

The interaction of electromagnetic radiation with one-electron atoms

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1 Introduction

We examine the interactions of radiation with a hydrogen-like atom as a simple example that displays many of the typical characteristics of how atoms and molecules in general interact with photons. We will examine the spectral line processes of *absorption*, *stimulated emission* (emission caused by passing radiation), *spontaneous emission* (radiation without any external stimulus), and the continuum process of photoelectric absorption.

In principle these processes should be described using quantum electrodynamics. However, this course is not at that level. We will describe the radiation field semi-classically (so we will have to study spontaneous emission using a statistical argument of Einstein), but use a quantum mechanical description of the atoms.

2 The Hamiltonian including the electromagnetic field

In a comprehensive treatment of electromagnetic theory using Maxwell's equations, it is found that the electric and magnetic fields may be derived from vector and scalar potentials \mathbf{A} and ϕ :

$$\begin{aligned}\mathbf{E}(\mathbf{r}, t) &= -\nabla\phi(\mathbf{r}, t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}, t) \\ \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t).\end{aligned}$$

We are interested in radiation away from sources, so we may set $\phi = 0$. We can show that the vector potential satisfies a wave equation

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} = 0.$$

Solutions of the wave equation for \mathbf{A} are

$$\mathbf{A}(\omega; \mathbf{r}, t) = \mathbf{A}_0(\omega)[\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)] + \text{c.c.}],$$

$$\begin{aligned}\mathbf{E} &= -2\omega A_0(\omega)\hat{\epsilon}\sin(\mathbf{k}\cdot\mathbf{r}-\omega t+\delta_\omega), \\ \mathbf{B} &= -2A_0(\omega)(\mathbf{k}\times\hat{\epsilon})\sin(\mathbf{k}\cdot\mathbf{r}-\omega t+\delta_\omega),\end{aligned}$$

where $\mathbf{A}_0(\omega) = A_0(\omega)\hat{\epsilon}$. The direction $\hat{\epsilon}$ specifies the direction of the polarization of the \mathbf{E} field.

For later reference, the energy flow per unit area through a surface normal to a wave is given by the Poynting vector, $(\mathbf{E}\times\mathbf{B})/\mu_0$. Averaged over a period of the wave, this defines the intensity of the radiation

$$I(\omega) = 2\varepsilon_0\omega^2 c A_0^2(\omega) = \left[\frac{N(\omega)\hbar\omega}{V} \right] c,$$

where $N(\omega)/V$ is the number of photons per unit volume and thus $N(\omega)\hbar\omega/V$ is the energy density in the radiation field.

It may be shown (but we won't do this) in our semi-classical treatment that the Schroedinger equation for a spinless charged particle in an electromagnetic field is given approximately by

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{i\hbar e}{m}\mathbf{A}\cdot\nabla \right] \Psi(\mathbf{r},t).$$

The effect of the radiation field is contained in the term with $\mathbf{A}\cdot\nabla$. We will look at the effects of this term using perturbation theory.

3 Transition rates between discrete states

As in the treatment of time-dependent perturbation from last week, take the perturbation to be the time-dependent term

$$H'(t) = -\frac{i\hbar e}{m}\mathbf{A}\cdot\nabla.$$

Let the system be initially in state a , and turn on a pulse of radiation at time $t = 0$. We have seen that the probability amplitude that the system will be in state b at a later time t is given by

$$c_b^{(1)}(t) = (i\hbar)^{-1} \int_0^t H'_{ba}(t') e^{i\omega_{ba}t'} dt'.$$

Using our expression for the vector potential,

$$\begin{aligned}c_b^{(1)}(t) &= -(e/m)A_0(\omega) [e^{i\delta_\omega} \langle\psi_b|e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\epsilon}\cdot\nabla|\psi_a\rangle \int_0^t dt' e^{i(\omega_{ba}-\omega)t'} \\ &\quad + e^{-i\delta_\omega} \langle\psi_b|e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\epsilon}\cdot\nabla|\psi_a\rangle \int_0^t dt' e^{i(\omega_{ba}+\omega)t'}].\end{aligned}$$

We have already examined integrals like the two time integrals that appear here, and we know that the first integral is negligible unless the term in the exponential $(\omega_{ba} - \omega)$ nearly vanishes. This is equivalent to the condition that $E_b = E_a + \hbar\omega$; in

other words, this term concerns transitions in which the final state energy is larger than the initial state by exactly the energy $\hbar\omega$ carried by one photon. This term thus describes *absorption* of radiation. The second term is only significant if $E_b = E_a - \hbar\omega$. In this case, the final energy is less than the initial energy, and one photon of energy $\hbar\omega$ has been emitted. Because this emission is caused by the incoming radiation, we call this process *stimulated emission*. Since only one of these two situations can be satisfied for a particular pair of states a and b , we may consider the two cases (and the two terms) separately.

3.1 Absorption

We have seen in the discussion of time-dependent perturbation theory that we got a constant transition probability per unit time only by assuming that a range of final state energies larger than the width of the function $F(\omega, t)$ was available. We will consider this case later (as photoionization). Here we want to look at transitions between two isolated bound states. In this case we can get the same simple behaviour as before by assuming that the radiation field is not monochromatic, but covers a significant range of frequencies with roughly constant intensity. Thus here we will take $I(\omega)$ to describe the energy per second and per unit angular frequency passing normally through a unit area.

If this radiation were emitted coherently by some single radiation source, we would have interference effects between interactions at different frequencies, and we would have to sum the $c_b^{(1)}(t)$'s before computing the total transition probability. However, here we assume the much more typical situation of radiation emitted in little packets by a large number of incoherent radiators (individual atoms), each with a different phase δ_ω . The radiation will therefore add incoherently; different frequencies will not interfere, and we may calculate the transition probability by integrating $|c_b^{(1)}(t)|^2$ over the range of wavelength of the incoming radiation.

Now consider the absorption term:

$$|c_b^{(1)}(t)|^2 = 2 \int d\omega \left[\frac{eA_0(\omega)}{m} \right]^2 |M_{ba}(\omega)|^2 F(t, \omega - \omega_{ba})$$

where $M_{ba} = \langle \psi_b | e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla | \psi_a \rangle$. The function F is the same one introduced in time-dependent perturbation theory. Taking the slowly varying terms outside the integral, integrating over the function F as before, and taking the time derivative, we find

$$W_{ba} = 2\pi \left[\frac{eA_0(\omega_{ba})}{m} \right]^2 |M_{ba}(\omega_{ba})|^2.$$

Using the relation between the amplitude of the vector potential and the intensity of the radiation field, this may be written as

$$W_{ba} = \frac{4\pi^2}{m^2c} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{I(\omega_{ba})}{\omega_{ba}^2} |M_{ba}(\omega_{ba})|^2$$

Note that the quantity

$$\sigma_{ba} = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{ba}} |M_{ba}(\omega_{ba})|^2,$$

defined by B & J (where $\alpha = (e^2/4\pi\epsilon_0)/\hbar c \approx 1/137$ is the fine structure constant) is *not* a cross section. It does not have the correct units, basically because $\hbar\omega_{ba}W_{ba}$ is the total energy removed from the beam by the transition per second, but $I(\omega)$ is the energy per unit angular frequency (and per unit time and area) incident on the atom. To make σ_{ba} into a cross section, W_{ba} must be multiplied by a (normalized) profile function $\phi(\omega)$ such that $\int \phi(\omega)d\omega = 1$.

3.2 Stimulated and spontaneous emission

The second term in the equation for $c_b^{(1)}(t)$ describes the probability of a photon being emitted by the atom as a result of the arriving radiation. With the same reasoning as above, we find

$$\bar{W}_{ab} = \frac{4\pi^2}{m^2c} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{I(\omega_{ba})}{\omega_{ba}^2} |\bar{M}_{ab}(\omega_{ba})|^2,$$

where it is easily seen that $\bar{M}_{ab}(\omega_{ba}) = -M_{ba}^*(\omega_{ba})$. We see that the probability per second of an atom in state a making a transition to b is identical to the probability per second that an atom in b will make a transition to a : this is an example of the principle of detailed balancing. However, in situations in or near thermal equilibrium, the upper state b will be less populated than the lower state a , and so stimulated emission will be a good deal less frequent than absorption. The additional process that allows the total number of upward transitions in thermal equilibrium to equal the number of downward transitions, is provided by *spontaneous emission*, a process which our semi-classical treatment of radiation does not predict. B & J provide an expression for this process.

4 The dipole approximation

We now look at how to compute the matrix element M_{ba} which appears in the expressions for transition rates. Consider the exponential term

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + (i\mathbf{k}\cdot\mathbf{r}) + (i\mathbf{k}\cdot\mathbf{r})^2/2! + \dots$$

The term $(\mathbf{k}\cdot\mathbf{r})$ is only non-zero over the extent of the interacting atom, roughly 1 Å. In contrast, $k = 2\pi/\lambda \sim 10^{-3} \text{ \AA}^{-1}$ for optical or near UV radiation. Hence $(\mathbf{k}\cdot\mathbf{r}) \sim 10^{-3}$, and so we replace $e^{i\mathbf{k}\cdot\mathbf{r}}$ by 1. This is known as the *electric dipole approximation*. With this replacement,

$$M_{ba} = \hat{\epsilon} \cdot \langle \psi_b | \nabla | \psi_a \rangle = \hat{\epsilon} \cdot \frac{i}{\hbar} \langle \psi_b | \mathbf{p} | \psi_a \rangle.$$

Now we make a clever transformation to replace the operator \mathbf{p} by an expression involving the unperturbed Hamiltonian. If the potential energy V in the (unperturbed)

Hamiltonian commutes with \mathbf{r} , we find that $\mathbf{p} = (m/i\hbar)[\mathbf{r}, H_0]$. This is easily shown. Consider the x -component of \mathbf{r} . It commutes with H_0 except for the term $p_x^2/2m$. Now $[x, p_x^2] = [x, p_x]p_x + p_x[x, p_x] = 2i\hbar p_x$, and similarly for the y and z components. This establishes the result we need. Then

$$M_{ba} = \hat{\epsilon} \cdot \frac{m}{\hbar^2} \langle \psi_b | \mathbf{r} H_0 - H_0 \mathbf{r} | \psi_a \rangle = \hat{\epsilon} \cdot \frac{m}{\hbar} \omega_{ba} \langle \psi_b | \mathbf{D} | \psi_a \rangle,$$

where we have applied H_0 to its two eigenstates ψ_a and ψ_b , set the resulting energy difference $E_a - E_b = -\omega_{ba}$, and introduced the *electric dipole operator* $\mathbf{D} = -e\mathbf{r}$, an operator which measures the extent to which the two states of interest have a dipole moment.

If the matrix element M_{ab} is non-zero in this approximation, the transition is *allowed*. If $M_{ab} = 0$ in the dipole approximation, it may still be non-zero by using one of the further terms in the expansion of the exponential, but because of the smallness of $\mathbf{k} \cdot \mathbf{r}$, it will be much weaker than an allowed transition. Such a transition is called *forbidden*. If M_{ab} vanishes exactly, the transition is *strictly forbidden* (although it may still occur via two-photon processes or other more devious routes).

The transition probability is now given by

$$W_{ba} = \frac{4\pi^2}{c\hbar^2} \left(\frac{1}{4\pi\epsilon_0} \right) I(\omega_{ba}) |\mathbf{D}_{ba}|^2 \cos^2 \theta,$$

where $\cos \theta$ is the angle between the polarization vector $\hat{\epsilon}$ of the radiation and the instantaneous dipole moment of the atom. Averaging over all directions, we finally arrive at

$$W_{ba} = \frac{4\pi^2}{3c\hbar^2} \left(\frac{1}{4\pi\epsilon_0} \right) I(\omega_{ba}) |\mathbf{D}_{ba}|^2.$$

This expression is identical to that for \bar{W}_{ab} . B & J report the expression for spontaneous emission.

5 Selection rules

We may explicitly evaluate the transition rates for radiative transitions between the levels of a hydrogenic atom. I will show one straightforward way to do this which will yield most of the *selection rules* obeyed by dipole transitions. Another more elegant method is discussed by B & J.

To get transition rates, we must evaluate the dipole matrix elements

$$|D_{ba}|^2 = e^2(x_{ba}^2 + y_{ba}^2 + z_{ba}^2)$$

where for example

$$x_{ba} = \int \int \int R_{n'l'}(r) x R_{nl}(r) Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) \sin \theta d\theta d\phi r^2 dr.$$

To evaluate this expression, use $x = r \sin \theta \cos \phi = r \sin \theta (e^{i\phi} + e^{-i\phi})/2$, so that

$$x_{ba} = \int_0^\infty R_{n'l'} R_{nl} r^3 dr \int_0^\pi C_{l'm'} P_{l'}^{m'} C_{lm} P_l^m \sin^2 \theta d\theta \int_0^{2\pi} e^{i(m-m')\phi} [(e^{i\phi} + e^{-i\phi})/2] d\phi,$$

where the C_{lm} 's contain the constants of the spherical harmonics.

We immediately see that the integral over ϕ vanishes unless $m - m' + 1$ or $m - m' - 1$ is 0. This is also the case for y_{ba} ; z_{ba} is non-zero if $m - m' = 0$. Thus dipole transitions are only possible between states with $m - m' = 0, \pm 1$.

The θ integral yields further restrictions. We may evaluate this using the recursion relation

$$(2l + 1) \sin \theta P_l^{m-1} = P_{l+1}^m - P_{l-1}^m.$$

For $m' = m - 1$, use this relationship to replace $P_{l'}^{m'} = P_{l'}^{m-1}$ in the integral. Using the orthogonality relationship

$$\int_0^\pi P_{l'}^m(\cos \theta) P_l^m(\cos \theta) \sin \theta d\theta = D_{lm} \delta_{l'l},$$

we see that x_{ba} vanishes unless $l' = l \pm 1$. For $m' = m + 1$, we replace the term P_l^m with the recursion relation, and obtain the same result, which is also found for the matrix elements y_{ba} and z_{ba} . Note that since states of even l have even parity, and states of odd l have odd parity, this selection rule also implies that electric dipole transitions only connect states of opposite parity.

The electric dipole operator does not depend on spin, and since different spin states are orthogonal, the transition probability is non-zero only if the spin component along the direction of quantization does not change.

6 Lifetimes of excited states

If an atom is in an excited state b , the total probability per second that it will change to some other state k is $\sum_k W_{kb}$. This will normally be a sum over spontaneous transitions (although if the atom is in an intense radiation field, it may be over spontaneous and stimulated emissions and absorptions; in this case there will also be terms in the sum bringing atoms *into* state b from other states). If there are $N(t)$ atoms in an ensemble in state b at time t , the number of transitions $\cdot N(t)$ out of b per second will be $N(t) \sum_k W_{kb}$, and if no transitions into b are occurring, we will have

$$N(t) = N(t=0)e^{-t/\tau}$$

where the *lifetime* τ is given by

$$\tau^{-1} = \sum_k W_{kb}.$$

The lifetime τ is the time in which $N(0)$ declines by a factor of e . Another frequently used time is the *half-life* $\tau_{1/2}$, which is the time for $N(0)$ to decline by a factor of 2. It is easily seen that $\tau_{1/2} = 0.693\tau$.

7 The photoelectric effect

Finally, we look at another process of wide importance, the absorption of radiation energetic enough to photoionize an atom, known as the photoelectric effect. Here

we consider only the simplest case of photons carrying much more energy than the ionization energy of the atom, $\hbar\omega \gg E_{\text{ion}}$ (but still satisfying $\hbar\omega \ll m_e c^2$).

To study this situation we go back to the derivation of the transition rate for absorption of radiation, but instead of considering an incoming radiation beam spread in frequency, with intensity per unit angular frequency $I(\omega)$, we now take I to specify the total intensity (energy per unit time and area) of angular frequency ω . In order to get our usual simple behaviour of W_{ba} , we notice that after absorption of a photoionizing photon, a large number of neighboring final atomic states will be available, since the removed electron will not be in a bound state, but in a continuum with $\bar{\rho}_b$ states per unit angular frequency and per steradian of solid angle. Thus we will sum the transition probabilities c_{ba} over final electron states rather than over neighboring frequencies ω . We find

$$W_{ba} = \frac{4\pi^2 \alpha \hbar}{m^2 \omega^2} I(\omega_{ba}) \bar{\rho}_b \int |M_{ba}|^2 d\Omega$$

and

$$\sigma = \frac{4\pi^2 \alpha \hbar^2}{m^2 \omega} \bar{\rho}_b \int |M_{ba}|^2 d\Omega,$$

where the angular integral arises because we must integrate over all outgoing electron directions.

Now for the initial state of the atom, we take a hydrogenic ground state $\psi_{rmls}(r) = (1/\pi)(Z/a_0)^{3/2} \exp(-Zr/a_0)$, and for the final state we take a plane wave unperturbed by the atomic potential (this is why we need to assume a photon energy much larger than the ionization energy), $\psi_b(\mathbf{k}_f, \mathbf{r}) = V^{-1/2} \exp(i\mathbf{k}_f \cdot \mathbf{r})$, normalized to an arbitrary volume V . The outgoing electron has wave number \mathbf{k}_f and energy $\hbar^2 k_{rml}^2 / 2m$. The density of final states (per unit angular frequency and per steradian) is given (a problem for you) by

$$\bar{\rho}_b = (2\pi)^{-3} V m k_f \hbar^{-1}.$$

The differential cross section for an electron to be emitted into $d\Omega$ is

$$d\sigma = (2\pi)^{-3} \frac{4\pi^2 \hbar \alpha}{m} \left(\frac{k_f}{\omega} \right) |V^{1/2} M_{ba}(\omega)|^2 d\Omega.$$

We must now evaluate the matrix element. Integrating by parts over V , we find

$$V^{1/2} M_{ba} = -i\hat{\epsilon} \cdot (\mathbf{k} - \mathbf{k}_f) \int e^{i(\mathbf{k}-\mathbf{k}_f) \cdot \mathbf{r}} \psi_{1s}(r) d\mathbf{r} = 8\pi \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} \frac{(Z/a_0)(ik_f \cos \gamma)}{[(Z/a_0)^2 + K^2]^2},$$

where $\mathbf{K} = \mathbf{k} - \mathbf{k}_f$ and γ is the angle between the wave vectors of the incoming photon and the outgoing electron. Then choosing the z -axis to be along the vector \mathbf{k} , so that $\cos \gamma = \sin \theta \cos \phi$, the differential cross section is

$$\frac{d\sigma}{d\Omega} = 32\alpha \left(\frac{\hbar}{m} \right) \left(\frac{k_f^3}{\omega} \right) \frac{Z^5 a_0^3 \sin^2 \theta \cos^2 \phi}{[Z^2 + K^2 a_0^2]^4}.$$

Now from our assumption that the binding energy is negligible, we have

$$\hbar\omega = \frac{\hbar k}{c} \approx \hbar^2 k_f^2 / 2m,$$

so

$$\frac{k}{k_f} \approx \frac{v_f}{2c}.$$

For the case we are considering, this is small and so we take $K^2 \approx k_f^2$. Furthermore, since $\hbar\omega \approx \hbar^2 k_f^2 / 2m \gg |E_{1s}| = Z^2(e^2/4\pi\epsilon_0)/2a_0$, we find

$$K^2 a_0^2 \approx k_f^2 a_0^2 \gg \frac{2m}{\hbar^2} |E_{1s}| a_0^2 = Z^2.$$

We thus neglect the Z^2 term in the denominator of $d\sigma/d\Omega$. Averaging over the $\cos^2 \phi$ term that comes from the direction of the polarization of the incident beam, we have finally

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{unpol}} \approx 16\alpha \left(\frac{\hbar}{m}\right) \frac{Z^5}{\omega(k_f a_0)^5} \sin^2 \theta.$$

To get the total cross section we integrate over all angles (θ, ϕ) and find

$$\sigma = \frac{16\sqrt{2}\pi}{3} \alpha^8 Z^5 \left(\frac{mc^2}{\hbar\omega}\right)^{7/2} a_0^2.$$

The essential point to notice is the dependence on $(\hbar\omega)^{-7/2}$. With increasing photon energy, the cross section for ionization falls rapidly. This behaviour is found quite generally for ionization from any level, although the detailed frequency dependence varies from case to case. The Z^5 dependence appears to suggest that the ionization cross section is larger for heavier ions, but since the minimum photon energy $\hbar\omega$ required to ionize an ion of atomic number Z goes as Z^2 , the maximum value of σ actually decreases as about Z^{-2} .

This equation, like others derived for hydrogen, may be used to obtain a first estimate of the situation for other ions. Thus, one may use this equation to estimate the cross section for ejection of K-shell electrons from a heavy ion.