

9.7: Quantizing Radiation

Introduction

In analyzing the photoelectric effect in hydrogen, we derived the rate of ionization of a hydrogen atom in a monochromatic electromagnetic wave of given strength, and the result we derived is in good agreement with experiment. Recall that the interaction Hamiltonian was

$$H^1 = \left(\frac{e}{mc} \right) \cos(\vec{k} \cdot \vec{r} - \omega t) \vec{A}_0 \cdot \vec{p} \\ = \left(\frac{e}{2mc} \right) (e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)}) \vec{A}_0 \cdot \vec{p}. \quad (9.7.1)$$

and we dropped the $e^{i\omega t}$ term because it would correspond to the atom giving energy to the field, and our atom was already in its ground state. However, if we go through the same calculation for an atom *not* initially in the ground state, then indeed an electromagnetic wave of appropriate frequency will cause a transition rate to a lower energy state, and $e^{i\omega t}$ is the relevant term.

But this is not the whole story. An atom in an excited state will eventually emit a photon and go to a lower energy state, even if there is *zero* external field. Our analysis so far does not predict this -- obviously, the interaction written above is only nonzero if \vec{A} is nonzero! So what are we missing?

Essentially, the answer is that the electromagnetic field itself is quantized. Of course, we know that, it's made up of photons. Recall Planck's successful analysis of radiation in a box: he considered all possible normal modes for the radiation, and asserted that a mode of energy ω could only gain or lose energy in amounts $\hbar\omega$. This led to the correct formula for blackbody radiation, then Einstein proved that the same assumption, with the same \hbar , accounted for the photoelectric effect. We now understand that these modes of oscillation of radiation are just simple harmonic oscillators, with energy $(n + \frac{1}{2})\hbar\omega$, and, just as a mass on a spring oscillator has fluctuations in the ground state, $\langle x \rangle = 0$ but $\langle x^2 \rangle \neq 0$, for these electromagnetic modes $\langle \vec{A} \rangle = 0$ but $\langle \vec{A}^2 \rangle \neq 0$.

The electromagnetic field itself is quantized.

These fluctuations in \vec{A} mean the interaction Hamiltonian is momentarily nonzero, and therefore can cause a transition.

Therefore, to find the spontaneous transition rate (as it's called) for an atom in a zero (classically speaking) electromagnetic field, we need to express the electromagnetic field in terms of normal modes (we'll take a big box), then quantize these modes as quantum simple harmonic oscillators, introducing raising and lowering operators for each oscillator (these will be photon creation and annihilation operators) then construct the appropriate quantum operator expression for \vec{A} to put in the electron-radiation interaction Hamiltonian.

The bras and kets will now be quantum states of the electron *and* the radiation field, in contrast to our analysis of the classical field above, where the radiation field didn't change. (Of course, it did, really, in that it lost one photon, but in the classical limit there are infinitely many photons in each mode, so that wouldn't register.)

We use the Coulomb gauge $\vec{\nabla} \cdot \vec{A} = 0$ satisfies

$$\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = 0. \quad (9.7.2)$$

Taking for convenience periodic boundary conditions in the big box, we can write \vec{A} (classically) as a Fourier series at $t = 0$:

$$\vec{A}(\vec{r}, t=0) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} (c_{\vec{k},\alpha}(0) \vec{\epsilon}_{\alpha} e^{i\vec{k} \cdot \vec{r}} + c_{\vec{k},\alpha}^*(0) \vec{\epsilon}_{\alpha}^* e^{-i\vec{k} \cdot \vec{r}}) \quad (9.7.3)$$

The time-dependence is given by putting in the whole plane wave: $e^{i\vec{k} \cdot \vec{r}} \rightarrow e^{i(\vec{k} \cdot \vec{r} - \omega t)}$, which time dependence can be taken into the coefficient, $c_{\vec{k},\alpha}(t) = c_{\vec{k},\alpha}(0) e^{-i\omega t}$, so

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} (c_{\vec{k},\alpha}(t) \vec{\epsilon}_{\alpha} e^{i\vec{k} \cdot \vec{r}} + c_{\vec{k},\alpha}^*(t) \vec{\epsilon}_{\alpha}^* e^{-i\vec{k} \cdot \vec{r}}) \quad (9.7.4)$$

The vector $\vec{\epsilon}_\alpha$ is the polarization of the plane wave. It's in the same direction as the electric field. Actually it varies with \vec{k} , because from $\vec{\nabla} \cdot \vec{A} = 0$, it's perpendicular to \vec{k} . That is, for a given \vec{k} there are two independent polarizations. For \vec{k} along the z -axis, they could be along the x -and y -axes, these would be called linear polarization, and is the standard approach. But we could also take the vectors $(1/\sqrt{2})(1, \pm i, 0)$. These correspond to *circular polarization*: equal x - and y -components but with the y-component 90 degrees ahead in phase. You may recognize the vectors $(1/\sqrt{2})(1, \pm i, 0)$ as the eigenvectors for the rotation operator around the z -axis -- the circularly polarized beam carries angular momentum, $\pm \hbar$ per photon, pointed along the direction of motion.

The energy density $\frac{1}{8\pi}(|\vec{E}|^2 + |\vec{B}|^2)$ can be expressed as a sum over the individual $(\vec{k}, \vec{\epsilon})$ modes.

Writing the electric and magnetic fields in terms of the vector potential,

$$\vec{E} = -(1/c)\partial\vec{A}/\partial t, \quad \vec{B} = \vec{\nabla} \times \vec{A}. \quad (9.7.5)$$

where

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} (c_{\vec{k},\alpha}(t)\vec{\epsilon}_\alpha e^{i\vec{k}\cdot\vec{r}} + c_{\vec{k},\alpha}^*(t)\vec{\epsilon}_\alpha^* e^{-i\vec{k}\cdot\vec{r}}) \quad (9.7.6)$$

and thereby expressing the total energy

$$\frac{V}{8\pi}(|\vec{E}|^2 + |\vec{B}|^2) = \frac{V}{4\pi} \left(\frac{\omega}{c}\right)^2 |\vec{A}|^2 \quad (9.7.7)$$

in terms of the $(\vec{k}, \vec{\epsilon})$ amplitudes $c_{\vec{k},\alpha}^*(t)$, $c_{\vec{k},\alpha}(t)$, then integrating the energy density over the whole large box the cross terms disappear from the orthogonality of the different modes and the total energy in the box -- the Hamiltonian -- is:

$$H = \frac{1}{2\pi} \sum_{\vec{k}} \sum_{\alpha} \left(\frac{\omega}{c}\right)^2 c_{\vec{k},\alpha}^* c_{\vec{k},\alpha}. \quad (9.7.8)$$

Note that although the Hamiltonian is (of course) time independent, the *coefficients* $c_{\vec{k},\alpha}$ here *are* time dependent, $c_{\vec{k},\alpha}(t) = c_{\vec{k},\alpha}(0)e^{-i\omega t}$.

But this is formally *identical* to a set of simple harmonic oscillators! Recall that for the classical oscillator, $p^2 + (m\omega x)^2 = 2mE$, the vector $z = m\omega x + ip$ has time dependence $z(t) = z_0 e^{-i\omega t}$, and the oscillator energy is proportional to $z^* z$ (x, p are the usual conjugate variables). Clearly, $c_{\vec{k},\alpha}(t)$ here corresponds to $z(t)$: same time dependence, same Hamiltonian. Therefore the real and imaginary parts of $c_{\vec{k},\alpha}(t)$ must *also* be conjugate variables, which can therefore be quantized exactly as for the simple harmonic oscillator.

From

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} (c_{\vec{k},\alpha}(t)\vec{\epsilon}_\alpha e^{i\vec{k}\cdot\vec{r}} + c_{\vec{k},\alpha}^*(t)\vec{\epsilon}_\alpha^* e^{-i\vec{k}\cdot\vec{r}}) \quad (9.7.9)$$

we see that the real part of $c_{\vec{k},\alpha}(t)$ basically gives the contribution of the \vec{k}, α and, recalling the time dependence $c_{\vec{k},\alpha}(t) = c_{\vec{k},\alpha}(0)e^{-i\omega t}$, the imaginary part is proportional to the contribution to $\partial\vec{A}(\vec{r}, t)/\partial t$, that is, to $\vec{E}(\vec{r}, t)$. Essentially, then, the real part of $c_{\vec{k},\alpha}(t)$, proportional to the \vec{k}, α Fourier component of the vector potential \vec{A} , is what corresponds to displacement x in a 1-D simple harmonic oscillator, and the imaginary part of $c_{\vec{k},\alpha}(t)$, the \vec{k}, α Fourier component of \vec{E} , corresponds to the momentum in the simple harmonic oscillator.

To carry out the quantization, we must express the classical Hamiltonian

$$H = \frac{1}{2\pi} \sum_{\vec{k}} \sum_{\alpha} \left(\frac{\omega}{c}\right)^2 c_{\vec{k},\alpha}^* c_{\vec{k},\alpha} \quad (9.7.10)$$

in the form

$$H = \sum_{\vec{k}} \sum_{\alpha} \frac{1}{2} (P_{\vec{k},\alpha}^2 + \omega^2 Q_{\vec{k},\alpha}^2) \quad (9.7.11)$$

with $P_{\vec{k},\alpha}$, $Q_{\vec{k},\alpha}$ being the imaginary and real parts of the oscillator amplitude $c_{\vec{k},\alpha}^-(t)$ (scaled appropriately) exactly parallel to the standard treatment of the simple harmonic oscillator:

$$Q_{\vec{k},\alpha} = \frac{1}{c\sqrt{4\pi}} (c_{\vec{k},\alpha}^- + c_{\vec{k},\alpha}^{*-}), \quad P_{\vec{k},\alpha} = -i\omega c 4\pi \sqrt{(c_{\vec{k},\alpha}^- - c_{\vec{k},\alpha}^{*-})}. \quad (9.7.12)$$

From the time-dependence $c_{\vec{k},\alpha}^-(t) = c_{\vec{k},\alpha}^-(0)e^{-i\omega t}$, these (classical) variables P, Q are *canonical*:

$$\frac{\partial H}{\partial Q_{\vec{k},\alpha}} = -\dot{P}_{\vec{k},\alpha}, \quad \frac{\partial H}{\partial P_{\vec{k},\alpha}} = \dot{Q}_{\vec{k},\alpha}. \quad (9.7.13)$$

The Hamiltonian can now be quantized by the standard procedure. The pairs of canonical variables P, Q (one pair to each mode \vec{k}, α) become operators, the Poisson brackets become commutators, the scale determined by Planck's constant:

$$[Q_{\vec{k},\alpha}, P_{\vec{k}',\alpha'}] = i\hbar \delta_{\vec{k},\vec{k}'} \delta_{\alpha,\alpha'}. \quad (9.7.14)$$

The next step is to express the electron radiation interaction $(e/mc)\vec{A} \cdot \vec{p}$ in terms of these field operators. Since the electromagnetic field is quantized, the interaction with the electron must be that the electron emits or absorbs quanta (photons). This is most directly represented by writing the interaction in terms of creation and annihilation (raising and lowering) operators:

$$\begin{aligned} a_{\vec{k},\alpha}^- &= \frac{1}{\sqrt{2\hbar\omega}} (\omega Q_{\vec{k},\alpha} + iP_{\vec{k},\alpha}) \\ a_{\vec{k},\alpha}^\dagger &= \frac{1}{\sqrt{2\hbar\omega}} (\omega Q_{\vec{k},\alpha} - iP_{\vec{k},\alpha}) \end{aligned} \quad (9.7.15)$$

These satisfy $[a, a^\dagger] = 1$.

(Notice that the annihilation operator $a_{\vec{k},\alpha}^-$ is nothing but the operator representation of the classical complex amplitude $c_{\vec{k},\alpha}^-$, with an extra factor to make it dimensionless, $c_{\vec{k},\alpha}^- \rightarrow c\sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k},\alpha}^-$. We discussed this same equivalence in the lecture on coherent states, which were eigenstates of the annihilation operator.)

Following the standard simple harmonic oscillator development, the operator $\hat{n}_{\vec{k},\alpha} = a_{\vec{k},\alpha}^\dagger a_{\vec{k},\alpha}^-$ has eigenstates with integer eigenvalues, $\hat{n}|n\rangle = n|n\rangle$, the contribution to the Hamiltonian from the mode \vec{k}, α is just $H_{\vec{k},\alpha} = (\hat{n}_{\vec{k},\alpha} + \frac{1}{2})\hbar\omega$, and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$, $a|n\rangle = \sqrt{n}|n-1\rangle$.

The bottom line is: the classical plane wave expansion of \vec{A} , with wave amplitudes $c_{\vec{k},\alpha}^-(t)$

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} (c_{\vec{k},\alpha}^-(t) \vec{\epsilon}_\alpha e^{i\vec{k} \cdot \vec{r}} + c_{\vec{k},\alpha}^{*-}(t) \vec{\epsilon}_\alpha^* e^{-i\vec{k} \cdot \vec{r}}) \quad (9.7.16)$$

is replaced on quantization by a parallel *operator* expansion, the wave amplitude $c_{\vec{k},\alpha}^-(t)$ becoming the (scaled) annihilation operator:

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \sum_{\alpha=1,2} c\sqrt{\frac{2\pi\hbar}{\omega}} (a_{\vec{k},\alpha}^-(t) \vec{\epsilon}_\alpha e^{i\vec{k} \cdot \vec{r}} + a_{\vec{k},\alpha}^\dagger(t) \vec{\epsilon}_\alpha^* e^{-i\vec{k} \cdot \vec{r}}). \quad (9.7.17)$$

Revisiting the Photoelectric Effect, now with a Quantized Field

Recall now that for the photoelectric effect in hydrogen, following Shankar we wrote the ingoing electromagnetic field $\vec{A}(\vec{r}, t) = \vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)$. The only relevant component was that going as $e^{i(\vec{k} \cdot \vec{r} - \omega t)}$. In this section, following standard usage (including Shankar) we take an ingoing field $\vec{A}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$ -- an irritating change by a factor of 2, but apparently unavoidable if we

want to follow Shankar's nonquantized photoelectric effect, then go on to the quantized case. Anyway, recall the matrix element to calculate the rate was (with ingoing wave now $\vec{A} = \vec{A}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$)

$$\langle \vec{k}_f | \left(\frac{e}{mc} \right) \vec{A}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} \cdot \vec{p} | 100 \rangle \quad (9.7.18)$$

On quantizing the field, from the end of the previous section

$$\vec{A}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} = \frac{c_{\vec{k},\alpha}(0)\vec{\varepsilon}}{\sqrt{V}} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \rightarrow c \sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k},\alpha} \frac{\vec{\varepsilon}}{\sqrt{V}} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \quad (9.7.19)$$

(the c at the beginning here being the speed of light).

Now that the electromagnetic field amplitude \vec{A}_0 is expressed as an annihilation operator, appropriate (photon number) bras and kets must be supplied for it to operate on. The relevant photon mode is \vec{k},α , so labeling the corresponding photon number states $|n_{\vec{k},\alpha}\rangle = |n\rangle_{\vec{k},\alpha}$ the matrix element that must appear in the Golden Rule is

$$\begin{aligned} & (\langle \vec{k}_f | \otimes \langle n-1 |_{\vec{k},\alpha}) \left(\frac{e}{mc} \right) e^{i\vec{k}\cdot\vec{r}} \vec{A}_0 \cdot \vec{p} (|100\rangle \otimes |n\rangle_{\vec{k},\alpha}) \\ &= \langle \vec{k}_f; n-1 | \left(\frac{e}{mc} \right) e^{i\vec{k}\cdot\vec{r}} c \sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k},\alpha} \frac{\vec{\varepsilon} \cdot \vec{p}}{\sqrt{V}} |100; n\rangle. \end{aligned} \quad (9.7.20)$$

(We've removed the $e^{i\omega t}$, that just contributes to the δ -function in the Golden Rule.)

Since $a_{\vec{k},\alpha} |n\rangle_{\vec{k},\alpha} = \sqrt{n_{\vec{k},\alpha}} |n-1\rangle_{\vec{k},\alpha}$, it is clear that quantizing the incoming electromagnetic wave amounts to replacing the classical vector potential for this wave

$$\vec{A}_0 \rightarrow c \vec{\varepsilon} \sqrt{\frac{2\pi\hbar n_{\vec{k},\alpha}}{\omega V}} \quad (9.7.21)$$

At the photon occupation level $n_{\vec{k},\alpha}$ the (macroscopic) energy in this single mode $\frac{1}{2\pi} \left(\frac{\omega}{c} \right)^2 c_{\vec{k},\alpha}^* c_{\vec{k},\alpha}$ becomes

$$\frac{1}{2\pi} \left(\frac{\omega}{c} \right)^2 c^2 \frac{2\pi\hbar}{\omega} a_{\vec{k},\alpha}^\dagger a_{\vec{k},\alpha} = n_{\vec{k},\alpha} \hbar\omega. \quad (9.7.22)$$

(Recall the Hamiltonian for the classical electromagnetic field is $H = \frac{1}{2\pi} \sum_{\vec{k}} \sum_{\alpha} \left(\frac{\omega}{c} \right)^2 c_{\vec{k},\alpha}^* c_{\vec{k},\alpha}$ in terms of the $c_{\vec{k},\alpha}$'s.)

From $a|n\rangle = \sqrt{n}|n-1\rangle$, the Golden Rule matrix element

$$\langle \vec{k}_f; n-1 | \left(\frac{e}{mc} \right) e^{i\vec{k}\cdot\vec{r}} c \sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k},\alpha} \frac{\vec{\varepsilon} \cdot \vec{p}}{\sqrt{V}} |100; n\rangle \quad (9.7.23)$$

is proportional to $\sqrt{n_{\vec{k},\alpha}}$, so the Golden Rule rate, which includes the square of the matrix element, will be exactly proportional to

$n_{\vec{k},\alpha}$. But from $\vec{A}_0 \rightarrow c \vec{\varepsilon} \sqrt{\frac{2\pi\hbar n_{\vec{k},\alpha}}{\omega V}}$, this is proportional to $|\vec{A}_0|^2$, and in fact *the quantum rate of absorption of radiation is exactly equal to the classical rate* over the whole range of field strengths.

Spontaneous Emission

However, this exact correspondence with the classical result does *not* hold for photon emission! In that case, the atom *adds* a photon to a mode which already contains n photons, say, and the relevant matrix element is $a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$, so the

equivalent classical vector \vec{A}_0 is $c \sqrt{\frac{(n_{\vec{k},\alpha}+1)2\pi\hbar}{\omega V}} \vec{\varepsilon}$. This is nonzero even if $n_{\vec{k},\alpha}$ is zero— hence *spontaneous* emission.

For spontaneous emission, then, the relevant matrix element is

$$\langle 100; 1 | \left(\frac{e}{mc} \right) e^{-i\vec{k}\cdot\vec{r}} c \sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k},\alpha}^\dagger \frac{\vec{\varepsilon} \cdot \vec{p}}{\sqrt{V}} |21m; 0\rangle. \quad (9.7.24)$$

The density of outgoing states for the emitted photon, taking box normalization with periodic boundary conditions as usual, is

$$\frac{V}{(2\pi)^3} k^2 dk d\Omega = \frac{V}{(2\pi)^3} \frac{\omega^2 d\omega d\Omega}{c^3} = \frac{V}{(2\pi)^3} \frac{\omega^2 dE d\Omega}{\hbar c^3} \quad (9.7.25)$$

so the density of states in energy contribution to the Golden Rule delta function is $\frac{V}{(2\pi)^3} \frac{\omega^2 d\Omega}{\hbar c^3}$, and the photon emission rate with polarization $\vec{\epsilon}$ into a solid angle $d\Omega$ will be:

$$\frac{2\pi}{\hbar} \left| \langle 100; 1 | \left(\frac{e}{mc} \right) e^{-i\vec{k} \cdot \vec{r}} c \sqrt{\frac{2\pi\hbar}{\omega}} a_{\vec{k}, \alpha}^\dagger \frac{\vec{\epsilon} \cdot \vec{p}}{\sqrt{V}} | 21m; 0 \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{\omega^2 d\Omega}{\hbar c^3}. \quad (9.7.26)$$

One slight difference in evaluating the matrix element from our treatment of the photoelectric effect is in the representation of the dipole interaction. Recall that there we gave the equivalent forms

$$\langle f | H^1 | i \rangle = \left(\frac{e}{mc} \right) \vec{A}_0 \cdot \langle f | \vec{p} | i \rangle e^{-i\omega t} = \left(\frac{e}{mc} \right) im\omega \vec{A}_0 \cdot \langle f | \vec{r} | i \rangle e^{-i\omega t} \quad (9.7.27)$$

and used the \vec{p} representation because the outgoing photoelectron was taken to be in a plane wave state, an eigenstates of \vec{p} . But for spontaneous emission, the electron goes from one bound state to another, so the \vec{r} form gives a more immediate picture of the interacting dipole with the external field, and in fact the integration between the states is generally a little more direct.

So in the matrix element we make the substitution $\vec{\epsilon} \cdot \vec{p} \rightarrow im\omega \vec{\epsilon} \cdot \vec{r}$, and must then evaluate the atomic matrix element $\langle 100 | \vec{\epsilon} \cdot \vec{r} | 21m \rangle$. The natural way to do this is to express the vectors in terms of spherical harmonics, that is, to write them as spherical vectors,

$$r_1^{\pm 1} = \mp(x \pm iy)/\sqrt{2} = r\sqrt{4\pi/3} Y_1^{\pm 1}, \quad r_1^0 = z = r\sqrt{4\pi/3} Y_1^0 \quad (9.7.28)$$

and similarly for $\vec{\epsilon}$. The integrals are then straightforward, but tedious.

An amusing point made by Sakurai is that the total transition probability for spontaneous emission is

$$\frac{1}{137} \frac{4}{3} \frac{\omega^3}{c^2} |\langle 100 | \vec{x} | 21m \rangle|^2 \quad (9.7.29)$$

and this same expression was obtained using the Correspondence Principle by Heisenberg, before quantum field theory was invented.

The calculated lifetime of the $n = 2$ state is 1.6×10^{-9} seconds.

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