Notes on Quantum Mechanics
Perturbation theory, quantum theory of radiation, radiative transitions

Module 4 of Refresher course conducted by Indian Academies of Sciences at
Bishop Moore College, Mavelikara, Kerala, May 5-17, 2014

Govind S. Krishnaswami, Chennai Mathematical Institute

- These are very brief and incomplete notes for lectures at the above Refresher Course. Please let me know (govind@cmi.ac.in) of any comments or corrections. 25 Oct, 2016.

Contents

1 References

- Here are some books on quantum mechanics.

1. H. S. Mani and G. K. Mehta, Introduction to Modern Physics.
2. Binayak Dutta-Roy, Elements of Quantum Mechanics.
3. L I Schiff, Quantum Mechanics, 3rd Ed. McGraw-Hill (1968).

4. P J E Peebles, Quantum Mechanics, Princeton Univ Press (1992).
5. B H Bransden and C J Joachain, Quantum Mechanics, 2nd Ed., Pearson (2000).
6. D. J. Griffiths, Introduction to Quantum Mechancis.
7. R. L. Liboff, Introductory Quantum Mechancis.
8. R Shankar, Principles of Quantum Mechanics, 2nd Ed. Plenum Press (1994).
9. P M Mathews and K Venkatesan, A textbook of quantum mechanics, Tata McGraw-Hill (1977).
10. P A M Dirac, The principles of quantum mechanics, 4th Ed., Oxford (1958).
11. Landau and Lifshitz, Quantum mechanics: Non-relativistic theory, 3rd Edition.
12. S. Weinberg, Lectures on Quantum Mechanics.
13. J. J. Sakurai, Advanced Quantum Mechanics, Addison Wesley (1967).
14. J. J. Sakurai, Modern Quantum Mechanics.
15. K. Huang, Quantum Field Theory, 2nd Ed. (2010).

2 Time-dependent hamiltonians and perturbation theory

• Suppose an atom is exposed to electromagnetic radiation for a certain duration (e.g. shine monochromatic light (e.g. from a laser) on an atom). How does it affect the atom? The atom is typically in a stationary state before the light was turned on. An interesting question is whether the atom will make a transition to another given stationary state and the rate of such transitions. In effect, from the time the laser is turned on, the hamiltonian of the atom has been perturbed by a time-dependent interaction of the electron with the oscillating electromagnetic field of the light beam[1]. Since the atom is neutral, this interaction energy is to leading order in the multipole expansion, given by the electric dipole energy $-\vec{p}\cdot\vec{E}$ where $\vec{p}$ is the electric dipole moment of the atom and $\vec{E} = \vec{E}_o \cos(\vec{k}\cdot\vec{r} - \omega t)$ is the electric field in the electromagnetic wave. For a hydrogen atom, $\vec{p} = e\vec{r}$ where $\vec{r}$ is the position vector of the electron (with respect to the nucleus) and $e < 0$ its charge. The magnetic force $ev \times B$ is smaller than the electric force eE by a factor of v/c. This is because, in an EM wave with wave vector $\mathbf{k} = k\hat{z}$, $\mathbf{E} = E_o \cos(kz - \omega t)\hat{x}$ and $\mathbf{B} = B_0 \cos(kz - \omega t)$. By Faraday's law of induction $\nabla \times E = -\frac{\partial \mathbf{B}}{\partial t}$, the amplitudes are related by $kE_o = \omega B_o$ or $B_o = E_o/c$ and $v/c \sim \alpha \sim \frac{1}{137} \ll 1$ for electrons in an atom[2]. So we ignore the magnetic force to first approximation.

• The wavelength of visible light ($\sim 400 - 700\,\mathrm{nm}$) is much larger than the size of atoms (~ 0.1 nm), so the electromagnetic field can be assumed spatially constant over the atom, but its time-dependence cannot be ignored. Indeed, as we learned from atomic spectroscopy, the frequency of visible (or UV/IR) light is such that $h\nu$ is of the order of the (electron volt) energy differences between atomic energy levels. What is more, atomic transitions occur in about a nano-second (we will show this), while the time period of visible light is about $T = 10^{-15}$ s, so the time dependence of the electromagnetic wave cannot be ignored.

• Here we develop techniques to treat physical situations where a time-dependent perturbation $gH_1(t)$ is applied to a system in a stationary state of its time-independent hamiltonian H_0. In

---

[1] We are treating the electron quantum mechanically but the light as a classical electromagnetic wave rather than as photons. Later, we will treat the EM field quantum mechanically.

[2] To see this, put the radius of the n^{th} Bohr orbit $r_n = \frac{n^2\hbar^2}{me^2}$ in the quantization condition for angular momentum $L = mv_n r_n = n\hbar$ to get $\frac{v_n}{c} = \frac{e^2}{n\hbar c} = \frac{\alpha}{n}$. We worked in Gaussian units here. Divide e^2 by $4\pi\epsilon_0$ to go to SI units.

the above example, we may treat the electric dipole interaction energy as a perturbation since the electric field in the light beam is typically much smaller (in commercial lasers used in eye surgery, it is about $10^7 - 10^8$ V/m) than the electric field felt by the electrons due to the nucleus $\sim \frac{13.6\text{V}}{.053\text{nm}} \sim 10^{11}\text{V/m} \sim \frac{\text{e}}{4\pi\epsilon_o \text{a}_o^2}$.

• Time dependent perturbations can be of various sorts. E.g. (1) periodic as in the case of monochromatic light shone on an atom. (2) adiabatic, where we have a perturbation which is very slowly varying compared to the time scales associated with H_0, (3) impulsive, where the perturbation lasts only a very short time as when an X-ray pulse is shone on an atom, possibly ionising it, or when a fast charged particle passes by an atom (4) sudden, for example where a sudden perturbation is applied resulting in a new time-independent hamiltonian. This happens when a neutron in the nucleus of an atom beta decays leaving behind a new isotope with a different atomic number.

• We will not solve these problems in detail, but will develop some of the formalism to treat them and illustrate with simple examples. In all cases, the main quantity of interest is the probability of transitions induced by the time-dependent perturbation.

2.1 Sudden perturbation: strong short-lived time dependence

A heavy isotope of hydrogen Tritium (nnpe) is unstable to beta decay $n \to p^+ + e^- + \bar{\nu}_e$. The resulting beta particle (electron) typically has a large kinetic energy ($\sim$ 1000 eV) and escapes from the atom in quick time[3]. The anti-neutrino also escapes very fast leaving behind a Helium-3 ion (${}^3_2\text{He}^+$ nppe, He-3 is a very stable isotope of Helium, no decay has been observed). The beta decay process happens almost instantaneously compared to atomic time-scales and in effect the hamiltonian of the system has suddenly changed from that of Tritium to that of a Helium ion. We are concerned with the electron wave function. Initially the Tritium atom was in one of its stationary states ψ_i^T (most often, its ground state). We would like to know the probability of a transition to any of the stationary states of ${}^3_2\text{He}^+$ after the decay.

• Such a sudden and drastic perturbation to a system, which takes it from one time-independent hamiltonian to another time-independent one can be modeled by

$$H(t) = \begin{cases} H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_o r} & \text{for } t < 0 \\ H_1 = \frac{p^2}{2m} - \frac{2e^2}{4\pi\epsilon_o r} & \text{for } t > 0 \end{cases} \tag{1}$$

So the hamiltonian operator behaves a bit like a step function with a finite discontinuity at $t = 0$. We wish to find the wave function after the sudden change (i.e. at $t = 0^+$), given that the system was in a stationary state of H_0 prior to the perturbation i.e., at $t = 0^-$. The Schrödinger equation $i\hbar\frac{\partial\psi}{\partial t} = H(t)\psi(t)$ can be usefully written as an integral equation

$$|\psi(t)\rangle = |\psi(0^-)\rangle - \frac{i}{\hbar}\int_0^t H(t')|\psi(t')\rangle\, dt' \tag{2}$$

Now we wish to take $t \to 0^+$. Though the hamiltonian suffers a sudden change, the change in each of its matrix elements is finite at $t = 0$, so the integral should vanish as $t \to 0^+$ (provided

---

[3] The beta particle is not mono-energetic, there is a continuous distribution of electron energies and neutrino energies up to about 18 KeV. On rare occasions, where the beta particle has very low energy, it may be captured by the He-3 ion to form a He-3 atom resulting only in a mono-energetic $\bar{\nu}_e$ escaping.

the wave function itself does not suffer an infinite discontinuity at $t = 0$). Thus we have

$$\lim_{t\to 0^+} |\psi(t)\rangle = \lim_{t\to 0^-} |\psi(t)\rangle \tag{3}$$

and the wave function is continuous at $t = 0$. Taking the projection on $|x\rangle$, for any fixed x, the wavefunction cannot have a finite discontinuity as t crosses 0. In other words, the change to the nucleus happened so fast that the electron wave function did not have time to change from its initial state ψ_i^T. Now, after the decay, the electron finds itself near a He-3 nucleus and if a measurement of the energy is made, one of the energy levels $E_n^{He_3^+}$ of He$_3^+$ is obtained, and the electron wave function collapses to the corresponding eigenstate $\psi_n^{He_3^+}$. The transition probability is

$$P_{i-\text{tritium}\to n-He_3^+} = |\langle\psi_n^{He}|\psi_i^T\rangle|^2 \tag{4}$$

Note that the energy difference between initial and final electronic states contributes to the energies of the emitted beta particle and anti-neutrino. To evaluate these transition probabilities we need to know the corresponding wave functions of Tritium and He$_3^+$. We know them since they are both hydrogenic atoms with $Z = 1$ and $Z = 2$. For example, the ground state wave functions are $\psi(\mathbf{r}) = \frac{2}{\sqrt{a^3}}\frac{1}{\sqrt{4\pi}}e^{-r/a}$ where $a = \frac{4\pi\epsilon_0\hbar^2}{mZe^2}$. The He-3 nucleus (npp, $Z = 2$) has twice the nuclear charge as the Tritium nucleus (nnp, $Z = 1$), so the Tritium atom (in its ground state) is much larger than the Helium ion (in its ground state). Indeed, the Bohr radius of a hydrogenic atom is $a = \frac{4\pi\epsilon_o\hbar^2}{mZe^2}$. So though the g.s. of He-3 is the most likely final state, it is also likely to make a transition to an excited state of He-3. The electronic energy difference (along with the nuclear mass defect) is carried away by the β-electron and $\bar{\nu}_e$.

• A sudden perturbation of this sort resulting in an abrupt and permanent change in the hamiltonian was not analyzed by treating the perturbation as small. But there are many situations where the perturbation may be treated as small. Let us develop a method to deal with such perturbations.

2.2 First order time-dependent perturbation theory

• Suppose a quantum system is initially in a stationary state $|\psi(0)\rangle = |u_i\rangle$ of the hamiltonian H_0. A time dependent perturbation $gH_1(t)$ is turned on at time $t = 0$ so that the total hamiltonian for $t \geq 0$ is

$$H(t) = H_0 + gH_1(t)\,\theta(t > 0) \tag{5}$$

We want to solve the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = H(t)\psi(t) \quad \text{with initial condition} \quad \psi(x, t = 0) = u_i(x). \tag{6}$$

We assume the stationary states of H_0 are known

$$H_0|u_n\rangle = E_n^{(0)}|u_n\rangle, \quad \text{and are orthonormal} \quad \langle u_n|u_m\rangle = \delta_{nm}, \tag{7}$$

and form a complete set. By completeness, we may expand the wave function at subsequent times as

$$\psi(t) = \sum_n c_n(t)\, u_n \quad \text{where normalization requires} \sum_n |c_n|^2 = 1. \tag{8}$$

In general, the coefficients $c_n(t)$ are complex and time-dependent. In the absence of the perturbation $(g = 0)$, we know $c_n(t) = c_n(0)e^{-iE_nt/\hbar}$. So we expect for $g \neq 0$ a correction of the form

$$c_n(t) = c_n(0)e^{-iE_nt/\hbar}\left(1 + \mathcal{O}(g)\right) \tag{9}$$

In the presence of the perturbation, the SE becomes for $t > 0$,

$$i\hbar \sum_m \dot{c}_m(t)|u_m\rangle = (H_0 + gH_1)\sum_m c_m(t)|u_m\rangle. \tag{10}$$

Taking the inner product with u_n we get

$$i\hbar\dot{c}_n(t) = c_n(t)E_n + g\sum_m \langle u_n|H_1(t)|u_m\rangle\, c_m(t). \tag{11}$$

This is a system of coupled first order ODEs for the coefficients $c_n(t)$. We know how they behave in the absence of the perturbation, so let us absorb the unperturbed harmonic time dependence and define

$$d_n(t) = c_n(t)e^{iE_nt/\hbar}. \tag{12}$$

Then d_n satisfy a simpler system of ordinary differential equations

$$\dot{d}_n(t) = -\frac{i}{\hbar}\sum_m \left\langle u_n\middle|gH_1(t)\middle|u_m\right\rangle e^{-i(E_m-E_n)t/\hbar}d_m(t) \tag{13}$$

with initial conditions $d_n(0) = c_n(0) = \delta_{ni}$ (since the system was initially in the eigenstate $|u_i\rangle$ of H_0). We will solve this system of equations for $d_n(t)$ essentially in a series in powers of g, $d_n(t) = \delta_{ni} + \mathcal{O}(g)$. To do so, it is convenient to write this as a system of integral equations. Integrating once in time from 0 to t and using $d_n(0) = \delta_{ni}$,

$$d_n(t) = \delta_{ni} - \frac{i}{\hbar}\int_0^t dt' \sum_m \left\langle u_n\middle|gH_1(t')\middle|u_m\right\rangle e^{-i(E_m-E_n)t'/\hbar}d_m(t') \tag{14}$$

So far we haven't made any approximation. The advantage of this formulation is that d_n is expressed as a zeroth order part plus a term of order g. We may solve this by iteration.

• To get a sense for what an iterative solution is, let us look at a toy version of this. Consider the equation $x = 1 + gx$ whose solution is $x = (1-g)^{-1}$. For $|g| < 1$, we may expand the solution in a series $x = 1 + g + g^2 + \cdots$. We could have obtained this series solution by iteration. The n^{th} iterate is given by

$$x^{(n)} = 1 + gx^{(n-1)}. \tag{15}$$

In favorable cases, the first few iterates already give a good approximation. In this case, the first few iterative approximations are

$$x^{(0)} = 1, \quad x^{(1)} = 1+g, \quad x^{(2)} = 1+g(1+g) = 1+g+g^2, \quad x^{(3)} = 1+g(1+g+g^2) = 1+g+g^2+g^3. \tag{16}$$

We see that we can recover the power series solution by iteration.

• Returning to (14), the first iterate involves putting the zeroth order solution $d_m = \delta_{mi}$ on the rhs. Thus to first order in g we have

$$d_n(t) = \delta_{ni} - \frac{gi}{\hbar}\int_0^t dt' \left\langle u_n\middle|H_1(t)\middle|u_i\right\rangle e^{-i(E_i-E_n)t'/\hbar} + \mathcal{O}(g^2). \tag{17}$$

This tells us how the initial state $\psi(0) = u_i$ evolves in time, since

$$\psi(t) = \sum_n c_n(t) u_n = \sum_n d_n(t) e^{-iE_n t/\hbar} u_n \quad \text{and} \quad \psi(0) = u_i. \tag{18}$$

$d_n(t)e^{-iE_n t/\hbar}$ is the component of the state at time t that is in the direction of the unperturbed eigenstate u_n. If the perturbation is switched off at time t, and a measurement of energy H_0 is made, then $|d_n(t)|^2$ is the probability of getting the value E_n. So $|d_n(t)|^2$ is the probability that the system makes a transition from initial state i to final state n due to the perturbation. If $i \neq n$, this transition probability is just the absolute square of the above time-integral of the matrix element of the perturbing hamiltonian between initial and final states

$$P(i \to n \neq i; t) = \frac{g^2}{\hbar^2} \left| \int_0^t dt' \left\langle u_n \middle| H_1(t') \middle| u_i \right\rangle e^{-i(E_i - E_n)t'/\hbar} \right|^2 + \mathcal{O}(g^3) \tag{19}$$

The probability that the final state is the same as the initial state $i = n$ can be estimated to order g^2 by using the normalization of the wave function $\sum_n |c_n(t)|^2 = \sum_n |d_n|^2 = 1$. So[4]

$$P(i \to i; t) = 1 - \sum_{n \neq i} P(i \to n, t). \tag{21}$$

- To go further, we must specify the perturbing hamiltonian $H_1(t)$. We will study some special cases.

2.3 Impulse approximation

- Here we consider a system in a stationary state subject to a sudden effect that is withdrawn quickly. For example, a fast electron may pass near a hydrogen atom, or an X-ray pulse may be shone on an atom for a short duration of time. These impulsive perturbations may end up ionizing the atom or exciting it to a new stationary state. We model an impulse at $t = 0$ by the hamiltonian

$$H = H_0 + gH_1\delta(t) \tag{22}$$

H_1 could be quite a big change compared to H_0, so one wonders if perturbation theory is applicable. But the change only lasts a short time and it is the integrated effect that enters the formula for the transition probability, so perturbation theory could serve as a good approximation. For $t > 0$ we find

$$d_f(t > 0) = \delta_{fi} - \frac{ig}{\hbar} \langle u_f | H_1 | u_i \rangle + \cdots \quad \Rightarrow \quad P(i \to f \neq i, t) = \frac{g^2}{\hbar^2} |\langle u_f | H_1 | u_i \rangle|^2 + \cdots \tag{23}$$

In particular, there can be no transition to final state f in the impulse approximation, if the perturbing hamiltonian has zero matrix element $(H_1)_{fi}$ between the initial and final states.

---

[4] Merely squaring the approximate formula for $d_i(t)$ (17) does not give the correct answer, as the term of order g^2 (say γg^2) in d_i that we have *not computed*, also contributes! Let $I = \int_0^t dt' \langle u_i | H_1(t) | u_i \rangle \in \mathbb{R}$, then

$$d_i(t) = 1 - \frac{igI}{\hbar} + \gamma g^2 + \cdots \quad \Rightarrow \quad |d_i|^2 = 1 + \frac{g^2 I^2}{\hbar^2} + 2g^2 \Re\gamma + \mathcal{O}(g^3). \tag{20}$$

In fact, if we do not account for this term γg^2, it would even appear that the probability to remain in the state i exceeds 1! Stated differently, normalization puts a constraint on what $\Re\gamma$ can be.

2.4 Harmonic perturbation

The effect of electromagnetic radiation on an atom is primarily due to the electric dipole interaction between the oscillating electric field of the EM wave and the dipole moment of the atom. For monochromatic light, the electric field $\vec{E} = \vec{E}_o \cos\omega t$ varies sinusoidally with time but is roughly constant over the dimensions of the atom (whose hamiltonian is H_0), so

$$gH_1 = -e\vec{r}\cdot\vec{E}_0 \cos\omega t \tag{24}$$

Note that the electromagnetic wave may be due to light that is shone on the atom or could also arise from light emitted by the atom. Even if light isn't shone on the atom by an external agency, there are virtual photons present due to quantum fluctuations of the vacuum and these could interact with the atom. We will deal with this case later when we quantize the EM field.

• We will consider a general sinusoidal perturbation of the form

$$H = H_0 + gH_1' \cos\omega t \quad \text{where} \quad H_1' \quad \text{is time independent.} \tag{25}$$

If we denote the energies of the initial and final eigenstates of H_0 as $E_{i,f} = \hbar\omega_{i,f}$, then

$$\begin{aligned} d_f &= \delta_{fi} - \frac{ig}{\hbar}\left\langle u_f \left| H_1' \right| u_i \right\rangle \int_0^t e^{-i(\omega_i-\omega_f)t'} \cos\omega t' \, dt' + \mathcal{O}(g^2) \\ &= \delta_{fi} + \frac{g}{2\hbar}\left\langle u_f \left| H_1' \right| u_i \right\rangle \left[\frac{e^{-i(\omega_i-\omega_f+\omega)t} - 1}{\omega_i - \omega_f + \omega} + \frac{e^{-i(\omega_i-\omega_f-\omega)t} - 1}{\omega_i - \omega_f - \omega} \right] + \mathcal{O}(g^2). \end{aligned} \tag{26}$$

To understand this result of perturbation theory, we ask for what angular frequency of the perturbation $\omega > 0$ (e.g. what color of incident light) the transition probability from initial state i to final state f is significant. This happens if the denominator of one of the two terms is nearly zero. If $\omega \approx \omega_f - \omega_i$, this corresponds to stimulated absorption of a photon by the atom in making a transition to an excited state. If $\omega \approx \omega_i - \omega_f$, this corresponds to decay of the atom from an excited state to a lower energy level while emitting a photon (stimulated emission).

• In either case, one of the two terms dominates and we have the transition probability from state i to state $f \neq i$ given by ($\pm$ refer to absorption and emission respectively)

$$P_{i\to f}(t) \approx \frac{g^2}{4\hbar^2} \left|\langle u_f \left| H_1 \right| u_i \rangle\right|^2 \frac{\left|e^{i(\Delta\omega \mp \omega)t} - 1\right|^2}{(\Delta\omega \mp \omega)^2} = \frac{g^2}{\hbar^2} \left|\langle u_f \left| H_1 \right| u_i \rangle\right|^2 \frac{\sin^2\left(\frac{\Delta\omega \mp \omega}{2} t\right)}{(\Delta\omega \mp \omega)^2} \quad \text{for} \quad \omega \approx \pm\Delta\omega. \tag{27}$$

We used $|e^{i\theta} - 1|^2 = 4\sin^2(\theta/2)$ and denoted the change in angular frequency as $\Delta\omega = \omega_f - \omega_i$.

• P is a probability in the sense that $\sum_f P_{i\to f} = 1$. However, P is not in general a probability distribution in the t or ω variables. $\int dt P(t) = \infty$ and $\int P(\omega) d\omega \neq 1$ in general.

• An interesting feature of this formula is the possibility of stimulated emission. Suppose there are two levels at energies $\hbar\omega_1 < \hbar\omega_2$ (say the g.s. and an excited state) and we shine light of frequency nearly equal to $\omega_2 - \omega_1$ on a population of such atoms which are mostly in the g.s. Atoms that are in state E_1 are then likely (with probability $P_{1\to 2}$) to absorb photons and get excited to state E_2. On the other hand, suppose many of the atoms were originally in the 'population inverted' excited state E_2 and we stimulate them by shining light of frequency $\omega \approx \omega_2 - \omega_1$. Then with the same probability as before, $P_{2\to 1} = P_{1\to 2}$, those atoms are likely to *emit* photons of frequency $\omega_2 - \omega_1$. So the emitted photons have roughly the same frequency as the stimulating photons. This is called stimulated emission. It leads to a cascade since a single photon can stimulate an atom to emit a photon of the same frequency and we have two photons. These two photons can stimulate two other atoms to emit, producing 4 photons, all of the same frequency $\omega_2 - \omega_1$. The maser (microwave amplification by stimulated emission of radiation) and laser is based on this phenomenon of stimulated emission [See the autobiography of a co-inventor of the laser, Charles Townes, How the laser happened, The adventures of a scientist].

• It is very interesting to study the dependence of the probability of transition on the duration of exposure t and the frequency ω of incident EM radiation. Suppose we hold ω fixed near $\pm\Delta\omega$ (the resonant frequency). The above formula says that the probability of the system being found in final state f at time t oscillates slowly in time with a frequency $\Delta\omega \mp \omega$, which by assumption is much smaller than ω. So we may maximize our chances of finding the atom in state f by waiting till time T_n given by one of

$$T_n = \frac{(2n+1)\pi}{\Delta\omega \mp \omega}, \quad n = 0, 1, 2, \cdots \tag{28}$$

For small times $t \ll \frac{2\pi}{\Delta\omega \mp \omega}$, the probability of a transition grows quadratically with time.

• On the other hand, suppose we fix a time t. Notice that as the frequency of light ω is tuned off from the 'resonant' frequency $\pm\Delta\omega$, the probability of a transition decays rapidly (quadratically in $\frac{1}{\Delta\omega \mp \omega}$). In fact, let us consider the 'average transition rate per unit time',

$$\frac{P_{i\to f}(t)}{t} \approx \frac{g^2}{\hbar^2} \left|\langle u_f \left| H_1 \right| u_i\rangle\right|^2 \frac{\sin^2\left(\frac{1}{2}(\Delta\omega \mp \omega)t\right)}{(\Delta\omega \mp \omega)^2 t}. \tag{29}$$

If we wait a time t large compared to the period of this oscillatory behavior $\frac{2\pi}{\Delta\omega \mp \omega}$, then the transition rate gets more sharply peaked at $\omega = \pm\Delta\omega$. Indeed, using a representation of the Dirac Delta function[5]

$$\frac{2}{\pi} \lim_{t\to\infty} \frac{\sin^2 \frac{1}{2}\Omega t}{\Omega^2 t} = \delta(\Omega), \quad \text{and putting } \Omega = \Delta\omega \mp \omega, \tag{30}$$

we get for a harmonic perturbation that lasts for a long time $0 \le t \le T$[6]

$$\text{Rate}_{i\to f} = \lim_{T\to\infty} \frac{P_{i\to f}(t)}{T} \approx \frac{g^2}{4\hbar^2} \left|\langle u_f \left| H_1 \right| u_i\rangle\right|^2 2\pi\delta(\Delta\omega \mp \omega). \tag{31}$$

---

[5] Let $D_t(\omega) = \frac{2}{\pi}\frac{\sin^2(\omega t/2)}{\omega^2 t}$. Then we see that $D_t(\omega) \to 0$ as $t \to \infty$ for any $\omega \neq 0$. Moreover, at $\omega = 0$, $D_t(0) = \frac{t}{2\pi} \to \infty$ as $t \to \infty$. So as $t \to \infty$, $D_t(\omega)$ tends to a distribution supported at $t = 0$. To show it is the Dirac delta distribution we need to show $\lim_{t\to\infty} \int_{\mathbb{R}} D_t(\omega) d\omega = 1$, but in fact this integral $U(t) = \int_{\mathbb{R}} D_t(\omega) d\omega = 1$ for all $t > 0$. First by rescaling $\omega = 2x/t$ we see that $U(t) = U(1)$. So it only remains to show that $U(1) = \frac{1}{\pi}\int_{\mathbb{R}} \frac{\sin^2 x}{x^2} dx = 1$. This may be established using contour integration. Indeed, $\frac{\sin^2 x}{x^2} = f(x) + f^*(x)$ where $f(x) = \frac{1-e^{2ix}}{4x^2}$. Moreover $f(x)$ has a simple pole at $x = 0$ with residue $-i/2$ (the residue is just the coefficient of the $1/x$ term in the Laurent series expansion of f around $x = 0$). We write the integral of $\frac{\sin^2 x}{x^2}$ as half the sum of two integrals over contours that are real except that they either just go above the origin or just below the origin. This is called the Cauchy principal value. In this manner we express $U(1)$ as $\frac{1}{\pi} \times 2 \times \Re\mathcal{P}\int_{\mathbb{R}} f(x)$. The Cauchy principal integral of f is obtained by closing the contour with a semicircle of radius R in the upper half plane where it is seen that $|f| < 1/2R^2$. Only the contour which goes below the origin encloses a pole and we get the desired result using the Cauchy residue theorem $\oint f(z)\, dz = 2\pi i \sum_j \text{Residue}_{w_j}(f)$ where w_j are the locations of the poles of f that lie within the contour of integration.

[6] Here $\omega > 0$ and $\Delta\omega = \omega_f - \omega_i$. Absorption: $-$sign, $\Delta\omega > 0$ and $\omega \approx \Delta\omega$. Emission $+$sign, $\omega_f < \omega_i$, $\omega \approx -\Delta\omega$.

This is called Fermi's Golden rule. For a harmonic perturbation, the average transition rate after a long time approaches a time independent value. It is proportional to the absolute square of the perturbing hamiltonian between initial and final states. It is significant only when the frequency of the perturbation matches the gap between the levels. So far we have considered the case where the initial and final states form a discrete set. Later, we will extend this to the case where the final states form a continuum.

2.4.1 Frequency-time relation for harmonic perturbations

We briefly discuss a relation between the frequency of a harmonic perturbation (e.g. EM waves) and the time for which it has acted to cause a transition between states of a system (e.g. an atom). This relation is often written in a form similar to the uncertainty principle, though it differs from the energy-time uncertainty inequality in many crucial ways.

• Recall that the probability of transitions from state i to state f due a harmonic perturbation $gH_1 \cos \omega t$ acting for a time t on a system with hamiltonian H_0 and energy levels $E_i = \hbar \omega_i$ is given to first order by

$$P_{i\to f}(t) \approx \frac{1}{\hbar^2} \left|\langle f|gH_1|i\rangle\right|^2 \frac{\sin^2\left(\frac{(\omega \pm \omega_{fi})t}{2}\right)}{(\omega \pm \omega_{fi})^2}. \qquad (32)$$

where $\omega_{fi} = \omega_f - \omega_i$ is the Bohr frequency associated with the transition between i and f. Let us consider the case of absorption (excitation) $\omega_{fi} > 0$, though a similar argument applies to emission (decay). We consider the transition probability (or the rate P/t) as a function of incident frequency ω. $P_{i\to f}(t)$ is quite sharply peaked around $\omega = \omega_{fi}$, but has a finite spread. In other words, it is not only the resonant frequency that is effective in inducing a transition, but a narrow range around it. Roughly, this band of frequencies lies somewhere in the interval between the two nearest zeros of $P_{i\to f}(t)$ around the central maximum at $\omega = \omega_{fi}$.

$$\text{These zeros occur at} \quad (\omega - \omega_{fi})\frac{t}{2} = \pm\pi. \qquad (33)$$

So the probability of excitation after a time t is most significant for a range of frequencies lying within

$$\omega_{fi} - \frac{2\pi}{t} \lesssim \omega \lesssim \omega_{fi} + \frac{2\pi}{t}. \qquad (34)$$

Note that these are not inviolable inequalities, frequencies which are outside this interval can also induce transitions from i to f, though with a much lower probability. Moreover, frequencies at the edges of this band cannot induce transitions since the probability goes to zero.

• Within these approximations, the frequencies lying in the central region of the band

$$|\omega - \omega_{fi}| \lesssim \frac{2\pi}{t} \qquad (35)$$

are particularly effective in inducing a transition from i to f after a time t. Let us denote the central half the above range of frequencies by $\delta\omega$ Then after a time t, frequencies lying in a band of width $\Delta\omega \approx 2\pi/t$ about ω_{fi} are effective in causing transitions from i to f:

$$\Delta\omega \; t \approx 2\pi \qquad (36)$$

Sometimes, we multiply through by $\hbar$ and express the frequency band as a range of energies $\Delta E \equiv \hbar\Delta\omega$

$$\Delta E\, t \approx h. \tag{37}$$

Sometimes, this is loosely called an uncertainty relation. But t here is not the uncertainty in a measurement of time. Moreover, this relation between the band of effective frequencies and the time the perturbation acted is not an inequality but just an estimate relevant to harmonic perturbations.

• The definitions of ΔE and t here are different from what they mean in the Mandelstam-Tamm version (see Griffiths, Introduction to Quantum Mechanics) of the energy-time uncertainty *inequality* $\Delta E \Delta t \geq \frac{\hbar}{2}$. In this inequality, ΔE is the standard deviation in possible measurements of energy of a system in a given state ψ. And Δt is the time it takes for the expectation value (in state ψ) of a chosen observable A to change by an amount equal to one standard deviation in the distribution of possible measured values of A: $\Delta t|\partial_t\langle A\rangle_\psi| = \Delta A$.

• Our new relation simply says that if the perturbation acts only for a short time, then a wide band of frequencies can cause transitions. Indeed, as is easily seen by taking $t \to 0$, for short times, $P_{i\to f}$ is independent of ω, all frequencies are equally effective in inducing transitions if they act for a very short time. But after the perturbation has acted for a long time, the band of effective frequencies is much narrower, tending eventually to the resonant frequency *alone*, as $t \to \infty$.

• In this discussion, the EM wave is treated classically. The photon concept does not play a role. This works in the high intensity regime where a large number of photons are present, and the energy in a monochromatic EM wave is supplied in a nearly continuous manner. Within this framework, energy is conserved. Irrespective of what the frequency of the EM wave is, an energy of $\hbar\omega_{fi}$ is absorbed by the atom in going from $i \to f$.

• One way to interpret this relation is to imagine an ensemble of atoms all in state i. A monochromatic harmonic perturbation is applied to each atom for a time t. However, we scan uniformly through a whole range of frequencies ω. So a bunch of atoms receive frequency ω_1, another bunch of atoms receive a slightly higher frequency and so on. So each bunch of atoms experiences a slightly different frequency of light. After a common time t some atoms would have been excited to a given final state f with energy E_f. The above argument says that the incident frequencies most effective in inducing a transition from $i \to f$ are clustered around $\omega = \omega_{fi}$ with an approximate spread given by $\Delta\omega \approx 2\pi/t$.

• Another way to interpret this formula: suppose all the atoms in state i receive light of the same frequency ω. But suppose there are several closely-spaced possible final states with energies E_f (to which transitions are not forbidden!). Let the harmonic perturbation act for a time t. Then we tabulate the energies E_f of the atoms that have made transitions to various possible excited states. Then we will find that among the atoms that have been excited, a vast majority would have been excited to states f with energies E_f satisfying

$$|E_f - (E_i + \hbar\omega)| \lesssim \frac{h}{t}. \tag{38}$$

In other words, the absorbed energies are centered around $\hbar\omega$ but with a spread of roughly h/t.

• Yet another way to look at it is to consider an ensemble of atoms or other particles in an unstable state i. However, suppose we do not know the energy E_i (or the mass of the unstable particle). We wait a time t (e.g. the life time) after which a fraction of the atoms have decayed, say via a specific channel to a particular (say stable) final state f, whose energy is known. In the process, radiation of some sort is also emitted and we measure how much energy is carried away by radiation in each decay. However, according to the above argument, in different members of the ensemble, we will find that a slightly different amount of energy has been carried away by radiation leading to a distribution of radiated energies that are clustered around a central value E_0 (determined experimentally), with a spread in energies given by $\Delta E \approx h/t$. In this manner, we can reconstruct a distribution of possible energies of the initial state E_i or a distribution of possible masses of the unstable particle i. We would predict that E_i would lie approximately in the interval

$$E_0 + E_f - \frac{h}{t} \lesssim E_i \lesssim E_0 + E_f + \frac{h}{t}. \tag{39}$$

3 Quantum theory of radiation

So far we have discussed the quantum theory of a matter particle like the electron, via the Schrodinger equation. Among other things, this was needed to accommodate the wave nature of electrons (Davisson-Germer electron diffraction) and to explain the stability of the ground state of the atom and the discrete atomic spectra. However, the earliest ideas of quantization arose from Planck's attempt to fit the spectrum of black body electromagnetic radiation. The photoelectric effect and Compton scattering reinforced the need to treat light quantum mechanically, light too displayed both wave and particle-like behaviour. However, we have not treated light quantum mechanically and have only a vague idea of what a photon is. Indeed, the quantization of the Electromagnetic field is more difficult than the quantization of particle mechanics, primarily because the EM field has an infinite number of degrees of freedom [namely, the electric and magnetic fields at each point of space]. On the other hand, a point particle has only three degrees of freedom, we need three coordinates (x, y, z) to locate the particle at any instant of time. Historically, the quantization of the EM field had to wait till the late 1920s and 1930s work of Dirac, Pauli, Heisenberg, Jordan, Fermi etc., while the quantum theory of a point particle was already formulated by Schrödinger and Heisenberg by 1926-27.

• Classical systems with infinitely many degrees of freedom are quite common. They include (1) the EM field; (2) transverse vibrations of a stretched string: the height of the string at each point along the string $h(x)$ must be specified; (3) heat conduction along a rod, the temperature $u(x)$ at each point x along the rod must be specified. (4) fluid flow, the velocity, pressure and density at each point of the container need to be specified. The classical equations of motion (evolution equations) for systems with infinitely many degrees of freedom are typically systems of partial differential equations. What are the PDEs that govern the time evolution of the above 4 systems? By contrast, the equations of motion for a system with finitely many degrees of freedom are systems of ordinary differential equations [e.g. Newton's equation for a particle is a set of three ODEs $m\ddot{x}_i = F_i$].

• What is more, the solution of the Schrödinger equation for the hydrogen atom spectrum suggests that an atom would remain forever in an excited stationary state. We have already seen that in the presence of an external EM field, atoms can be stimulated to make transitions between stationary states. The rate of stimulated emission or absorption is proportional to the intensity of light (energy density of the stimulating EM radiation). However, spectroscopists have known for long that atoms in excited states spontaneously decay in about a nanosecond through emission of light, even in the absence of any stimulation. How is this to be explained theoretically? Einstein showed that to understand thermodynamic equilibrium between atoms and radiation (whose spectral distribution is governed by Planck's blackbody law) in a cavity, the rate for spontaneous decay from excited states must be non-zero. Remarkably, Einstein's 1917 argument preceded the formulation of quantum mechanics (Schrodinger and Heisenberg) and the development of time dependent perturbation theory (by Dirac)! Let us recall his argument. However, Einstein's argument does not explain how there can be spontaneous decay even in the absence of external EM fields. The explanation for this is provided by the quantum theory of radiation. Even in the vacuum state where the mean electric and magnetic fields are zero, there are vacuum fluctuations which, in a sense, 'induce' spontaneous emission!

• Note that spontaneous absorption is almost never seen to occur, an atom in its ground state in vacuum is rarely found to spontaneously get excited. A statistical mechanics argument for this may be offered, using the principle of equal a priori probabilities: in equilibrium, all states of a system with the same energy are equally likely. Consider an atom in the presence of electromagnetic radiation present in the vacuum. Suppose the energy difference between the ground and first excited state of the atom is ΔE. There is only one way in which this quantum of energy can be possessed by the atom: by being in the first excited state. On the other hand, this energy can be kept in the radiation field in very many ways, essentially, since the electromagnetic field has very many degrees of freedom, the electric and magnetic fields at each point of space. Since a priori all these possibilities are equally probable, it is infinitely more likely for the quantum of energy to be stored in the electromagnetic field than in the atom. This explains why atoms are typically found in their ground states and are not seen to spontaneously absorb radiation from the vacuum and get excited.

3.1 Atoms and radiation in equilibrium: Einstein's A and B coefficients

• Suppose we have a box of atoms in thermal equilibrium with EM radiation at temperature T. We already know that EM radiation in equilibrium at temp T has a frequency distribution of energy density $u(\nu)d\nu$ given by Planck's black body law. For simplicity, suppose the atoms can be in one of two states, with N_u in the upper state and N_l in the lower state. In equilibrium these numbers do not change with time. However, this is a dynamic equilibrium where atoms in the upper state decay to l via stimulated emission (due to the EM waves in the cavity) and possibly by spontaneous emission. At the same time, atoms in the lower state get exited to u via stimulated absorption. The rates (per atom) for these processes are denoted in the obvious way. The rate of change of N_u is (ignoring spontaneous absorption)

$$0 = \frac{dN_u}{dt} = -R^{\text{sp}}_{u\to l} N_u - R^{\text{st}}_{u\to l} N_u + R^{\text{st}}_{l\to u} N_l. \tag{40}$$

From our study of time dependent perturbation theory, we have seen that the rates of stimulated emission/absorption are equal $R^{\text{st}}_{u\to l} = R^{\text{st}}_{l\to u}$, both being proportional to the absolute squares of the transition matrix elements $\langle u|H_1|l\rangle, \langle l|H_1|u\rangle$ (which are complex conjugates due to hermiticity of the perturbing hamiltonian). However, this fact was not available to Einstein. He deduced it as we will see below. However, these stimulated emission rates should be proportional to the energy density $u(\nu)$ of EM waves at the transition frequency[7]. So Einstein defined the

---

[7] This is a consequence of Fermi's Golden rule, the transition rate is proportional to the square of the transition matrix element, which is proportional to the square of the electric field for electric dipole transitions.

so-called B coefficients which are the rates (per atom) for stimulated transitions per unit radiant energy density:

$$R^{\rm st}_{u\to l} = B_{u\to l}\; u(\nu) \quad \text{and} \quad R^{\rm st}_{l\to u} = B_{l\to u}\; u(\nu) \tag{41}$$

where we denote the energy difference by $h\nu = E_u - E_l$. Furthermore, he denoted the rate of spontaneous emission per atom by $R^{\rm sp}_{u\to l} = A$. Thus the rates per atom for the two transitions are

$$w_{l\to u} = B_{l\to u} u(\nu) \quad \text{and} \quad w_{u\to l} = B_{u\to l} u(\nu) + A. \tag{42}$$

Then the statement of equilibrium $\frac{dN_u}{dt} = 0$ is the equality

$$N_l w_{l\to u} = N_u w_{u\to l} \quad \text{or} \quad N_l B_{l\to u} u(\nu) = N_u B_{u\to l} u(\nu) + N_u A \tag{43}$$

We find

$$u(\nu) = \frac{A N_u}{N_l B_{l\to u} - N_u B_{u\to l}} = \frac{A/B_{u\to l}}{\frac{N_l}{N_u}\frac{B_{l\to u}}{B_{u\to l}} - 1} \tag{44}$$

Now since the atoms are in thermal equilibrium at temperature T, the populations N_l, N_u are proportional to the Boltzmann factors

$$\frac{N_l}{N_u} = e^{-(E_l - E_u)/kT} = e^{h\nu/kT}. \tag{45}$$

Thus

$$u(\nu) d\nu = \frac{A/B_{u\to l}}{e^{h\nu/kT}\frac{B_{l\to u}}{B_{u\to l}} - 1} d\nu. \tag{46}$$

In order to fix the A and B coefficients (which are independent of T) we will compare this with the classically known energy density in black-body radiation. At high temperatures or in the semi-classical limit $h\nu/kT \to 0$, the equilibrium distribution of energy density in cavity radiation is given by the Rayleigh-Jeans law [we indicate below one way to derive the Rayleigh-Jeans formula]

$$u_{RJ}(\nu) d\nu = \frac{8\pi\nu^2}{c^3} kT\, d\nu \quad \text{or} \quad u_{RJ}(\omega) d\omega = \frac{8\pi\omega^2}{(2\pi)^2 c^3} kT\, d\omega \tag{47}$$

For this to agree with our formula at high temperatures, we need several conditions to be satisfied. First, the rate of spontaneous emission $A \neq 0$, we will explain this by studying the quantum theory of radiation. Second, the two B coefficients must be equal $B_{u\to l} = B_{l\to u} \equiv B$. Under this assumption,

$$u(\nu) d\nu \overset{\text{high T}}{\longrightarrow} \frac{A}{B}\frac{kT}{h\nu}\, d\nu. \tag{48}$$

Comparing with the RJ formula we find the ratio of spontaneous and stimulated emission rates

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} \tag{49}$$

Thus we have expressed the spontaneous emission rate in terms of the stimulated emission rate. The latter can be calculated by treating the stimulating EM wave as a perturbation to the atomic hamiltonian.

• As a byproduct of this argument, we may also obtain the Planck black body spectrum by plugging in this value for $\frac{A}{B}$ in $u(\nu)$:

$$u(\nu)d\nu = \frac{A}{B}\frac{d\nu}{e^{h\nu/kT}-1} = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT}-1}d\nu \tag{50}$$

which is precisely the Planck distribution ($\omega = 2\pi\nu, h\nu = \hbar\omega$).

• Let us indicate how one may obtain the Rayleigh Jeans formula. One counts the number of possible modes of EM radiation with frequency in the interval $[\nu, \nu + d\nu]$ in a cavity of unit volume. Then one appeals to classical equipartition to assign an energy kT to each of these modes. Then the RJ energy density at temperature T is just the product of the number of modes and kT. We could count the number of modes (standing waves) in a cavity purely classically and get the answer $8\pi\nu^2/c^3$. But let us use quantum mechanical reasoning. The number of photons with momentum between $[\mathbf{p}, \mathbf{p} + d\mathbf{p}]$ and $[\mathbf{r}, \mathbf{r} + d\mathbf{r}]$ is

$$2 \times \frac{d^3p\, d^3r}{h^3}. \tag{51}$$

The reasoning is that there is one quantum state for each cell of phase space of volume h^3. The uncertainty principle forbids us from localizing a particle to within a cell of Planck volume h^3 in phase space. The factor of 2 accounts for the two possible polarizations of photons. We will soon explain what a photon is, and what its polarization is. It follows that the number of photon states per unit volume with wave vector in [**k**, **k**+ d**k**] is

$$2 \times \frac{\hbar^3 d^3k}{h^3} = 2 \times \frac{d^3k}{(2\pi)^3} \tag{52}$$

So the number of photon states with wave number between $[k, k + dk]$ and direction of wave vector lying in solid angle $d\Omega_k$ is

$$2 \times \frac{k^2 dk d\Omega_k}{(2\pi)^3}. \tag{53}$$

Converting to frequency $k = \omega/c = 2\pi\nu/c$, the number of photons with frequency in the interval $[\nu, \nu + d\nu]$ and any direction of wave vector is

$$2 \times \frac{4\pi\nu^2 d\nu}{c^3} = \frac{8\pi\nu^2\, d\nu}{c^3}. \tag{54}$$

Multiplying by the classical equipartition assignment of energy kT per mode, we get the Rayleigh-Jeans distribution.

3.2 Definition of mean lifetime of an excited state due to spontaneous emission

• Suppose an atom is initially in the excited (upper energy) state u and has available to it several lower energy states $l_1, l_2, \ldots l_n$ to which it can spontaneously decay. Each of these is called a decay channel or decay mode. Suppose the spontaneous transition probability from $u \to l_i$ per unit time, i.e., the spontaneous decay rate is $R^{\text{sp}}_{u\to l_i}$. This spontaneous decay rate will depend on the electromagnetic radiation present in the vacuum, just as the rate for stimulated emission depends on the electromagnetic radiation incident on the atom. The spontaneous decay rate $R^{\text{sp}}_{u\to l_i}$ was called the A-coefficient by Einstein.

- If there are initially N_u atoms in upper state u, then in a time dt the increase in N_u

$$dN_u = -\left(R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}\right) N_u \, dt \tag{55}$$

Thus the expected number of atoms remaining in upper state u at time t is

$$N_u(t) = N_u(t=0) \, \exp\left[-\left(R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}\right) t\right] \tag{56}$$

The time constant for this exponential depletion of population is called the lifetime of the upper state

$$\tau = \frac{1}{R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}} \tag{57}$$

It is the time after which (on average) a fraction $1/e \approx 1/2.718 \approx 0.37$ the population has decayed to *any* of the available lower states, and only about 63% remain in upper state u. If selection rules do not permit any lower state to decay to, then the rates are zero and the lifetime τ infinite and the state is stable.

- To understand the spontaneous decay of excited states of the atom (and compute their lifetime) we will develop the quantum theory of radiation and study its interaction with electrons in an atom.

3.3 Classical radiation from Maxwell's equations in radiation gauge

- Maxwell's equations for the vacuum electric and magnetic fields in rationalized Heaviside-Lorentz units are[8]

$$\nabla\cdot\mathbf{B} = 0, \quad \nabla\times E = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}, \quad \nabla\cdot\mathbf{E} = \rho \quad \text{and} \quad \nabla\times\mathbf{B} = \frac{\mathbf{j}}{c} + \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}. \tag{58}$$

where for consistency of the two inhomogeneous equations the charge and current density must satisfy the continuity equation $\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0$. The first two homogeneous Maxwell equations state the absence of magnetic monopoles, and Faraday's law of induction. The second pair of inhomogeneous equations are Gauss' law and Ampere's law with Maxwell's correction term involving the time derivative of the electric field (the displacement current). Gauss was German, Ampere French, Faraday English and Maxwell Scottish. The motion of a charge e in an electromagnetic field is governed by the Lorentz force law

$$\mathbf{F} = e\left[\mathbf{E} + \frac{\mathbf{v}}{c}\times\mathbf{B}\right]. \tag{59}$$

---

[8] We use rationalized Heaviside-Lorentz units. In HLU charges are normalized so that Coulomb's law takes the form $\mathbf{F} = \frac{q_1 q_2 \hat r}{4\pi r^2}$. The electric field of a point charge is $\mathbf{E} = \frac{q}{4\pi r^2}\hat r$ and the Biot-Savart law reads $\mathbf{B} = \frac{1}{4\pi c}\oint \frac{I d\mathbf{l}\times\mathbf{r}}{r^3}$. Charges in HLU are related to CGS (esu or statcouloumb) units via $q_{hlu} = \sqrt{4\pi} q_{esu}$ while the fields and potentials are $E_{hlu} = \frac{E_{cgs}}{\sqrt{4\pi}}$, $B_{hlu} = \frac{B_{cgs}}{\sqrt{4\pi}}$ and $A_{hlu} = \frac{A_{cgs}}{\sqrt{4\pi}}$. It follows that the expression for the conjugate momentum $\pi = \mathbf{p} - e\mathbf{A}/c$ and the Lorentz force law $\mathbf{F} = q(\mathbf{E} + \frac{\mathbf{v}}{c}\times\mathbf{B})$ take the same form in both Gaussian and rationalized units. The magnitude of the charge of the electron is $e_{cgs} = 4.8\times 10^{-10}$ esu. Sommerfeld's fine structure constant in HLU is $\alpha = \frac{e^2}{4\pi\hbar c}$. Putting in the values $c = 3\times 10^{10}$ cm/s and $\hbar = 1.05\times 10^{-27}$ erg.s we find $\alpha = \frac{4.8^2\times 10^{-20}}{1.05\times 3\times 10^{-17}} = 7.3\times 10^{-3} \approx 1/137$. In going from formulae in SI units to HLU, ϵ_0, μ_0 are put equal to one, since they have been absorbed into the definition of charge, and all times come with a factor of c.

• The first pair of homogeneous Maxwell equations are identically satisfied if the fields are expressed in terms of scalar and vector potentials $(\phi, \mathbf{A})$

$$\mathbf{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A}. \tag{60}$$

However, the gauge potentials $(\phi, \mathbf{A})$ are not uniquely determined by the $\mathbf{E}$ and $\mathbf{B}$ fields, more on this momentarily. In terms of the gauge potentials, the Ampere-Maxwell equation becomes (use $\nabla \times (\nabla \times \mathbf{A}) = -\nabla^2 \mathbf{A} + \nabla(\nabla \cdot \mathbf{A})$)

$$-\nabla^2 \mathbf{A} + \nabla(\nabla \cdot \mathbf{A}) = \frac{\mathbf{j}}{c} - \frac{1}{c}\partial_t \nabla\phi - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2}. \tag{61}$$

So introducing the scalar and vector potentials means that the first pair of homogeneous Maxwell equations have already been solved. The gauge potentials play a very important role in the quantum theory. The hamiltonian for the interaction of a charged particle with the EM field is written in terms of $\mathbf{A}$, rather than in terms of $\mathbf{E}$ or $\mathbf{B}$.

• The inhomogeneous Maxwell equations can be written in a relativistically covariant form by introducing the 4-vectors $A^\mu = (\phi, \mathbf{A})$ and $j^\mu = (c\rho, \mathbf{j})$ and the field strength tensor $F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu$. Then the inhomogeneous Maxwell equations become $\partial_\mu F^{\mu\nu} = \frac{1}{c} j^\nu$ along with the consistency condition $\partial_\mu j^\mu = 0$ which expresses local charge conservation.

• However, $\mathbf{A}$ and ϕ are not uniquely determined by the measurable electric and magnetic fields. Two gauge potentials $(\phi, \mathbf{A})$ and $(\phi', \mathbf{A}')$ which differ by a gauge transformation

$$\mathbf{A}' = \mathbf{A} + \nabla\theta, \quad \phi' = \phi - \frac{1}{c}\frac{\partial \theta}{\partial t}. \tag{62}$$

correspond to the same electromagnetic fields. Gauge transformations form a group $\mathcal{G}$ which acts on the space of gauge potentials $\mathcal{A} = \{(\phi, \mathbf{A})\}$. Each orbit (equivalence class of gauge potentials) corresponds to an electromagnetic field $(\mathbf{E}, \mathbf{B})$ and the space of electromagnetic fields is the quotient $\mathcal{A}/\mathcal{G}$. A choice of orbit representatives is called a gauge choice. It is obtained by imposing condition(s) on the gauge potentials which are satisfied by one set of gauge potentials from each equivalence class.

• A convenient gauge choice is Coulomb gauge $\nabla \cdot \mathbf{A} = 0$. Given a vector potential $\mathbf{A}'$ we find its representative in Coulomb gauge by making the gauge transformation $\mathbf{A} = \mathbf{A}' - \nabla\theta$ with θ chosen to satisfy Poisson's equation $\nabla^2\theta = \nabla \cdot \mathbf{A}'$.

• Gauss' law simplifies in Coulomb gauge: $\nabla \cdot E = -\nabla^2\phi - \frac{\partial \nabla\cdot\mathbf{A}}{\partial t} = 0$ becomes $-\nabla^2\phi = \rho$, whose solution involves the Coulomb potential (this is why $\nabla \cdot A = 0$ is called the Coulomb gauge!) $\phi(\mathbf{r}, t) = \frac{1}{4\pi}\int d^3r' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}$. In particular, in Coulomb gauge, the scalar potential $\phi(\mathbf{r}, t)$ is not a dynamical quantity, it is entirely fixed by the instantaneous charge density. Now let us specialize to the case where there are no charges present in the interior and boundary of the region of interest, so that $\rho = 0$. Then $\phi = 0$. In the absence of charges, Coulomb gauge is called radiation gauge ($\phi = 0$, $\nabla \cdot \mathbf{A} = 0$), since electromagnetic radiation is most easily described in this gauge. Indeed, $\nabla \cdot \mathbf{A} = 0$ or $\mathbf{k} \cdot \tilde{\mathbf{A}}_k = 0$ in Fourier space means there are only two (transverse) components of the vector potential that are dynamical. These correspond to the two independent polarizations of electromagnetic radiation. In radiation gauge, the Ampere-Maxwell equation becomes

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = \nabla^2 \mathbf{A} + \frac{\mathbf{j}}{c}, \qquad \text{(provided } \nabla \cdot \mathbf{A} = 0, \phi = \rho = 0). \tag{63}$$

This is the vector wave equation in the presence of a current source $\mathbf{j}$. One is often interested in EM waves in vacuum, in which case $\mathbf{j}=0$ and we get the homogeneous vector wave equation.

$$\Box\mathbf{A} \equiv \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} - \nabla^2\mathbf{A} = 0, \qquad \text{(provided } \nabla\cdot\mathbf{A}=0, \mathbf{j}=0, \phi=\rho=0). \tag{64}$$

3.3.1 Fourier decomposition of $\mathbf{A}(\mathbf{r},t)$, transversality condition and polarization

The wave equation describes EM waves, including traveling plane waves. Since the equation is linear, a super position of plane waves is also a solution. This suggests that we may express the general solution of the wave equation as a superposition of plane waves. This is what Fourier analysis does for us. We first imagine that the EM field is considered in a large cubical box of volume V and write the vector potential as a Fourier series

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}}\sum_{\mathbf{k}}\mathbf{A}_{\mathbf{k}}(t)e^{i\mathbf{k}\cdot\mathbf{r}} \tag{65}$$

The Fourier coefficient $\mathbf{A}_{\mathbf{k}}(t)$ is called the Fourier mode corresponding to wave vector $\mathbf{k}$. The pre-factors $c/\sqrt{V}$ are not very important and for later convenience: the formula for the electric field $-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}$ becomes simpler. The allowed values of $\mathbf{k}$ are determined by the boundary conditions, but are not important to us since we will eventually let $V\to\infty$ so that all $\mathbf{k}$ are allowed. For simplicity, we consider the radiation field in a cubical cavity of volume V with periodic boundary conditions. This allows us to work with Fourier series. We will eventually let the sides of the box go to infinity, and the Fourier series will become Fourier integrals. The distinction is not important for us here.

• The advantage of the Fourier expansion is that the wave equation $\Box\mathbf{A}=0$ reduces to a system of ODEs, for each mode $\mathbf{k}$

$$\ddot{\mathbf{A}}_{\mathbf{k}}(t) + c^2\mathbf{k}^2\mathbf{A}_{\mathbf{k}}(t) = 0 \quad\Rightarrow\quad \ddot{\mathbf{A}}_{\mathbf{k}}(t) = -\omega_k^2\mathbf{A}_{\mathbf{k}}(t). \tag{66}$$

Thus each mode $A_{\mathbf{k}}$ evolves independently in time like a classical oscillator of angular frequency $\omega_k = c|\mathbf{k}|$. We anticipate that the time dependence of the vector potential may be written as a linear combination of $e^{i\omega_k t}$ and $e^{-i\omega_k t}$. However $\mathbf{A}_{\mathbf{k}}$ is a vector, not a scalar, so it has a direction. Which way does it point? This brings in the concept of polarization.

• The Coulomb gauge condition $\nabla\cdot\mathbf{A}=0$ becomes

$$\nabla\cdot\mathbf{A} = \frac{ic}{\sqrt{V}}\sum_{\mathbf{k}}\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}}(t)e^{i\mathbf{k}\cdot\mathbf{r}} \equiv 0. \quad\Rightarrow\quad \sum_{\mathbf{k}}\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} = 0 \quad \text{for all} \quad \mathbf{r} \tag{67}$$

The only way for this to happen is for the individual Fourier coefficients to vanish, i.e., $\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}}=0$ for each $\mathbf{k}$. In other words, the Fourier modes $\mathbf{A}_{\mathbf{k}}$ must each be transversal (orthogonal) to the corresponding wave vectors. Thus the Coulomb gauge condition is also called the transversality condition. We will soon see that $\mathbf{k}$ is the direction of propagation of the corresponding EM wave, so we see that $\mathbf{A}_{\mathbf{k}}$ must be transverse to its wave vector.

• So we may write $\mathbf{A}_{\mathbf{k}} = \sum_\lambda A_{\mathbf{k},\lambda}\epsilon_\lambda$ as a linear combination of two basis polarization vectors $\vec{\epsilon}_1, \vec{\epsilon}_2$, which are perpendicular to $\mathbf{k}$. For convenience we choose them to be mutually orthogonal so that $\epsilon_1, \epsilon_2, \hat{k}$ form an orthonormal system:

$$\hat{\mathbf{k}}\cdot\epsilon_\lambda = 0, \quad \epsilon_\lambda\cdot\epsilon_{\lambda'} = \delta_{\lambda,\lambda'}, \quad \epsilon_1\times\epsilon_2 = \hat{\mathbf{k}} = \frac{\mathbf{k}}{k} \tag{68}$$

$\epsilon_{1,2}(\mathbf{k})$ of course depend on $\mathbf{k}$, but for brevity, we do not display the $\mathbf{k}$-dependence explicitly.

- A single-mode EM field with $\mathbf{A}_{\mathbf{k},\lambda} \propto \epsilon_\lambda$ would correspond to an EM wave with the electric field $\mathbf{E}_\mathbf{k} \propto -\frac{1}{c}\dot{\mathbf{A}}_\mathbf{k}$ pointing along ("polarized along") the ϵ_λ direction. The corresponding magnetic field is $\mathbf{B}_\mathbf{k} \propto \mathbf{k} \times \mathbf{A}_\mathbf{k}$. We see that for a fixed Fourier mode $\mathbf{k}$, the electric $\mathbf{E}_k \propto \dot{\mathbf{A}}_\mathbf{k}$ and magnetic fields $\mathbf{B}_\mathbf{k} \propto \mathbf{k} \times \mathbf{A}_\mathbf{k}$ are both orthogonal to $\mathbf{k}$, i.e., $\mathbf{k} \cdot \mathbf{E}_\mathbf{k} = 0$ and $\mathbf{k} \cdot \mathbf{B}_\mathbf{k} = 0$. This is the statement that EM waves are transversely polarized. One choice of basis for polarization vectors is[9]

$$\epsilon_1 = \hat{x}, \quad \epsilon_2 = \hat{y} \quad \text{and} \quad \hat{\mathbf{k}} = \hat{z}. \tag{70}$$

Since $\epsilon_1, \epsilon_2, \hat{\mathbf{k}}$ form an orthonormal basis for 3d Euclidean space, we may write the identity matrix as a sum of projections to the subspaces spanned by each

$$I = \epsilon_1 \epsilon_1^t + \epsilon_2 \epsilon_2^t + \hat{\mathbf{k}}\hat{\mathbf{k}}^t \quad \text{or} \quad \delta_{ij} = (\epsilon_1)_i(\epsilon_1)_j + (\epsilon_2)_i(\epsilon_2)_j + \frac{k_i k_j}{k^2} \tag{71}$$

Thus the transverse projection operator (it appears in the Poisson brackets below) may be expressed as

$$\delta_{ij} - \frac{k_i k_j}{k^2} = \sum_{\lambda=1,2} \epsilon_i^\lambda \epsilon_j^\lambda. \tag{72}$$

3.3.2 Electromagnetic energy, Lagrangian, conjugate momentum and Poisson brackets

- The energy in the electromagnetic field in the radiation gauge becomes

$$H = \frac{1}{2}\int \left(\mathbf{E}^2 + \mathbf{B}^2\right) d^3r = \frac{1}{2}\int \left(\frac{1}{c^2}\dot{\mathbf{A}}^2 + (\nabla \times \mathbf{A})^2\right) d^3r \equiv \int \mathcal{H}\, d^3r. \tag{73}$$

The instantaneous configuration of the radiation field is specified by the vector potential $\mathbf{A}(\mathbf{r},t)$, subject to $\nabla \cdot \mathbf{A} = 0$. Comparing with the point-particle energy $H = \frac{1}{2}m\dot{q}^2 + V(q) = T + V$, the electric energy is the kinetic energy and the magnetic energy is a potential energy. The corresponding Lagrangian is $T - V$:

$$L = \frac{1}{2}\int \left(\mathbf{E}^2 - \mathbf{B}^2\right) d^3\mathbf{r} = \frac{1}{2}\int \left(\frac{1}{c^2}\dot{\mathbf{A}}^2 - (\nabla \times \mathbf{A})^2\right) d^3\mathbf{r} \equiv \int \mathcal{L}\, d^3\mathbf{r}. \tag{74}$$

Recall that the momentum conjugate to a coordinate q is $\frac{\partial L}{\partial \dot{q}}$. So the momentum conjugate to A_i is $\pi_i = \frac{\partial \mathcal{L}}{\partial \dot{A}_i} = -\frac{1}{c}E_i$. It is tempting to write Poisson brackets $\{A_i(\mathbf{r},t), -\frac{1}{c}E_j(\mathbf{r},t)\} = \delta_{ij}\delta^3(\mathbf{r}-\mathbf{r}')$. However, this would not be consistent with the radiation gauge condition, which requires that the divergence of the lhs must vanish. In fact the divergence of the lhs in both $\mathbf{r}$ and $\mathbf{r}'$ must vanish since $\nabla \cdot \mathbf{A} = 0$ and $\nabla \cdot \mathbf{E} = 0$ in the absence of charges.

- Poisson bracket relations that respect the transversality constraints are

$$\left\{\frac{1}{c}E_i(\mathbf{r},t), A_j(\mathbf{r}',t)\right\} = \delta_{ij}^T(\mathbf{r}-\mathbf{r}'), \quad \left\{A_i(\mathbf{r},t), A_j(\mathbf{r}',t)\right\} = \left\{E_i(\mathbf{r},t), E_j(\mathbf{r}',t)\right\} = 0. \tag{75}$$

---

[9] It is also interesting to choose a complex basis of 'right' and 'left' circular polarization vectors. E.g. if $\vec{\epsilon}_1 = \hat{x}, \vec{\epsilon}_2 = \hat{y}$,

$$\epsilon_+ = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y}) \quad \text{and} \quad \epsilon_- = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y}), \quad \text{while} \quad \hat{k} = \hat{z}. \tag{69}$$

These are orthonormal in the sense $\epsilon_\lambda^* \cdot \epsilon_{\lambda'} = \delta_{\lambda,\lambda'}$, $\hat{z} \cdot \epsilon_\pm = 0$.

Here $\delta^T_{ij}(\mathbf{r}-\mathbf{r'})$ is the transverse projection of the delta function:

$$\delta^T_{ij}(\mathbf{r}-\mathbf{r'}) = \int \frac{d^3k}{(2\pi)^3}\left(\delta_{ij} - \frac{k_i k_j}{\mathbf{k}^2}\right) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r'})} = \frac{1}{V}\sum_{\mathbf{k}}\left(\delta_{ij} - \frac{k_i k_j}{\mathbf{k}^2}\right) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r'})}. \tag{76}$$

The transverse delta function is symmetric and divergence-free $\frac{\partial}{\partial \mathbf{r}_i}\delta^T_{ij}(\mathbf{r}-\mathbf{r'}) = -\frac{\partial}{\partial \mathbf{r}'_i}\delta^T_{ij}(\mathbf{r}-\mathbf{r'}) = 0$.

- These Poisson brackets may seem a bit ad hoc. The justification for any set of Poisson brackets is that they must give the correct equations of motion with the appropriate hamiltonian (and satisfy anti-symmetry and the Jacobi identity). We will verify later that these p.b. imply the vector wave equation for $\mathbf{A}$ (this is easier to check in Fourier space).

- Let us return to the Fourier expansion of the vector potential and write the electromagnetic energy in terms of the modes $\mathbf{A}_\mathbf{k}$[10]

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}}\sum_{\mathbf{k}} \mathbf{A}_\mathbf{k}(t) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{78}$$

- The electric and magnetic fields are

$$\mathbf{E} = -\frac{1}{\sqrt{V}}\sum_{\mathbf{k}} \dot{\mathbf{A}}_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{and} \quad \mathbf{B} = \frac{ic}{\sqrt{V}}\sum_{\mathbf{k}} (\mathbf{k}\times\mathbf{A}_\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{79}$$

- The electric (kinetic) energy is (we use $\int d^3\mathbf{r}\ e^{i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}} = V\delta_{\mathbf{k}\mathbf{k'}}$ and $\mathbf{A}_{-\mathbf{k}} = \mathbf{A}^*_\mathbf{k}$)

$$\text{K.E.} = \frac{1}{2}\int \mathbf{E}^2 d^3\mathbf{r} = \frac{1}{2V}\sum_{\mathbf{k},\mathbf{k'}} \dot{\mathbf{A}}_\mathbf{k}\dot{\mathbf{A}}_{\mathbf{k'}}\int d^3\mathbf{r}\ e^{i(\mathbf{k}+\mathbf{k'})\cdot\mathbf{r}} = \frac{1}{2}\sum_{\mathbf{k}}\dot{\mathbf{A}}_\mathbf{k}\dot{\mathbf{A}}_{-\mathbf{k}} = \frac{1}{2}\sum_{\mathbf{k}}|\dot{\mathbf{A}}_\mathbf{k}|^2. \tag{80}$$

While the magnetic (potential) energy is

$$\text{P.E.} = -\frac{1}{2}\frac{c^2}{V}\sum_{\mathbf{k},\mathbf{k'}}(\mathbf{k}\times\mathbf{A}_\mathbf{k})\cdot(\mathbf{k'}\times\mathbf{A}_{\mathbf{k'}})\int e^{i(\mathbf{k}+\mathbf{k'})\cdot\mathbf{r}}d^3\mathbf{r} = \frac{c^2}{2}\sum_{\mathbf{k}}(\mathbf{k}\times\mathbf{A}_\mathbf{k})\cdot(\mathbf{k}\times\mathbf{A}_{-\mathbf{k}}) = \frac{c^2}{2}\sum_{\mathbf{k}}|\mathbf{k}\times\mathbf{A}_\mathbf{k}|^2. \tag{81}$$

Thus the electromagnetic energy is

$$H = \frac{1}{2}\sum_{\mathbf{k}}\left(|\dot{\mathbf{A}}_\mathbf{k}|^2 + \omega_k^2|\hat{k}\times\mathbf{A}_\mathbf{k}|^2\right) \quad \text{where} \quad \omega_k = c|\mathbf{k}|. \tag{82}$$

Comparing with the hamiltonian of a particle of mass $m=1$ in a harmonic oscillator potential, $H_{\text{sho}} = \frac{1}{2}\dot{q}^2 + \frac{1}{2}\omega^2 q^2$ we see that the electromagnetic energy is a sum of energies of a collection of oscillators $\mathbf{A}_\mathbf{k}$. This may also be seen from the equation of motion $\Box\mathbf{A} = 0$.

---

[10] Since $\mathbf{A}$ is real, the Fourier coefficients must satisfy the symmetry $\mathbf{A}^*_{-\mathbf{k}} = \mathbf{A}_\mathbf{k}$. Why is this true? This is a general fact about Fourier series. Suppose $f(x) = \sum_{n=-\infty}^{\infty} f_n e^{inx}$. Then $f^*(x) = \sum_n f^*_n e^{-inx}$. But now let us relabel the dummy index of summation as $n' = -n$, then $f^*(x) = \sum_{n'=-\infty}^{\infty} f^*_{-n'} e^{in'x} = \sum_n f^*_{-n} e^{inx}$. But this must equal $f(x)$ for all x, and this is possible only if the Fourier coefficients are all the same, i.e., if $f_n = f^*_{-n}$. To make the reality of $A(\mathbf{r},t)$ manifest, we could also write

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{2}\frac{c}{\sqrt{V}}\sum_{\mathbf{k}}\left(\mathbf{A}_\mathbf{k}(t)e^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{A}^*_\mathbf{k}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}\right) \tag{77}$$

3.3.3 Solution of vector wave equation as superposition of polarized plane waves

• Indeed, the advantage of the Fourier expansion is that the wave equation $\Box \mathbf{A} = 0$ reduces to a system of decoupled ODEs, for each mode $\mathbf{k}$ and each independent polarization λ. Upon dotting with $\vec{\epsilon}_\lambda$,

$$\ddot{\mathbf{A}}_{\mathbf{k}}(t) + c^2\mathbf{k}^2\mathbf{A}_{\mathbf{k}}(t) = 0 \quad \text{becomes} \quad \ddot{A}_{\mathbf{k},\lambda}(t) = -\omega_k^2 A_{\mathbf{k},\lambda}(t) \quad \text{where} \quad \omega_k = c|\mathbf{k}|. \tag{83}$$

Thus each mode $A_{\mathbf{k},\lambda}$ evolves independently in time like a classical oscillator of angular frequency ω_k

$$A_{\mathbf{k},\lambda}(t) = c_{\mathbf{k},\lambda} e^{-i\omega_k t} + c^*_{\mathbf{k},\lambda} e^{i\omega_k t}. \tag{84}$$

The real and imaginary parts of $c_{\mathbf{k},\lambda}$ are the two constants of integration. Thus

$$\mathbf{A}_{\mathbf{k}}(t) = \sum_\lambda \vec{\epsilon}_\lambda \left[c_{\mathbf{k},\lambda} e^{-i\omega_k t} + c^*_{\mathbf{k},\lambda} e^{i\omega_k t}\right]. \tag{85}$$

If we were working with complex polarization vectors $\epsilon_\pm$ we would have

$$\mathbf{A}_{\mathbf{k}}(t) = \sum_\lambda \left[c_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda e^{-i\omega_k t} + c^*_{\mathbf{k},\lambda} \vec{\epsilon}^{\,*}_\lambda e^{i\omega_k t}\right]. \tag{86}$$

For simplicity, let us stick to real polarization vectors. Using these Fourier coefficients we synthesize the vector potential that is the general solution of the vector wave equation incorporating the Coulomb gauge condition[11]

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \left[c_{\mathbf{k},\lambda} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_k t)} + c^*_{\mathbf{k},\lambda} e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega_k t)}\right] \tag{88}$$

$\mathbf{A}$ has been expressed as a linear combination of plane waves $\epsilon_\lambda e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ traveling in the direction of their respective wave vectors $\mathbf{k}$, and with polarization λ. The corresponding electric field is (here and elsewhere + c.c. denotes addition of the complex conjugate)

$$\mathbf{E}(\mathbf{r},t) = -\frac{1}{c}\dot{\mathbf{A}} = \frac{i}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \omega_k \left(c_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - c.c.\right) \tag{89}$$

Here the constant Fourier coefficients $c_{\mathbf{k},\lambda}, c^*_{\mathbf{k},\lambda}$ are determined by initial conditions on A, E. With a slight abuse of notion, it is convenient to define

$$c_{\mathbf{k},\lambda}(t) = c_{\mathbf{k},\lambda} e^{-i\omega_{\mathbf{k}} t}, \quad c^*_{\mathbf{k},\lambda}(t) = c^*_{\mathbf{k},\lambda} e^{i\omega_{\mathbf{k}} t} \quad \text{where} \quad c_{\mathbf{k},\lambda}, c^*_{\mathbf{k},\lambda} \quad \text{are the initial values.} \tag{90}$$

3.3.4 Change of phase space variables from $\mathbf{A}, \mathbf{E}$ to Fourier modes $c_{\mathbf{k},\lambda}, c^*_{\mathbf{k},\lambda}$

It is clear that the Fourier modes $c_{\mathbf{k},\lambda}(t), c^*_{\mathbf{k},\lambda}(t)$ of definite wave number and polarization have a simpler (simple harmonic) time-dependence than the position space E, A fields (which are

---

[11] • When $V \to \infty$, these Fourier series become integrals $\frac{1}{V}\sum_{\mathbf{k}} \to \int \frac{d^3k}{(2\pi)^3}$ with $\mathbf{k}$ taking all values. For instance,

$$\mathbf{A}(\mathbf{r},t) = c\int \frac{d^3\mathbf{k}}{(2\pi)^3} \sum_\lambda [c(\mathbf{k},\lambda)\epsilon_\lambda e^{(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{c.c}] \quad \text{where} \quad c(\mathbf{k},\lambda) = \sqrt{V} c_{\mathbf{k},\lambda}. \tag{87}$$

linear combinations of several modes). Moreover, the hamiltonian does not couple distinct Fourier modes. This motivates a change of phase space variables from A and E to c, c^*. We *define*[12]

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &= \frac{c}{\sqrt{V}}\sum_{\mathbf{k},\lambda}\vec{\epsilon}_\lambda\left[c_{\mathbf{k},\lambda}(t)e^{i\mathbf{k}\cdot\mathbf{r}}+c^*_{\mathbf{k},\lambda}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}\right]\\ \mathbf{E}(\mathbf{r},t) &= \frac{i}{\sqrt{V}}\sum_{\mathbf{k},\lambda}\vec{\epsilon}_\lambda\omega_k\left(c_{\mathbf{k}\lambda}(t)e^{i\mathbf{k}\cdot\mathbf{r}}-c^*_{\mathbf{k}\lambda}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}\right)\end{aligned} \tag{91}$$

These changes of variables are chosen so that the transversality constraints on A and E are automatically satisfied. Note that the electric field is not obtained by differentiating A in time, it is an independent field. On the other hand, the magnetic field is obtained by taking curl of A, it is a dependent field.

• A significant advantage of c, c^* over A, E is that they have simpler p.b. than A and E. Upon quantization c, c^* are related to annihilation and creation operators for photons with definite wave vector and polarization.

• The equal-time Poisson brackets among the components A_i and E_j are satisfied if the modes $c_{\mathbf{k},\lambda}(t), c^*_{\mathbf{k},\lambda}(t)$ satisfy the following equal time p.b.

$$\left\{c_{\mathbf{k},\lambda}(t), c^*_{\mathbf{k}',\lambda'}(t)\right\} = \frac{1}{2i\omega_k}\,\delta_{\mathbf{k}\mathbf{k}'}\,\delta_{\lambda\lambda'}, \quad \left\{c_{\mathbf{k},\lambda}(t), c_{\mathbf{k}',\lambda'}(t)\right\} = \left\{c^*_{\mathbf{k},\lambda}(t), c^*_{\mathbf{k}',\lambda'}(t)\right\} = 0. \tag{92}$$

Apart from some constant factors, this must remind us of commutators between SHO annihilation and creation operators $[a, a^\dagger] = 1, [a, a] = [a^\dagger, a^\dagger] = 0$. Let us indicate how this is verified in one case. All dynamical variables A, E, c, c^* are evaluated at the same time t which we suppress

$$\begin{aligned}\left\{\frac{1}{c}E_i(\mathbf{r}), A_j(\mathbf{r}')\right\} &= \frac{i}{V}\sum_{\mathbf{k},\lambda,\mathbf{k}',\lambda'}\omega_k\left\{c_{\mathbf{k},\lambda}(\epsilon_\lambda)_i e^{i\mathbf{k}\cdot\mathbf{r}}-\text{c.c.},\ c_{\mathbf{k}'\lambda'}(\epsilon_{\lambda'})_j e^{i\mathbf{k}'\cdot\mathbf{r}'}+\text{c.c}\right\}\\ &= \frac{i}{iV}\sum_{\mathbf{k},\lambda,\mathbf{k}',\lambda'}\frac{\omega_k}{2\omega_k}\left[\delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}\epsilon_{\lambda i}\epsilon_{\lambda' j}e^{i(\mathbf{k}\cdot\mathbf{r}-\mathbf{k}'\cdot\mathbf{r}')}+\text{c.c.}\right]\\ &= \frac{1}{2V}\left(\sum_{\mathbf{k}}\left(\delta_{ij}-\frac{k_ik_j}{k^2}\right)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}+\text{c.c.}\right) = \frac{1}{2V}2V\delta^T_{ij}(\mathbf{r}-\mathbf{r}') = \delta^T_{ij}(\mathbf{r}-\mathbf{r}').\end{aligned}$$

We used the completeness/transverse projection formula $\sum_\lambda \epsilon_{\lambda i}\epsilon_{\lambda j} = \delta_{ij} - \hat{k}_i\hat{k}_j$. In the last line, the Fourier series is a real function of $\mathbf{r}-\mathbf{r}'$, since $\delta_{ij} - \hat{k}_i\hat{k}_j$ is an even function of momentum. So the addition of the complex conjugate just doubles it. One may similarly check that the components of the electric field Poisson commute with each other and so too do the components of the vector potential.

---

[12] Of course, we know the time dependence of $c(t), c^*(t)$ from solving the equations of motion. But that explicit time-dependence is not needed now, it simply motivates the following change of phase space dynamical variables. Equal time Poisson brackets between dynamical variables do not depend on their time-dependence nor on what the hamiltonian is.

3.3.5 Hamiltonian in terms of Fourier modes $c_{\mathbf{k}\lambda}, c^*_{\mathbf{k}\lambda}$

• Let us express the classical hamiltonian in terms of the Fourier modes. We will show below that

$$H = \frac{1}{2}\int (\mathbf{E}^2 + \mathbf{B}^2) d^3\mathbf{r} = 2\sum_{\mathbf{k},\lambda} \omega_k^2 c^*_{\mathbf{k},\lambda} c_{\mathbf{k},\lambda} \tag{93}$$

• To obtain this formula for the hamiltonian, let us work for simplicity with a real o.n. basis for polarizations $\epsilon_1 \times \epsilon_2 = \hat{k}$. The expressions for $\mathbf{A}, \mathbf{E}, \mathbf{B}$ in terms of c, c^* are

$$\begin{aligned}
\mathbf{A}(\mathbf{r}, t) &= \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \left[c_{\mathbf{k},\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + c^*_{\mathbf{k},\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \\
\mathbf{E}(\mathbf{r}, t) &= \frac{i}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \omega_k \left(c_{\mathbf{k}\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} - c^*_{\mathbf{k}\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}}\right) \\
\mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A} = \frac{i}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k}} \hat{k} \times \vec{\epsilon}_\lambda \left(c_{\mathbf{k}\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} - c^*_{\mathbf{k}\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}}\right)
\end{aligned} \tag{94}$$

Now we compute the electric energy using orthogonality $\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} d^3r = V\delta_{\mathbf{k},\mathbf{k}'}$ and $\epsilon_\lambda \epsilon_{\lambda'} = \delta_{\lambda,\lambda'}$.

$$\begin{aligned}
\frac{1}{2}\int \mathbf{E}^2 d^3\mathbf{r} &= -\frac{1}{2V} \sum_{\mathbf{k},\mathbf{k}',\lambda,\lambda'} \epsilon_\lambda \cdot \epsilon'_\lambda \omega_{\mathbf{k}}\, \omega_{\mathbf{k}'} \int \left[c_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} - c^*_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \left[c_{\mathbf{k}'\lambda'} e^{i\mathbf{k}'\cdot\mathbf{r}} - c^*_{\mathbf{k}'\lambda'} e^{-i\mathbf{k}'\cdot\mathbf{r}}\right] d^3\mathbf{r} \\
&= -\frac{1}{2} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}}^2 \left[c_{\mathbf{k}\lambda} c_{-\mathbf{k}\lambda} + c^*_{\mathbf{k}\lambda} c^*_{-\mathbf{k}\lambda} - 2|c_{\mathbf{k}\lambda}|^2\right].
\end{aligned} \tag{95}$$

The magnetic energy is

$$\frac{1}{2}\int \mathbf{B}^2 d^3\mathbf{r} = -\frac{1}{2V} \sum_{\mathbf{k},\mathbf{k}',\lambda,\lambda'} \omega_{\mathbf{k}} \omega_{\mathbf{k}'} (\hat{k} \times \epsilon_\lambda) \cdot (\hat{k}' \times \epsilon'_\lambda) \int \left[c_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} - c^*_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \left[c_{\mathbf{k}'\lambda'} e^{i\mathbf{k}'\cdot\mathbf{r}} - c^*_{\mathbf{k}'\lambda'} e^{-i\mathbf{k}'\cdot\mathbf{r}}\right] d^3\mathbf{r}.$$

It is clear that the spatial integrals will produce either $\delta_{\mathbf{k},-\mathbf{k}'}$ or $\delta_{\mathbf{k},\mathbf{k}'}$ in the various terms. Now we use $\hat{k} = \pm\hat{k}'$, orthogonality of wave and polarization vectors, and the scalar and vector triple product identities to simplify

$$(\hat{k} \times \epsilon_\lambda) \cdot (\hat{k}' \times \epsilon'_\lambda) = \hat{k}' \cdot (\epsilon'_\lambda \times (\hat{k} \times \epsilon_\lambda)) = \hat{k}' \cdot [\hat{k}(\epsilon_{\lambda'} \cdot \epsilon_\lambda) - \epsilon_\lambda(\epsilon_{\lambda'} \cdot \hat{k})] = (\hat{k}' \cdot \hat{k})\, \delta_{\lambda\lambda'}. \tag{96}$$

So the magnetic energy becomes

$$\frac{1}{2}\int \mathbf{B}^2 d^3\mathbf{r} = -\frac{1}{2} \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k}}^2 [-c_{\mathbf{k},\lambda} c_{-\mathbf{k},\lambda} - c^*_{\mathbf{k},\lambda} c^*_{-\mathbf{k},\lambda} - 2|c_{\mathbf{k},\lambda}|^2]. \tag{97}$$

We see that the cc and c^*c^* terms cancel between the electric and magnetic energies giving $H = 2\sum_{\mathbf{k},\lambda} \omega_{\mathbf{k}}^2 c^*_{\mathbf{k},\lambda}$. To make the energy look like that of a collection of harmonic oscillators, we define rescaled Fourier modes

$$c_{\mathbf{k},\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\, a_{\mathbf{k},\lambda}, \quad \text{and} \quad c^*_{\mathbf{k},\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\, a^*_{\mathbf{k},\lambda}. \tag{98}$$

Then the hamiltonian and p.b. become

$$H = \sum_{\mathbf{k},\lambda} \hbar\omega_k \left(a^*_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}\right), \qquad \left\{a_{\mathbf{k},\lambda}, a^*_{\mathbf{k}',\lambda'}\right\} = \frac{1}{i\hbar}\delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}, \quad \left\{a_{\mathbf{k},\lambda}, a_{\mathbf{k}',\lambda'}\right\} = \left\{a^*_{\mathbf{k},\lambda}, a^*_{\mathbf{k}',\lambda'}\right\} = 0. \tag{99}$$

Note that the introduction of factors of $\hbar$ does not make this a quantum theory, we are simply choosing to measure the energy of each mode in units of $\hbar\omega_k$. We will quantize this hamiltonian dynamical system soon by replacing classical dynamical variables by operators on Hilbert space and p.b. by commutators $\{.,.\} \to \frac{1}{i\hbar}[.,.]$. These re-scalings ensure that the quantum hamiltonian and commutators take a standard form.

• Simple as the hamiltonian and p.b. are, we must still check that they imply the correct time dependence for a and a^*, previously obtained by solving the vector wave equation, i.e., $a_{\mathbf{k},\lambda}(t) = e^{-i\omega_{\mathbf{k}}t} a_{\mathbf{k},\lambda}(0)$. Hamilton's equation for evolution is

$$\dot a_{\mathbf{k}\lambda} = \{a_{\mathbf{k},\lambda}, H\} = \left\{ a_{\mathbf{k},\lambda}, \sum_{l,\mu} \hbar\omega_l a^*_{l\mu} a_{l\mu} \right\} = \sum_{l\mu} \hbar\omega_l a_{l\mu} \frac{\delta_{\mathbf{k},\mathbf{l}}\delta_{\lambda,\mu}}{i\hbar} = -i\omega_k a_{\mathbf{k}\lambda}. \tag{100}$$

The solution of this equation is $a_{\mathbf{k},\lambda}(t) = a_{\mathbf{k},\lambda}(0) e^{-i\omega_k t}$. Thus we have verified that the Hamiltonian and p.b. we have postulated for the classical radiation field lead to the correct time-evolution. This justifies the 'ad-hoc' introduction of the transverse delta function in the p.b. between **A** and **E**.

• Let us motivate the passage to the quantum theory by recalling how to 'canonically' quantize a harmonic oscillator using creation and annihilation operators.

3.4 Quantization of the harmonic oscillator using creation and annihilation operators

• Newton's equation for a particle of mass m executing simple harmonic motion is $m\ddot q = -\omega^2 q$. The energy of such a harmonic oscillator is $E = \frac{1}{2}m\dot q^2 + \frac{1}{2}m\omega^2 q^2$. In terms of the momentum $p = m\dot q$, the hamiltonian is $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$. Position and momentum satisfy the p.b. $\{q,p\} = 1$, $\{q,q\} = \{p,p\} = 0$.

• Since $\hbar\omega$ has dimensions of energy, even classically we may write $H = \hbar\omega(\frac{p^2}{2m\hbar\omega} + \frac{1}{2}\frac{m\omega q^2}{\hbar})$. Defining a constant with unit of inverse length $\beta = \sqrt{\frac{m\omega}{\hbar}}$ we have the dimensionless coordinate and momentum $\xi = \beta q$ and $\mathtt{p} = \frac{p}{\hbar\beta}$ with p.b. $\{\xi, \mathtt{p}\} = \frac{1}{\hbar}$ and $H = \frac{1}{2}\hbar\omega(\xi^2 + \mathtt{p}^2)$. We now define the complex combinations

$$a = \frac{\xi + i\mathtt{p}}{\sqrt{2}} \quad \text{and} \quad a^* = \frac{\xi - i\mathtt{p}}{\sqrt{2}} \quad \text{with} \quad \{a, a^*\} = -\frac{i}{\hbar} \quad \text{and} \quad H = \hbar\omega a^* a = \hbar\omega |a|^2. \tag{101}$$

In the quantum theory, q, p become operators. In the Schrodinger representation $p = -i\hbar\frac{\partial}{\partial q}$ and the p.b. $\{q,p\} = 1$ is replaced by the commutator $[q,p] = i\hbar$ (i.e., multiply the rhs by $i\hbar$). It follows that $[\xi, \mathtt{p}] = i$. In the Schrodinger representation $\mathtt{p} = -i\frac{\partial}{\partial \xi}$, check that this gives the desired commutator $[\xi, \mathtt{p}] = i$.

• Now if $a^\dagger = (\xi - i\mathtt{p})/\sqrt{2}$ denotes the hermitian adjoint of the operator a (quantum version of a^*), then $[a, a^\dagger] = 1$. Moreover,

$$a^\dagger a = \frac{1}{2}\left(\xi^2 + \mathtt{p}^2 + i[\xi, \mathtt{p}]\right) = \frac{1}{2}\left(\xi^2 + \mathtt{p}^2 - 1\right) \tag{102}$$

- The hamiltonian operator

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = \frac{1}{2}\hbar\omega(\xi^2 + \mathtt{p}^2) \tag{103}$$

may be written as $H = \hbar\omega(a^\dagger a + \frac{1}{2})$. We have used that fact that $aa^\dagger - a^\dagger a = 1$. $N = a^\dagger a$ is the number operator. We may check using the commutation relations that

$$[N, a] = [a^\dagger a, a] = [a^\dagger, a]a = -a \quad \text{and} \quad [N, a^\dagger] = [a^\dagger a, a^\dagger] = a^\dagger[a, a^\dagger] = a^\dagger. \tag{104}$$

It follows that

$$[H, a] = -\hbar\omega a \quad \text{and} \quad [H, a^\dagger] = \hbar\omega a^\dagger. \tag{105}$$

$a, a^\dagger$ are called the annihilation and creation operators (or lowering and raising operators) because of the way we may interpret these relations. Suppose $|\psi\rangle$ is an energy eigenstate with energy eigenvalue E. Then assuming $a|\psi\rangle$ is not the zero vector, $a|\psi\rangle$ is also an energy eigenstate with a little lower energy $E - \hbar\omega$, since

$$H(a|\psi\rangle) = aH|\psi\rangle - \hbar\omega a|\psi\rangle = (E - \hbar\omega)(a|\psi\rangle) \tag{106}$$

Similarly, $a^\dagger|\psi\rangle$ is also an energy eigenstate with a slightly higher energy $E + \hbar\omega$.

- Now the SHO hamiltonian is a positive operator, in the sense that its diagonal matrix element in any state is positive:

$$\langle\phi|H|\phi\rangle = \frac{1}{2}\hbar\omega + \langle\phi|a^\dagger a|\phi\rangle = \frac{1}{2}\hbar\omega + \langle a\phi|a\phi\rangle = \frac{1}{2}\hbar\omega + ||a\phi\rangle||^2 \geq \frac{1}{2}\hbar\omega. \tag{107}$$

Since eigenvalues are simply expectation values in normalized eigenstates, the energy eigenvalues must all be $\geq \frac{1}{2}\hbar\omega$. Now, if there is one energy eigenstate $|\psi\rangle$ with eigenvalue E, then by repeated application of the lowering operator a, we may produce an energy eigenstate with negative energy, contradicting the positivity of H. To avoid this problem, successive application of a must result in a state $|0\rangle$ (taken to have unit norm) which is annihilated by the lowering operator. This state is the ground state of the hamiltonian $H|0\rangle = \frac{1}{2}\hbar\omega|0\rangle$ with energy $E_0 = \frac{1}{2}\hbar\omega$. $|0\rangle$ is also called the vacuum state. The first excited state is $|1\rangle = a^\dagger|0\rangle$, with an energy $E_1 = \frac{3}{2}\hbar\omega$.

- Note that the ground or vacuum state is not the zero vector. The zero vector $\psi(x) = 0$ is not a state describing a particle, since it has zero probability to be found any where. But the simple harmonic oscillator describes one particle at all times, so every physical state of the SHO must satisfy the normalization condition $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$. One may find the position space wave function of the ground state, i.e., $\langle x|0\rangle = \psi_0(x)$ using the condition $a\psi(x) = \frac{1}{\sqrt{2}}(\xi + \partial_\xi)\psi = 0$. This implies $\psi'/\psi = -\xi$ or $\psi = Ae^{-\xi^2/2} = Ae^{-\beta^2 x^2/2}$. Find the value of constant A to ensure the ground state is normalized to one. Note that though the average value of x in the ground (vacuum) state is zero on account of evenness (parity symmetry) of $\psi_0(x)$, the position does suffer fluctuations, $\langle x^2\rangle_0 \neq 0$. Similarly, one checks that $\langle p\rangle_0 = 0$ but $\langle p^2\rangle_0 \neq 0$.

- We check using the commutation relation $aa^\dagger - a^\dagger a = 1$ that $|1\rangle$ has unit norm

$$\langle 1|1\rangle = \langle 0|aa^\dagger|0\rangle = \langle 0|0\rangle + \langle 0|a^\dagger a|0\rangle = 1. \tag{108}$$

Similarly, the second excited state is $\propto a^\dagger|1\rangle$. The square of its norm is

$$\langle 0|aaa^\dagger a^\dagger|0\rangle = \langle 0|a(a^\dagger a + 1)a^\dagger|0\rangle = \langle 0|aa^\dagger|0\rangle + \langle 0|(a^\dagger a + 1)aa^\dagger|0\rangle = 1 + 1 = 2. \tag{109}$$

So the normalized second excited state is $|2\rangle = \frac{1}{\sqrt{2}} a^\dagger a^\dagger|0\rangle$, with an energy $\frac{5}{2}\hbar\omega$. Proceeding this way[13], one finds that the n^{th} excited state (normalized to one) is $|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle$ with an energy eigenvalue $E_n = \hbar\omega(n+\frac{1}{2})$.

• In the Schrödinger picture, the states evolve with time, as specified by the Schrodinger equation $i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = H|\psi(t)\rangle$, while observables like H, x, p are time-independent. Energy levels are stationary, in the sense that they evolve by a phase

$$|n(t)\rangle = e^{-iE_n t/\hbar}|n(0)\rangle. \tag{110}$$

• In the Heisenberg picture, states are time-independent while observables carry the time dependence. By definition, the state in the Heisenberg picture is just the Schrödinger state at $t=0$. So

$$|\phi(t)\rangle_s = e^{-iHt/\hbar}|\phi(0)\rangle \quad \Rightarrow \quad |\phi(t)\rangle_s = e^{-iHt/\hbar}|\phi\rangle_h. \tag{111}$$

The Heisenberg picture operator A_h corresponding to the Schrödinger picture operator A_s is defined as

$$A_h(t) = e^{iHt/\hbar}A_s e^{-iHt/\hbar} = U^\dagger A_s U, \quad \text{where we denote} \quad U = e^{-iHt/\hbar}. \tag{112}$$

It follows that the hamiltonian is the same in both pictures $H_s = H_h \equiv H$. Further, the states and operators in the two pictures coincide at $t=0$.

• Matrix elements and expectation values (which carry physical significance) may be computed in either picture, resulting in the same values

$$_h\langle\phi|A_h(t)|\psi\rangle_h =_s \langle\phi(t)|UU^\dagger A_s UU^\dagger|\psi(t)\rangle_s =_s \langle\phi(t)|A_s|\psi(t)\rangle_s. \tag{113}$$

Just as the Schrodinger equation governs the evolution of states in the Schrodinger picture, the time evolution of an observable A_h is governed by the Heisenberg equation of motion

$$i\hbar\frac{\partial A_h}{\partial t} = [A_h, H]. \tag{114}$$

Let us derive the Heisenberg equation of motion. Recall $A_h(t) = U^\dagger A_s U$

$$i\hbar\partial_t A_h = i\hbar(\partial_t U^\dagger)A_s U + i\hbar U^\dagger A_s \partial_t U = -HU^\dagger A_s U + U^\dagger A_s U H = -HA_h + A_h H = [A_h, H]. \tag{115}$$

Here we used $U = e^{-iHt/\hbar}$ so that $i\hbar\partial_t U = HU = UH$ since H and U commute. And taking the hermitian adjoint, $-i\hbar\partial_t U^\dagger = HU^\dagger$.

• The Heisenberg equation of motion is the quantum version of Hamilton's classical equations written in p.b. form. Start with $\{A, H\} = \frac{\partial A}{\partial t}$ and replace p.b. by commutators and multiply the rhs by $i\hbar$.

• Let us use the Heisenberg equation of motion[14] to find the time evolution of the SHO creation and annihilation operators in the Heisenberg picture.

$$i\hbar\frac{\partial a_h}{\partial t} = [a_h, H] = ([a, H])_h = \hbar\omega a_h \quad \Rightarrow \quad \frac{\partial a_h}{\partial t} = -i\omega a_h \quad \Rightarrow \quad a_h(t) = e^{-i\omega t}a_h(0) \tag{116}$$

Similarly (or taking the hermitian conjugate), we get $a_h^\dagger(t) = e^{i\omega t}a_h^\dagger(0)$. This is the same time evolution as in a classical harmonic oscillator.

---

[13] The normalization factors may be obtained by first showing that $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $a|n\rangle = \sqrt{n}|n-1\rangle$.

[14] We also use $[H, a] = -\hbar\omega a, [H, a^\dagger] = \hbar\omega a^\dagger$ and the relation $[B_h, H] = [U^\dagger B U, H] = U^\dagger[B, H]U = ([B, H])_h$ on account of $[H, U] = 0$ where $U = e^{-iHt/\hbar}$.

3.5 Quantization of radiation field in radiation gauge

- Heisenberg's and Schrödinger's development of point particle quantum mechanics shows that the position and momentum of a particle are subject to quantum fluctuations. This is also motivated by Heisenberg's microscope thought-experiment which suggests that the determination of position with greater accuracy would make the determination of momentum more uncertain. The electromagnetic field is also subject to quantum fluctuations. This was motivated by Weisskopf's microscope thought-experiment. Here, we try to pin point the position of a charged point particle by measuring the electric field it produces, and fix its momentum by measuring the magnetic field produced by the current of the moving charge. If the electric and magnetic fields could be simultaneously determined, then we might be able to fix the instantaneous position and momentum of the particle, violating the Heisenberg uncertainty principle. To avoid this problem, we expect the electric and magnetic fields to display quantum fluctuations. This gives us a reason to quantize the radiation field. Once quantized, we will be able to identify the photon as a state of the quantized radiation field. However, it is harder to quantize the radiation field than a point particle. This is primarily because a particle or system of particles has a finite number of degrees of freedom, while the EM field has an infinite number of degrees of freedom (the electric and magnetic fields at each point in space). Another new feature is the possibility for photons to be created or absorbed. The number of atomic electrons in Schrodinger's treatment is fixed. But in radiative transitions the number of photons is not conserved. So the Hilbert space must include a vacuum state of no photons, states with one photon, states with two photons etc. Let us set up a scheme to deal with these possibilities.

- We will quantize the radiation field by the canonical procedure of replacing Poisson brackets with commutators, as we did for the harmonic oscillator. Indeed, the radiation field can be regarded as an infinite collection of harmonic oscillators, one for each mode labelled by wave vector and polarization $(\mathbf{k}, \lambda)$.

$$H = 2 \sum_{\mathbf{k},\lambda} \omega_k^2 c_{\mathbf{k}\lambda}^* c_{\mathbf{k}\lambda} \tag{117}$$

where the vector potential is

$$\mathbf{A}(\mathbf{r}, t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k}\lambda} \vec{\epsilon}_\lambda \left[c_{\mathbf{k}\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + c_{\mathbf{k}\lambda}^* e^{-i\mathbf{k}\cdot\mathbf{r}} \right]. \tag{118}$$

Recall the p.b. among the modes of the EM field

$$\left\{ c_{\mathbf{k},\lambda}, c_{\mathbf{k}',\lambda'}^* \right\} = \frac{1}{2i\omega_k} \delta_{\mathbf{k}\mathbf{k}'} \, \delta_{\lambda\lambda'}, \quad \left\{ c_{\mathbf{k},\lambda}, c_{\mathbf{k}',\lambda'} \right\} = \left\{ c_{\mathbf{k},\lambda}^*, c_{\mathbf{k}',\lambda'}^* \right\} = 0. \tag{119}$$

To make the Hamiltonian and p.b. look simpler and to follow a notation similar to the one used in quantizing the SHO, we define re-scaled Fourier modes for the radiation field

$$c_{\mathbf{k},\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\, a_{\mathbf{k},\lambda}, \quad \text{and} \quad c_{\mathbf{k},\lambda}^* = \sqrt{\frac{\hbar}{2\omega_k}}\, a_{\mathbf{k},\lambda}^*. \tag{120}$$

Then the hamiltonian becomes

$$H = \sum_{\mathbf{k}\lambda} \hbar\omega_k a_{\mathbf{k}\lambda}^* a_{\mathbf{k}\lambda}. \tag{121}$$

Then the Fourier decomposition of the vector potential reads

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar}{2\omega_k}} \vec{\epsilon}_\lambda \left[a_{\mathbf{k},\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + a^*_{\mathbf{k}\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}} \right] \tag{122}$$

and the equal-time p.b. among the $a_{\mathbf{k},\lambda}, a^*_{\mathbf{k},\lambda}$ are

$$\left\{ a_{\mathbf{k},\lambda}, a^*_{\mathbf{k}',\lambda'} \right\} = \frac{1}{i\hbar} \delta_{\mathbf{k},\mathbf{k}'} \delta_{\lambda,\lambda'}, \quad \text{while} \quad \left\{ a_{\mathbf{k},\lambda}, a_{\mathbf{k}',\lambda'} \right\} = \left\{ a^*_{\mathbf{k},\lambda}, a^*_{\mathbf{k}',\lambda'} \right\} = 0. \tag{123}$$

Now we canonically quantize this system by analogy with the SHO. The p.b. among the a, a^* are replaced by commutators between a , multiplying the RHS by $i\hbar$. Thus we get the canonical commutation relations

$$[a_{\mathbf{k},\lambda}, a^\dagger_{\mathbf{k}',\lambda'}] = \delta_{\mathbf{k},\mathbf{k}'} \delta_{\lambda,\lambda'}, \quad \text{while} \quad [a_{\mathbf{k},\lambda}, a_{\mathbf{k}',\lambda'}] = [a^\dagger_{\mathbf{k},\lambda}, a^\dagger_{\mathbf{k}',\lambda'}] = 0. \tag{124}$$

The expansion of the vector potential operator now reads

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar}{2\omega_k}} \vec{\epsilon}_\lambda \left[a_{\mathbf{k},\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger_{\mathbf{k}\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}} \right]. \tag{125}$$

We will find its time dependence shortly. There are similar expansions for the electric and magnetic field operators as linear combinations of creation and annihilation operators. The quantum version of the A, E Poisson brackets are the commutators $[E_i, E_j] = [A_i A_j] = 0$ and

$$[E_i(\mathbf{r},t), A_j(\mathbf{r}',t)] = i\hbar c \delta^T_{ij}(\mathbf{r}-\mathbf{r}'). \tag{126}$$

• The expression for the hamiltonian operator is ambiguous in the quantum theory since $a, a^\dagger$ do not commute. Classically we may write several equivalent expressions, $H = \sum \hbar\omega_k a^*_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} = \sum \hbar\omega_k a_{\mathbf{k}\lambda} a^*_{\mathbf{k}\lambda} = \frac{1}{2} \sum \hbar\omega_k (a^*_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} + a_{\mathbf{k}\lambda} a^*_{\mathbf{k}\lambda})$. If a, a^* are replaced by $a, a^\dagger$ then one gets hamiltonian operators that differ by an additive constant. If we use the first expression, then $\hat{H} = \sum_{\mathbf{k},\lambda} \hbar\omega_k a^\dagger_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}$. But if we use the third (symmetric expression for H, which also corresponds to $\frac{1}{2}(E^2 + B^2)$) then the quantum hamiltonian is

$$\hat{H} = \sum_{\mathbf{k},\lambda} \hbar\omega_k \left(a^\dagger_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda} + \frac{1}{2} \right) \quad \text{since} \quad a_{\mathbf{k},\lambda} a^\dagger_{\mathbf{k},\lambda} = a^\dagger_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda} + 1. \tag{127}$$

The additive constant $\sum_{\mathbf{k},\lambda} \frac{1}{2}\hbar\omega_k$ is called the zero point energy. In the infinite volume limit, it is infinite. However, this is a constant addition to the energy, and can be eliminated by redefining the zero of energy. Henceforth, we define $H = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}}\, a^\dagger_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}$. This definition is convenient since it assigns energy zero to the vacuum state.

3.5.1 Hilbert space of photon states

• To find the spectrum of the hamiltonian, we proceed as we did for the SHO. Indeed, the hamiltonian of the quantized radiation field is a sum of harmonic oscillators, one for each ‘mode’ labelled by $\mathbf{k}, \lambda$. From the commutation relations, we find as before, that

$$[H, a_{\mathbf{k},\lambda}] = -\hbar\omega_k a_{\mathbf{k},\lambda} \quad \text{and} \quad [H, a^\dagger_{\mathbf{k},\lambda}] = \hbar\omega_k a^\dagger_{\mathbf{k},\lambda}. \tag{128}$$

It follows that $a_{\mathbf{k},\lambda}, a^\dagger_{\mathbf{k},\lambda}$ lower and raise the energy by $\hbar\omega_k$. Thus we have a vacuum state $|0\rangle$ with energy zero, which is annihilated by *all* the lowering operators $a_{\mathbf{k},\lambda}|0\rangle = 0$. (This also means $\langle 0|a^\dagger_{\mathbf{k},\lambda} = 0$ for all $\mathbf{k}, \lambda$.) As before, $N_{\mathbf{k},\lambda} = a^\dagger_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}$ is a number operator. It has non-negative integers as its eigenvalues, which count the number of photons with wave vector $\mathbf{k}$ and polarization ϵ_λ in an eigenstate. $\mathbf{k}, \lambda$ are together good quantum numbers for photons. $N_{\mathbf{k},\lambda}|0\rangle = 0$. The operator whose eigenvalues are the total number of photons is $\hat{N} = \sum_{\mathbf{k},\lambda} N_{\mathbf{k},\lambda}$. We say that the vacuum state has no photons of any wave vector or polarization. However, the vacuum state is not the zero vector, it has unit norm $\langle 0|0\rangle = 1$. We will see that though the average electric and magnetic fields in the vacuum state are zero, they have non-zero fluctuations in the vacuum state. The free space around us (ignoring the EM fields from cell phone towers etc) is to a reasonable approximation the vacuum state of the photon field. If we measure the electric field, we will get small non-zero values which on average are zero. These small non-zero values are due to quantum fluctuations. This is just like saying that x and p are on average zero in the ground state of the harmonic oscillator. Nevertheless $\langle x^2\rangle$ and $\langle p^2\rangle$ are non-zero in the ground state of the SHO. The position x of the particle is the counterpart of the vector potential A, while the particle momentum p is the analog of ($-1/c$ times) the electric field.

• A state with one photon of wave vector $\mathbf{k}$ and polarization λ is $|1_{\mathbf{k},\lambda}\rangle = a^\dagger_{\mathbf{k},\lambda}|0\rangle$. This 1-photon state has energy $\hbar\omega_k$.

• Similarly, a state with two photos is

$$|1_{\mathbf{k},\lambda}, 1_{\mathbf{k}',\lambda'}\rangle = a^\dagger_{\mathbf{k},\lambda} a^\dagger_{\mathbf{k}',\lambda'}|0\rangle. \tag{129}$$

It is an eigenstate of the hamiltonian with energy $\hbar(\omega_k + \omega_{k'})$. Since creation operators commute, it does not matter in what order we write the creation operators, so

$$|1_{\mathbf{k}',\lambda'} 1_{\mathbf{k},\lambda}\rangle = |1_{\mathbf{k},\lambda}, 1_{\mathbf{k}',\lambda'}\rangle. \tag{130}$$

In other words, the state function of a system of two photons is symmetric with respect to exchange of the quantum numbers of the two photons: photons behave as bosons.

• The above two photon state has norm one if the quantum numbers are distinct, i.e., $(\mathbf{k}, \lambda) \neq (\mathbf{k}', \lambda')$. If the quantum numbers are the same, then the normalized 2-photon state is

$$|2_{\mathbf{k},\lambda}\rangle = \frac{1}{\sqrt{2!}}(a^\dagger_{\mathbf{k},\lambda})^2|0\rangle. \tag{131}$$

This follows from the commutation relations of creation and annihilation operators just as in the case of the harmonic oscillator.

• More generally a normalised multi-photon state with $n, n', n'', \ldots$ photons with quantum numbers $(\mathbf{k}, \lambda), (\mathbf{k}', \lambda'), (\mathbf{k}'', \lambda''), \ldots$ is

$$|n_{\mathbf{k},\lambda}, n'_{\mathbf{k}',\lambda'}, n''_{\mathbf{k}'',\lambda''}, \ldots\rangle = \frac{(a^\dagger_{\mathbf{k},\lambda})^n}{\sqrt{n!}} \frac{(a^\dagger_{\mathbf{k}',\lambda'})^{n'}}{\sqrt{n'!}} \frac{(a^\dagger_{\mathbf{k}'',\lambda''})^{n''}}{\sqrt{n''!}} \ldots |0\rangle. \tag{132}$$

Again, by the commutativity of the creation operators, these multi-photon states are symmetric under exchange of any pair, they describe bosons. These multi-photon states together span the Hilbert space of the quantized radiation field. It is called the bosonic Fock space of photons. The basis we have chosen to describe the Fock space is called the occupation number/photon number basis, since the basis states have definite numbers of photons with specified wave vector and polarization. It is in this way that the quantum theory accommodates the particle-like nature of photons discovered by Planck, Einstein et. al. On the other hand, a linear combination such as $|1_{\mathbf{k},\lambda}\rangle - |2_{\mathbf{k}',\lambda'}\rangle$ is also a valid state of the radiation field, but it does not have a definite number of photons, a measurement of the number of photons may result either in the answer one or two. Such states play a role in the ability of the quantum theory to accommodate the wave-like character of light, as we will see.

3.5.2 Fluctuations of E and B fields, EM Waves from matrix elements

• In the quantum theory the transverse photon vector potential field in radiation gauge is the hermitian operator

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \sqrt{\frac{\hbar}{2\omega_k}} \left[a_{\mathbf{k},\lambda}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger_{\mathbf{k}\lambda}(t) e^{-i\mathbf{k}\cdot\mathbf{r}} \right]. \tag{133}$$

The time dependence of $\mathbf{A}$ as well as the electric and magnetic field operators is determined by that of the creation and annihilation operators. To find their time-dependence, we use the Heisenberg equation of motion which is the quantised version of Hamilton's equation $\dot{a} = \{a, H\}$ obtained by the replacement $\{\cdot,\cdot\} \to [\cdot,\cdot]/i\hbar$

$$i\hbar \frac{da_{\mathbf{k},\lambda}}{dt} = [a_{\mathbf{k},\lambda}, H] = \hbar\omega_k a_{\mathbf{k},\lambda} \quad \Rightarrow \quad a_{\mathbf{k},\lambda}(t) = e^{-i\omega_k t} a_{\mathbf{k},\lambda}(0) \tag{134}$$

Similarly, $a^\dagger_{\mathbf{k},\lambda}(t) = e^{i\omega_k t} a^\dagger_{\mathbf{k},\lambda}(0)$. We may regard $a_{\mathbf{k},\lambda}(t)$ as the annihilation operator in the Heisenberg picture while $a_{\mathbf{k},\lambda}(0)$ is the annihilation operator in the Schrodinger picture. We will often omit the argument of a, and hope it is clear from the context. Thus our Fourier mode expansion of the quantized vector potential is

$$\mathbf{A}(\mathbf{r},t) = \frac{c}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \vec{\epsilon}_\lambda \sqrt{\frac{\hbar}{2\omega_k}} \left[a_{\mathbf{k},\lambda}(0) e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} + a^\dagger_{\mathbf{k}\lambda}(0) e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} \right]. \tag{135}$$

We notice that the time dependence is the same as in classical radiation theory (this is generally true when the hamiltonian is quadratic in fields and commutators are canonical). It follows that $\mathbf{E}$ and $\mathbf{B}$ are the hermitian field operators

$$\begin{aligned} \mathbf{E}(\mathbf{r},t) &= -\frac{\dot{\mathbf{A}}}{c} = i \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar\omega_k}{2V}} \vec{\epsilon}_\lambda \left(a_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} - a^\dagger_{\mathbf{k}\lambda} e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} \right) \\ \mathbf{B}(\mathbf{r},t) &= \nabla \times \mathbf{A} = i \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar\omega_k}{2V}} (\hat{k} \times \vec{\epsilon}_\lambda) \left(a_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} - a^\dagger_{\mathbf{k}\lambda} e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} \right) \end{aligned} \tag{136}$$

Being linear combinations of creation and annihilation operators, the electric and magnetic fields do not commute either with the number operator or hamiltonian (nor with each other). Their eigenstates do not have definite energy or number of photons in general. On the other hand, states of definite energy (like the vacuum) are not eigenstates of $\mathbf{E}$ or $\mathbf{B}$. For instance, acting on the vacuum the electric field operator produces a linear combination of one photon states with all possible wave vectors and polarizations.

$$\mathbf{E}(\mathbf{r},t)|0\rangle = -i \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar \omega_k}{2V}} \vec{\epsilon}_\lambda e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} |1_{\mathbf{k},\lambda}\rangle \tag{137}$$

It follows that the matrix element of the electric (or magnetic field) between the vacuum and 1 photon state $1_{\mathbf{k},\lambda}$ is a transversely polarized plane EM wave

$$\langle 1_{\mathbf{k},\lambda}|\mathbf{E}(\mathbf{r},t)|0\rangle = -i\sqrt{\frac{\hbar\omega}{2V}} \epsilon_\lambda e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \quad \text{and} \quad \langle 1_{\mathbf{k},\lambda}|\mathbf{B}(\mathbf{r},t)|0\rangle = -i\sqrt{\frac{\hbar\omega}{2V}} (\epsilon_\lambda \times \hat{k})\, e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{138}$$

Since plane waves satisfy Maxwell's equations, we see that these matrix elements of the electric and magnetic fields in the quantum theory satisfy the same wave equations (Maxwell's equations) as the classical electric and magnetic fields. The wave nature of light follows from Maxwell's equations. So this is one of the ways in which the quantum theory of the photon field accommodates the wave nature of light while also manifesting the particle-like nature of photons. From the viewpoint of the quantum theory, we may regard Maxwell's equations as determining these matrix elements of the fields. This is a useful point of view, since it also applies to the Klein-Gordon and Dirac equations.

• Historically, the Dirac and KG equations were introduced as relativistic quantum equations to describe a single electron or single pion. This interpretation was inconsistent in situations with significant relativistic effects: due to the possibility for particle creation and annihilation, particle number is not conserved and it does not make sense to look for a theory of a definite number of particles. The apparent successes of the '1 particle' Dirac equation (like the prediction of the magnetic moment of the electron or fine structure of the hydrogen spectrum) are all in the regime where relativistic effects are very small. In the current view, the Dirac and KG equations are not one particle wave equations like the non-relativistic Schrodinger equation, but rather classical wave-field equations, on the same footing as Maxwell's equations. The appearance of factors of $\hbar$ in the Dirac and KG equations does not make them 'quantum', but is due to a conventional choice of units for momenta and energies. Strictly, these classical relativistic field equations do not admit particle interpretation at all. However, when quantised via the process of 'field' quantization (somewhat misleadingly also known as 'second' quantization) that we have just carried out for the EM field, we arrive at the quantised Dirac and KG fields. States in the Hilbert space of these quantum fields now admit physical interpretation in terms of particles. Remarkably, the matrix elements of these quantised fields (Dirac, KG, Maxwell) between the vacuum and 1 particle states, satisfy the classical wave-field equations that one started with.

• By contrast, the 1 particle (or n-particle) non-relativisitic Schrodinger wave equation is already quantised. Unlike KG, Dirac or Maxwell, it is not to be regarded as a classical field equation awaiting quantization. It already deals with operators and states in Hilbert space.

• As the Weisskopf microscope thought experiment suggested, the electromagnetic field displays quantum fluctuations. To see this, consider the simplest of states, the vacuum $|0\rangle$ with no photons. In this state, $\langle 0|\mathbf{A}|0\rangle = 0$ since the annihilation operators will kill the ket-vacuum while the creation operators kill the bra-vacuum. Since $\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \nabla \times \mathbf{A}$, the electric and magnetic fields also have zero expectation values in the vacuum state. However, just as $\langle 0|x^2|0\rangle > 0, \langle 0|p^2|0\rangle > 0$ in the g.s of the SHO, one checks that $\langle 0|\mathbf{B}^2|0\rangle > 0$ and $\langle 0|\mathbf{E}^2|0\rangle > 0$

since $\mathbf{E}^2, \mathbf{B}^2$ include terms of the form $aa^\dagger$ which have non-zero vacuum expectation values. It follows that there are vacuum fluctuations in the electromagnetic fields, even when their mean values are zero. E.g., free space around us (ignoring the EM fields from cell phone towers etc) is to a reasonable approximation the vacuum state of the photon field. If we measure the electric field, we will get small non-zero values which on average are zero. These small non-zero values are due to quantum fluctuations.

• Question: How is $\langle 0|\mathbf{E}^2|0\rangle > 0$ and $\langle 0|\mathbf{B}^2|0\rangle > 0$ consistent with $\langle 0|H|0\rangle = 0$? Ans: our hamiltonian $H = \sum \hbar\omega a^\dagger a$ differs from $\int \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2) = \sum \frac{1}{2}\hbar\omega(aa^\dagger + a^\dagger a)$ by an additive constant ('zero point energy' $\sum \frac{1}{2}\hbar\omega_{\mathbf{k}}$). The non-zero vacuum fluctuations in $\mathbf{E}$ and $\mathbf{B}$, in a sense, add up to give this 'zero point energy'.

• Heuristically we may say that in the vacuum, though there are no real photons, there can be virtual photons that pop in and out of existence here and there, for short periods of time. These virtual photons are a way to visualize, for example, the evaluation of the expectation value $\langle 0|aa^\dagger|0\rangle$. Virtual photons are not directly detected, they are not present in the initial or final state. But virtual photons have real effects such as (1) The measurable vacuum fluctuations in the electric and magnetic fields. (2) The Casimir force between metal plates in vacuum. (3) The spontaneous gamma decay of atoms, nuclei and hadrons from excited states. While stimulated emission of photons from excited atoms is understandable, it was found that excited atoms can spontaneously emit photons. In a sense, virtual photons 'stimulate' the atom to 'spontaneously' decay.

4 Interaction of atomic electrons with radiation

4.1 Overview of atomic structure & transitions

• Let us begin with a brief overview of atomic structure and transitions. Though weak interactions do play a tiny role (especially in parity-violating effects), atomic structure is determined to an excellent approximation simply by applying non-relativistic quantum mechanics to the Coulomb interaction between electrons and nuclei, while imposing Pauli's exclusion principle. The mass of the nucleus m_N is too large compared to m_e to affect atomic wave functions and energies much. To a good approximation, they depend only on the charge (via the fine structure constant $\alpha = e^2/4\pi\hbar c$) and mass of the electron m_e and the nuclear charge Z. There are two length scales associated with atomic electrons, their reduced Compton wavelength $\hbar/mc = 1/m \approx 4 \times 10^{-14}$m and the atomic size (Bohr radius $a_0 = 1/\alpha m$). The typical atomic size, binding energy and speed of electrons in atoms can be estimated using the Bohr model of the H-atom, or variationally by using Heisenberg's uncertainty principle. Heuristically (replacing $\langle 1/r\rangle$ by $1/\langle r\rangle$ etc.), the expectation value of energy is $E \approx \frac{(\Delta p)^2}{2m} - \frac{\alpha}{\Delta x}$. Using $\Delta p \Delta x \sim 1$ we get $E \approx \frac{1}{2m(\Delta x)^2} - \frac{\alpha}{\Delta x}$. Minimizing in Δx we get $a_0 \approx (\Delta x)_{\min} = \frac{1}{\alpha m}$. The resulting energy is $E_{\min} \sim -\frac{1}{2}m\alpha^2 \equiv -1\text{Ry} = -13.6$ eV. Putting $|E| \approx \frac{1}{2}mv^2$ we find that the speed of an electron in an atom is roughly $v = \alpha$ in units of c. We notice that (1) the size of the atom is much larger than the Compton wavelength of its constituents $a_0 = 1/\alpha m_e \gg 1/m_e \gg 1/m_N$; (2) the electron moves non-relativistically and (3) the binding energy $\frac{1}{2}m\alpha^2$ is much less than the rest energy of the constituents ($\text{Ry} \ll m_e c^2 \ll m_N c^2$). These are general features of a non-relativistic bound state. To a good approximation, a nucleus is a non-relativistic bound state of nucleons, the solar system is a non-relativistic bound state of sun and planets. A hadron is very different: it is a relativistic bound state of quarks and gluons.

• The solution of the Schrödinger equation for the hydrogen spectrum suggests that an atom would remain forever in an excited stationary state. In the presence of an external EM field, atoms can be stimulated to make transitions between stationary states. The rate of stimulated emission or absorption is proportional to the intensity of light (energy density of the stimulating EM radiation). However, spectroscopists have known for long that atoms in excited states spontaneously decay in about a nanosecond through emission of light, even in the absence of any stimulation. How is this to be explained theoretically? Einstein showed that to understand thermodynamic equilibrium between atoms and radiation (whose spectral distribution is governed by Planck's blackbody law) in a cavity, the rate for spontaneous decay from excited states must be non-zero. Remarkably, Einstein's 1917 argument preceded the formulation of quantum mechanics and the development of time dependent perturbation theory (by Dirac)! However, Einstein's argument does not explain how there can be spontaneous decay even in the absence of external EM fields. The explanation for this is provided by the quantum theory of radiation. Even in the vacuum state where the mean electric and magnetic fields are zero, there are vacuum fluctuations which, in a sense, 'induce' spontaneous emission[15]!

• The interaction of atomic electrons with radiation leads to decay of atoms in excited states to lower energy levels via spontaneous emission of photons. As for any non-relativistic bound state, the reduced wavelength $\lambda = 1/\Delta E$ of photons emitted is large compared to the atomic size a_0. To see this, note that the energy difference $\Delta E \sim \frac{1}{2} m\alpha^2 \sim 1/2ma_0^2$. So $\lambda/a_0 \sim ma_0 = 1/\alpha = 1/v \gg 1$. The radiation field of the decaying atom may be expressed as a multipole expansion in powers of the small parameter $a_0/\lambda \sim \alpha$. We will see that the leading term corresponds to electric dipole radiation (E1), which is followed by electric quadrupole E2 and magnetic dipole (M1) terms.

• Not all transitions between atomic levels are allowed, there are selection rules based on parity and angular momentum conservation. In one photon emission, the angular momentum j_i of the atom in its initial state must equal the combined angular momentum of the photon (j_γ) and final state atom (j_f). By the rules for combining angular momenta we must have $|j_f - j_\gamma| \leq j_i \leq |j_f + j_\gamma|$. Dipole radiation has $J_\gamma = 1$, so dipole transitions must satisfy the selection rule $\Delta j = 0, \pm 1$. Now a 1 photon state (dipole or not) cannot have zero angular momentum, $j_\gamma \neq 0$. It follows that j_i, j_f cannot both be zero, there are no 1-photon transitions between a pair of zero angular momentum states. Parity conservation implies $\Pi_i = \Pi_f \Pi_\gamma$. We will see that $\Pi_\gamma = -1$ for E1 ($\Pi_\gamma = 1$ for M1), so it follows that parity must be reversed in E1 transitions.

---

[15] Note that spontaneous absorption is almost never seen to occur, an atom in its ground state in vacuum is rarely found to spontaneously get excited. A statistical mechanics argument for this may be offered, using the principle of equal a priori probabilities: in equilibrium, all states of a system with the same energy are equally likely. Consider an atom in the presence of electromagnetic radiation present in the vacuum. Suppose the energy difference between the ground and first excited state of the atom is ΔE. There is only one way in which this quantum of energy can be possessed by the atom: by being in the first excited state. On the other hand, this energy can be kept in the radiation field in very many ways, essentially, since the electromagnetic field has very many degrees of freedom, the electric and magnetic fields at each point of space. Since a priori all these possibilities are equally probable, it is infinitely more likely for the quantum of energy to be stored in the electromagnetic field than in the atom. This explains why atoms are typically found in their ground states and are not seen to spontaneously absorb radiation from the vacuum and get excited.

4.2 Coupling of atomic electrons to the EM field

• To systematically study the interaction of electrons in an atom with the radiation field, we begin with the atomic hamiltonian H_0 and treat the interaction with the EM field as a perturbation H_1. For simplicity, let us consider a one electron atom such as hydrogen, ignoring the spin of the electron. In rationalized Heaviside-Lorentz units,

$$H_0 = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi r} \tag{139}$$

We know that the eigenstates of H_0 are $|nlm\rangle$ with energies

$$E_{nlm} = -\frac{me^4}{2(4\pi)^2 n^2 \hbar^2} = -\frac{e^2}{2(4\pi) n^2 a_0} = -\frac{mc^2\alpha^2}{2n^2} \quad \text{where} \quad a_0 = \frac{(4\pi)\hbar^2}{e^2 m} \quad \text{and} \quad \alpha = \frac{e^2}{4\pi\hbar c} \tag{140}$$

are the Bohr radius and fine structure constant. Here the principal quantum number n takes the values $1, 2, \ldots$ corresponding to the K,L,M shells. The angular momentum/azimuthal quantum number $l = 0, 1, \ldots n-1$ corresponds to the s, p, d, f orbitals and the magnetic quantum number $m_l = -l, -l+1, \ldots, l-1, l$ corresponds to the various possible projections of the angular momentum on the z-axis. Each level has a degeneracy of n^2. If we included the spin of the electron, then the energies are not altered but the degeneracies are doubled to $2n^2$ on account of the two possible spin projections on the z-axis $m_s = \pm\frac{1}{2}$. If we have a hydrogenic atom with Z protons in the nucleus e^2 is replaced by Ze^2.

• According to the Schrodinger equation, all the eigenstates $|n, l, m\rangle$ are stable if the hydrogen atom is considered in isolation. However, when we consider the hydrogen atom coupled to the electromagnetic field, we find that all except the ground state $|100\rangle$ are unstable to decay by emission of one or more photons, as is experimentally observed. The decay may be either stimulated by external EM radiation or 'spontaneous'. Even in the vacuum state, the electromagnetic field displays quantum fluctuations and these quantum fluctuations can cause spontaneous emission.

• The interaction of a charged particle with an EM field is given by the Lorentz force law. The interaction of an electron (charge e) with an EM field (given by the vector potential $\mathbf{A}$) may be derived from a Hamiltonian. It is obtained by replacing the electron momentum $\mathbf{p}$ by $\mathbf{p} - e\mathbf{A}/c$. This is called the minimal coupling or Lorentz prescription (it can be proved by checking that the resulting equation of motion for $\mathbf{r}(t)$ is Newton's equation with the Lorentz force). Thus

$$\frac{\mathbf{p}^2}{2m} \to \frac{1}{2m}\left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right)^2 = \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}\left(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}\right) + \frac{e^2}{2mc^2}\mathbf{A}^2. \tag{141}$$

• In the quantum theory, $\mathbf{p} = -i\hbar\nabla$. So $\mathbf{p}$ and $\mathbf{A}(\mathbf{r})$ do not commute in general, $[p_i, A_j] = -i\hbar\partial_i A_j$. In particular,

$$\mathbf{p}\cdot\mathbf{A} - \mathbf{A}\cdot\mathbf{p} = \sum_i [p_i, A_i] = -i\hbar\nabla\cdot\mathbf{A}. \tag{142}$$

However, in Coulomb gauge, $\nabla\cdot\mathbf{A} = 0$, so $\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}$. Thus the hamiltonian becomes

$$H = \left(\frac{p^2}{2m} - \frac{e^2}{4\pi r}\right) - \frac{e}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 = H_0 - \frac{e}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 \tag{143}$$

where H_0 is the standard hydrogen hamiltonian including kinetic energy and Coulomb potential. The first interaction term linear in $\mathbf{A}$ is usually the dominant one, responsible for decay by single photon emission in perturbation theory (e.g. electric dipole radiation). The quadratic term in A is usually a small correction, it is called the dielectric term. It is responsible for simultaneous two photon emission processes. We will ignore it. It becomes more important when the effect due to the first term vanishes (as in the decay of the 2S state of hydrogen).

• In addition to this 'minimal' electromagnetic coupling of the electron, there is Pauli's magnetic moment interaction between the spin of the electron and the magnetic field

$$\frac{e\hbar}{2mc}\sigma\cdot\mathbf{B} \quad \text{where} \quad \mathbf{B} = \nabla\times\mathbf{A}. \tag{144}$$

Though an ad hoc addition to the hamiltonian in the non-relativistic treatment of the atom, Pauli's magnetic moment interaction also arises via the minimal coupling Lorentz prescription in Dirac's relativistic theory of the electron. The magnetic moment interaction is usually smaller than the electric dipole interaction and we will ignore it. It is responsible for magnetic dipole radiation from atoms.

4.3 Why $\mathbf{p} \to \mathbf{p} - \frac{eA}{c}$ for charged particle in an EM field?

An electromagnetic field is described by electric $\vec{E}(r,t)$ and magnetic $\vec{B}(r,t)$ fields which may be obtained from scalar $\phi(r,t)$ and vector $\vec{A}(r,t)$ potentials

$$\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}, \qquad \vec{B} = \vec{\nabla}\times\vec{A} \tag{145}$$

Suppose a test charge e moves in such an external field (produced by some other charges and currents), then it feels the Lorentz force and follows a trajectory given by Newton's second law

$$m\ddot{r} = \vec{F} = e\vec{E} + \frac{e}{c}\vec{v}\times\vec{B}, \tag{146}$$

Now we wish to derive this equation of motion from a classical Hamiltonian. Having a hamiltonian helps in the passage to the quantum theory. The hamiltonian that does this job is

$$H = \frac{1}{2m}\left(p - \frac{eA}{c}\right)^2 + e\phi = \frac{p\cdot p}{2m} + \frac{e^2 A\cdot A}{2mc^2} - \frac{ep\cdot A}{mc} + e\phi. \tag{147}$$

Let us work out Hamilton's equations $\dot{r}_j = \frac{\partial H}{\partial p_j}$, $\dot{p}_j = -\frac{\partial H}{\partial r_j}$ and show that they reduce to the Lorentz force law. Hamilton's equations are

$$m\dot{r}_j = m\frac{\partial H}{\partial p_j} = p_j - \frac{e}{c}A_j \;\text{ and }\; -\dot{p}_j = \frac{\partial H}{\partial r_j} = e\frac{\partial\phi}{\partial r_j} + \frac{e^2}{mc^2}A_i\frac{\partial A_i}{\partial r_j} - \frac{e}{mc}p_i\frac{\partial A_i}{\partial r_j} \tag{148}$$

We need $m\ddot{r}_j$, which is

$$m\ddot{r}_j = \dot{p}_j - \frac{e}{c}\dot{A}_j = -e\frac{\partial\phi}{\partial r_j} - \frac{e^2}{mc^2}A_i\frac{\partial A_i}{\partial r_j} + \frac{e}{mc}p_i\frac{\partial A_i}{\partial r_j} - \frac{e}{c}\dot{A}_j. \tag{149}$$

Here $\dot{A}_j = \frac{\partial A_j}{\partial t} + \frac{dr_i}{dt}\frac{\partial A_j}{\partial x_i}$. Let us denote the velocity of the particle by $v_i = \dot{r}_i = \frac{dr_i}{dt}$. Substituting for $p_i = m\dot{r}_i + \frac{e}{c}A_i$

$$m\ddot{r}_j = eE_j + e\frac{v_i}{c}\frac{\partial A_i}{\partial r_j} - \frac{e}{c}(v \cdot \nabla)A_j. \tag{150}$$

From vector calculus,

$$(v \cdot \nabla)A = \nabla(v \cdot A) - v \times (\nabla \times A) \tag{151}$$

Thus

$$m\ddot{r}_j = eE_j + \frac{e}{c}(v \times B)_j + \frac{e}{c}\left(v_i\frac{\partial A_i}{\partial r_j} - \frac{\partial(v \cdot A)}{\partial r_j}\right). \tag{152}$$

The term in parentheses vanishes since

$$\frac{\partial v_i}{\partial r_j} = \frac{\partial \dot{r}_i}{\partial r_j} = \frac{d}{dt}\frac{\partial r_i}{\partial r_j} = \frac{d}{dt}\delta_{ij} = 0. \tag{153}$$

Thus, Hamilton's equations for $H = \frac{\pi^2}{2m} + e\phi$ where $\pi = p - eA$ are equivalent to Newton's equation for a particle subject to the Lorentz force in an electromagnetic field. This interaction of a charged particle with an electromagnetic field is called minimal-coupling.

4.4 Golden rule for radiative emission rate in first order perturbation theory

We would like to study a radiative transition of an atom from an initial (excited) state $|i\rangle$ to a final state $|f\rangle$ while emitting a single photon with wave vector and polarization $\mathbf{k}, \lambda$. There is the analogous absorption process as well. The hamiltonian that governs these processes in the leading approximation mentioned above is

$$H = \left(\frac{p^2}{2m} - \frac{e^2}{4\pi r}\right) - \frac{e}{mc}\mathbf{A} \cdot \mathbf{p} = H_0 + H_1(t). \tag{154}$$

$\mathbf{A}(\mathbf{r}, t)$ is dependent on time. So we have a time dependent perturbation to the atomic hamiltonian, which we wish to treat to first order. For emission, our initial state at $t = 0$, $|i\rangle \otimes |0\rangle$ consists of an atom in state $|i\rangle$ and the radiation field in its vacuum state $|0\rangle$. After a time T, we ask for the amplitude to make a transition to the state $|f\rangle \otimes |1_{\mathbf{k},\lambda}\rangle$ consisting of the atom in state $|f\rangle$ and the radiation field in the given 1-photon state. From 1st order perturbation theory, assuming $i \neq f$, the transition probability is the absolute square of the

$$\text{Amplitude}(f, 1_{\mathbf{k}\lambda} \leftarrow i; T) = -\frac{i}{\hbar}\int_0^T \langle f, 1_{\mathbf{k},\lambda}|H_1(t)|i\rangle \; e^{-i(E_i - E_f)t/\hbar}\, dt + \cdots \tag{155}$$

Recalling that

$$\mathbf{A}(\mathbf{r}, t) = \frac{c}{\sqrt{V}}\sum_{\mathbf{k}',\lambda'}\sqrt{\frac{\hbar}{2\omega_{k'}}}\vec{\epsilon}_{\lambda'}\left[a_{\mathbf{k}',\lambda'}e^{i(\mathbf{k}'\cdot\mathbf{r} - \omega_{k'}t)} + a^{\dagger}_{\mathbf{k}'\lambda'}e^{-i(\mathbf{k}'\cdot\mathbf{r} - \omega_{k'}t)}\right], \tag{156}$$

we see that only the term involving the creation operator $a^{\dagger}_{\mathbf{k}',\lambda'}e^{i\omega_{k'}t}$ for $\mathbf{k}' = \mathbf{k}$ and $\lambda' = \lambda$ can have a non-vanishing matrix element between the vacuum initial state and the final 1-photon state $|1_{\mathbf{k}\lambda}\rangle$. On the other hand, for absorption of a photon with wave vector $\mathbf{k}$ and polarization λ, only the annihilation operator term $a_{\mathbf{k},\lambda}e^{-i\omega_k t}$ can contribute.

• Thus, without loss of generality, we may factor $H_1(t) = \tilde{H}_1 e^{\pm i\omega_k t}$ where $\tilde{H}_1$ is time-independent. The $+$ sign is for emission and $-$ sign for absorption. Thus the amplitude for emission is

$$\text{Ampl}_{f,1_{\mathbf{k}\lambda}\leftarrow i}(T) = \frac{1}{i\hbar}\langle f, 1_{\mathbf{k}\lambda}|\tilde{H}_1|i\rangle \int_0^T e^{-i(E_i-E_f-\hbar\omega_k)t/\hbar} = \frac{1}{\hbar}\langle f, 1_{\mathbf{k}\lambda}|\tilde{H}_1|i\rangle \frac{\left[e^{-i(E_i-E_f-\hbar\omega_k)T/\hbar} - 1\right]}{(E_i - E_f - \hbar\omega_k)/\hbar} \tag{157}$$

The transition probability is its absolute square

$$\text{Prob}_{f,1_{\mathbf{k}\lambda}\leftarrow i}(T) = \frac{|\langle f|\tilde{H}_1|i\rangle|^2}{\hbar^2}\frac{4\sin^2(\Omega T/2)}{\Omega^2}. \tag{158}$$

where $\Omega = (E_i - E_f - \hbar\omega_k)/\hbar$ and $|e^{i\theta} - 1|^2 = 4\sin^2(\theta/2)$. Plot $\sin^2(\Omega T/2)/\Omega^2$ as a function of Ω for various times T and notice that this function is increasingly concentrated around $\Omega = 0$ as T grows. For long times T, the transition probability is significant only when $\Omega = (E_i - E_f - \hbar\omega_k)/\hbar \approx 0$. Recalling the representation of the Dirac δ function,

$$\frac{2}{\pi}\lim_{T\to\infty}\frac{\sin^2\frac{1}{2}\Omega T}{\Omega^2 T} = \delta(\Omega). \tag{159}$$

we see that for long times, the transition probability is proportional to the time:

$$\text{Prob}_{f,1_{\mathbf{k}\lambda}\leftarrow i}(T) \to \frac{2\pi}{\hbar}|\langle f|\tilde{H}_1|i\rangle|^2\; T\; \delta(E_i - E_f - \hbar\omega_k) \tag{160}$$

We used $\hbar^{-1}\delta(\Omega) = \delta(\hbar\Omega)$. Dividing by T, the transition probability per unit time (or transition rate) approaches a constant for long times

$$\text{Rate}_{f,1_{\mathbf{k}\lambda}\leftarrow i} \to \frac{2\pi}{\hbar}|\langle f|\tilde{H}_1|i\rangle|^2\; \delta(E_i - E_f - \hbar\omega_k) \tag{161}$$

The same formula holds for absorption with the change $-\hbar\omega_k \to +\hbar\omega_k$.

• In the case of emission, when the volume of our box $V \to \infty$, there is a continuous energy spectrum of possible final state photons which could have wave vectors pointing in various directions. So it is interesting to find the transition rate for photons emitted into an elemental solid angle $d\Omega$ around the direction (θ, ϕ) and having an energy lying between $\hbar\omega$ and $\hbar(\omega+d\omega)$. This rate is given by the product of the above rate by the number of photon states in this range. We will eventually sum/integrate over all the possible states (energies, directions and polarizations) of the emitted photon to find the total decay rate, but we go in steps.

• Now the energy of a photon is $E = \hbar\omega_k = \hbar c|\mathbf{k}|$. So photon states in a given energy range lie in a spherical shell in $\mathbf{k}$-space. In general, we associate one quantum state to a phase region of volume $d^3\mathbf{r}d^3\mathbf{p}/h^3$. So the number of photon states in a volume V (with fixed polarization - we will sum over polarizations later) with wave vectors in the range $[\mathbf{k}, \mathbf{k} + d\mathbf{k}]$ is ($\mathbf{p} = \hbar\mathbf{k}$)

$$dn = \frac{V\, d^3\mathbf{p}}{(2\pi)^3\hbar^3} = \frac{V\, d^3\mathbf{k}}{(2\pi)^3} = \frac{1}{(2\pi)^3}V\, k^2\, dk\, d\Omega \tag{162}$$

upon transforming to spherical polar coordinates. For photons emitted into the solid angle $d\Omega$, let us denote the number of photon states with energy in the interval $[E, E + dE]$ by $\rho(E,\Omega)dEd\Omega$. Then

$$\rho(E,\Omega)\, dE\, d\Omega = dn = \frac{1}{(2\pi)^3}V\, k^2\, dk\, d\Omega. \tag{163}$$

Thus, the density of states ($E = \hbar\omega = \hbar ck$)

$$\rho(E,\Omega)\, dE\, d\Omega = \frac{1}{(2\pi)^3} V\, k^2\, d\Omega\, \frac{dk}{dE}\, dE = \frac{Vk^2 d\Omega}{(2\pi)^3 \hbar c} dE = \frac{V\omega^2 d\Omega}{(2\pi)^3 \hbar c^3} dE. \tag{164}$$

Multiplying by the previously obtained rate and integrating over photon energies (which is fixed by the energy conserving δ-function), we obtain Fermi's Golden Rule for the emission rate of a photon with polarisation λ and wave vector $\mathbf{k}$ pointing in the solid angle $d\Omega$ around the direction defined by θ, ϕ:

$$w(\Omega) d\Omega = d\Omega \frac{2\pi}{\hbar} \int |\langle f|\tilde{H}_1|i\rangle|^2\, \delta(E_i - E_f - \hbar\omega_k) \rho(E,\Omega) dE = \frac{2\pi}{\hbar} |\langle f|\tilde{H}_1|i\rangle|^2 \rho(E_{\mathbf{k}},\Omega)\, d\Omega \tag{165}$$

where $E_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} = E_i - E_f$. The letter w is a commonly used symbol to denote the rate of a process in physics. This formula for w is called Fermi's golden rule.

• Now let us apply this to the case of photon emission. The relevant interaction hamiltonian is the coefficient of the creation operator $a^\dagger_{\mathbf{k},\lambda} e^{i\omega_{\mathbf{k}} t}$ in $-(e/mc)\mathbf{A}\cdot\mathbf{p}$:

$$\tilde{H}_1 = -\frac{e}{mc} \frac{c}{\sqrt{V}} \sqrt{\frac{\hbar}{2\omega_k}} e^{-i\mathbf{k}\cdot\mathbf{r}}\, \vec{\epsilon}_\lambda \cdot \mathbf{p}. \tag{166}$$

Note that $\langle 1_{\mathbf{k}\lambda}|a^\dagger_{\mathbf{k}\lambda}|0\rangle = 1$, so we do not indicate the photon creation operator or photon state any more. Thus the rate for photon emission into $d\Omega$ is

$$w(\Omega) d\Omega = \frac{2\pi}{\hbar} \frac{e^2\hbar}{2m^2\omega_k V} |\langle f|e^{-i\mathbf{k}\cdot\mathbf{r}} \vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle|^2 \frac{V\omega_k^2}{(2\pi)^3} \frac{d\Omega}{\hbar c^3} = \frac{e^2\omega_k}{8\pi^2 m^2 \hbar c^3} |\langle f|e^{-i\mathbf{k}\cdot\mathbf{r}} \vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle|^2\, d\Omega \tag{167}$$

Notice that the factor of V in the density of states cancels the $1/V$ from the square of the matrix element leaving a finite limit as $V \to \infty$.

4.5 Electric dipole approximation

To determine the emission rate, we must evaluate the matrix element

$$\langle f|e^{-i\mathbf{k}\cdot\mathbf{r}}\, \vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle \tag{168}$$

between the initial and final atomic states $|i\rangle, |f\rangle$. Here $\mathbf{k}, \vec{\epsilon}_\lambda$ are the photon wave vector and polarization while $\mathbf{r}, \mathbf{p}$ are the position and momentum operators of the electron. Computing this matrix element between atomic energy eigenstates is in general quite difficult since it involves the exponential of the position operator. To make progress we would like to expand the exponential in a series.

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = 1 - i\mathbf{k}\cdot\mathbf{r} - (\mathbf{k}\cdot\mathbf{r})^2 + \cdots . \tag{169}$$

This is a reasonable approximation if we are considering EM radiation in the visible/UV/IR region of the spectrum. The wave number of $k = \frac{2\pi}{\lambda}$ of visible light corresponds to wave lengths of several thousands of angstroms while atomic wave functions are spread over lengths of the order of an angstrom. So the order of magnitude of

$$\langle \mathbf{k}\cdot\mathbf{r}\rangle \text{ is } \frac{\text{size of atom}}{\text{wave length of light}} \sim 10^{-3}. \tag{170}$$

The electric dipole approximation E1 consists in approximating $e^{-i\mathbf{k}\cdot\mathbf{r}}$ by 1. Retaining the next term $e^{-i\mathbf{k}\cdot\mathbf{r}} \approx 1 - i\mathbf{k}\cdot\mathbf{r}$ is called the electric quadrupole approximation E2. We expect the quadrupole term to be a thousand times smaller than the dipole term.

• To compute the transition rate in the long wavelength E1 approximation, we need to find the matrix element

$$\langle f|\vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle = \vec{\epsilon}_\lambda \cdot \langle f|\mathbf{p}|i\rangle. \tag{171}$$

The matrix elements of position between hydrogen energy levels are somewhat easier to compute (by direct integration), than the momentum matrix elements. We may relate them using a trick: the commutator of the hydrogen hamiltonian with position is proportional to momentum:

$$[\mathbf{r}, H_0] = [\mathbf{r}, \frac{p^2}{2m}] = i\frac{\hbar}{m}\mathbf{p} \tag{172}$$

Bearing in mind that $|i\rangle$ and $|f\rangle$ are eigenstates of H_0 with energies $E_{i,f}$ we get

$$i\frac{\hbar}{m}\langle f|\mathbf{p}|i\rangle = \langle f|[\mathbf{r}, H_0]|i\rangle = (E_i - E_f)\langle f|\mathbf{r}|i\rangle = \hbar\omega_k\langle f|\mathbf{r}|i\rangle. \tag{173}$$

Thus

$$\langle f|\vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle = -im\omega\vec{\epsilon}_\lambda \cdot \langle f|\mathbf{r}|i\rangle \quad \text{and} \quad |\langle f|\vec{\epsilon}_\lambda \cdot \mathbf{p}|i\rangle|^2 = m^2\omega^2|\vec{\epsilon}_\lambda \cdot \langle f|\mathbf{r}|i\rangle|^2 \tag{174}$$

So the transition rate in the E1 approximation becomes

$$w(\Omega)d\Omega = \frac{e^2\omega^3}{8\pi^2\hbar c^3}|\vec{\epsilon}_\lambda \cdot \langle f|\mathbf{r}|i\rangle|^2 \, d\Omega_k. \tag{175}$$

4.6 Selection rules for E1 transitions

• Selection rules state that the matrix element for electric dipole transitions $\langle f|\mathbf{r}|i\rangle$ vanish for certain initial and final states. So there can be no E1 transitions for certain quantum numbers of the initial and final states.

• The parity selection rule states that an E1 transition is forbidden if the initial and final atomic levels $|i\rangle, |f\rangle$ have the same parity. To see this first recall that parity acts as

$$\mathbf{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}) \quad \text{and} \quad \mathbf{P}^2 = I \quad \Rightarrow \quad \mathbf{P}^{-1} = \mathbf{P}. \tag{176}$$

It follows that parity anti-commutes with position, for

$$(\mathbf{P}\mathbf{r} + \mathbf{r}\mathbf{P})\psi(\mathbf{r}) = -\mathbf{r}\psi(-\mathbf{r}) + \mathbf{r}\psi(-\mathbf{r}) = 0. \tag{177}$$

Therefore $\mathbf{P}^{-1}\mathbf{r}\mathbf{P} = \mathbf{P}\mathbf{r}\mathbf{P} = -\mathbf{r}$. Using this, the dipole matrix element satisfies

$$\langle f|\mathbf{r}|i\rangle = -\langle f|\mathbf{P}\mathbf{r}\mathbf{P}|i\rangle = -P_f P_i\langle f|\mathbf{r}|i\rangle \quad \Rightarrow \quad (1 + P_f P_i)\langle f|\mathbf{r}|i\rangle = 0. \tag{178}$$

Hence, either the matrix element vanishes or the product of parities $P_f P_i$ is -1. So the parity must change in an E1 transition.

• Recall that the parity of the hydrogen level $|nlm\rangle$ is $(-1)^l$. So the E1 transition $|nlm\rangle \to |n'l'm'\rangle$ is forbidden if $l + l'$ is odd. In particular, $l' - l = 0$ is forbidden. So for instance there cannot be E1 transitions between two S-wave states or two P-wave states or two D-wave states etc. In fact, combining with the angular momentum selection rule (see below), this implies $\Delta l = \pm 1$.

• Angular momentum selection rule. As we argue heuristically below, in E1 transitions the emitted photon carries angular momentum $j_\gamma = 1$ in units of $\hbar$. (See QM2 lecture notes for a more detailed treatment or see a book on quantum mechanics) Suppose j_i, j_f are the total angular momentum quantum numbers of the initial and final electronic states. Then the selection rule states that an E1 transition is forbidden if

$$\Delta j = j_f - j_i \neq 0, \pm 1. \tag{179}$$

Moreover the transition from $j_i = 0$ to $j_f = 0$ is also forbidden. Heuristically, in the matrix element $\langle f|\mathbf{r}|i\rangle$, the operator $\mathbf{r}$ behaves as if it has angular momentum one[16]. Then we are adding the angular momentum j_i of the initial state to this, $j_i \otimes 1$ and we know that if $j_i \neq 0, \frac{1}{2}$, the resulting system behaves as if it has angular momentum $j_f = j_i - 1$ or j_i or $j_i + 1$. So j_i and j_f must differ by 0 or ± 1. If $j_i = \frac{1}{2}$ then j_f must be $\frac{1}{2}$ or $3/2$. If $j_i = 0$ then $j_f = 1$, so $0 \to 0$ E1 transition is forbidden.

• In particular, the 'metastable' 2S state of hydrogen is stable to radiative decay in the E1 approximation. In fact, it is stable to decay via all 1 photon electric and magnetic multipole transitions, it decays via 2 photon emission. This accounts for its unusually long mean lifetime of 0.12 seconds.

4.7 Polarization and direction averaged E1 emission rate

So far we have found that the E1 transition rate $i \to f$ accompanied by the emission of a photon into solid angle $d\Omega$ with polarization λ is

$$w(\Omega) d\Omega = \frac{e^2\omega^3}{8\pi^2\hbar c^3} |\vec{\epsilon}_\lambda \cdot \langle f|\mathbf{r}|i\rangle|^2 \, d\Omega. \tag{180}$$

From here on, we are interested in the rate of emission, irrespective of the direction or polarization of the outgoing photon. To do this averaging, it is convenient to write the square of the dot product in terms of the angle Θ_λ between the unit polarization vector $\vec{\epsilon}_\lambda$ and the dipole vector matrix element $\langle f|\mathbf{r}|i\rangle \equiv \mathbf{r}_{fi}$

$$|\mathbf{r}_{fi} \cdot \epsilon_\lambda| = |\mathbf{r}_{fi}| \, \cos\Theta_\lambda. \tag{181}$$

Then

$$w(\Omega) \, d\Omega = \frac{e^2\omega^3}{8\pi^2\hbar c^3} |\mathbf{r}_{fi}|^2 \, \cos^2\Theta_\lambda \, d\Omega \tag{182}$$

To do the sum over polarizations λ, let us work in a real right-handed orthonormal basis $\epsilon_1, \epsilon_2, \hat{\mathbf{k}}$ with $\epsilon_1 \times \epsilon_2 = \hat{\mathbf{k}}$ and define spherical polar coordinates θ, ϕ: $\mathbf{r}_{fi}$ makes an angle θ with $\mathbf{k}$ and the projection of $\mathbf{r}_{fi}$ onto the $\epsilon_1 - \epsilon_2$ plane makes an angle ϕ with ϵ_1. Then

$$\cos\Theta_1 = \sin\theta\cos\phi \quad \text{and} \quad \cos\Theta_2 = \sin\theta\sin\phi. \tag{183}$$

---

[16] To motivate this, notice that $\mathbf{r} = (x, y, z) = r(\cos\theta, \sin\theta\cos\phi, \sin\theta\sin\phi)$ so $\frac{1}{r}(z, x \pm iy) = (\cos\theta, \sin\theta e^{\pm i\phi})$ which we notice are proportional to the $l = 1$ spherical harmonics $Y_{10}, Y_{1,\pm 1}$.

Then the sum over polarizations just gives a $\sin^2\theta$ factor

$$\sum_{\lambda=1}^{2} w(\Omega)d\Omega = \frac{e^2\omega^3}{8\pi^2\hbar c^3}|\mathbf{r}_{fi}|^2\,(\cos^2\Theta_1+\cos^2\Theta_2)d\Omega\; = \frac{e^2\omega^3}{8\pi^2\hbar c^3}|\mathbf{r}_{fi}|^2\,\sin^2\theta\,d\Omega \tag{184}$$

- There is another way of summing over polarizations to show that

$$\sum_\lambda |\vec{\epsilon}_\lambda\cdot\langle f|\mathbf{r}|i\rangle|^2 = |\mathbf{r}_{fi}|^2\sin^2\theta \tag{185}$$

where θ is the angle between the dipole matrix element and $\mathbf{k}$. To do this we abbreviate $\langle f|\mathbf{r}|i\rangle \equiv \mathbf{r} = (r_1, r_2, r_3)$, write in components and use the completeness of the orthonormal system $\epsilon_1, \epsilon_2, \hat{k}$:

$$\sum_\lambda |\vec{\epsilon}_\lambda\cdot\langle f|\mathbf{r}|i\rangle|^2 = \sum_\lambda r_i\epsilon_{\lambda i}r_j^*\epsilon_{\lambda j} = \sum_{i,j=1}^{3} r_i r_j^*\sum_\lambda \epsilon_{\lambda i}\epsilon_{\lambda j} = \sum r_i r_j^*(\delta_{ij}-\hat{k}_i\hat{k}_j) = |r|^2 - |\mathbf{r}\cdot\hat{\mathbf{k}}|^2 = r^2\sin^2\theta. \tag{186}$$

- Before performing the average over directions we remark that to obtain the energy radiated per unit time into solid angle $d\Omega$ we must multiply the above polarization averaged rate by the energy per photon $\hbar\omega$

$$\text{Power}_{d\Omega} = \frac{e^2\omega^4}{8\pi^2 c^3}|\mathbf{r}_{fi}|^2\,\sin^2\theta\,d\Omega \tag{187}$$

The power is proportional to the fourth power of ω and to the square of the matrix element of the electric dipole moment of the electron $e\mathbf{r}$. Moreover, it has a $\sin^2\theta$ angular dependence where θ is the angle between the dipole moment matrix element and the direction of propagation $\hat{k}$. No energy is radiated along the direction of the dipole moment ('it is darkest underneath the candle'!). This is reminiscent of the formula for the intensity of energy radiated by an oscillating electric dipole[17] $\mathbf{p}(t) = 2p_0\cos\omega t\;\hat{z}$ in classical E & M, which may be described by the flux of the time-averaged Poynting vector $\langle\mathbf{S}\rangle$ across the element $r^2 d\Omega\hat{r}$. In HL units (see Griffiths and put $\epsilon_0 = 1$)

$$\langle\mathbf{S}\rangle\cdot r^2 d\Omega\hat{r} = \frac{\omega^4}{8\pi^2c^3}p_0^2\frac{\sin^2\theta}{r^2}\hat{r}\cdot r^2 d\Omega\hat{r} = \frac{\omega^4}{8\pi^2c^3}p_0^2\sin^2\theta d\Omega. \tag{188}$$

Here $2p_0 = 2q_0 s$ is the maximum value of the dipole moment and s is the separation between the oscillating charges $\pm 2q(t) = \pm 2q_0\cos\omega t$.

- The ω^4 dependence is also expected classically from the Larmor formula which states that the power radiated is proportional to the square of acceleration [acceleration $\sim\omega^2$ from the formula for $\mathbf{p}(t)$].

- Returning to the rate of E1 transitions $w_{d\Omega}$, we follow the polarization sum by the integral over directions

$$\int_0^\pi\int_0^{2\pi}\sin^2\theta\sin\theta\,d\theta\,d\phi = 2\pi\int_{-1}^{1}\sin^2\theta\,d(\cos\theta) = 2\pi\times 2\int_0^1(1-t^2)\,dt = \frac{8\pi}{3}. \tag{189}$$

So the polarization and direction averaged emission rate is

$$w = \sum_\lambda\int w_{d\Omega} = \frac{e^2\omega^3}{3\pi\hbar c^3}|\mathbf{r}_{fi}|^2 = \left(\frac{e^2}{4\pi\hbar c}\right)\frac{4\omega^3}{3c^2}|\mathbf{r}_{fi}|^2 = \frac{4\alpha\omega^3}{3c^2}|\mathbf{r}_{fi}|^2 \tag{190}$$

---

[17] The factors of 2 are because $e^{i\omega t}+e^{-i\omega t} = 2\cos\omega t$ and we used exponentials in the quantum theory.

It has dimensions of inverse time. Here $\alpha = \frac{e^2}{4\pi\hbar c}$ is the fine structure constant. We have computed this rate to first order in perturbation theory in the electric dipole approximation. Multiplying by the photon energy $\hbar\omega$ we also get the power radiated in all directions

$$\text{Power} = \frac{e^2\omega^4}{3\pi c^3}|\mathbf{r}_{fi}|^2. \tag{191}$$

This too is reminiscent of the classical formula for the power radiated by the above oscillating electric dipole. In HL units (see Griffiths and mind the factor of two in the definition of dipole moment)

$$\langle\text{Power}\rangle_{\text{classical}} = \int \langle\mathbf{S}\rangle \cdot \hat{r}\, r^2 d\Omega = \frac{\omega^4 p_0^2}{3\pi c^3}. \tag{192}$$

This increase in power with the fourth power of the frequency is used to explain the blueness of sunlight scattered by the atmosphere.

• Sakurai points out that Heisenberg obtained the formula for the rate w prior to the development of the quantum theory of radiation, by a use of the correspondence principle.

4.8 Life-time of 2p state of hydrogen: Lyman α transition

• The mean lifetime τ of state $|i\rangle$ is defined as the reciprocal of the sum of transition rates to all possible final states $|f\rangle$ allowed by the selection rules and energy conservation

$$\frac{1}{\tau_i} = \sum_f w_{f\leftarrow i}. \tag{193}$$

The sum over final states $\sum_f w_{f\leftarrow i}$ is called the total decay rate of the state i, the summands being the partial decay rates. $\Gamma_{f\leftarrow i} = \hbar w_{f\leftarrow i}$ is called the partial energy width, $\Gamma_{tot} = \sum_f \Gamma_{f\leftarrow i}$ is called the total energy width of the unstable state i. The lifetime $\tau = \hbar/\Gamma_{tot}$. Note that we do not speak of partial life-times.

• Now consider the first excited states of hydrogen, they are of course degenerate, including the 2s and 2p levels. The only lower level they can decay to is 1s (Note that 2p → 2s has zero rate since $\omega = 0$). The 2s → 1s electric dipole transition is forbidden since they have the same parity. The 2p to 1s E1 transition is allowed by the selection rules. Spectroscopists call it the Lyman α transition. The Lyman α transition has been a useful tool in cosmology. The Lyman alpha 'forest': absorption lines in light from very far away quasars due to excitation of hydrogen in inter-stellar gas. One sees not one line but several lines, indeed a forest of lines, because of the shifting of spectral lines due to relative motions of the various clouds of intervening gas. But all the lines are believed to correspond to the same Lyman α atomic transition.

• τ_{2p} in the E1 approximation is given by

$$\tau_{2p}^{-1} = w = \frac{4\alpha\omega^3}{3c^2}|\langle 1s0|\mathbf{r}|2pm_l\rangle|^2 \tag{194}$$

The rate is the same for all the values of $m_l = 0, \pm 1$. Let us compute it for $m_l = 0$. Recall that the hydrogen wave functions are given by $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$. We have

$$R_{1s} = \frac{2}{\sqrt{a^3}}e^{-r/a}, \quad Y_{00} = \frac{1}{\sqrt{4\pi}}, \quad R_{2p} = \frac{1}{\sqrt{24a^3}}\frac{r}{a}e^{-r/2a}, \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{195}$$

Note that the R_{2p} decays twice as slowly as R_{1s}, excited states are more spread out. Also $R_{2p}(r)$ has one more node than R_{1s} as we expect of the first excited state. The pre-factors are fixed by normalisation $\int |\psi|^2 r^2 dr d\Omega = 1$, $\int |Y_{lm}|^2 d\Omega = 1$. So

$$\langle 1s0|\mathbf{r}|2p0\rangle = \int dr d\theta d\phi \; r^2 \sin\theta \; \frac{1}{\sqrt{4\pi}}\sqrt{\frac{3}{4\pi}} \cos\theta \; \frac{2}{\sqrt{a^3}} e^{-r/a} \; \frac{1}{\sqrt{24a^3}} \frac{r}{a} e^{-r/2a} \; (x, y, z) \tag{196}$$

Now $\mathbf{r} = (x, y, z) = r(\cos\theta, \sin\theta\cos\phi, \sin\theta\sin\phi)$. We see that only z component contributes to the matrix element, the x, y components vanish since they are proportional to the integrals $\int_0^{2\pi} \cos\phi d\phi$ and $\int_0^{2\pi} \sin\phi \; d\phi$. So we only need

$$\langle 1s0|z|2p0\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \; \frac{1}{\sqrt{4\pi}} \cdot \cos\theta \cdot \sqrt{\frac{3}{4\pi}} \cos\theta \int_0^{\infty} dr \, r^2 \frac{2}{\sqrt{a^3}} e^{-r/a} \cdot r \cdot \frac{1}{\sqrt{24a^3}} \frac{r}{a} e^{-r/2a}. \tag{197}$$

where $a = \frac{\hbar}{mc\alpha} = \frac{4\pi\hbar^2}{me^2} = .53$ Angstroms is the Bohr radius. Doing the integrals we get a matrix element that is of order of the Bohr radius

$$\langle 1s0|z|2p0\rangle = \frac{256}{243\sqrt{2}} a = 0.74a = 3.9\times 10^{-9}\text{cm} \quad \Rightarrow \quad |\mathbf{r}_{fi}|^2 = 0.55a^2 = 1.52\times 10^{-17}\text{cm}^2. \tag{198}$$

The energy of the emitted photon is

$$\hbar\omega = E_{2p} - E_{1s} = -\frac{mc^2\alpha^2}{2}\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = \frac{3mc^2\alpha^2}{8} = -\frac{e^2}{8\pi a}\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = \frac{3e^2}{32\pi a} = 13.6 \times \frac{3}{4} = 10.2\,\text{eV}. \tag{199}$$

Since $\hbar = 6.52 \times 10^{-16}$ eV.s, $\omega = 1.56 \times 10^{16}$/s corresponding to the wave length $\lambda = 2\pi c/\omega =$ 1216 Angstroms of the Lyman α line. With $\alpha = 1/137$ and $c = 3 \times 10^{10}$ cm/s we get the numerical values of the 2p-1s Lyman α transition rate and mean lifetime of the 2p level

$$w = \frac{4\alpha\omega^3}{3c^2}|\mathbf{r}_{fi}|^2 = 0.6 \times 10^9 \; s^{-1} \quad \Rightarrow \quad \tau_{2p} \approx 1.6\,\text{ns} \tag{200}$$

• The energy widths of excited levels that decay via E1 transitions are of order $\Gamma = \hbar/\tau \sim \frac{\alpha\omega^3}{c^2}|\mathbf{r}_{fi}|^2$. Now the dipole matrix element is of order the Bohr radius $|\mathbf{r}_{fi}|^2 \sim a_0^2$ while $\hbar\omega$ is of the order of a Rydberg $\text{Ry} = \frac{1}{2}mc^2\alpha^2$. Let us write the width in natural units, where $a_0 = \frac{1}{\alpha m}$. We get $\Gamma \sim \text{Ry}\,\alpha^3 = m\alpha^5$. This gives a simple way of estimating its numerical value, $\tau \sim \frac{1}{m\alpha}\frac{1}{\alpha^4}$. We can restore factors of $c, \hbar$ by not ing that $c\tau$ is a length, so it must be a multiple of the Compton wave length of the electron, so $c\tau = \frac{\hbar}{mc\alpha}\frac{1}{\alpha^4}$. The first factor is the Bohr radius a_0. Putting in $a_0 = .53$ Angstroms, $\alpha = 1/137$ and $c = 3 \times 10^8$ m/s we get $\tau \sim 10^{-9}$ s.

• A similar calculation can be performed to find the rates for E1 transitions between other hydrogen levels that are not forbidden by the selection rules. For small values of n, the dipole matrix element $|\mathbf{r}_{fi}|$ is of order the Bohr radius and $\omega \approx 10^{16}$ Hz, resulting in lifetimes on the order of nanoseconds or tens of nanoseconds. Some of these allowed decays are 2p-1s, 3s-2p, 3p-1s, 3p-2s, 3d-2p e.t.c.

• When a decay is forbidden in the electric dipole approximation we go to the next approximation: the electric quadrupole approximation E2 coming from the second term in $e^{-i\mathbf{k}\cdot\mathbf{r}} = 1 - i\mathbf{k}\cdot\mathbf{r} + \dots$. One must also consider the magnetic dipole approximation M1 due to Pauli's coupling of the magnetic dipole moment of electrons to the radiation field. The lifetimes of excited states that decay to leading order via E2 and M1 transitions are about a million times as long as those that decay via E1

$$\tau_{\mathrm{E2,M1}} \sim \left(\frac{\lambda}{a_0}\right)^2 \tau_{\mathrm{E1}} \sim 10^{-3}\ \mathrm{s}. \tag{201}$$

• The 2s level cannot decay in the E1 approximation due to the parity selection rule, the only lower level 1s has the same parity. In fact is is forbidden to decay even via E2 or M1. It eventually decays via 2 photon emission. This is in fact the superposition of two amplitudes, one coming from treating the interaction hamiltonian $-\frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$ to second order in perturbation theory and by treating the dielectric term ($\frac{e^2}{2mc^2}\mathbf{A}^2$) in first order perturbation theory. The 2s level consequently has a long lifetime $\tau_{2s} \approx .12$ s.