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## Photoelectric Effect in Hydrogen

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### Introduction

In the photoelectric effect, incoming light causes an atom to eject an electron. We consider the simplest possible scenario: that the atom is hydrogen in its ground state. The interesting question is: for an incoming light wave of definite frequency and amplitude, what is the probability of ionization of a hydrogen atom in a given time? In other words, assuming we can use time-dependent perturbation theory, what is the ionization rate?

Formally, we know what to do. We must find the interaction Hamiltonian  $H^1$ , then use Fermi's Golden Rule for the transition rate with a periodic perturbation:

$$R_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H^1 | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

But it's not that easy! For one thing, the outgoing electron will be in some kind of plane wave state, so whatever convention we adopt for normalizing such states appears in the rate. But also the  $\delta$  function is tricky for excitation into the continuum: just how many of these plane wave states satisfy  $E_f = E_i + \hbar\omega$ ? We shall discover that with a consistent formalism, these two difficulties cancel each other.

### The Interaction Hamiltonian

Taking the incoming wave to be an electromagnetic field having vector potential

$$\vec{A}(\vec{r}, t) = \vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)$$

The interaction Hamiltonian is given by replacing the electron kinetic energy term  $\vec{p}^2 / 2m$  with  $(\vec{p} - q\vec{A}/c)^2 / 2m$ . The relevant new term is

$$-(1/2m) \left( q/c (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) \right) = (e/mc) \vec{A} \cdot \vec{p}$$

since  $q = -e$  and  $\vec{\nabla} \cdot \vec{A} = 0$  in our gauge.

Therefore

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

The two different terms in this expression, having time dependences  $e^{-i\omega t}$  and  $e^{i\omega t}$  will give  $\delta$  functions  $\delta(E_f - E_i - \hbar\omega)$  and  $\delta(E_f - E_i + \hbar\omega)$  respectively in the transition rate. The  $e^{-i\omega t}$  term therefore corresponds to absorption of a photon, since we are looking at a process in which the electron gains energy,  $E_f > E_i$ . The  $e^{i\omega t}$  term is for the process where an atom in an excited state emits a photon into the beam and *drops* in energy.

So the relevant interaction Hamiltonian is

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

### Plane Waves: Density of States

We make the assumption that the final state is a plane wave state  $|\vec{k}_f\rangle \propto e^{i\vec{k}_f\cdot\vec{r}}$ .

The most straightforward way of handling the plane wave states is to confine the whole system to an extremely large cubical box of side  $L$ , and impose *periodic* boundary conditions (so that plane traveling wave states are allowed).

The big box has volume  $V = L^3$ , so the appropriately normalized plane wave states are

$$|\vec{k}\rangle = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}} = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}.$$

As will become apparent, we need to count how thickly these states are distributed, both in momentum space (or  $k$ -space) and in energy. We'll begin by reviewing the one-dimensional problem—the three-dimensional case is a simple generalization.

Recall that for particles in *one* dimension confined to a line of length  $L$  with periodic boundary conditions, the allowed values of wave number  $k$  were given by  $e^{ikL} = 1$ , so  $k = 2n\pi/L$  with  $n$  an integer. Thus considering only intervals  $\Delta k \gg 2\pi/L$ , the “density of states” in  $k$  is  $L/2\pi$ : an interval of length  $\Delta k$  contains  $(L/2\pi)\Delta k = \rho(k)\Delta k$  states, where here  $\rho(k) = L/2\pi$ . The density of states in *energy*,  $\rho(E)$ , follows from differentiating  $E = \hbar^2 k^2 / 2m$ . Writing

$\Delta E = (\hbar^2 k / m)\Delta k$ , gives the incremental change  $\Delta E$  in  $E$  for a given incremental change  $\Delta k$  in  $k$ , so the two intervals  $\Delta E$  and  $\Delta k$  must contain the same number of states, that is,

$\rho(E)\Delta E = \rho(k)\Delta k$ . It then follows from  $\rho(k) = L/2\pi$  that the one-dimensional density of states in energy

$$\rho_{1D}(E) = (L/2\pi)(m/\hbar^2 k) = (L/2\pi\hbar)\sqrt{m/2E}.$$

Note this *one-dimensional* density of states goes to infinity as  $E$  goes to zero.

In *three* dimensions, with a cube of side  $L$  and periodic boundary conditions, the density of states in  $k$ -space is  $(L/2\pi)^3$ . The allowed states can be visualized as the points of a cubic lattice,

$(k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$ , the  $n$ 's being integers, so each allowed state has associated with it the volume of a small cube  $(2\pi/L)^3$ .

To find the three-dimensional density of states in energy, using  $E = \hbar^2 \vec{k}^2 / 2m$ , again  $\Delta E = (\hbar^2 k / m) \Delta k$  but now to find the number of states in a small energy range we must multiply by  $4\pi k^2$ , since the states in the energy range lie between two close concentric spheres in  $k$ -space. This gives

$$\rho(E) = (L/2\pi)^3 4\pi k^2 (m/\hbar^2 k) = (L/2\pi)^3 4\pi k (m/\hbar^2) = (V/2\pi^2) (m/\hbar^3) \sqrt{2mE}.$$

Notice that in contrast to the one-dimensional case, the three-dimensional density of states goes to *zero* at zero energy. (*Exercise*: What happens in two dimensions?)

(Of course, if we are detecting the ejected electron with apparatus restricted to a solid angle  $d\Omega$ , the  $4\pi$  is replaced by  $d\Omega$ .)

The orthogonality condition between the plane wave states is

$$\langle \vec{k} | \vec{k}' \rangle = \delta_{\vec{k}, \vec{k}'}$$

the ordinary Kronecker delta function—not Dirac's—since the  $k$ 's are an enumerated set,

$$(k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$$

the  $n$ 's being integers.

### Finding the Matrix Element

The ground state wave function for hydrogen is

$$|100\rangle = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}.$$

The matrix element entering Fermi's Golden Rule  $R_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H^1 | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$  is therefore:

$$\langle \vec{k}_f | \left( \frac{e}{2mc} \right) e^{i\vec{k}\cdot\vec{r}} \vec{A}_0 \cdot \vec{p} | 100 \rangle = \int d^3r (1/L)^{3/2} e^{-i\vec{k}_f\cdot\vec{r}} \left( \frac{e}{2mc} \right) e^{i\vec{k}\cdot\vec{r}} \vec{A}_0 \cdot (-i\hbar\vec{\nabla}) \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$$

Actually the  $e^{i\vec{k}\cdot\vec{r}}$  term is not very important—the wavelength of incoming photons for the usual photoelectric effect is far greater than the size of the hydrogen atom in its ground state (which our integral is limited to) so  $e^{i\vec{k}\cdot\vec{r}} \cong 1$ , and we can drop that term.

One point we've overlooked is that the electromagnetic wave has a *magnetic* field just as strong as the electric field, so what about the interaction of this magnetic field with the electron's magnetic moment? This turns out to be much weaker than the  $\left( \frac{e}{2mc} \right) \vec{A}_0 \cdot \vec{p}$  term: the magnetic interaction

$$\vec{\mu}_B \cdot \vec{B} = \left( \frac{e}{2mc} \right) \vec{S} \cdot \vec{B},$$

and the ratio of this magnetic contribution to the electric one is

$$\frac{\left( \frac{e}{2mc} \right) \vec{S} \cdot \vec{B}}{\left( \frac{e}{2mc} \right) \vec{A}_0 \cdot \vec{p}} \cong \frac{\hbar \vec{\sigma} \cdot \vec{\nabla} \times \vec{A}}{\vec{A} \cdot \vec{p}} \cong \frac{\hbar k}{p},$$

with  $p \sim \hbar/a_0$ , so this ratio is of order  $a_0/\lambda$ ,  $\lambda$  being the wavelength of the incoming light, around 100 nm to ionize hydrogen. So, we can safely ignore the magnetic interaction.

This interaction Hamiltonian  $H^1 = \left( \frac{e}{2mc} \right) \vec{A}_0 \cdot \vec{p} e^{-i\omega t}$  is called the *dipole approximation*, because it can also be written in terms of the atom's dipole moment  $e\vec{r}$  as follows:

If  $|i\rangle, |f\rangle$  are eigenstates of  $H = \vec{p}^2/2m + V(\vec{r})$ , then from  $[\vec{r}, \vec{p}] = i\hbar$ ,  $[\vec{r}, H] = (i\hbar/m)\vec{p}$ , and

$$\begin{aligned} \langle f | \vec{p} | i \rangle &= (m/i\hbar) \langle f | \vec{r}H - H\vec{r} | i \rangle \\ &= (m/i\hbar) (E_i - E_f) \langle f | \vec{r} | i \rangle \\ &= im\omega \langle f | \vec{r} | i \rangle. \end{aligned}$$

This means that

$$\langle f | H^1(t) | i \rangle = \left( \frac{e}{2mc} \right) \vec{A}_0 e^{-i\omega t} \cdot \langle f | \vec{p} | i \rangle = \left( \frac{e}{2mc} \right) im\omega \vec{A}_0 e^{-i\omega t} \cdot \langle f | \vec{r} | i \rangle,$$

then recall  $\vec{E} = -(1/c) \partial \vec{A} / \partial t = (i\omega/2c) \vec{A}_0 e^{-i\omega t}$ , from which  $\langle f | H^1(t) | i \rangle = \langle f | -\vec{\mu} \cdot \vec{E}(t) | i \rangle$ , with  $\vec{\mu} = -e\vec{r}$ , the atom's electric dipole moment.

Nevertheless, for the particular interaction we are considering here, the  $\vec{p} = -i\hbar \vec{\nabla}$  representation proves more convenient. (We'll use the  $\vec{\mu} = -e\vec{r}$  representation in later work.)

We must evaluate:

$$(1/L)^{3/2} \left( \frac{e}{2mc} \right) \sqrt{\frac{1}{\pi a_0^3}} \int d^3 r e^{-i\vec{k}_f \cdot \vec{r}} \vec{A}_0 \cdot (-i\hbar \vec{\nabla}) e^{-r/a_0}.$$

Integration by parts gives the gradient operator acting on the plane wave state,

$$\int d^3 r e^{-i\vec{k}_f \cdot \vec{r}} \vec{A}_0 \cdot (-i\hbar \vec{\nabla}) e^{-r/a_0} = -(\vec{A}_0 \cdot \vec{p}_f) \int d^3 r e^{-i\vec{k}_f \cdot \vec{r}} e^{-r/a_0}.$$

The integral is now a Fourier transform of the hydrogen ground state wave function, and is straightforward: choose the  $z$ -axis in the direction of  $\vec{k}_f$ , the  $\varphi$ -integration gives  $2\pi$ , the  $\theta$ -integration has  $\sin \theta d\theta = -d(\cos \theta)$ , etc. The result is  $(8\pi/a_0)/(a_0^{-2} + k_f^2)^2$ .

Finally, we can put this into Fermi's Golden Rule:

$$R_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| (1/L)^{3/2} \left( \frac{e}{2mc} \right) \sqrt{\frac{1}{\pi a_0^3}} (\vec{A}_0 \cdot \vec{p}_f) \left( \frac{8\pi/a_0}{(a_0^{-2} + k_f^2)^2} \right) \right|^2 \delta(E_f - E_i - \hbar\omega).$$

To detect the ejected electron, we will have a detector sensitive to some small solid angle,  $d\Omega$ , not to some precise value of  $\vec{p}_f$ . There will also be some tiny uncertainty in  $|\vec{p}_f|$ , equivalent to an energy uncertainty, because for one thing the ejection takes place after a finite time. This means the  $\delta$ -function actually has finite width, and by taking our normalizing box big enough, there will be many states within this width—so, effectively, the  $\delta$ -function is measuring the density of possible outgoing states (see discussion at end). Recall the density of states in energy for outgoing solid angle  $d\Omega$  is

$$\rho(E, d\Omega) = (L/2\pi)^3 k^2 (m/\hbar^2 k) d\Omega = (L/2\pi)^3 k (m/\hbar^2) d\Omega,$$

giving

$$R_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| (1/L)^{3/2} \left( \frac{e}{2mc} \right) \sqrt{\frac{1}{\pi a_0^3}} (\vec{A}_0 \cdot \vec{p}_f) \left( \frac{8\pi/a_0}{(a_0^{-2} + k_f^2)^2} \right) \right|^2 (L/2\pi)^3 k_f (m/\hbar^2) d\Omega.$$

Notice first that the  $L^3$  terms cancel, reassuringly, our result cannot depend on the size of the box chosen for the plane wave states. Writing  $p_f = \hbar k_f$ , and of course  $p_f^2/2m = E_i + \hbar\omega$ , we find

$$R_{i \rightarrow f} = \frac{4mp_f}{\pi a_0^5 \hbar^4} \left( \frac{e}{mc} \right)^2 (\vec{A}_0 \cdot \vec{p}_f)^2 \left( \frac{1}{a_0^{-2} + (p_f/\hbar)^2} \right)^4 d\Omega.$$

Note that the rate is angle-dependent, since  $(\vec{A}_0 \cdot \vec{p}_f)^2 = A_0^2 p_f^2 \cos^2 \theta$ : ejection is most likely parallel to the electric field. The *total* ionization rate is given by integrating the rate over all angles, and on the unit sphere  $\overline{\cos^2 \theta} = \overline{z^2} = 1/3$ , so in the above,  $(\vec{A}_0 \cdot \vec{p}_f)^2 d\Omega \rightarrow 4\pi A_0^2 p_f^2 / 3$ .

### The Photoelectric Cross Section

Imagine now sending this radiation into a gas of hydrogen atoms, many of them, but not enough to shade each other from the radiation significantly. Energy will be absorbed from the beam as atoms ionize. What is the rate at which the beam loses energy? A convenient way of visualizing this rate of loss of energy is to replace each atom by a tiny perfectly absorbent disc oriented with its normal parallel to the beam, the size of these discs such that the beam loses energy at the same rate as it would by ionization. The area of the disc equivalent to one atom is called the *photoelectric cross section*.

The energy density in the beam of radiation is

$$\frac{1}{8\pi} (|\vec{E}|^2 + |\vec{B}|^2) = \frac{1}{8\pi} \left( 2 \frac{\omega^2}{c^2} \vec{A}_0^2 \cos^2(\vec{k} \cdot \vec{r} - \omega t) \right)$$

Denoting the photoelectric cross section by  $\sigma$ ,

$$\text{energy absorbed per second} = \sigma \times c \times \text{energy density},$$

and averaging  $\cos^2$ , this gives the energy absorption rate per atom to be  $A_0^2 \omega^2 \sigma / 8\pi c$ .

However, if the rate of ionization of one atom is  $R_{i \rightarrow f}$ , and that ionization takes energy  $\hbar\omega$  from the beam, the rate of energy absorption is just  $\hbar\omega R_{i \rightarrow f}$ , so the ionization cross section is given by

$$A_0^2 \omega^2 \sigma / 8\pi c = \hbar\omega R_{i \rightarrow f}$$

This gives

$$\begin{aligned}
\sigma &= \frac{8\pi c}{A_0^2 \omega^2} \hbar \omega R_{i \rightarrow f} \\
&= \frac{8\pi c}{A_0^2 \omega^2} \hbar \omega \frac{4mp_f}{\pi a_0^5 \hbar^4} \left(\frac{e}{mc}\right)^2 \frac{4\pi A_0^2 p_f^2}{3} \left(\frac{1}{a_0^{-2} + (p_f/\hbar)^2}\right)^4 \\
&= \frac{128}{\omega} \frac{e^2}{a_0^5 \hbar^3} \frac{\pi p_f^3}{3mc} \left(\frac{1}{a_0^{-2} + (p_f/\hbar)^2}\right)^4.
\end{aligned}$$

### Appendix: the Golden Rule Delta Function and the Density of States

For our big box model, the states are infinite in number, but can be counted by going outwards from the origin in  $k$ -space, and adopting some convention for ordering those of equal energy. We can label the states with  $\vec{n} = (n_x, n_y, n_z)$ , a vector with integer components placing the state in  $k$ -space, and denote its energy  $E_{\vec{n}}$ . The contribution of this state to the density of states is a Dirac  $\delta$ -function  $\delta(E - E_{\vec{n}})$ , that is to say, this state contributes 1 to the density of states at the point  $E_{\vec{n}}$  on the energy axis. Therefore the density of states in energy  $\rho(E) = \sum_{\vec{n}} \delta(E - E_{\vec{n}})$ , well approximated by the smooth function we derived above.

Now consider the integral over final plane wave states needed in the evaluation of the Golden Rule formula. *That*  $\delta$ -function has finite width (from the time-energy uncertainty principle), so by taking our big box big enough we can have many plane wave states within the width of the Golden Rule  $\delta$ -function: to picture this, let's represent it by a function equal to  $\Delta$  over an interval  $1/\Delta$ , zero otherwise. Then integrating this Golden Rule  $\delta$ -function with  $\rho(E)$  will give a contribution  $\Delta$  from each state inside the interval of width  $1/\Delta$ . If the states were uniformly distributed in energy, this would give the total number of states in an interval of unit energy—and that is the definition of the density of states.

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