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Contents

1 Quantization of Free Radiation Field.

Canonical quantization of the free radiation field a la Dirac leads to Einstein and Planck's quantization of the energy of the radiation field in terms of the fundamental quantum of energy, $\varepsilon_k = \hbar\omega_k = \hbar c|\mathbf{k}|$, where $h = 2\pi\hbar$ is Planck's constant and c is the speed of light. This procedure also shows that each quantum of the radiation field carries momentum $\hbar\mathbf{k}$ and angular momentum $\pm\hbar$ for the two helicity states, $\mathbf{e}_{\mathbf{k}\pm}$, and thus to the particle interpretation of the quanta as *photons* carrying momentum, energy and spin angular momentum. The multi-mode Fock states,

$$|\{n_k\}\rangle = \prod_k \frac{(a_k^\dagger)^{n_k}}{\sqrt{n_k!}}|0\rangle \ , \tag{1}$$

are energy eigenstates for pure radiation. Note that I use the short-hand notation, $k = (\mathbf{k}, \lambda)$. Consider the pure radiation field in thermal equilibrium with an external heat bath held at fixed temperature, T. Since photon number in any mode is not a conserved quantity, thermal equilibrium of the radiation at temperature T is described by the density matrix for the Canonical ensemble,

$$\rho_c = \frac{1}{\mathscr{Z}} e^{-\beta H} = \prod_k \frac{1}{\mathscr{Z}_k} e^{-\beta H_k} \ , \tag{2}$$

where $\beta = 1/k_B T$ and k_B is Boltzmann's constant. The factorization of the density matrix occurs because there are no interactions between photons and the Hamiltonian is simply, $H = \sum_k \varepsilon_k (a_k^\dagger a_k + \frac{1}{2})$. Note that the single mode partition function is given by $\mathscr{Z}_k = \mathrm{Tr}\left\{e^{-\beta H_k}\right\}$.

1.1 Single-Mode Partition Function.

Express the single-mode partition function as a sum over the number of photons in the Fock states.

The single mode partition function is given by

$$\mathscr{Z}_k = \sum_{n_k=0}^{\infty} \langle n_k | e^{-\beta\hbar\omega_k\left(\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}\right)} | n_k \rangle = e^{-\beta\hbar\omega_k/2} \sum_{n_k=0}^{\infty} \langle n_k | e^{-\beta\hbar\omega_k \hat{N}_k} | n_k \rangle \ , \tag{3}$$

where $\hat{N}_k = \hat{a}_k^\dagger \hat{a}_k$ is the occupation number operator for mode k. If we expand the exponential into an infinite sum, we see we have terms with $\hat{N}_k^m$ where m is an integer, which when acting on the state $|n_k\rangle$ simply returns the occupation number n_k to the same power. This infinite series representing the exponential can then be written as the exponential with the operator replaced with its eigenvalue. Therefore the single mode partition function is

$$\mathscr{Z}_k = e^{-\beta\hbar\omega_k/2} \sum_{n_k=0}^{\infty} e^{-\beta\hbar\omega_k n_k} = e^{-\beta\hbar\omega_k/2}\left(\frac{e^{\beta\hbar\omega_k}}{e^{\beta\hbar\omega_k} - 1}\right) \ , \tag{4}$$

which if we multiply and divide by $e^{-\beta\hbar\omega_k}$, we obtain

$$\mathscr{Z}_k = e^{-\beta\hbar\omega_k/2}\left(\frac{1}{1 - e^{-\beta\hbar\omega_k}}\right) = \frac{1}{2}\mathrm{csch}\left(\frac{\beta\omega\hbar}{2}\right) \ . \tag{5}$$

1.2 Mean Number of Photons per Mode.

Evaluate the mean number of photons for mode of k in equilibrium with a heat bath at temperature T,

$$\bar{n}_k = \frac{1}{\mathscr{Z}_k} \operatorname{Tr}\left\{ e^{-\beta H_k} a_k^\dagger a_k \right\} \ , \tag{6}$$

in terms of k_B, T, $\hbar$, c and $|\mathbf{k}|$. Note: You need only evaluate the sum over photon occupation for the partition function in order to compute $\bar{n}_k$.

The trace of the indicated operator is given by

$$\sum_{n_k=0}^{\infty} \langle n_k | e^{-\beta H_k} a_k^\dagger a_k | n_k \rangle = \sum_{n_k=0}^{\infty} \langle n_k | e^{-\beta \hbar \omega_k (\hat{N}_k + \frac{1}{2})} \hat{N}_k | n_k \rangle = e^{-\beta \hbar \omega_k / 2} \sum_{n_k=0}^{\infty} n_k e^{-\beta \hbar \omega_k n_k} \ , \tag{7}$$

using the same reasoning as the previous section to deal with the exponential. The form of this sum is well-known, and thus the average occupation number per mode is given by

$$\bar{n}_k = \frac{1}{\mathscr{Z}_k} e^{-\beta \hbar \omega_k / 2} \frac{e^{-\beta \hbar \omega_k}}{\left(1 - e^{-\beta \hbar \omega_k}\right)^2} \ , \tag{8}$$

after we divide by the single-mode partition function (using the first expression in Equation 5) we obtain

$$\bar{n}_k = \frac{e^{-\beta \hbar \omega_k}}{1 - e^{-\beta \hbar \omega_k}} \ , \tag{9}$$

which if we multiply and divide by an exponential of the same argument, only positive, we obtain

$$\bar{n}_k = \frac{1}{e^{\beta \hbar \omega_k} - 1} \ , \tag{10}$$

which is the Bose-Einstein distribution, which we expect for photons.

1.3 Frequency Distribution.

The mean energy density of radiation in thermal equilibrium can be expressed as an integral over the *spectral energy density*, ρ_ω,

$$\bar{\varepsilon}(T) = \int_0^\infty \mathrm{d}\omega \rho_\omega \ . \tag{11}$$

Derive the formula for the distribution ρ_ω by summing the mean energy in each mode over all modes $\mathbf{k}$ and photon polarization states, λ.

The average energy per mode is given by

$$\bar{\varepsilon}_k = \frac{1}{\mathscr{Z}_k} \operatorname{Tr}\left\{ e^{-\beta H_k} H_k \right\} = \frac{1}{\mathscr{Z}_k} \operatorname{Tr}\left\{ e^{-\beta \hbar \omega_k (\hat{N}_k + \frac{1}{2})} \hbar \omega_k \left(\hat{N}_k + \frac{1}{2} \right) \right\} \ , \tag{12}$$

using the Fock basis to evaluate the trace, we have

$$\bar{\varepsilon}_k = \frac{1}{\mathscr{Z}_k} \sum_{n_k=0}^{\infty} \langle n_k | e^{-\beta \hbar \omega_k \left(\hat{N}_k + \frac{1}{2} \right)} \hbar \omega_k \left(\hat{N}_k + \tfrac{1}{2} \right) | n_k \rangle = \frac{e^{-\beta \hbar \omega_k / 2}}{\mathscr{Z}_k} \sum_{n_k=0}^{\infty} e^{-\beta \hbar \omega_k n_k} \hbar \omega_k \left(n_k + \tfrac{1}{2} \right) \ . \tag{13}$$

We can separate this sum into two terms: the energy due to the radiation $\bar{\varepsilon}_{\text{rad}}$ and the energy of the vacuum ε_0:

$$\bar{\varepsilon}_k = \bar{\varepsilon}_{\text{rad}}(\mathbf{k}) + \varepsilon_0 \ , \tag{14}$$

and so the average radiation energy is simply

$$\bar{\varepsilon}_{\text{rad}}(\mathbf{k}) = \frac{e^{-\beta\hbar\omega_k/2}}{\mathscr{Z}_k} \sum_{n_k=0}^{\infty} e^{-\beta\hbar\omega_k n_k} \hbar\omega_k n_k \ . \tag{15}$$

If we compare this with Equation 7, we see the average radiation energy of a single mode is given by

$$\bar{\varepsilon}_{\text{rad}}(\mathbf{k}) = \hbar\omega_k \bar{n}_k \ , \tag{16}$$

and so the average radiation energy over all modes is

$$\bar{\varepsilon}_{\text{rad}} = \sum_{\mathbf{k},\lambda} \hbar\omega_k \bar{n}_k \ , \tag{17}$$

which we may approximate as an integral if the spacing in $|\mathbf{k}|$ is small enough:

$$\bar{\varepsilon}_{\text{rad}} = 2 \int \frac{1}{(2\pi)^3} \mathrm{d}^3k \hbar\omega_k \bar{n}_k = \frac{2}{(2\pi)^3} \int_0^\infty k^2 \mathrm{d}k \hbar\omega_k \bar{n}_k \int_{\mathrm{d}\Omega_{\hat{\mathbf{k}}}} \mathrm{d}\Omega \ , \tag{18}$$

where we acquired a factor of two by carrying out the sum over both polarization states λ. The angular integration simply gives a factor of 4π, and using the dispersion relation $\omega = ck$, we can write this as an integral over the frequency

$$\bar{\varepsilon}_{\text{rad}} = \frac{8\pi}{(2\pi)^3} \hbar \int_0^\infty \frac{\omega^2 \mathrm{d}\omega}{c^3} \omega \bar{n}_k = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 \mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} \ , \tag{19}$$

after substituting in Equation 10. If we compare this to the given definition of the spectral energy density, we find

$$\rho_\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \ . \tag{20}$$

1.4 Radiant Energy Density.

Show that the total radiant energy density at temperature T scales as

$$\bar{\varepsilon}(T) = \sigma T^p \ . \tag{21}$$

Determine the power p, and evaluate the Stefan-Boltzmann constant, σ, in units of $J \cdot m^{-3} \cdot K^{-p}$. Hint: Once you obtain the scaling law for $\bar{\varepsilon}(T)$, σ will be determined by fundamental constants and a dimensionless integral, $\mathscr{S}$, which can be expressed as an infinite series of the form,

$$\mathscr{S} = \sum_{m=1}^{\infty} \int_0^\infty x^{p-1} e^{-mx} \mathrm{d}x \ , \quad p > 1 \ . \tag{22}$$

Use the properties of the Gamma and Riemann Zeta functions to calculate $\mathscr{S}$[1].

[1] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1970.

Let us begin from Equation 19, defining $x = \beta\hbar\omega$, giving the radiant energy density to be

$$\bar{\varepsilon}_{\text{rad}} = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\left(\frac{x}{\beta\hbar}\right)^3 \frac{\mathrm{d}x}{\beta\hbar}}{e^x - 1} = \frac{1}{\pi^2(\hbar c)^3}\frac{1}{\beta^4}\int_0^\infty \frac{x^3\mathrm{d}x}{e^x - 1} \ . \tag{23}$$

If we note the inverse temperature can be written $1/\beta = k_B T$, where k_B is the Boltzmann constant, the radiant energy density as a function of temperature is

$$\bar{\varepsilon}_{\text{rad}} = \left[\frac{k_B^4}{\pi^2(\hbar c)^3}\int_0^\infty \frac{x^3\mathrm{d}x}{e^x - 1}\right] T^4 \ , \tag{24}$$

and since everything but the temperature is a constant, we may define the Stefan-Boltzmann constant as

$$\sigma = \frac{k_B^4}{\pi^2(\hbar c)^3}\int_0^\infty \frac{x^3\mathrm{d}x}{e^x - 1} \ . \tag{25}$$

Let us turn our attention to evaluating the dimensionless integral - we can maneuver it into the given form (Equation 22) by showing

$$\frac{x^3\mathrm{d}x}{e^x - 1} = x^{(4-1)}\sum_{m=1}^\infty e^{-mx} \ . \tag{26}$$

Start by considering the following sum:

$$\sum_{m=0}^\infty e^{-mx} = \frac{e^x}{e^x - 1} = \frac{1}{1 - e^{-x}} \ , \tag{27}$$

but the sum can also be written

$$\sum_{m=0}^\infty e^{-mx} = 1 + \sum_{m=1}^\infty e^{-mx} \ , \tag{28}$$

so combining the two we see

$$\sum_{m=1}^\infty e^{-mx} = \frac{1}{1 - e^{-x}} - 1 = \frac{1 - (1 - e^{-x})}{1 - e^{-x}} = \frac{e^{-x}}{1 - e^{-x}} = \frac{1}{e^x - 1} \ , \tag{29}$$

so in fact, Equation 26 holds true. Now the integral can be written

$$\int_0^\infty \frac{x^3\mathrm{d}x}{e^x - 1} = \sum_{m=1}^\infty \int_0^\infty x^{(4-1)}e^{-mx}\mathrm{d}x \ , \tag{30}$$

let us evaluate this making a substitution $u = mx$:

$$\sum_{m=1}^\infty \int_0^\infty \left(\frac{u}{m}\right)^3 e^{-u}\frac{\mathrm{d}u}{m} = \sum_{m=1}^\infty \frac{1}{m^4}\int_0^\infty u^3 e^{-u}\mathrm{d}u = \sum_{m=1}^\infty \frac{\Gamma(4)}{m^4} = \Gamma(4)\zeta(4) \ , \tag{31}$$

where $\zeta(q)$ is the Riemann zeta function. The Stefan-Boltzmann constant is then

$$\sigma = \frac{k_B^4}{\pi^2(\hbar c)^3}\Gamma(4)\zeta(4) = \frac{k_B^4}{\pi^2(\hbar c)^3}\left(\frac{3!\pi^4}{90}\right) = \frac{k_B^4\pi^2}{15(\hbar c)^3} = 7.5657 \times 10^{-16}\ \mathrm{J}\cdot\mathrm{m}^{-3}\cdot\mathrm{K}^{-4} \ . \tag{32}$$

2 Selection Rules for Transitions of Hydrogenic Atoms.

Derive the selection rules for electric dipole (E_1), magnetic dipole (M_1) and electric quadrupole (E_2) transitions for Hydrogenic atoms. Show that the spontaneous decay of the $2s$ state of hydrogen by one-photon emission is strictly forbidden in the non-relativistic limit.

The atomic Hamiltonian of an electron in a Hydrogenic atom is given by

$$\hat{\mathcal{H}}_{\text{atom}} = \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\hat{\mathbf{r}}) \ , \tag{33}$$

where $\hat{V}(\hat{\mathbf{r}})$ is the Coulomb potential due to the nuclear charge Ze. This atom couples to the free radiation field denoted by the vector potential operator $\hat{\mathbf{A}}(\hat{\mathbf{r}}, t)$, using the Coulomb gauge ($\boldsymbol{\nabla} \cdot \hat{\mathbf{A}} = 0$), which replaces the momentum operator $\hat{\mathbf{p}}$ with the kinetic momentum operator $\hat{\mathbf{\Pi}} = \hat{\mathbf{p}} - (e/c)\hat{\mathbf{A}}$. The system Hamiltonian becomes

$$\hat{\mathcal{H}} = \frac{1}{2m}\left(\hat{\mathbf{p}} - (e/c)\hat{\mathbf{A}}\right)^2 + \hat{V}(\hat{\mathbf{r}}) + \hat{\mathcal{H}}_{\text{rad}} \ , \tag{34}$$

where the radiation Hamiltonian is given by

$$\hat{\mathcal{H}}_{\text{rad}} = \int \mathrm{d}V \frac{1}{8\pi}\left\{\left|-\frac{1}{c}\frac{\partial \hat{\mathbf{A}}}{\partial t}\right|^2 + \left|\boldsymbol{\nabla} \times \hat{\mathbf{A}}\right|^2\right\} \ . \tag{35}$$

We may now focus on the interaction Hamiltonian, found by expanding the kinetic term in the atomic Hamiltonian:

$$\hat{\mathcal{H}}_{\text{int}} = -\frac{e}{2c}\left\{\frac{\hat{\mathbf{p}}}{m} \cdot \hat{\mathbf{A}} + \hat{\mathbf{A}} \cdot \frac{\hat{\mathbf{p}}}{m}\right\} + \frac{e^2}{2mc^2}|\hat{\mathbf{A}}|^2 \ , \tag{36}$$

note the pure momentum term is not included in the interaction Hamiltonian (it is part of the original atomic Hamiltonian). It has been shown previously that $[\hat{\mathbf{p}}, \hat{\mathbf{A}}] = 0$, so the first term simplifies. The system Hamiltonian can now be expressed as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{atom}} + \hat{\mathcal{H}}_{\text{rad}} + \hat{\mathcal{H}}_{\text{int}} \ . \tag{37}$$

The quantized free radiation field operator $\hat{\mathbf{A}}$ of a single mode $k \equiv (\mathbf{k}, \lambda)$ is given by

$$\hat{\mathbf{A}}_k(\hat{\mathbf{r}}, t) = \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\left\{\hat{a}_k \mathbf{e}_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \hat{a}_k^\dagger \mathbf{e}_k^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right\} \ , \tag{38}$$

which implies the second term (modulus square of this operator) in the interaction Hamiltonian involves terms that only have products of two creation or annihilation operators. Therefore this term corresponds to two-photon processes, which we are not concerned with, and may be neglected, allowing the interaction Hamiltonian to be written as

$$\hat{\mathcal{H}}_{\text{int}} = -\frac{e}{c}\left\{\hat{\mathbf{A}} \cdot \frac{\hat{\mathbf{p}}}{m}\right\} = -\frac{e}{c}\sum_{\mathbf{k},\lambda}\left\{\hat{\mathbf{A}}_k \cdot \frac{\hat{\mathbf{p}}}{m}\right\} \tag{39}$$

$$= -\frac{e}{mc}\sum_{\mathbf{k},\lambda}\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\left\{\hat{a}_k(\mathbf{e}_k \cdot \hat{\mathbf{p}})e^{i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)} + \hat{a}_k^\dagger(\mathbf{e}_k^* \cdot \hat{\mathbf{p}})e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}\right\} \ . \tag{40}$$

Using Fermi's Golden rule, the interaction rate for an individual mode is given by

$$\Gamma_{n\to n'}(\mathbf{k}) = \frac{2\pi}{\hbar}\left|\langle n'; N_k+1|\hat{\mathcal{H}}_{\text{int}}|n; N_k\rangle\right|^2 \delta[(E_{n'}+(N_k+1)\hbar\omega_k)-(E_n+N_k\hbar\omega_k)] \ . \tag{41}$$

Let us examine the matrix element

$$\begin{aligned}\langle n'; N_k+1|\hat{\mathcal{H}}_{\text{int}}|n; N_k\rangle = \\ -\frac{e}{mc}\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\langle n'; N_k+1|\hat{a}_k(\mathbf{e}_k\cdot\hat{\mathbf{p}})e^{i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}+\hat{a}_k^\dagger(\mathbf{e}_k^*\cdot\hat{\mathbf{p}})e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}|n; N_k\rangle \ ,\end{aligned} \tag{42}$$

note that we can act the creation or annihilation operator to the left:

$$\langle N_k+1|\hat{a}_k|N_k\rangle = \left[\hat{a}_k^\dagger|N_k+1\rangle\right]^\dagger|N_k\rangle = \sqrt{N_k+2}\,\langle N_k+2|N_k\rangle = 0 \tag{43}$$

$$\langle N_k+1|\hat{a}_k^\dagger|N_k\rangle = [\hat{a}_k|N_k+1\rangle]^\dagger|N_k\rangle = \sqrt{N_k+1}\,\langle N_k|N_k\rangle = \sqrt{N_k+1} \ , \tag{44}$$

and see that the first term in Equation 39 does not contribute. Using this result, the matrix element becomes

$$\langle n'; N_k+1|\hat{\mathcal{H}}_{\text{int}}|n; N_k\rangle = -\frac{e}{c}\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\sqrt{N_k+1}\,\langle n'|(\mathbf{e}_k^*\cdot\frac{\hat{\mathbf{p}}}{m})e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}|n\rangle \ , \tag{45}$$

and thus the rate for a single mode is

$$\Gamma_{n\to n'}(\mathbf{k}) = \frac{2\pi}{\hbar}\left|-\frac{e}{c}\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\sqrt{N_k+1}\,\langle n'|(\mathbf{e}_k^*\cdot\frac{\hat{\mathbf{p}}}{m})e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}|n\rangle\right|^2\delta[\hbar\omega-\hbar\omega_k] \tag{46}$$

$$= \frac{2\pi}{\hbar}\left(\frac{e}{c}\right)^2\frac{2\pi\hbar c^2}{V\omega_k}(N_k+1)\left|\langle n'|\mathbf{e}_k^*\cdot\frac{\hat{\mathbf{p}}}{m}e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}|n\rangle\right|^2\delta[\hbar\omega-\hbar\omega_k] \ , \tag{47}$$

upon further simplification, we obtain

$$\Gamma_{n\to n'}(\mathbf{k}) = \frac{4\pi^2e^2}{V\omega_k}(N_k+1)\left|\langle n'|\mathbf{e}_k\cdot\frac{\hat{\mathbf{p}}}{m}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|n\rangle\right|^2\delta[\hbar\omega_k-\hbar\omega] \ , \tag{48}$$

noting that the time components of the exponential cancel in the modulus squared, which also allows us to replace the constants in the operator with their complex conjugates. Note the above form is for a transition that emits a photon, whereas for a transition that absorbs a photon, we have that $N_k+1\to N_k$, but the functional form remains the same. To find the total rate, we integrate over all k and pick up a factor of two for the polarization sum:

$$\Gamma_{n\to n'} = \int\frac{\mathrm{d}^3k}{(2\pi)^3}\frac{8\pi e^2}{\omega_k}(N_k+1)\left|\langle n'|\mathbf{e}_k\cdot\frac{\hat{\mathbf{p}}}{m}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|n\rangle\right|^2\delta(k-\omega/c)\frac{1}{\hbar c} \ . \tag{49}$$

All of the physics of the transition is contained in the matrix element, which we will define as

$$\mathcal{M}_{nn'} = \langle n'|\mathbf{e}_k\cdot\frac{\hat{\mathbf{p}}}{m}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|n\rangle = \langle n'|\mathbf{e}_k\cdot\frac{\hat{\mathbf{p}}}{m}|n\rangle + \langle n'|\mathbf{e}_k\cdot\frac{\hat{\mathbf{p}}}{m}(i\mathbf{k}\cdot\hat{\mathbf{r}})|n\rangle \ , \tag{50}$$

after expanding the exponential and retaining the first two terms. Using Einstein notation, the second term can be written

$$\frac{i}{m}\langle n'|(\mathbf{e}_k)^\alpha \hat{\mathbf{p}}^\alpha \mathbf{k}^\beta \hat{\mathbf{r}}^\beta)|n\rangle = \frac{ie_k^\alpha k^\beta}{m}\langle n'|\hat{p}^\alpha \hat{r}^\beta|n\rangle \ , \tag{51}$$

and rewriting the remaining operator yields

$$\hat{p}^\alpha \hat{r}^\beta = \frac{1}{2}(\hat{p}^\alpha \hat{r}^\beta - \hat{p}^\beta \hat{r}^\alpha) + \frac{1}{2}(\hat{p}^\alpha \hat{r}^\beta + \hat{p}^\beta \hat{r}^\alpha) \ . \tag{52}$$

We may then write the matrix element from the Golden rule as

$$\mathcal{M}_{nn'} = \langle n'|\mathbf{e}_k \cdot \frac{\hat{\mathbf{p}}}{m}|n\rangle + \frac{ie_k^\alpha k^\beta}{2m}\langle n'|\hat{p}^\alpha \hat{r}^\beta - \hat{p}^\beta \hat{r}^\alpha|n\rangle + \frac{ie_k^\alpha k^\beta}{2m}\langle n'|\hat{p}^\alpha \hat{r}^\beta + \hat{p}^\beta \hat{r}^\alpha|n\rangle \tag{53}$$

$$\mathcal{M}_{nn'} = \mathcal{M}_{nn'}^{(E1)} + \mathcal{M}_{nn'}^{(M1)} + \mathcal{M}_{nn'}^{(E2)} \ , \tag{54}$$

and we may identify the terms as the electric dipole transition (E1), the magnetic dipole transition (M1), and the electric quadrupole transition (E2), respectively.

2.1 Electric Dipole.

It may not be obvious the first matrix element corresponds to an electric dipole operator. However, consider the commutator of the position operator and the atomic Hamiltonian:

$$[\hat{\mathbf{r}}, \hat{\mathcal{H}}_{\text{atom}}] = [\hat{\mathbf{r}}, \hat{\mathbf{p}}^2/2m] + [\hat{\mathbf{r}}, \hat{V}(\hat{\mathbf{r}})] = i\hbar\frac{\hat{\mathbf{p}}}{m} + [\hat{\mathbf{r}}, \hat{V}(\hat{\mathbf{r}})] \ , \tag{55}$$

but since the potential only depends on the position operator, their commutator is zero. We are left with the relation

$$\frac{\hat{\mathbf{p}}}{m} = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{\mathcal{H}}_{\text{atom}}] = \frac{1}{i\hbar}\left(\hat{\mathbf{r}}\hat{\mathcal{H}}_{\text{atom}} - \hat{\mathcal{H}}_{\text{atom}}\hat{\mathbf{r}}\right) \ , \tag{56}$$

which makes the matrix element

$$\mathcal{M}_{nn'}^{(E1)} = \frac{1}{i\hbar}\langle n'|\mathbf{e}_k \cdot \frac{\hat{\mathbf{p}}}{m}|n\rangle = \frac{1}{i\hbar}\langle n'|\hat{\mathbf{r}}\hat{\mathcal{H}}_{\text{atom}} \cdot \mathbf{e}_k|n\rangle - \frac{1}{i\hbar}\langle n'|\hat{\mathcal{H}}_{\text{atom}}\hat{\mathbf{r}} \cdot \mathbf{e}_k|n\rangle \tag{57}$$

$$= \frac{1}{i\hbar}\langle n'|(\hat{\mathbf{r}} \cdot \mathbf{e}_k)\hat{\mathcal{H}}_{\text{atom}}|n\rangle - \frac{1}{i\hbar}\langle n'|\hat{\mathcal{H}}_{\text{atom}}(\hat{\mathbf{r}} \cdot \mathbf{e}_k)|n\rangle = \frac{E_n - E_{n'}}{i\hbar}\langle n'|\hat{\mathbf{r}} \cdot \mathbf{e}_k|n\rangle \ , \tag{58}$$

which is clearly the electric dipole operator. Transitions are allowed when this matrix element is nonzero (as long as there are no degenerate energy levels). In Hydrogenic atoms, there is the principal quantum number n, the total angular momentum ℓ, and the projection of the angular momentum onto the z axis, m, so the states[2] $|n\rangle \to |n\ell m\rangle$. We are therefore interested in the behavior[3] of the matrix element

$$\langle n'\ell'm'|\hat{\mathbf{r}} \cdot \mathbf{e}_k|n\ell m\rangle = \int (r^2 \mathrm{d}r\mathrm{d}\Omega_{\hat{\mathbf{r}}}) R_{n'\ell'}^*(r) Y_{\ell'm'}^*(\theta,\phi)(\mathbf{r} \cdot \mathbf{e}_k) R_{n\ell}(r) Y_{\ell m}(\theta,\phi) \ , \tag{59}$$

[2] A state $|n\ell m\rangle$ can be represented in the coordinate basis as $R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$ - denoting the radial and angular parts separately, and is properly normalized.

[3] Only interested in cases in which the matrix element is zero, specific values of the matrix element for each state $|n\ell m\rangle$ are different and do not affect the selection rules.

which in general will depend on the coordinate operators $\hat{x}, \hat{y}, \hat{z}$. But it is easily shown that the coordinates are related to spherical harmonics by

$$z \sim Y_{1,0}(\theta, \phi) \tag{60}$$

$$x \pm iy \sim Y_{1,\pm 1}(\theta, \phi) \ , \tag{61}$$

therefore these relations can be elevated to the quantum mechanical operators in the same way. We may then represent the scalar product of the electron position and the polarization direction as a generic $\ell = 1$ spherical harmonic, $Y_{1t}(\theta, \phi)$. If we insert this into the integral shown above, and separate into radial and angular components, we see

$$\mathcal{M}^{(E1)}_{nn'} \propto \int r^2 \mathrm{d}r(r) R^*_{n'\ell'}(r) R_{n\ell}(r) \int \mathrm{d}\Omega_{\hat{\mathbf{r}}} Y^*_{\ell' m'}(\theta, \phi) Y_{1t}(\theta, \phi) Y_{\ell m}(\theta, \phi) \ , \tag{62}$$

with $t \in \{-1, 0, 1\}$. In general, there is a sum over t due to the fact the polarization vector may have components in all three Cartesian directions. The radial integral does not provide information on selection rules because there is no orthonormality condition, as there is with the spherical harmonics. Therefore, we can conclude that all selection rules for electric dipole transitions in a Hydrogenic atom are due to the angular integral implicit in the corresponding matrix element. The integral of three spherical harmonics over the unit sphere is given[4] by

$$\sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \ , \tag{63}$$

where the 6-element objects are Wigner 3j-symbols. These symbols are nonzero if the following four conditions are satisfied:

1. $m_1 \in \{-|\ell_1|, \ldots, |\ell_1|\}$, $m_2 \in \{-|\ell_2|, \ldots, |\ell_2|\}$, and $m_3 \in \{-|\ell_3|, \ldots, |\ell_3|\}$
2. $m_1 + m_2 = -m_3$
3. $|\ell_1 - \ell_2| \leq \ell_3 \leq \ell_1 + \ell_2$
4. $\ell_1 + \ell_2 + \ell_3 \in \mathbb{Z}$

For the product in Equation 62, the angular integral becomes

$$\sqrt{\frac{(2\ell' + 1)(3)(2\ell + 1)}{4\pi}} \begin{pmatrix} \ell' & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & 1 & \ell \\ m' & t & m \end{pmatrix} \ , \tag{64}$$

due to the integral nature of orbital spin quantum numbers, condition (4) is automatically satisfied, and (1) is satisfied by the relation of the total angular momentum quantum number and the angular momentum projection quantum number. Thus we are only concerned with the conditions (2) and (3). Using (2) we get that $m = t + m'$ bu $t \in \{0, \pm 1\}$, so we obtain the selection rule for the projection quantum number:

$$\Delta m = \{0, \pm 1\} \ . \tag{65}$$

Using (3) in a similar manner we get that $\Delta \ell = \{0, \pm 1\}$, but we know $Y_{1t}(\theta, \phi)$ is odd under parity ($\ell \to -\ell$) for all [allowed] t. If we have $\Delta \ell = 0$, the initial and final states' spherical harmonics are either both odd or even, so their product is even, which is then multiplied by the odd Y_{1t}, and integrated over all space (see Equation 62), resulting in an overall odd integrand. The integral over all space of odd functions is zero, so $\Delta \ell = 0$ is forbidden. Thus, we are left with the selection rule for the total orbital angular momentum quantum numbers for electric dipole transitions:

$$\Delta \ell = \pm 1 \ . \tag{66}$$

[4] Weisstein, Eric W. "Spherical Harmonic." From MathWorld–A Wolfram Web Resource. http://mathworld.wolfram.com/SphericalHarmonic.html

2.2 Magnetic Dipole.

The magnetic dipole transitions are dependent on the matrix element

$$\mathcal{M}^{(M1)}_{nn'} = \frac{ie^\alpha_k k^\beta}{2m} \langle n'|\hat{p}^\alpha \hat{r}^\beta - \hat{p}^\beta \hat{r}^\alpha|n\rangle = -i\frac{\mathbf{e}_k \times \mathbf{k}}{2m} \langle n'|\hat{\mathbf{L}}|n\rangle \ , \tag{67}$$

wherre $\hat{\mathbf{L}}$ is the orbital angular momentum operator. We can identify this as the magnetic dipole operator by noting that the magnetic moment of the elctron is given by

$$\hat{\boldsymbol{\mu}} = \frac{e}{2mc}\hat{\mathbf{L}} \ , \tag{68}$$

and the magnetic field is in the direction $\mathbf{e}_k \times \mathbf{k}$. We see the matrix element is proportional to

$$\mathcal{M}^{(M1)}_{nn'} \propto \langle n'|(\mathbf{e}_k \times \mathbf{k}) \cdot \hat{\mathbf{L}}|n\rangle \ , \tag{69}$$

and in general the result of the cross product may have components in all the Cartesian coordinates. We see the z component would result in an operator proportional to $\hat{L}_z$, while we may define the coordinates $x \pm iy$ for the two orthogonal directions, which result in operators proportional to $\hat{L}_\pm$. We are then interested in the matrix elements of the form

$$\langle n'\ell'm'|\hat{L}_z|n\ell m\rangle \tag{70}$$

$$\langle n'\ell'm'|\hat{L}_\pm|n\ell m\rangle \ , \tag{71}$$

which will determine the selection rules for the magnetic dipole transition. The states $|n\ell m\rangle$ are eigenstates of the angular momentum projection operator, so the first matrix element (for $\hat{L}_z$) is nonzero for $n = n', \ell = \ell'$, and $m = m'$. The angular momentum projection raising or lowering operators have the following actions on the eigenstates:

$$\hat{L}_- |n\ell, m\rangle \propto |n\ell, m-1\rangle \tag{72}$$

$$\hat{L}_+ |n\ell, m\rangle \propto |n\ell, m+1\rangle \ , \tag{73}$$

and thus require that $n = n', \ell = \ell'$, and $m = m' \pm 1$ for each element to be nonzero (otherwise the matrix element results in the inner product of two orthogonal states). The total matrix element for the magnetic dipole transition $\mathcal{M}^{(M1)}_{nn'}$ is a linear combination of the three matrix elements indicated above. For the entire element to be nonzero, we must have the following conditions be satisfied

$$|\Delta n| = 0 \qquad |\Delta \ell| = 0 \qquad |\Delta m| = \{0, \pm 1\} \ , \tag{74}$$

which are the selection rules for magnetic dipole transitions.

2.3 Electric Quadrupole.

The electric quadrupole transitions are dependent on the matrix element

$$\mathcal{M}^{(E2)}_{nn'} = \frac{ie^\alpha_k k^\beta}{2m} \langle n'|\hat{p}^\alpha \hat{r}^\beta + \hat{p}^\beta \hat{r}^\alpha|n\rangle \ , \tag{75}$$

which if we employ a similar trick as Equation 55 we can write this as

$$\mathcal{M}^{(E2)}_{nn'} = \frac{ie^\alpha_k k^\beta}{2m} \langle n'|\frac{m}{2i\hbar}\left[\hat{r}^\alpha \hat{r}^\beta + \hat{r}^\beta \hat{r}^\alpha, \hat{\mathcal{H}}_{\text{atom}}\right]|n\rangle = \frac{e^\alpha_k k^\beta}{4\hbar}(\hbar\omega) \langle n'|\hat{r}^\alpha \hat{r}^\beta + \hat{r}^\beta \hat{r}^\alpha|n\rangle \ , \tag{76}$$

where $\hbar\omega$ is the difference in energy between state $|n\rangle$ and $|n'\rangle$, and corresponds to a single photon with frequency ω. We should note that since $\mathbf{e}_k \parallel \mathbf{k}$ we have $e_k^\alpha k^\beta = 0$ for $\beta = \alpha$, and so there are no diagonal terms, which allow us to add a term with a Kronecker delta with no effect:

$$\mathcal{M}_{nn'}^{(E2)} = \frac{e_k^\alpha k^\beta}{4\hbar}(\hbar\omega)\,\langle n'|\hat{r}^\alpha\hat{r}^\beta + \hat{r}^\beta\hat{r}^\alpha - \frac{2}{3}\hat{r}^2\delta_{\alpha\beta}|n\rangle \ . \tag{77}$$

We may now define the operator

$$\hat{Q}_{\alpha\beta} = e\left(\hat{r}^\alpha\hat{r}^\beta + \hat{r}^\beta\hat{r}^\alpha - \frac{2}{3}\hat{r}^2\delta_{\alpha\beta}\right) \ , \tag{78}$$

which we note is traceless and symmetric, so there are only five independent components. If we note that for a state with a given n and ℓ there are 5 independent basis vectors $m \in \{0, \pm1, \pm2\}$, which implies that the operator $\hat{Q}_{\alpha\beta}$ is the tensor representation of an $\ell = 2$ operator. Using this operator, the electric quadrupole transition matrix element is

$$\mathcal{M}_{nn'}^{(E2)} = \omega\frac{e_k^\alpha k^\beta}{4e}\,\langle n'|\hat{Q}_{\alpha\beta}|n\rangle \ . \tag{79}$$

We see the terms in this matrix element with $\alpha = \beta$ are zero, so we are left with terms that look like

$$\langle n'|\hat{x}\hat{y}|n\rangle \ , \tag{80}$$

and other permutations of $\{\hat{x}, \hat{y}, \hat{z}\}$. Since all of these position operators can be represented as a linear combinations of $\ell = 1$ spherical harmonics, the matrix element has, in general, terms which are of the form

$$\langle n'\ell'm'|Y_{1s}Y_{1t}|n\ell m\rangle \ , \tag{81}$$

and due to the way spherical harmonics multiply (addition of angular momentum rules) this product results in a linear combination of, in general, all of the spherical harmonics for $\ell = 0, 1, 2$. However, since the operator $\hat{Q}_{\alpha\beta}$ is traceless, we cannot have the Y_{00} spherical harmonic. Any matrix can be written as a linear combination of terms proportional to the identity matrix and terms proportional to traceless matrices. However, if the matrix we are interested in is itself traceless, all the coefficients of the identity matrix must be zero. Since the first spherical harmonic is a constant and thus proportional to the identity operator, these terms do not contribute to the total matrix element. Furthermore, since each term in the operator is proportional to the product of two $\ell = 1$ spherical harmonics, this operator is even under parity ($\ell \to -\ell$). Since the $\ell = 1$ spherical harmonics are odd under parity, there can also be no terms proportional to these spherical harmonics. We then see that the operator $\hat{Q}$ is a linear combination of only $\ell = 2$ spherical harmonics. The terms in this operator are each proportional to:

$$\int \mathrm{d}\Omega Y_{\ell'm'}^* Y_{2u} Y_{\ell m} \ , \tag{82}$$

with $u \in \{0, \pm1, \pm2\}$. We can immediately see, by parity, that $\Delta\ell = \pm1$ is not allowed. The inner and outer spherical harmonics, for $\Delta\ell = \pm1$, will always be opposite parity, so their product is odd, and the $\ell = 2$ spherical harmonic is even under parity, so the product is still odd. We then integrate an odd function over all space, which is identically zero. Therefore using the rules multiplication of spherical harmonics (the resulting ℓ value can range from $|\ell - 2|$ to $\ell + 2$, and with m taking

integer values between the positive and negative of the resulting ℓ value), and excluding $\Delta\ell = \pm 1$, the product results in integrals proportional to

$$\int \mathrm{d}\Omega Y^*_{\ell' m'} Y_{(\ell\pm 2),\{m\pm 2, m\pm 1, m\}} \tag{83}$$

$$\int \mathrm{d}\Omega Y^*_{\ell' m'} Y_{\ell, m} \ , \tag{84}$$

we can immediately read off the selection rules

$$\Delta m = \{\pm 2, \pm 1, 0\} \qquad \Delta\ell = \{\pm 2, 0\} \ , \tag{85}$$

for electric quadrupole transitions.

2.4 Spontaneous Decay of $2s$ state of Hydrogen.

The $2s$ state has quantum numbers $n = 2, \ell = 0, m = 0$, and the only state it could decay to is the $1s$ state which has quantum numbers $n = 1, \ell = 0, m = 0$. This transition has $|\Delta\ell| = 0$ and $|\Delta m| = 0$, which excludes electric dipole ($|\Delta\ell| = 1$). The magnetic dipole interaction, which depends on the orientation of the magnetic field, allows $\Delta\ell = 0$, but no change in principal quantum number so it is forbidden. This leaves only (to first order) the electric quadrupole channel. If we compare this to Equation 82 with $\ell' = \ell = 0$, we see

$$\int \mathrm{d}\Omega Y^*_{00} Y_{2u} Y_{00} \propto \int \mathrm{d}\Omega Y^*_{00} Y_{2u} \ , \tag{86}$$

using the addition of angular momentum properties to multiply the spherical harmonics. It is clear to see that due to the orthonormality of spherical harmonics, that this integral is identically zero. Therefore the $2s_0 \to 1s_0$ decay is strictly forbidden through all transition channels (to first order). Furthermore, we can show that $\ell' = 0 \to \ell = 0$ transitions are forbidden by all electric multipoles. In the general case, the nth multipole is a spin n operator, and therefore is proportional to Y_{na}. Using Equation 82, we see the matrix element for higher order electric multipoles is proportional to

$$\int \mathrm{d}\Omega Y^*_{00} Y_{na} Y_{00} \propto \int \mathrm{d}\Omega Y^*_{00} Y_{na} \ , \tag{87}$$

which is zero by orthonormality.
This condition enforces **for all transition channels** there can be no $\ell' = 0 \to \ell = 0$ transitions.

3 Transitions of Hydrogenic Atoms.

Consider the spontaneous decay of a Hydrogenic atom with nuclear charge Z from a $2p$ level to the ground state.

3.1 Wavelength of Emitted Photon.

For the $2p \to 1s$ transition of He^+ what is the wavelength of the radiation that is produced?

The energy levels of a Hydrogenic atom are given by

$$\varepsilon_n = \frac{Z^2}{n^2}\frac{mc^2\alpha^2}{2} = \frac{Z^2}{n^2}\varepsilon_0 \ , \tag{88}$$

where $n \in \mathbb{N}$ (excluding zero) and ε_0 is the Rydberg constant -13.6 eV. The energy of the emitted photon in the decay of the He^+ ($Z = 2$) state to the ground state is

$$\Delta\varepsilon = Z^2\left(\frac{1}{2^2} - \frac{1}{1^2}\right)\varepsilon_0 = -3\varepsilon_0 \ , \tag{89}$$

note $\varepsilon_0 < 0$. The corresponding wavelength of a photon with this energy is given by

$$\lambda = \frac{2\pi\hbar c}{|\Delta\varepsilon|} = \frac{2}{3}\pi\frac{\hbar c}{\varepsilon_0} = \frac{2}{3}\pi(14.50326)\text{nm} = 30.376 \text{ nm} \ , \tag{90}$$

which is in the ultraviolet regime.

3.2 Fermi's Golden Rule: Ionized Helium.

Write down the Golden rule formula and relevant matrix element for the transition rate for the spontaneous decay of a $2p$ level of a Hydrogenic ion to the $1s$ state via one photon emission. Here you can neglect spin and spin-orbit coupling. Specify the dominant multipole of the radiation field that determines the rate.

The $2p$ states can be denoted $|n\ell m\rangle = |21m\rangle$ and the $1s$ state as $|100\rangle$. This transition has $|\Delta\ell| = 1$ and $|\Delta m| = \{0, \pm 1\}$, so by the selection rules derived in problem two, the dominant multiple is the electric dipole. Fermi's rule gives the rate for the spontaneous decay of the $2s$ state to the ground state to be

$$\Gamma_{2p\to 1s} = \frac{2\pi}{\hbar}\left|\langle 1s; N_k + 1|\hat{\mathcal{H}}|2p; N_k\rangle\right|^2 \delta((E_{1s} + \hbar\omega) - E_{2p}) \ , \tag{91}$$

where $\hat{\mathcal{H}} = (e/mc)\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}$ is the interaction Hamiltonian between the electron and the free radiation field (given by Equation 36, and ω is the frequency of the emitted photon. After evaluating the action of the interaction Hamiltonian and the states of the radiation field, we are left with Equation 49. For this specific transition, the rate, by Fermi's Golden rule is

$$\Gamma_{2p\to 1s} = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\sum_\lambda \frac{4\pi e^2}{\omega_k}(N_k + 1)\left|\langle 100|\mathbf{e}_k \cdot \frac{\hat{\mathbf{p}}}{m}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|21m\rangle\right|^2 \delta((E_{1s} + \hbar\omega) - E_{2p}) \ . \tag{92}$$

where $m \in \{-1, 0, 1\}$. We have shown in class that the lifetimes for all $2p$ states are the same. The states $2p_{\{-1,0,1\}}$ only differ by orientation, and thus the lifetimes must be the same. For simplicity, we may only consider the $2p_0$ state, with no loss of information. We have previously stated that

this decay proceeds through the electric dipole transition so we can use the method in section 2.1 to write the rate as

$$\Gamma_{2p\to 1s} = \int \frac{\mathrm{d}^3k}{(2\pi)^3} \sum_\lambda \frac{4\pi e^2}{\omega_k}(N_k+1) \left| \frac{E_{210}-E_{100}}{i\hbar} \langle 100|\hat{\mathbf{r}}\cdot\mathbf{e}_k|210\rangle \right|^2 \delta((E_{1s}+\hbar\omega)-E_{2p}) \ . \quad (93)$$

3.3 Lifetime of $2p_0$ State of He^+.

Given that the same transition for hydrogen has a lifetime of 1.6×10^{-9} seconds calculate the lifetime for the $2p\to 1s$ transition for He^+.

The energy difference squared in Equation 93 becomes

$$|\Delta E|^2 = \left| Z^2\left(\frac{1}{2^2}-\frac{1}{1^2}\right)\varepsilon_0 \right|^2 = \frac{9}{16}Z^4\varepsilon_0^2 \ , \quad (94)$$

where Z is the atomic number, in this case 2. The rate to a single final state for Hydrogen is given by Shankar equation 18.5.88 (Principles of Quantum Mechanics, 2 ed. Page 519). This expression must be modified such that the Bohr radius $a_0 \to a_0/Z$, and we obtain

$$\Gamma_{2p\to 1s}(k) = \frac{2\pi}{\hbar}\left(\frac{e^2}{mc}\right)^2 \frac{\hbar c^2}{4\pi^2} m^2\omega \frac{2^{15}}{3^{11}}\frac{a_0^2}{Z^2}\delta((E_{1s}+\hbar\omega)-E_{2p}) \quad (95)$$

where we have yet to integrate over all photon momenta $\mathbf{k}$ and polarization λ. If we integrate the delta function over k and pick up a factor of two for the polarization we see

$$2\int_0^\infty k^2 \mathrm{d}k\mathrm{d}\Omega_{\hat{\mathbf{k}}}\delta((E_{1s}+\hbar\omega)-E_{2p}) = 2\frac{4\pi k^2}{\hbar c} \ . \quad (96)$$

Using the dispersion relation, $k=\omega/c$, and noting that $\hbar\omega$ is the energy of the emitted photon, equivalent to $|\Delta E|^2$. We see that $\hbar ck=\omega$, so the total rate is

$$\Gamma_{2p\to 1s} = \frac{2\pi}{\hbar}\left(\frac{e^2}{mc}\right)^2 \frac{\hbar c^2}{4\pi^2} m^2(\hbar ck)\frac{2^{16}}{3^{11}}\frac{a_0^2}{Z^2}\frac{4\pi k^2}{\hbar c} = e^4\frac{2^{17}}{3^{11}}\frac{a_0^2}{Z^2}k^3 = e^4\frac{2^{17}}{3^{11}}\frac{a_0^2}{Z^2}\left(\frac{\frac{3}{4}Z^2\varepsilon_0}{\hbar c}\right)^3 \ . \quad (97)$$

Thus we see

$$\Gamma_{2p\to 1s} \propto Z^4 \ , \quad (98)$$

and the rate for He^+ is

$$\tau^{\mathrm{He+}} = \frac{1}{\Gamma^{\mathrm{He+}}_{2p\to 1s}} = \frac{1}{2^4\Gamma^{\mathrm{H}}_{2p\to 1s}} = \frac{\tau^{\mathrm{H}}}{16} \ , \quad (99)$$

so given that the lifetime for the $2p$ state of Hydrogen is 1.6×10^{-9} seconds, the lifetime of the same state in singly ionized Helium is 10^{-10} seconds.

3.4 Likelihood of Transition changing Spin Projection.

The interaction of the radiation field with an atom also occurs via the magnetic moment of the electron. For Hydrogenic atoms this interaction is

$$\hat{H}_{\mathrm{int}} = -\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\hat{\mathbf{B}} \ , \quad (100)$$

where $\hat{\mathbf{B}}$ is the magnetic field operator for the photon field and $\boldsymbol{\sigma}$ is the Pauli spin operator for the electron, $-e$ and m are the charge and mass of the electron, respectively. Consider the $2p \to 1s$ transition with a spin-flip, *e.g.*, $|2p_0, m_s\rangle \to |1s_0, m_s'\rangle$. Calculate (up to a prefactor of order unity) the ratio $\Gamma_{2p\uparrow\to 1s\downarrow}/\Gamma_{2p\uparrow\to 1s\uparrow}$.

First let us note we may ignore factors of Z for they will exactly cancel when we take the ratios of the rates. The total interaction Hamiltonian is

$$\hat{\mathcal{H}}_{\text{int}} = -\frac{e}{c}\left(\hat{\mathbf{A}}\cdot\frac{\hat{\mathbf{p}}}{m}\right) - \frac{e\hbar}{2mc}\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{B}}\right) \ , \tag{101}$$

and the initial and final states are given by

$$|i\rangle = |21m_\ell\rangle \otimes |m_s\rangle \otimes |0_k\rangle \equiv |21m_\ell; m_s; 0_k\rangle \tag{102}$$

$$|f\rangle = |100\rangle \otimes |m_s'\rangle \otimes |1_k\rangle \equiv |100; m_s'; 1_k\rangle \ . \tag{103}$$

The matrix element relevant to Fermi's Golden rule is $\langle f|\hat{\mathcal{H}}_{\text{int}}|i\rangle$, which separates into two terms:

$$-\frac{e}{c}\langle 100; m_s'; 1_k|\hat{\mathbf{A}}\cdot\frac{\hat{\mathbf{p}}}{m}|21m_\ell; m_s; 0_k\rangle - \frac{e\hbar}{2mc}\langle 100; m_s'; 1_k|\boldsymbol{\sigma}\cdot\hat{\mathbf{B}}|21m_\ell; m_s; 0_k\rangle \ , \tag{104}$$

we will refer to the first as term **1** and the second as term **2**. First we consider **2** which interacts with the spin state, the spatial state, and the field:

$$\langle 100; m_s'; 1_k|\boldsymbol{\sigma}\cdot\hat{\mathbf{B}}|21m_\ell; m_s; 0_k\rangle \ , \tag{105}$$

where the magnetic field operator is given by

$$\hat{\mathbf{B}} = \sum_{\mathbf{k},\lambda} i\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}\left(\hat{a}_k(\mathbf{k}\times\mathbf{e}_k)e^{i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)} - \hat{a}_k^\dagger(\mathbf{k}\times\mathbf{e}_k^*)e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}\right) \ , \tag{106}$$

and we see the first term will produce an orthogonal state when we insert it into the matrix element. We will take this to be normalized over volume and set V to unity. Additionally because only one mode interacts in the transition, we can consider the operator $\hat{\mathbf{B}}$ as one mode. Since we will be taking the modulus squared of this matrix element, the exponential factor in time will become unity. The matrix element in **2** can be expressed as

$$\frac{2}{\hbar}\langle 100; m_s'|\hat{\mathbf{S}}\cdot(\mathbf{k}\times\mathbf{e}_k^*)\, e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}}|21m_\ell; m_s\rangle \otimes \langle 1_k|\hat{a}_k^\dagger|0_k\rangle \ , \tag{107}$$

where $\hat{\mathbf{S}}$ is the spin operator vector. The matrix element of field states is simply unity. Let us define a vector along the direction of the magnetic field $\mathbf{h} = \mathbf{k}\times\mathbf{e}_k^*$, so that the dot product with the spin operator yields the linear combination

$$h_x\hat{S}_x + h_y\hat{S}_y + h_z\hat{S}_z = h_+\hat{S}_+ + h_-\hat{S}_- + h_z\hat{S}_z \ , \tag{108}$$

if we use the coordinates z and $x \pm iy$. It is evident that $h_\pm = \frac{1}{2}(h_x \mp ih_y)$. Using this, the matrix element becomes

$$\langle 100; m_s'|\left(h_+\hat{S}_+ + h_-\hat{S}_- + h_z\hat{S}_z\right)e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}}|21m_\ell; m_s\rangle \ , \tag{109}$$

and we are free to expand the exponential to first order, yielding the sum of the matrix elements

$$0^{th}\text{ order}: \ \langle m_s'|h_+\hat{S}_+ + h_-\hat{S}_- + h_z\hat{S}_z|m_s\rangle \otimes \langle 100|\mathbb{1}|21m_\ell\rangle \tag{110}$$

$$1^{st}\text{ order}: \ \langle m_s'|h_+\hat{S}_+ + h_-\hat{S}_- + h_z\hat{S}_z|m_s\rangle \otimes \langle 100| - i\mathbf{k}\cdot\hat{\mathbf{r}}|21m_\ell\rangle \ . \tag{111}$$

Obviously the electric dipole term vanishes because the operator is the identity to the spatial states, and thus we see the term **2** can be written as

$$\frac{e\hbar}{2mc}\sqrt{\frac{2\pi\hbar c^2}{\omega}}\frac{2}{\hbar}\langle m_s'|h_+\hat{S}_+ + h_-\hat{S}_- + h_z\hat{S}_z|m_s\rangle \otimes \langle 100|\mathbf{k}\cdot\hat{\mathbf{r}}|21m_\ell\rangle \tag{112}$$

Let us now define the components of the wave vector that are parallel with the components of the "magnetic field" vector $\mathbf{h}$. Clearly $k_i = \mathbf{k}\cdot\hat{\mathbf{x}}_i$, where i are the Cartesian components. We then have that

$$k_\pm = \mp\frac{1}{\sqrt{2}}\left(k_x \pm k_y\right) \ , \tag{113}$$

so we have a matrix element equivalent to the electric dipole term. Let us consider the spatial matrix element in Equation 112:

$$\langle 100|\mathbf{k}\cdot\hat{\mathbf{r}}|21m_\ell\rangle = \int \mathrm{d}^3r\ \psi^*_{100}(\mathbf{k}\cdot\hat{\mathbf{r}})\psi_{21m_\ell} \ , \tag{114}$$

for which we turn to Shankar (section 18.5) to evaluate the integral:

$$\sqrt{\frac{4\pi}{3}}\int R_{10}rR_{21}r^2\mathrm{d}r\int Y^*_{00}\left(-k_+Y_{1,-1} + k_zY_{1,0} - k_+Y_{1,1}\right)Y_{1m_\ell}\mathrm{d}\Omega$$
$$= \left(\frac{3}{2}\right)^{1/2}\frac{2^8}{3^5}\frac{a_0}{3^{1/2}}\left(k_+\delta_{m,1} + k_z\delta m,0 + k_+\delta m,-1\right), \tag{115}$$

where the $\delta_{a,b}$ represent the Kronecker delta (see Shankar equation 18.5.86). In a simmilar fashion to Shankar, we take the modulus squared of this quantity and then average over the possible m_ℓ values (1,0,-1), the integral reduces to

$$\frac{2^{15}}{3^{10}}\frac{k_+^2 + k_-^2 + k_z^2}{3} = \frac{2^{15}}{3^{11}}a_0^2k^2 \ , \tag{116}$$

where k is the magnitude of the wave vector. Let us now return to the spin matrix element, which is a linear combination of the three relevant spin operators:

$$h_z\langle m_s'|\hat{S}_z|m_s\rangle + h_+\langle m_s'|\hat{S}_+|m_s\rangle + h_-\langle m_s'|\hat{S}_-|m_s\rangle \ , \tag{117}$$

We see the first term contributes when there is no spin-flip, the second contributes when the initial state has spin projection $-\frac{1}{2}$ and the initial has spin projection $+\frac{1}{2}$, and finally the third contributes when initial state has spin projection $+\frac{1}{2}$ and the initial has spin projection $-\frac{1}{2}$. We are interested in the transition $2p_\uparrow \to 1s_\downarrow$, so only the final term contributes to the rate. We may evaluate the spin matrix element using

$$\hat{S}_\pm|s,m_s\rangle = \hbar\sqrt{s(s+1) - m(m\pm1)}\,|s,m_s\pm1\rangle \ , \tag{118}$$

in this case we have $s = 1/2$ and $m_s = 1/2$, so

$$\hat{S}_-|+\tfrac{1}{2}\rangle = \hbar\sqrt{\tfrac{3}{4} - \tfrac{1}{2}(-\tfrac{1}{2})}\,|-\tfrac{1}{2}\rangle = \hbar|-\tfrac{1}{2}\rangle \ , \tag{119}$$

so the matrix element $\langle-\frac{1}{2}|\hat{S}_-|+\frac{1}{2}\rangle$ is $\hbar$. Therefore the modulus squared (ignoring the factor of $\hbar$) of the spin component is simply

$$|h_-|^2 = \left|\frac{1}{2}(h_x + ih_y)\right|^2 = \frac{1}{4}(h_x^2 + h_y^2) = \frac{1}{4}\left(|\mathbf{h}|^2 - h_z^2\right) \ , \tag{120}$$

and the magnitude of the "magnetic field" vector is

$$|\mathbf{h}| = |\mathbf{k} \times \mathbf{e}_k^*| = k \ , \tag{121}$$

because the polarization basis vector has unit magnitude. We may take the projection of this vector onto the z axis by introducing the polar angle θ:

$$h_z = |\mathbf{h}| \cos\theta = k \cos\theta \ , \tag{122}$$

and so Equation 120 becomes

$$|h_-|^2 = \frac{1}{4}(k^2 - k^2\cos^2\theta) = \left(\frac{k}{2}\right)^2 (1 - \cos^2\theta) \ . \tag{123}$$

We now collect all the results and write the modulus squared of the matrix element relevant in the Golden rule as

$$\left(\frac{e\hbar}{2mc}\right)^2 \left|\langle f|\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{B}}|i\rangle\right|^2 = \left(\hbar^2 \left(\frac{k}{2}\right)^2 (1 - \cos^2\theta)\right) \left(\frac{2^{15}}{3^{11}} a_0^2 k^2\right) \left(\frac{e\hbar}{2mc}\sqrt{\frac{2\pi\hbar c^2}{\omega}}\frac{2}{\hbar}\right)^2 \tag{124}$$

$$= \frac{k^4}{\omega}(1 - \cos^2\theta)\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^3 e^2 \pi}{m^2} = k^3(1 - \cos^2\theta)\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^3 e^2 \pi}{m^2 c} \ , \tag{125}$$

after using the dispersion relation $\omega = ck$. From Fermi's Golden rule, the rate to a single final state is given by

$$\Gamma(k) = \frac{2\pi}{\hbar}\left\{k^3(1 - \cos^2\theta)\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^3 e^2 \pi}{m^2 c}\right\} \delta((E_{1s} + \hbar c k) - E_{2p}) \ , \tag{126}$$

which we must integrate over all possible final k and sum over polarization states λ. We will integrate in spherical coordinates such that $\mathrm{d}^3k = k^2 \mathrm{d}k\mathrm{d}\phi\mathrm{d}(\cos\theta)$, but we also pick up a factor of $(2\pi)^{-3}$ for integrating in k space, yielding

$$\Gamma_{2p\uparrow\to 1s\downarrow} = (2)2\pi \int_0^\infty \frac{k^2 \mathrm{d}k}{(2\pi)^3}\frac{2\pi}{\hbar}\left\{k^3\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^3 e^2 \pi}{m^2 c}\right\} \delta((E_{1s} + \hbar c k) - E_{2p}) \int_{-1}^{1} \mathrm{d}(\cos\theta)(1 - \cos^2\theta) \ ,$$

where the prefactor of 2 comes from summing over the polarization states. Some simplification, and evaluating the angular integral yields

$$\Gamma_{2p\uparrow\to 1s\downarrow} = \left\{\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^2 e^2}{m^2 c}\right\} \int_0^\infty k^5 \mathrm{d}k \delta((E_{1s} + \hbar c k) - E_{2p}) \left(\frac{4}{3}\right) \ , \tag{127}$$

so performing the k integral yields

$$\int_0^\infty k^5 \mathrm{d}k \delta((E_{1s} + \hbar c k) - E_{2p}) = \frac{k^5}{\hbar c} \ . \tag{128}$$

We then obtain the result

$$\Gamma_{2p\uparrow\to 1s\downarrow} = \left\{\left(\frac{2^{14}}{3^{11}}\right) a_0^2 \frac{\hbar^2 e^2}{m^2 c}\right\} \frac{k^5}{\hbar c}\left(\frac{4}{3}\right) = \left(\frac{2^{16}}{3^{12}}\right) a_0^2 \frac{\hbar e^2}{m^2 c^2} k^5 = \frac{2^{16}}{3^{12}} a_0^2 \frac{\hbar^2}{m^2 c} \alpha k^5 \ . \tag{129}$$

Now we consider **1**, and we see the operator does not interact with the spin vector space, so it may be written as

$$-\frac{e}{c}\langle 100;1_k|\hat{\mathbf{A}}\cdot\frac{\hat{\mathbf{p}}}{m}|21m_\ell;0_k\rangle\otimes\langle m_s'|\mathbb{1}|m_s\rangle \ , \tag{130}$$

so we see this term only contributes when there is no spin-flip. For transitions without a spin-flip, this matrix element can be evaluated as in problem #2. Following the procedure there, we expand the resulting exponential to first order, but keep only the zeroth order term because the first order term is zero for the $2p\to 1s$ transition (*i.e.*, expand the exponetnial as $e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}}=1-i\mathbf{k}\cdot\hat{\mathbf{r}}+\ldots$ and only the unity term contributes because $|\Delta\ell|=1$ so it is M1 and E2 forbidden). Let us consider a transition withoit a spin flip, so the spin matrix element is one, and the total matrix element is nonzero, then from Equation 58 we have

$$-\frac{e}{c}\langle 100;m_s';1_k|\hat{\mathbf{A}}\cdot\frac{\hat{\mathbf{p}}}{m}|21m_\ell;m_s;0_k\rangle=-\frac{e}{c}\frac{\frac{3}{4}Z^2\varepsilon_0}{i\hbar}\langle 210|\hat{\mathbf{r}}\cdot\mathbf{e}_k|100\rangle=\frac{3Z^2e}{4i\hbar c}|\varepsilon_0|\langle 210|\hat{\mathbf{r}}|100\rangle \ . \tag{131}$$

If we are interested in the rate for a transition with no spiin-flip, then we must take the modulus squared of the sum of terms **1** and **2**. However, if we note that in order to get nonzero matrix elements for the spin interaction (see Equation 110) we have to expand the exponential to first order, we see this interaction is supressed by a factor of α^2 (magnetic dipole and electric quadrupole relative strengths). Therefore, term **2** is negligible compared to term **1** for transitions withouut a spin-flip, and so the rate is simply

$$\Gamma_{2p\uparrow\to 1s\uparrow}=\frac{2\pi}{\hbar}\left|-\frac{e}{c}\langle 100;m_s';1_k|\hat{\mathbf{A}}\cdot\frac{\hat{\mathbf{p}}}{m}|21m_\ell;m_s;0_k\rangle\right|^2\delta((E_{1s}+\hbar\omega)-E_{2p}) \ , \tag{132}$$

and using the result from Shankar[5] (also section 3.3) we see

$$\Gamma_{2p\uparrow\to 1s\uparrow}=\frac{2^{16}}{3^{11}}\alpha ck^3a_0^2=\left(\frac{2}{3}\right)^8\alpha^5\frac{mc^2}{\hbar} \ . \tag{133}$$

Note that there is an energy shift due to the alignment of the electron spin with the magnetic field. However, for this case, with no spin-flip, the energies of both final and initial states are shifted by the same amount, so the result from Shankar remains valid.

Let us take the ratio of Equation 129 to Equation 133. It is important to note that the k values are different for both the rates due to the fact there is an energy shift due to the alignment of the spin in the transition $2p\uparrow\to 1s\downarrow$, this effect is negligible, so we see an approximate ratio is

$$\frac{\frac{2^{16}}{3^{12}}a_0^2\frac{\hbar^2}{m^2c}\alpha k^5}{\frac{2^{16}}{3^{11}}\alpha ck^3a_0^2}=\frac{2^{16}}{3^{12}}\frac{3^{11}}{2^{16}}\frac{\hbar^2}{m^2c}k^2=\frac{\hbar^2}{3m^2c^2}k^2 \ . \tag{134}$$

The energy of the emitted photon from the non spin-flip transition is $\hbar\omega=\frac{3}{4}\varepsilon_0$, and thus

$$k=\frac{\hbar\omega}{\hbar c}=\frac{3}{4}\frac{\varepsilon_0}{\hbar c}=\frac{3e^2}{8a_0\hbar c} \ , \tag{135}$$

and the ratio of the rates is therefore

$$\frac{\hbar^2}{3m^2c^2}\left(\frac{3e^2}{8a_0\hbar c}\right)^2=\frac{3}{64}\frac{e^4}{m^2\left(\frac{\hbar^2}{me^2}\right)^2c^4}=\frac{3}{64}\left(\frac{e^2}{\hbar c}\right)^4=\frac{3\alpha}{64}=1.33\times 10^{-10} \ . \tag{136}$$

[5]Shankar, Principles of Quantum Mechanics, 2 ed. Page 520.

4 Lifetime of Excited Hyperfine State.

The excited hyperfine levels of interstellar hydrogen are believed to be populated via binary collision scattering. As a result microwave radiation corresponding to transitions between the hyperfine levels is observed. Calculate the lifetime of the excited hyperfine level via single photon emission. Hint: check selection rules and identify the relevant radiation channel, *i.e.*, E_1, M_1, E_2, etc.

Let the total magnetic moment of the electron-proton system be $\boldsymbol{\mu}$, which is the sum of the magnetic moments of the electron and proton:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \boldsymbol{\mu}_p = -g_e \frac{\mu_B}{\hbar}\mathbf{S} + g_p \frac{\mu_N}{\hbar}\mathbf{I} \ , \tag{137}$$

where $g_e \simeq 2$ and $g_p \simeq 5.86$ are the Landé g-factors for the electron and proton, μ_B and μ_N are the Bohr and nuclear magnetons, and $\mathbf{S}$ and $\mathbf{I}$ are the spin of the electron and proton, respectively. This overall magnetic moment interacts with the magnetic field of the free radiation field as $\boldsymbol{\mu} \cdot \mathbf{B}$, and thus if we elevate these to quantum mechanical opertors, the rate is given by Fermi's Golden rule:

$$\Gamma = \frac{2\pi}{\hbar}\left|\langle f|\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{B}}|i\rangle\right|^2 \delta(E_f - E_i) \ , \tag{138}$$

where $\{|f\rangle, E_f\}$ and $\{|i\rangle, E_i\}$ are the final and initial states, and their energies, respectively. Note that we do not need to consider the interaction Hamiltonian of the kinetic momentum because, as shown in section 3.4, when the spin state changes, the matrix element $\langle f|\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}|i\rangle$ vanishes[6]. The state vectors are the direct products of a spatial state, a spin state, and a field state:

$$|t\rangle = |n\ell m_\ell\rangle \otimes |F, M\rangle \otimes |\{N_k\}\rangle \ \ , \tag{139}$$

where $\{n, \ell, m_\ell\}$ are the principal, orbital angular momentum, and orbital projection quantum numbers. The quantum numbers F, M define the hyperfine state, where F is the total spin of the electron-proton system, and F is its projection onto the z axis. Finally, $\{N_k\}$ represents the field configuration, *i.e.*, the occupancy number of each field mode k. Consider a Hydrogen atom in an arbitrary spatial state, for a transition from the excited hyperfine state to the ground state, through one photon emission, the initial and final states are

$$|i\rangle = |n\ell m_\ell\rangle \otimes |1, M\rangle \otimes |N_k\rangle \tag{140}$$

$$|f\rangle = |n\ell m_\ell\rangle \otimes |0, 0\rangle \otimes |N_k + 1\rangle \ \ , \tag{141}$$

where we only consider one mode k (the mode of the emitted photon) because all other modes are spectators to this decay. However, for simplicity we will consider only the $1s$ state, so there is no orbital coupling to the magnetic field, and no spin-orbit interaction. Note that there is no change in the spatial state of the atom, so the energy of the emitted photon $\hbar\omega$ is simply the energy splitting between the excited hyperfine state and the ground hyperfine state. Since none of the spatial quantum numbers are changed this is forbidden by electric dipole, but allowed by magnetic dipole. Additionally, if the atom is not in an s state ($\ell = 0$), then this transition is allowed by electric quadrupole as well. Let us now consider the hyperfine spin state vectors $|MF\rangle$, which are

[6]The kinetic momentum operator is the identity to spin states:

$$\langle f|\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}|i\rangle = \langle n\ell m|\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}|n'\ell' m'\rangle \otimes \langle 1M|\mathbb{1}|00\rangle = 0$$

linear combinations of the individual spins of the proton and electron. There is the symmetric triplet, with total spin $F = 1$:

$$|1,1\rangle = |\uparrow\rangle_p \otimes |\uparrow\rangle_e \tag{142}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}}\left\{|\uparrow\rangle_p \otimes |\downarrow\rangle_e + |\downarrow\rangle_p \otimes |\uparrow\rangle_e\right\} \tag{143}$$

$$|1,-1\rangle = |\downarrow\rangle_p \otimes |\downarrow\rangle_e \ , \tag{144}$$

and the antisymmetric singlet, with total spin $F = 0$:

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left\{|\uparrow\rangle_p \otimes |\downarrow\rangle_e - |\downarrow\rangle_p \otimes |\uparrow\rangle_e\right\} \ . \tag{145}$$

We are using the notation that $|\uparrow\rangle$ is a projection state with eigenvalue $+\hbar/2$ and $|\downarrow\rangle$ is a projection state with eigenvalue $-\hbar/2$.

We are only concerned with the mode that participates in the decay, k, and the magnetic field operator for this mode is

$$i\sqrt{\frac{2\pi\hbar c^2}{V\omega}}\left(\hat{a}_k(\mathbf{k}\times\mathbf{e}_k)e^{i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)} - \hat{a}_k^\dagger(\mathbf{k}\times\mathbf{e}_k^*)e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}\right) \ , \tag{146}$$

where ω is the frequency of the photon in this mode. We may normalize this with respect to volume, and set V to unity. Thus, the matrix element from Fermi's Golden rule is

$$i\sqrt{\frac{2\pi\hbar c^2}{\omega}}\,\langle 100;0,0;N_k+1|\hat{\boldsymbol{\mu}}\cdot\left(\hat{a}_k(\mathbf{k}\times\mathbf{e}_k)e^{i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)} - \hat{a}_k^\dagger(\mathbf{k}\times\mathbf{e}_k^*)e^{-i(\mathbf{k}\cdot\hat{\mathbf{r}}-\omega t)}\right)|100;1,M;N_k\rangle$$

but we can immediateely take evaluate the field component:

$$\langle N_k+1|\hat{a}_k|N_k\rangle - \langle N_k+1|\hat{a}_k^\dagger|N_k\rangle = 0 - \sqrt{N_k+1}\,\langle N_k+1|n_k+1\rangle = -\sqrt{N_k+1}\ . \tag{147}$$

Knowing that we will be taking the modulus squared of the resulting matrix element, we may discard the factor of i out front, and the negative due to subtraction. Additionally, the $e^{i\omega t}$ term is effectively a constant regarding the matrix element, so it may be factored out, now when it's modulus is squared, we acquire a factor of unity. The resulting matrix element, including relevant prefactors is

$$\sqrt{\frac{2\pi\hbar c^2}{\omega}}\sqrt{N_k+1}\,\langle 100;0,0|\hat{\boldsymbol{\mu}}\cdot(\mathbf{k}\times\mathbf{e}_k)e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|100;1,M\rangle \ , \tag{148}$$

where we have taken the complex conjugate of the operator, knowing that we will be taking the square of its modulus. Let us define a direction $\mathbf{h}$ such that

$$\mathbf{h} = \mathbf{k}\times\mathbf{e}_k \ , \tag{149}$$

which has magnitude k (unless it is zero, which is uninteresting because the matrix element will be zero). For simplicity, we will take the case where there were no photons in the mode of the emitted photon before the decay. Additionally, the magnitude of the wave vector is simply ω/c and so we can write the matrix element as

$$\sqrt{\frac{2\pi\hbar c^2}{\omega}}\,\langle 100;0,0|(\hat{\boldsymbol{\mu}}\cdot\mathbf{h})e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}|100;1,M\rangle \ . \tag{150}$$

To zero order, we may consider the spin of the proton fixed, and therefore neglect it, so that

$$\boldsymbol{\mu} \to \boldsymbol{\mu}_e = -g_e \frac{\mu_B}{\hbar} \mathbf{S} \ , \tag{151}$$

we may also expand the exponential to zero order, in which case, the spin operator will be the identity to the spatial states. As such, the matrix element from the Golden rule is

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \langle 0,0|(\hat{\mathbf{S}} \cdot \mathbf{h})|1,M\rangle \otimes \langle 100|\mathbb{1}|100\rangle \ , \tag{152}$$

where again we have dropped the negative sign because all relevant quantities depend only on the square of the matrix element. In a similar fashion to Equation 110, we have

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \langle 0,0|h_+ \hat{S}_+ + h_- \hat{S}_- + h_z \hat{S}_z|1,M\rangle \ , \tag{153}$$

so the three possible matrix elements are

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] (h_+ \hat{S}_+ + h_- \hat{S}_- + h_z \hat{S}_z) \left[|\uparrow\uparrow\rangle\right] \tag{154}$$

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] (h_+ \hat{S}_+ + h_- \hat{S}_- + h_z \hat{S}_z) \left[\frac{1}{\sqrt{2}} \{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\}\right] \tag{155}$$

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] (h_+ \hat{S}_+ + h_- \hat{S}_- + h_z \hat{S}_z) \left[|\downarrow\downarrow\rangle\right] \ , \tag{156}$$

where the first arrow denotes the projection of the proton spin and the second denotes the electron spin. Noting the action of the spin operators this becomes

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] h_- \hat{S}_- \left[|\uparrow\uparrow\rangle\right] = g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} h_- \frac{\hbar}{\sqrt{2}} \tag{157}$$

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] h_z \hat{S}_z \left[\frac{1}{\sqrt{2}} \{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\}\right] = g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \frac{h_z}{2} (-\hbar) \tag{158}$$

$$g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} \left[\frac{1}{\sqrt{2}} \{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\}\right] h_+ \hat{S}_+ \left[|\downarrow\downarrow\rangle\right] = -g_e \frac{\mu_B}{\hbar} \sqrt{\frac{2\pi\hbar c^2}{\omega}} h_+ \frac{\hbar}{\sqrt{2}} \ . \tag{159}$$

We will label the results $s_{++}, s_{\pm}, s{-}{-}$, and we see

$$s_{++} = 2\mu_B \sqrt{\frac{\pi\hbar c^2}{\omega}} h_- \quad s_{\pm} = -\sqrt{2}\mu_B \sqrt{\frac{\pi\hbar c^2}{\omega}} h_z \quad s_{--} = -2\mu_B \sqrt{\frac{\pi\hbar c^2}{\omega}} h_+ \ . \tag{160}$$

If we take the modulus squared of each, add them and average (divide by three), we obtain the expression

$$2\mu_B^2 \frac{\pi\hbar c^2}{3\omega} \left(2h_-^2 + h_z^2 + 2h_+^2\right) = 2\frac{e^2\hbar^2}{12m^2c^2} \frac{\pi\hbar c^2}{\omega} \left(2h_-^2 + h_z^2 + 2h_+^2\right) = \frac{\pi e^2\hbar^3}{3m^2\omega} \left(h_-^2 + \frac{1}{2}h_z^2 + h_+^2\right) \ .$$

The magnitudes of each of the h components squared must add to k, and we know $h_z = k\cos\theta$, we therefore see the above expression simplifies to

$$\frac{\pi e^2\hbar^3}{3m^2\omega} \left(\left|\frac{1}{2}(h_x + ih_y)\right|^2 + \left|\frac{1}{2}(h_x - ih_y)\right|^2 + \frac{h_z^2}{2}\right) = \frac{\pi e^2\hbar^3}{3m^2\omega} \left(\frac{1}{4}\left(2h_x^2 + 2h_y^2\right) + \frac{h_z^2}{2}\right) \ , \tag{161}$$

simplifying to

$$\frac{\pi e^2\hbar^3}{6m^2\omega}\left(h_x^2+h_y^2+h_z^2\right)=\frac{\pi e^2\hbar^3}{6m^2\omega}k^2=\frac{\pi e^2\hbar^3}{6m^2c}k\ . \tag{162}$$

We may now apply Fermi's Golden rule to obtain the rate to a single final state

$$\Gamma(k)=\frac{2\pi}{\hbar}\frac{\pi e^2\hbar^3}{6m^2c}k\delta((E_0+\hbar ck)-E_1)\ , \tag{163}$$

where E_1 is the energy for $F=1$ and E_0 is the answer for $F=0$. We may now integrate over all final k, and pick up a factor of two for the sum over polarizations

$$\Gamma=\frac{4\pi}{\hbar}\frac{\pi e^2\hbar^3}{6m^2c}\int\frac{\mathrm{d}^3k}{(2\pi)^3}k\delta((E_0+\hbar ck)-E_1)\ , \tag{164}$$

using spherical coordinates and immediately integrating over the azimuthal and polar angles, we have

$$\Gamma=(4\pi)\frac{4\pi}{\hbar}\frac{\pi e^2\hbar^3}{6m^2c}\int_0^\infty\frac{k^2\mathrm{d}k}{(2\pi)^3}k\delta((E_0+\hbar ck)-E_1)=\frac{e^2\hbar^2}{3m^2c}\int_0^\infty k^3\mathrm{d}k\delta((E_0+\hbar ck)-E_1)\ . \tag{165}$$

As we have evaluated before, the k integral is

$$\int_0^\infty k^3\mathrm{d}k\delta((E_0+\hbar ck)-E_1)=\frac{k^3}{\hbar c}\ , \tag{166}$$

where $k=|\Delta E_{\mathrm{hf}}|/\hbar c$. Alternatively, knowing the hyperfine transition results in a 21 cm emission, we have

$$k=\frac{2\pi}{\lambda}\simeq 0.3\ \mathrm{cm}^{-1}. \tag{167}$$

The total rate is then

$$\Gamma=\frac{e^2\hbar^2}{3m^2c}\frac{k^3}{\hbar c}=\frac{e^2\hbar}{3m^2c^2}k^3\ , \tag{168}$$

and the lifetime is then

$$\tau=\frac{3m^2c^2}{e^2\hbar k^3}\ . \tag{169}$$