 1, 0, -1$ and the final state is the $1s$ state. For an initial $2p$ state which is *unpolarised*, each m value is equally likely and we must average over the probabilities for each m with equal weight:

$$\frac{1}{3} \sum_{m=-1}^{+1} |\langle 100|\underline{r}|21m\rangle|^2 = \frac{1}{3}\left[\frac{2^{15}}{3^{10}}\, a_0^2 + \frac{2^{15}}{3^{10}}\, a_0^2 + \frac{2^{15}}{3^{10}}\, a_0^2\right] = \frac{2^{15}}{3^{10}}\, a_0^2$$

Thus the desired rate is

$$R_{2p\to 1s} = \frac{4}{3}\, \alpha \frac{\omega^3}{c^2} \frac{2^{15}}{3^{10}}\, a_0^2 = \frac{2^{17}}{3^{11}}\, \alpha \frac{\omega^3}{c^2} a_0^2$$

where the transition frequency, ω, may be obtained from the Bohr formula for the energy levels of the hydrogen atom:

$$\omega = (E_{2p} - E_{1s})/\hbar = -\frac{1}{2}\,\alpha^2 \frac{mc^2}{4\hbar} + \frac{1}{2}\,\alpha^2 \frac{mc^2}{\hbar} = \frac{3}{8}\,\alpha^2 \frac{mc^2}{\hbar}$$

We can express the Bohr radius in terms of the fine structure constant: $a_0 = \hbar/mc\alpha$ to give, finally,

$$\boxed{R_{2p\to 1s} = \frac{2^{17}}{3^{11}}\,\frac{\alpha}{c^2}\,\frac{3^3}{2^9}\,\alpha^6\,\frac{m^3c^6}{\hbar^3}\,\frac{\hbar^2}{m^2c^2\alpha^2} = \left(\frac{2}{3}\right)^8\,\frac{mc^2}{\hbar}\,\alpha^5}$$