CHAPTER 15

1. With the perturbing potential given, we get

$$C(1s \to 2p) = \frac{eE_0}{i\hbar} \langle \phi_{210} | z | \phi_{100} \rangle \int_0^\infty dt e^{i\omega t} e^{-\gamma t}$$

where $\omega = (E_{21} - E_{10})$. The integral yields $1/(\gamma - i\omega)$ so that the absolute square of $C(1s \to 2p)$ is

$$P(1s \to 2p) = e^2 E_0^2 \frac{|\langle \phi_{210} | z | \phi_{100} \rangle|^2}{\hbar^2 (\omega^2 + \gamma^2)}$$

We may use $|\langle \phi_{210} | z | \phi_{100} \rangle|^2 = \frac{2^{15}}{3^{10}} a_0^2$ to complete the calculation.

2. Here we need to calculate the absolute square of

$$\frac{1}{i\hbar} \int_0^T dt e^{i\omega_{21} t} \sin \omega t \times \frac{2}{a} \lambda \int_0^a dx \sin \frac{2\pi x}{a} (x - \frac{a}{2}) \sin \frac{\pi x}{a}$$

Let us first consider the time integral. We will assume that at $t = 0$ the system starts in the ground state. The time integral then becomes

$$\int_0^\infty dt e^{i\omega_{21} t} \sin \omega t = \frac{1}{2i} \int_0^\infty dt \{ e^{i(\omega_{21} + \omega)t} - e^{i(\omega_{21} - \omega)t} \} = \frac{\omega}{\omega^2 - \omega_{21}^2}$$

We have used the fact that an finitely rapidly oscillating function is zero on the average. In the special case that ω matches the transition frequency, one must deal with this integral in a more delicate manner. We shall exclude this possibility.

The spatial integral involves

$$\frac{2}{a} \int_0^a dx \sin \frac{2\pi x}{a} \sin \frac{\pi x}{a} (x - \frac{a}{2}) =$$

$$\frac{1}{a} \int_0^a \left(\cos \frac{\pi x}{a} - \cos \frac{3\pi x}{a} \right) (x - \frac{a}{2})$$

$$= \frac{1}{a} \int_0^a dx \left[\frac{d}{dx} \left\{ \left(\frac{a}{\pi} \sin \frac{\pi x}{a} - \frac{a}{3\pi} \sin \frac{3\pi x}{a} \right) (x - \frac{a}{2}) \right\} - \left(\frac{a}{\pi} \sin \frac{\pi x}{a} - \frac{a}{3\pi} \sin \frac{3\pi x}{a} \right) \right]$$

$$= \frac{1}{a} \left[\frac{a^2}{\pi^2} \cos \frac{\pi x}{a} - \frac{a^2}{9\pi^2} \cos \frac{3\pi x}{a} \right]_0^a = -2 \frac{a}{\pi^2} \frac{8}{9}$$

The probability is therefore

$$P_{12} = \left(\frac{\lambda}{\hbar}\right)^2 \left(\frac{16a}{9\pi^2}\right)^2 \frac{\omega^2}{(\omega_{21}^2 - \omega^2)^2}$$

(b) The transition from the n = 1 state to the n = 3 state is *zero*. The reason is that the eigenfunctions for all the odd values of n are all symmetric about $x = a/2$, while the potential $(x - a/2)$ is antisymmetric about that axis, so that the integral vanishes. In fact, quite generally all transition probabilities (even → even) and (odd → odd) vanish.

(c) The probability goes to zero as $\omega \to 0$.

3. The only change occurs in the absolute square of the time integral. The relevant one is

$$\int_{-\infty}^{\infty} dt e^{i\omega_{21}t} e^{-t^2/\tau^2} = \sqrt{\pi} e^{-\omega^2\tau^2/4}$$

which has to be squared.
When $\tau \to \infty$ this vanishes, showing that the transition rate vanishes for a very slowly varying perturbation.

4. The transition amplitude is

$$\begin{aligned} C_{n\to m} &= \frac{\lambda}{i\hbar}\langle m|\sqrt{\frac{\hbar}{2M\omega}}(A + A^+)|n\rangle \int_0^{\infty} dt e^{i\omega(m-n)t} e^{-\alpha t}\cos\omega_1 t \\ &= -i\lambda\sqrt{\frac{1}{2M\hbar\omega}}\left(\delta_{m,n-1}\sqrt{n} + \delta_{m,n+1}\sqrt{n+1}\right)\frac{\alpha - i\omega(m-n)}{(\alpha - i\omega(m-n))^2 + \omega_1^2} \end{aligned}$$

(a) Transitions are only allowed for $m = n \pm 1$.

(b) The absolute square of the amplitude is, taking into account that $(m - n)^2 = 1$,

$$\frac{\lambda^2}{2M\hbar\omega}(n\delta_{m,n-1} + (n+1)\delta_{m,n+1)}\frac{\alpha^2 + \omega^2}{(\alpha^2 + \omega_1^2 - \omega^2)^2 + 4\alpha^2\omega^2}$$

When $\omega_1 \to \omega$, nothing special happens, except that the probability appears to exceed unity when α^2 gets to be small enough. This is not possible physically, and what this suggests is that when the external frequency ω_1 matches the oscillator frequency, we get a resonance condition as α approaches zero. Under those circumstances first order perturbation theory is not applicable.
When $\alpha \to 0$, then we get a frequency dependence similar to that in problem 2.

5. The two particles have equal and opposite momenta, so that

$$E_i = \sqrt{(pc)^2 + m_i^2 c^4}$$

The integral becomes

$$\frac{1}{(2\pi\hbar)^6}\int d\Omega \int_0^\infty p^2 dp\, \delta\big(Mc^2 - E_1(p) - E_2(p)\big)$$

and it is only the second integral that is of interest to us. Let us change variables to

$$u = E_1(p) + E_2(p)$$

then

$$du = \frac{pc^2}{E_1}dp + \frac{pc^2}{E_2}dp = (E_1 + E_2)\frac{pdp}{E_1 E_2}$$

and the momentum integral is

$$\int_0^\infty p^2 dp\, \delta\big(Mc^2 - E_1(p) - E_2(p)\big) = \int_{(m_1+m_2)c^2}^\infty p\frac{E_1 E_2 du}{uc^2}\delta(Mc^2 - u)$$
$$= p\frac{E_1 E_2}{Mc^4}$$

To complete the expression we need to express *p* in terms of the masses.

We have

$$(m_2 c^2)^2 + p^2 c^2 = (Mc^2 - \sqrt{(m_1 c^2)^2 + p^2 c^2})^2$$
$$= (Mc^2)^2 - 2Mc^2 E_1(p) + (m_1 c^2)^2 + p^2 c^2$$

This yields

$$E_1(p) = \frac{(Mc^2)^2 + (m_1 c^2)^2 - (m_2 c^2)^2}{2Mc^2}$$

and in the same way

$$E_2(p) = \frac{(Mc^2)^2 + (m_2 c^2)^2 - (m_1 c^2)^2}{2Mc^2}$$

By squaring both sides of either of these we may find an expression for p^2.
The result of a short algebraic manipulation yields

$$p^2 = \frac{c^2}{4M^2}(M - m_1 - m_2)(M - m_1 + m_2)(M + m_1 - m_2)(M + m_1 + m_2)$$

6. The wave function of a system subject to the perturbing potential

$$\lambda\, V(t) = V\, f(t)$$

where $f(0) = 0$ and $\lim_{t\to\infty} f(t) = 1$, with $df(t)/dt << \omega\, f(t)$, is given by

$$|\psi(t)\rangle = \sum_m C_m(t) e^{-iE_m^0 t/\hbar} |\phi_m\rangle$$

and to lowest order in V, we have

$$C_m(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i\omega t'} f(t')\langle\phi_m | V | \phi_0\rangle$$

where $\omega = (E_m^0 - E_0^0)/\hbar$ and at time $t = 0$ the system is in the ground state. The time integral is

$$\int_0^t dt' e^{i\omega t'} f(t') = \int_0^t dt' f(t') \frac{d}{dt'}\frac{e^{i\omega t'}}{i\omega} = \frac{1}{i\omega}\int_0^t dt' \frac{d}{dt'}(e^{i\omega t'} f(t')) - \frac{1}{i\omega}\int_0^t dt' e^{i\omega t'} df(t')/dt'$$

The second term is much smaller than the term we are trying to evaluate, so that we are left with the first term. Using $f(0) = 0$ we are left with $e^{i\omega t}/i\omega$, since for large times $f(t) = 1$. When this is substituted into the expression for $C_{\underline{m}}(t)$ we get

$$C_m(t) = -\frac{e^{i\omega t}}{(E_m^0 - E_0^0)}\langle\phi_m | V | \phi_0\rangle \qquad m \neq 0$$

Insertion of this into the expression for $|\psi(t)>$ yields

$$|\psi(t)\rangle = |\phi_0\rangle + e^{-iE_0^0 t/\hbar}\sum_{m\neq 0}\frac{\langle\phi_m | V | \phi_0\rangle}{E_0^0 - E_m^0}|\phi_m\rangle$$

On the other hand the ground state wave function, to first order in V is

$$|w_0\rangle = |\phi_0\rangle + \sum_{n\neq 0}\frac{\langle\phi_n | V | \phi_0\rangle}{E_0^0 - E_n^0}|\phi_n\rangle$$

It follows that

$$\langle w_0 | \psi(t)\rangle = 1 + e^{-iE_0^0 t/\hbar}\sum_{m\neq 0}\frac{\langle\phi_0 | V | \phi_m\rangle\langle\phi_m | V | \phi_0\rangle}{(E_0^0 - E_m^0)^2}$$

Thus to order *V* the right side is just one.
A fuller discussion may be found in D.J.Griffiths *Introduction to Quantum Mechanics.i*

7. The matrix element to be calculated is

$$M_{fi} = -\frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 \int d^3r_2 ... \int d^3r_A \Phi_f^*(r_1, r_2, ..r_A) \int d^3r \frac{e^{-i\mathbf{p}.\mathbf{r}/\hbar}}{\sqrt{\mathbf{V}}}$$
$$\sum_{i=1}^{Z} \frac{1}{|\mathbf{r}-\mathbf{r}_i|} \psi_{100}(\mathbf{r}) \Phi_i(r_1, r_2, ..r_A)$$

The summation is over $I = 1,2,3,..Z$, that is, only over the proton coordinates. The outgoing electron wave function is taken to be a plane wave, and the Φ are the nuclear wave functions. Now we take advantage of the fact that the nuclear dimensions are tiny compared to the electronic ones. Since $|\mathbf{r}_I| << |\mathbf{r}|$, we may write

$$\frac{1}{|\mathbf{r}-\mathbf{r}_i|} = \frac{1}{r} + \frac{\mathbf{r} \bullet \mathbf{r}_i}{r^3} + ...$$

The $1/r$ term gives no contribution because $\langle \Phi_f | \Phi_i \rangle = 0$. This is a short-hand way of saying that the initial and final nuclear states are orthogonal to each other, because they have different energies. Let us now define

$$\mathbf{d} = \sum_{j=1}^{Z} \int d^3r_1 \int d^3r_2 .. \int d^3r_A \Phi_f^*(r_1, r_2, ..) \mathbf{r}_j \Phi_i(r_1, r_2, ..)$$

The matrix element then becomes

$$M_{fi} = -\frac{e^2}{4\pi\varepsilon_0}\int d^3r \frac{e^{-i\mathbf{p}.\mathbf{r}/\hbar}}{\sqrt{V}} \frac{\mathbf{d}\bullet\mathbf{r}}{r^3} \psi_{100}(\mathbf{r})$$

The remaining task is to evaluate this integral.
First of all note that the free electron energy is given by

$$\frac{p^2}{2m} = \Delta E + |E_{100}|$$

where ΔE is the change in the nuclear energy. Since nuclear energies are significantly larger than atomic energy, we may take for p the value $p = \sqrt{2m\Delta E}$.
To proceed with the integral we choose $\mathbf{p}$ to define the z axis, and write $p/\hbar = k$. We write the $\mathbf{r}$ coordinate in terms of the usual angles θ and ϕ. We thus have

$$\int d^3 r e^{-i\mathbf{p}.\mathbf{r}/\hbar} \frac{\mathbf{d}.\mathbf{r}}{r^3}\psi_{100}(\mathbf{r}) =$$

$$\int d\Omega \int_0^\infty dr e^{-ikr\cos\theta}(d_x \sin\theta\cos\phi + d_y \sin\theta\sin\phi + d_z \cos\theta)\frac{2}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

The solid angle integration involves $\int_0^{2\pi} d\phi$, so that the first two terms above disappear. We are thus left with

$$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} 2\pi d_z \int_{-1}^{1} d(\cos\theta)\int_0^\infty dr \cos\theta e^{-ikr\cos\theta}e^{-Zr/a_0} =$$

$$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} 2\pi(\mathbf{d}.\hat{\mathbf{p}})\int_{-\mathbf{1}}^{\mathbf{1}} d(\cos\theta)\frac{\cos\theta}{(Z/a_0 + ik\cos\theta)}$$

The integral, with the change of variables $\cos\theta = u$ becomes

$$\int_{-1}^{1} du \frac{u}{Z/a_0 + iku} =$$

$$\int_{-1}^{1} du \frac{u(Z/a_0 - iku)}{(Z/a_0)^2 + k^2u^2} =$$

$$-ik\int_{-1}^{1} du \frac{u^2}{(Z/a_0)^2 + k^2u^2}$$

$$\frac{-i}{k^2}\int_{-k}^{k} dw \frac{w^2}{(Z/a_0)^2 + w^2} = -\frac{2i}{k^2}\left[k - \frac{a_0}{Z}\arctan(\frac{a_0 k}{Z})\right]$$

Note now that $\frac{ka_0}{Z} = \frac{k\hbar}{mcZ\alpha} = \sqrt{\frac{2\Delta E}{Z^2 mc^2\alpha^2}} = \frac{1}{Z}\sqrt{\frac{\Delta E}{(13.6eV)}}$. If Z is not too large, then the factor is quite large, because nuclear energies are in the thousands or millions of electron volts. In that case the integral is simple: it is just

$$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2\pi)\frac{\mathbf{d}\bullet\mathbf{p}}{p^2}(-2i\hbar)\left[1 - \frac{\pi\hbar Z}{2a_0 p}\right]$$

We evaluate the rate using only the first factor in the square bracket. We need the absolute square of the matrix element which is

$$(-\frac{e^2}{4\pi\varepsilon_0\sqrt{V}})^2 16\pi\hbar^2\left(\frac{Z}{a_0}\right)^3\frac{(\mathbf{d}.\mathbf{p})^2}{p^4}$$

The transition rate per nucleus is

$$R_{fi} = \frac{2\pi}{\hbar}\int \frac{d^3 pV}{(2\pi\hbar)^3}\,\delta(\frac{p^2}{2m} - \Delta E)\,|\,M_{fi}\,|^2$$
$$= \frac{2\pi}{\hbar}\int \frac{d^3 pV}{(2\pi\hbar)^3}\,\delta(\frac{p^2}{2m} - \Delta E)\frac{1}{V}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 16\pi\hbar^2\left(\frac{Z}{a_0}\right)^3 \frac{(\mathbf{d}\bullet\mathbf{p})^2}{p^4}$$

In carrying out the solid angle integration we get

$$\int d\Omega(\mathbf{d}\bullet\mathbf{p})^2 = \frac{4\pi}{3}\,|\,\mathbf{d}\,|^2\; p^2$$

so that we are left with some numerical factors times $\int dp\,\delta(p^2 / 2m - \Delta E) = \sqrt{\frac{m}{2\Delta E}}$
Putting all this together we finally get

$$R_{fi} = \frac{16}{3}(Z\alpha)^3 \frac{d^2}{a_0^2}\sqrt{\frac{mc^2}{2\Delta E}}\,\frac{mc^2}{\hbar}$$

We write this in a form that makes the dimension of the rate manifest.