COLLISIONS OF LIGHT WITH ATOMS

P. A. Franken

The University of Michigan

Ann Arbor, Michigan

INTRODUCTION

It is my purpose in these notes to review some well but apparently not widely known facts about the suitability of ordinary electromagnetic theory and simple quantum mechanics for the treatment of such phenomena as resonance fluorescence and the photoelectric effect. I pretend to no particular originality, and I wish to acknowledge at the outset my gratitude for many informative discussions over the years with Ed Jaynes, Willis Lamb, Gabriel Weinreich and others too numerous to mention. Let me finally stress that any resemblance between these notes and the lecture that I actually did not present at the symposium is fortuitous at best.

The contention is that it is unnecessary to introduce the photon concept into many familiar calculations and descriptions of modern atomic physics. Even though the photon myth has considerable pedagogic utility, it rarely introduces calculational simplification and often obscures the physics. I am not seeking to make a philosophical point, or argue that one set of axioms for physics is more epistemologically fragrant than another. Rather, I shall restrict myself to demonstrating that the phenomena of resonance fluorescence and the photoelectric effect can be accommodated with the familiar classical formulation of the electromagnetic field together with ordinary quantum mechanics for the description of the relevant particles. I have

selected these two problems because they appear, more than many others, to demand the introduction of a photon concept ab initio.

RESONANCE FLUORESCENCE

In this process the photon concept seems natural because of the apparent random delay between what appears to be two distinctly different events. First, the atom ingests a photon from some attacking beam and is thereupon in a state of "excitement". Then sometime later (the microsecond region, perhaps--a very long time in atomic units) this electronic passion is relieved by the process called "spontaneous emmission". The entire phenomenon embraces, so to speak, two apparently distinct events and therefore strongly suggests the utility of photons: their ingestion, "storage" and subsequent emission.

We shall examine resonance fluorescence by first solving the general (but non-relativistic) case of electromagnetic scattering by atoms. We shall assume an atom to be exposed to a plane polarized electromagnetic wave characterized by an electric field $E = E_0 \cos \omega t$. In Gaussian units* this leads to a Poynting's vector with magnitude S given by:
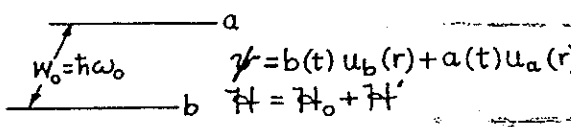
$$S = \frac{c E_0^2}{8\pi} \text{ erg sec}^{-1}\text{cm}^{-2} \qquad (1)$$

This electromagnetic wave induces a dipole moment in the atom which oscillates at the frequency ω of the driving wave, although not necessarily in phase. We shall calculate this induced moment which will then permit the ready classical calculation of the radiation $\mathcal{P}$ emitted by the atom. The ratio $\mathcal{P}/S$ is, by definition, the scattering cross section.

Without loss of generality we shall consider a somewhat emasculated atom. To wit, only possessed of a ground state (b) and one excited state (a), with energy separation W_0. This situation is exhibited in fig. 1, on the following page, which also contains the beginnings of a proper calculation.

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*It is alleged that the calculations which follow can be accomplished in MKS units but the author remains unconvinced.

FIGURE 1

Please note, first off, that the substitution $W_0 = \hbar\omega_0$ is simply an algebraic anticipation; the photon idea has not evidenced itself at all. The wave function describes the atom at all times, and we shall invoke ordinary first order time dependent perturbation theory. The perturbation term $\mathcal{H}'$ is $e\vec{E}\cdot\vec{r}$, as shown, and thereby explicitly assumes the dipole approximation. We do this to avoid fooling around with an expansion of $(\vec{P} - e\vec{A}/c)^2$. (The dipole approximation is excellent for optical frequencies and atoms, since the electromagnetic wavelength is literally thousands of times larger than atomic dimensions.) The standard expansion into complex form as shown is for ultimate simplicity and the unit vector $\hat{f}$ is collinear with $\vec{E}$, and is often referred to as the polarization vector. The last line of figure (1) results from substitution into Schroedinger's equation, the usual integration over space on both sides, keeping all terms, and the addition of that strange beast at the end which I shall discuss in a moment. The matrix element $\mathcal{H}'_{aa}$ vanishes for atoms (because of spherical symmetry or, if you prefer, parity) and, even if the symmetry were destroyed so that the matrix element would be significant, the term could still be dropped because the coefficient $\underline{a}$ is genuinely small compared to $\overline{b}$ (the spirit of 1st order perturbation theory). Now the damping term $-(\frac{1}{2})\Gamma a$ is just the Wigner-Weisskopf term that provides a phenomenological description of spontaneous emission, or damping if you will, that is consistent with perturbation theory to first order. There is no <u>mechanism</u>

in this term; it simply asserts that if an excited
state exists it will, in the absence of perturbations
such as appear in the present problem, decay exponen-
tially. Ed Jaynes has a very nice "classical"
derivation of this term which is achieved by consider-
ing the excited atom in a box of arbitrary size and
allowing the atom to interact with the resonance
radiation that begins to build up in the box (private
communication). In any event, I am not pulling a
swindle by inserting this term somewhat arbitrarily at
this point. Thrashing about within the full limits of
1st order perturbation theory, yes; but deceit, by no
means.

For convenience we set the energy of the ground
state equal to zero. This, together with the basic
premise of 1st order perturbation theory, permits
setting b(t) = 1. Thus the last line in figure 1
readily submits to integration and yields the steady
state solution exhibited in figure 2:

$$\text{STEADY STATE:}$$

$$a(t) = \frac{eE_o}{2i\hbar} \langle u_a^* | \hat{f} \cdot \vec{r} | u_b \rangle \cdot$$

$$\left[\frac{e^{i\omega t}}{(1/2)\Gamma + i(\omega_o + \omega)} + \frac{e^{-i\omega t}}{(1/2)\Gamma + i(\omega_o - \omega)} \right]$$

$$\text{seek } |\vec{P}| = \langle \psi^* | e\hat{f} \cdot \vec{r} | \psi \rangle$$

FIGURE 2

The notation is conventional (perhaps old-fashioned,
even) and it is worth noting that the first of the two
time dependent terms is the so-called "anti-resonant"
one which is not dropped at this point because we will
want to explore the final expressions at frequencies
ω quite disparate from ω_O, in which regime the two
terms become comparable.
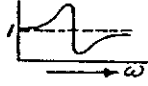
-- As indicated in figure (2) we seek the expectation value of the dipole moment (which will clearly have an ω time dependence). This expectation value is given by the simple formula shown in the last line of the figure if we assume the atom is spherically symmetric so that the atomic polarization is indeed collinear with the electromagnetic polarization vector $\hat{f}$. (If we were dealing with a molecule that was not spherically symmetric, then we would not have such a simple expression and would have to mash through lots of unhappy tensor-type stuff. The conclusions would not be shattered, however, which is why I have taken the liberty of sticking to the spherically symmetric case.)

Following the recipe given in the last line of figure (2) we achieve the result shown at the top of figure (3):

$$|\vec{P}| = \underbrace{(\text{mess of stuff})}_{P_0} \cos(\omega t + \phi)$$

$$\sigma = \frac{8\pi}{3} \cdot \frac{\omega^4}{c^4} \cdot \frac{e^4 \omega_0^2 \langle u_a^* | \hat{f} \cdot \vec{r} | u_b \rangle^4}{\hbar^2 \left\{ \left[\frac{\Gamma^2}{4} + (\omega_0^2 - \omega^2) \right]^2 + \Gamma^2 \omega^2 \right\}}$$

FIGURE 3

The "mess of stuff" is literally that, a fierce garbage of atomic constants, ω, ω_0, matrix elements and the like. However, the important point is that we now have a classical expression for the dipole moment P of the form $P = P_0 \cos(\omega t + \emptyset)$ which enables us to assert that the atom radiates a power $\mathcal{P}$ given by:

$$\mathcal{P} = \frac{P_0^2 \omega^4}{3c^3} \text{ erg sec}^{-1} \tag{2}$$

(If the derivation of equation (2) is not in your reference work on classical electromagnetic theory, throw the book away.) Since the cross section is just

$\mathcal{P}/S$, as noted earlier, the result shown at the bottom of figure (3) is readily obtained. (No physics has been skipped in getting to this point, just a mild tedium of algebra.)

Before discussing this cross section let me call your attention to the phase $\emptyset$ occurring in the expression for the dipole moment in figure 3, because there is an interesting dividend involved. The phase factor, as does P_0, exhibits a somewhat unfriendly algebraic complexity. However, it approaches 0 as $\omega << \omega_0$, it equals zero for $\omega = \omega_0$, and approaches π as $\omega >> \omega_0$. In classical terms, this means the induced moment is in phase with the driving field for low driving frequencies, $90°$ out of phase at "resonance", and $180°$ out of phase at very high frequencies. It is this behavior that accounts for anomolous dispersion, as sketched in the figure.

Returning to the cross section given in figure (3), it might seem surprising that the denominator does not appear to be Lorentzian. Actually it is, near resonance; this is readily shown in a few steps when cognizance is taken of the fact that Γ is many orders of magnitude less than either ω or ω_0. The reason that there is more complexity in the actual expression is that we have kept the anti-resonant as well as the resonant term shown in figure (2). And that is a good thing to do when you want to explore the extreme frequency limits as shown in figure (4):

For $\omega << \omega_0$

$$\sigma \to \frac{8\pi}{3} \frac{\omega^4}{c^4} \frac{e^4 \langle 11 \rangle^4}{\hbar^2 \omega_0^2}$$

For $\omega >> \omega_0$, take H: $n = 1 \, \& \, 2$

$$\sigma \to \frac{8\pi}{3} \left(\frac{e^2}{mc^2} \right)^2 \left(\sim \frac{1}{30} \right)$$

FIGURE 4

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The expression above the line in this figure is just the Rayleigh scattering cross section with its characteristic frequency dependence. Furthermore, the factor that follows ω^4/c^4 is just the quantum mechanical expression for the square of the polarizability of a two level system so that the expression we are dealing with is, in fact, quantitatively exact.

In order to evaluate the cross section in the high frequency limit it is necessary to consider a particular system. I have taken Hydrogen with the 1S and 2P states as the two levels and ground through the algebra to obtain the expression given below the line in figure 4. The result is a cross section approximately 1/30 that of the classical Thomson scattering of electromagnetic radiation from a free electron. (I don't know whether to be surprised that just taking two of the infinite number of levels into account yields as much as 1/30 of the Thomson limit or as little as 1/30.)

Now that we have verified that the cross section behaves as expected in the classical limits of very high and very low frequencies it is time to turn to the question of whether or not the derived cross section really describes the phenomena associated with resonance fluorescence. In order to have particular experiments to explore I shall assume we have an atom with a decay rate Γ equal to approx 10^6 sec^{-1}. This corresponds to a mean "lifetime" of 10^{-6} seconds and a "halfwidth" $\Delta\nu$ in the absorption cross section of approximately 10^6 Hz. (For convenience I have clearly set both π as well as 2π equal to unity, but that is not nearly as egregious as the high energy physicist's assault on the velocity of light.) These parameters, together with a sketch of some experiments we shall now discuss, are presented in figure 5 on the following page. The open bell shaped curve at the top of this figure represents the cross section vs. frequency. First off, the theory we have developed is distinctly steady state. This suggests what might appear to be a liability in describing "events", as opposed to infinite atomic somnolence. Not so. For example, consider an atom irradiated with a spectrum significantly narrower than the cross section halfwidth as indicated by the shaded curve in the figure. The present theory predicts the same frequencies in the scattered spectrum, as does quantum electrodynamics. (Indeed, those of you enamored of second quantization will recognize my sketch as being virtually a copy

of that which appears on Page 201 of the Gospel accord-
ing to Heitler.)

The description of distinctly transient phenomena
requires some discussion, but not much. Consider the
situation displayed in the lower part of figure 5 in
which the atom is exposed to a very brief pulse of
radiation, so that we can really define a time (to
within 10^{-12} seconds) when the atom suddenly became
excited. We also know, from experiment, that the
photodetector will respond, on the average, a micro-
second later. Dilemma? Of course not. The atom can
only scatter those Fourier components in the beam
that are accommodated by the scattering cross section.
To wit, some 10^6 Hz "bandwidth" and, therefore. the
train of radiation is "stretched" to some 10^{-6} seconds.
The photodetector is a quantum mechanical system and
can go "click" with a distribution (assuming the
experiment to be repeated often) that is exponential in
time.   This is because the probability per unit time of
a photodetector going click is proportional to the in-
tensity of the radiation it is exposed to, and the
Fourier transform of the Lorentzian is an exponential.
The process is entirely analogous to a narrow band
audio system exposed to a pistol shot. It rings. And
it's classical.

Let me conclude this section by asserting that all
of the spectroscopic phenomena I know of can be treated
with the techniques illustrated in this section.
Specifically, the photonless marriage of a classical
electromagnetic field to a quantized atomic system.
Optical pumping, level-crossing spectroscopy, double
resonance, etc., all yield with grace to this massage.

THE PHOTOELECTRIC EFFECT

I have saved this discussion for the end partly
because it is usually the principal bastion of the
photon devotee, and partly because it is the most
trivial to handle. The three features of the photo-
electric effect that, together, created such agony that
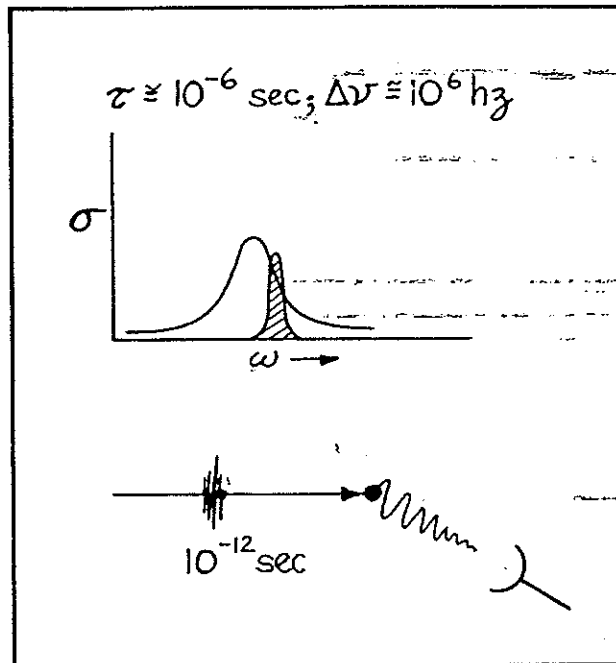photons just had to be invoked are summarized in figure
6.

$$\tau \gtrsim 10^{-6} \text{ sec}; \ \Delta\nu \cong 10^{6} \text{ hz}$$

FIGURE 5

PHOTOELECTRIC EFFECT:

1.) Einstein equation

$$(\tfrac{1}{2})mv^2 = \hbar\omega - \phi$$

2.) $R \sim I$

3.) No systematic time delay

FIGURE 6

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The first point is famous. The second point is that
the intensity of the light influences only the rate,
and not the energy distribution of the emitted electrons.
The third observation is simply that if we have a beam
of light stimulating the emission of, say, 100 photons
per second that the first electron can be ejected
right after the light is turned on, rather than having
to "wait" for 10^{-2} seconds. (This last point really
provided the supreme agony in fully classical days; it
is interesting to note in passing, by the way, that the
stated motivation for the Forrester et al experiments
on the photoelectric "mixing" of light beams was to
explore the possibility of time delays in the 10^{-10}
second regime.)

Well, we can end all this distress quite easily.
I will consider only the photoelectric effect for a
single atom and leave the problem of some 10^{23} atoms
as an exercise for the non-believer. The situation is
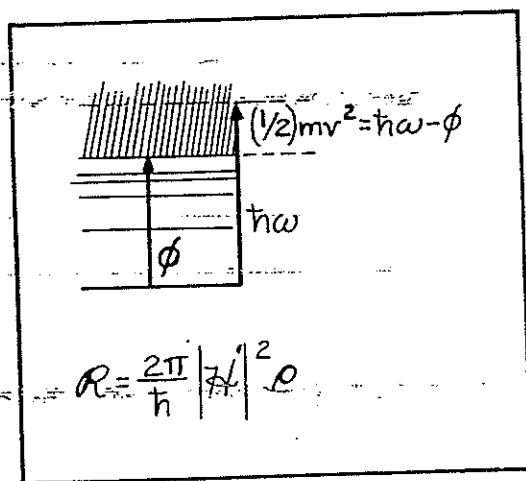shown in figure 7:

$$\frac{1}{2}mv^2 = \hbar\omega - \phi$$

$$\hbar\omega$$

$$\phi$$

$$R = \frac{2\pi}{\hbar}\left|\mathcal{H}'\right|^2 \rho$$

FIGURE 7

The ionization potential of the atom is ϕ, and the
continuum is indicated by the shaded region. If this
atom is exposed to electromagnetic radiation of fre-
quency ω then the ordinary perturbation theory used in
the previous section will yield the fact that only the
level shown in the continuum will be excited, and that
this level lies $\hbar\omega$ ergs above the ground state. (The
Planck constant came in from the use of Schroedinger's

equation for the atom, not from any photonic backfield-
in-motion play). This continuum level corresponds to
a free electron with a kinetic energy as written in
the figure so that we now have the Einstein equation.
As simple as that. The second point of the rate being
proportional to the intensity is guaranteed by the
Fermi "golden rule", written in the figure, because the
square of the perturbation matrix element is proportion-
al to E_0, and thus to the intensity. As for time delays,
quantum mechanics teaches us that the rate is established
when the perturbation is turned on.

How different physics might have been if atoms
had suffered quantum mechanics before fields did!
However, there is certainly no question that the
student of elementary physics should be exposed to the
photon concept, because that is certainly the easy way
of doing the photoelectric effect. And it also provides
him with a useful precursor to the shock of wave-
particle duality. I should mention, in closing, that
black body radiation presents no problem because the
radiation in an enclosure is produced by electrons in
the wall that obey quantum mechanics. Thus there are,
in fact, wave packets of total energy $\hbar\omega$. But these
were made, and not invoked. And therein lies whatever
physics is contained in this paper.