I. The interaction of electromagnetic fields with matter.

The Lagrangian for the charge $q$ in electromagnetic potentials $V$ and $\vec{A}$ is,

$$L = \frac{1}{2}mv^2 - qV + \frac{q}{c} \vec{A} \cdot \vec{v},$$

where the interaction is through the scalar potential ($qV$) and the vector potential ($\vec{J} \cdot \vec{A} = q\vec{v} \cdot \vec{A}$); the fields in terms of the potentials are,

$$\vec{B} = \vec{\nabla} \times \vec{A}, \quad \vec{E} = -\vec{\nabla}V - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}.$$ (1)

Canonical momenta are defined by,

$$p_i = \frac{\partial L}{\partial \dot{x}_i} = m\dot{x}_i + \frac{q}{c} A_i,$$

or

$$\vec{p} = m\vec{v} + \frac{q}{c} \vec{A}.$$ (2)

The Hamiltonian can thus be written as $H = \sum_i p_i \dot{x}_i - L$, or

$$H = \frac{1}{2m}(\vec{p} - q\vec{A}/c)^2 + qV.$$ (2)

To go over to quantum mechanics, one turns the canonical momentum into a quantum operator by the transcription $\vec{p} \rightarrow \hbar / i \vec{\nabla}$.

II. Maxwell’s equations in free space and their solutions.

The Maxwell equations in free space (Gaussian units) are,

$$\vec{\nabla} \cdot \vec{E} = 0 \quad \vec{\nabla} \cdot \vec{B} = 0,$$

$$\vec{\nabla} \times \vec{B} = \frac{1}{c} \frac{\partial \vec{E}}{\partial t} \quad \vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}.$$ (1)

The two equations on the left imply that in free space the (time-dependent) fields can be written in terms of the potentials, as in (1), but where the scalar potential is zero and
(Coulomb Gauge) \( \vec{\nabla} \cdot \vec{A} = 0 \). The Hamiltonian for the fields only can therefore be written in terms of the vector potential alone as,

\[
H_{\text{fields}} = \frac{1}{8\pi} \int d^3r \left( \vec{E}^2 + \vec{B}^2 \right)
\]

\[
= \frac{1}{8\pi} \int d^3r \left[ \left( -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right)^2 + (\vec{\nabla} \times \vec{A})^2 \right].
\]

(3)

The second pair of the Maxwell equations imply that the vector potential satisfies the wave equation,

\[
\frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} - \vec{\nabla}^2 \vec{A} = 0.
\]

(4)

Solutions of (4) are plane waves with \( \omega = ck \):

\[
\vec{A}(\vec{r}, t) = \vec{A}_0 e^{i(k \cdot \vec{r} - \omega t)}.
\]

The general solution in free space is therefore,

\[
\vec{A}(\vec{r}, t) = \sum_{\vec{k}, \lambda} \left[ C_{k, \lambda} \vec{\epsilon}_{k, \lambda} e^{i(k \cdot \vec{r} - \omega t)} + C^*_{k, \lambda} \vec{\epsilon}_{k, \lambda} e^{-i(k \cdot \vec{r} - \omega t)} \right] / \sqrt{V},
\]

where the wavevector and polarization vectors form an orthogonal triplet,

\[
\vec{k} \cdot \vec{\epsilon}_{k, \lambda} = 0, \quad \vec{\epsilon}_{k, 1} \cdot \vec{\epsilon}_{k, 2} = 0, \quad \vec{\epsilon}_{k, 1} \times \vec{\epsilon}_{k, 2} = \vec{k}/k.
\]

For convenience, define new dimensionless coefficients \( a, a^* \) from,

\[
C_{k, \lambda} = c \sqrt{\frac{2\pi \hbar}{\omega}} a_{k, \lambda}.
\]

Then the general solution of the wave equation becomes,

\[
\vec{A}(\vec{r}, t) = \sum_{\vec{k}, \lambda} c \sqrt{\frac{2\pi \hbar}{\omega V}} \left[ a_{k, \lambda} \vec{\epsilon}_{k, \lambda} e^{i(k \cdot \vec{r} - \omega t)} + \text{c.c.} \right],
\]

(5)

together with the associated orthonormality of the plane waves,

\[
\int d^3r e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{k}' \cdot \vec{r}} = V \delta_{\vec{k}, \vec{k}'}.
\]

Substitution of (5) into (3) results in a very simplified form of the Hamiltonian,

\[
H_{\text{fields}} = \sum_{k, \lambda} (a^*_{k, \lambda} a_{k, \lambda} + \frac{1}{2}) \hbar \omega.
\]

(6)
III. Photons

To quantize the theory defined by (5) and (6) we promote the $a$-coefficients to creation and destruction operators,

$$a_{k,\lambda} \rightarrow \hat{a}_{k,\lambda}, \quad a^*_{k,\lambda} \rightarrow \hat{a}^\dagger_{k,\lambda},$$

equipped with Bose commutation relations,

$$[\hat{a}_{k,\lambda}, \hat{a}^\dagger_{k',\lambda'}] = \delta_{k,k'}\delta_{\lambda,\lambda'}.$$

The Hamiltonian then becomes a sum of number operators counting photon numbers of differing wavevector and polarization. The infinite "zero-point" energy which is the sum over $1/2$ is discarded as unphysical. States of an indefinite number of photons ("Fock states") are defined from the action of the creation and destruction operators:

**general state:** $|n_{E_1,\lambda_1}, n_{E_2,\lambda_2}, \cdots\rangle$,

$$\hat{a}_{k,\lambda} |n_{k,\lambda}\rangle = \sqrt{n_{k,\lambda}} |n_{k,\lambda} - 1\rangle$$

$$\hat{a}^\dagger_{k,\lambda} |n_{k,\lambda}\rangle = \sqrt{n_{k,\lambda} + 1} |n_{k,\lambda} + 1\rangle.$$

Other physical observables may also of course be written in terms of the new operators; for example, the electromagnetic momentum operator,

$$\vec{P} = \frac{1}{4\pi c} \int d^3r (\vec{E} \times \vec{B}) = \sum_{k,\lambda} \hbar \vec{k} \hat{a}^\dagger_{k,\lambda} \hat{a}_{k,\lambda}.$$

The complete Hamiltonian, which treats the atom only nonrelativistically, is then,

$$\hat{H} = \frac{1}{2m_e} (\vec{p} - \frac{e}{c} \vec{A})^2 - \frac{\hbar^2}{2m_e} \nabla^2 + \frac{1}{8\pi} \int d^3r \left[ \left( \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right)^2 + (\nabla \times \vec{A})^2 \right]$$

$$\equiv \hat{H}_0 + \hat{H}_{\text{int}},$$

(7)

where

$$\hat{H}_0 = (-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{r^2}) + \hat{H}_{\text{field}},$$

whose eigenstates (without electron spin) are,

$$|n, \ell, m\rangle \text{ photon numbers},$$

and the interaction Hamiltonian is,

$$\hat{H}_{\text{int}} = \frac{e}{m_e c} \vec{A} \cdot \frac{\hbar}{\ell} \nabla + \frac{e^2}{2m_e c^2} \vec{A}^2.$$

(8)
Equation (8) follows because of the identity \( \nabla \cdot (A \psi) = (\nabla \cdot A) \psi + (A \cdot \nabla) \psi \) and that we are working in a gauge where \( \nabla \cdot A = 0 \). Also, the above neglects the interaction of the electron and proton fields which is down by a factor of \( m_e/m_p \).

IV. Perturbation Theory

The interactions given in (8) are sufficient to calculate quantum electrodynamic effects. Here, we will be content with first-order, time-dependent theory which results in the Fermi Golden Rule approximation for the transition rate between two quantum states labelled \( i \) and \( f \),

\[
\Gamma = \sum_{\lambda} \int \frac{2\pi}{\hbar} |\langle f|\hat{H}_i|i\rangle|^2 \rho \, d\epsilon \, \delta(\epsilon_f - \epsilon_i \pm \hbar \omega). \tag{9}
\]

The density of states \( \rho \) for photons required is,

\[
\rho(\epsilon) d\epsilon = \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega \, d\Omega. \tag{10}
\]

V. Spontaneous Emission

The states of the unperturbed hydrogen atom \( |n, \ell, m\rangle \) are stationary; if left alone the states will remain forever. However, in the quantum theory of fields governed by (6) and (8) there are always photons present even in a vacuum; their presence may cause spontaneous emission from an excited initial state. In particular, the first order term \( A \) in \( \hat{H}_i \) contains a linear combination of creation and destruction operators and thus creates or destroys a single photon. The \( A^2 \) term contains quadratic combinations of the photon operators and can thus contribute to two photon processes. Note that the exact time-development operator in the interaction picture is the time-ordered exponential,

\[
\hat{U}(t) = T \exp \left\{ -\frac{i}{\hbar} \int_0^t \hat{H}_i(t') \, dt' \right\},
\]

which has all possible numbers of photons created or destroyed.

Let us now consider a spontaneous transition between a \( 2P \) state and the \( 1S \) ground state of the hydrogen atom. Then \( |i\rangle = |2, 1, m\rangle \), and \( |f\rangle = |1, 0, 0\rangle \). The essential matrix element needed for first order theory is,

\[
\langle f|\hat{H}_i|i\rangle = \langle 1, \lambda| \langle 1, 0, 0|\hat{H}_i|2, 1, m\rangle |0\rangle \]

\[
= \frac{e}{m_e \sqrt{2\pi \hbar \omega V}} \int d^3 r \Psi_{100}^\ast(r) e^{-ik \cdot r} \bar{\epsilon}_{k,\lambda} \cdot \frac{\hbar}{i} \nabla \Psi_{210}(r) \langle 1, \lambda | \partial_{k,\lambda} | 0 \rangle. \tag{11}
\]
Note that if there were one photon initially present, the photon part for stimulated emission would be \( \langle 2_k,\lambda | \hat{a}^\dagger_{k,\lambda} | 1_k,\lambda \rangle = \sqrt{2} \), and thus the stimulated emission rate (to first order) would be larger by a factor of 2 from the spontaneous emission rate that we obtain below.

VI. Spontaneous emission rate in the electric dipole approximation

For optical transitions in the range of 4000 – 6000 Å, such as the \( 2P \rightarrow 1S \) transition in hydrogen, \( \vec{k} \cdot \vec{r} \ll 1 \), so that one may make the approximation \( \exp\{-i\vec{k} \cdot \vec{r}\} \simeq 1 \) \((r \simeq a_0 \simeq 1 \text{ Å})\). Thus, we may write the transition rate per unit solid angle, for polarization \( \lambda \), as,

\[
\frac{d^2\Gamma_\lambda}{d\Omega \, dw} = \frac{2\pi}{\hbar} (e \sqrt{\frac{2\pi \hbar}{\omega V}})^2 \int d^3r \Psi^*_{100} \vec{e}_{k,\lambda} \cdot \vec{p} \Psi_{21m} \left| \sum \frac{e^2}{mc^2}\rho \right|^2
\]

The matrix element of the momentum operator may be conveniently computed as follows:

\[
\vec{p} = \frac{im}{\hbar} [\vec{p}^2/2m - \epsilon^2/r, \vec{r}]
\]

and thus

\[
\langle 100 | \vec{p} | 21m \rangle = \frac{im}{\hbar} \langle [H_0, \vec{r}] \rangle
\]

\[
= \frac{im}{\hbar} (E_2 - E_1) \langle \vec{r} \rangle
\]

\[
= i\omega m \langle \vec{r} \rangle
\]

We now need to compute,

\[
\frac{d\Gamma_\lambda}{d\Omega} = \frac{2\pi}{\hbar} \int d\omega \left( e \sqrt{\frac{2\pi \hbar}{\omega V}} \right)^2 e^2 \omega^2 \frac{\epsilon^2}{c^2} \left| \int d^3r \Psi^*_{100} \vec{e}_{k,\lambda} \cdot \vec{r} \Psi_{21m} \right|^2 \times
\]

\[
\times \left( \frac{V}{2\pi} \right)^2 \omega^2 \frac{\epsilon^2}{\hbar c^3} \delta(\epsilon_f - \epsilon_i - \hbar \omega).
\]

For unpolarized photons, and random values of \( m_\ell = 0, \pm 1 \), we average over all possible initial states: we take \( \frac{1}{2} \sum_{m=0, \pm 1} \). Also,

\[
\vec{r} \cdot \vec{e} = \sum_{q=0, \pm 1} r_q \epsilon_{-q} (-1)^q
\]

\[
= r \sqrt{\frac{4\pi}{3}} \left( \frac{\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{1,-1} - \frac{\epsilon_x - i \epsilon_y}{\sqrt{2}} Y_{1,1} + \epsilon_z Y_{1,0} \right),
\]

and

\[
Y_{1,1} = -Y_{1,-1} \quad Y_{1,0} = \frac{1}{\sqrt{4\pi}} \int d\Omega \, Y^*_1 m Y_{1,m'} = \delta_{m m'}.
\]
The integral above is therefore,

\[
\int d^3 r \, R_{1,0} \frac{r}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} \text{ (same as above) } R_{2,1} Y_{1,m}
\]

\[
= \sqrt{1/3} \left( -\frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m,1} + \frac{\epsilon_x - i\epsilon_y}{\sqrt{2}} \delta_{m,-1} + \epsilon_z \delta_{m,0} \right) \int_0^\infty dr \, r^3 R_{1,0} R_{2,1}.
\]

The last radial integral has the value \( \sqrt{3/2}(2^8/3^5)a_0 \). So taking \( \frac{1}{3} \sum_m |m|^2 \) in the last expression yields

\[
\frac{2}{3^{10}} a_0^2 \cdot \frac{1}{3} (\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2) = \frac{2^{15}}{3^{11}} a_0^2.
\]

Putting together all of the above pieces into (12) and restoring the sum over polarizations produces,

\[
\Gamma_{2p \to 1s} = \sum \chi \int d\Omega \, \frac{\alpha \omega^3}{2\pi \epsilon^2} \frac{2^{15}}{3^{11}} a_0^2
\]

\[
= \frac{\alpha \omega^3}{\epsilon^2} \frac{2^{17}}{3^{11}} a_0^2,
\]

where \( \alpha = e^2/\hbar c \approx 1/137 \) is the fine structure constant. The final result for the transition probability is,

\[
\Gamma_{2p \to 1s} = \left( \frac{2}{3} \right)^8 \alpha^5 \left( \frac{m\epsilon^2}{\hbar} \right) \approx 0.6 \times 10^9 \text{ Hz}.
\]

The mean transition time for spontaneous emission from \( 2P \) to \( 1S \) is,

\[
\tau_{2p \to 1s} = \frac{1}{\Gamma_{2p \to 1s}} = 1.6 \times 10^{-9} \text{ sec}.
\]

VII. Q.E.D. processes: Feynman Diagrams

Electron Self Energy:

\[\fbox{+ \ \ \ \ \ \ \ + \ \ \ \ \ \ \ +} \]

\[\fbox{\text{e}^+ \text{e}^- \text{ Scattering:}}\]