Photoelectric effect in hydrogen

Consider a hydrogen atom in its ground state $|1s0\rangle$, centered at the origin, exposed to an incident electromagnetic wave in Coulomb gauge ($\nabla \cdot \vec{A} = 0$)

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

If $\omega$ is large enough, this can ionize the atom. Let's try to calculate the ionization rate using Fermi's golden rule:

$$R_{i \rightarrow f} = \frac{dP_{i \rightarrow f}}{dt} = \frac{2\pi}{\hbar} \left| \langle f^0 | \hat{H}' | i^0 \rangle \right|^2 \delta(E_f^0 - E_i^0 - \omega)$$

We don't need the term $\sim \delta(E_f^0 - E_i^0 + \omega)$ arising from the $\mathcal{E}$ part of the cosine because we are already in the lowest state of the atom.

The final state is a positive energy eigenstate in the continuum. We should use a Coulomb wave (i.e., a positive energy ($E > 0$) solution of the Coulomb Hamiltonian). It turns out that, for subtle reasons that we don't have time to explore in detail (see Botte and Sargent, The Theory of One- and Two-Electron Atoms, Plenum 1977), for excitation from $s$-states (but not $p$-states), we can replace the true Coulomb wave by a plane wave, $|f^0\rangle \rightarrow \frac{e^{-i\vec{k} \cdot \vec{r}}}{(2\pi\hbar)^{3/2}}$. 

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We write the interaction Hamiltonian in Coulomb gauge as (remember $\mathbf{p} \to \mathbf{p} - \frac{1}{2} \mathbf{A}$)

$$
\hat{H}'(r) = -\left(\frac{e}{c}\right) \frac{1}{2m} \left( \mathbf{A} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \mathbf{A} \right) \quad \text{(ignore term } \nabla \mathbf{A}^2 \text{ which is second order in } \mathbf{A})
$$

$$
\left(\nabla \mathbf{A} = 0\right)
= \frac{e}{mc} \mathbf{A} \cdot \hat{\mathbf{p}} = \frac{e}{mc} \cos(k^0 \mathbf{r} - \omega t) \mathbf{A}_0 \cdot \hat{\mathbf{p}}
$$

$$
= \frac{e}{2mc} \left[ e^{i(k^0 \mathbf{r} - \omega t)} + e^{-i(k^0 \mathbf{r} - \omega t)} \right] \mathbf{A}_0 \cdot \hat{\mathbf{p}}
$$

(ignoring term $\sim e^{i\omega t}$)

$$
\rightarrow \mathbf{A} \cdot \hat{\mathbf{p}} e^{-i\omega t} = \hat{H}'(\mathbf{r}) e^{-i\omega t}
$$

$$
\Rightarrow \langle f^0 | \hat{H}' | i^0 \rangle = \frac{e}{2mc} \frac{1}{(2\pi)^3} \sqrt{\frac{1}{\pi a_0^3}} \int d^3r \: e^{-i \mathbf{p} \cdot \mathbf{r}} e^{\frac{ik^0 \mathbf{r}}{\hbar}} \mathbf{A}_0 \cdot \left( -i \hbar \nabla \right) e^{-i\omega t}
$$

The factor $e^{\frac{ik^0 \mathbf{r}}{\hbar}}$ adds a momentum $\mathbf{k}$ to the atom. How does the electromagnetic wave impart momentum on the atom? How does this affect the energetics?

To ionize the atom, we must transfer an energy of order $1\text{Ry}$:

$$
\hbar \omega \sim \frac{e^2}{a_0} \Rightarrow \hbar k \sim \frac{e^2}{a_0 c}
$$
In the ground state, the electron has a typical momentum (from the uncertainty relation)

\[ p \sim \frac{h}{a_0} \]

\[ \Rightarrow \frac{\text{thc}}{p} \sim \frac{e^2}{a_0 c} \cdot \frac{a_0}{\text{thc}} = \frac{e^2}{\text{hc}} = \alpha = \frac{1}{137} \]

So \[ \frac{\text{thc}}{p} \ll 1 \] when we use the final state electron at an energy of \( O(137 \text{ Ry}) \). So let's work in this energy domain where we can use this approximation.

In principle we should also account for the interaction of the electron spin with the \( B \)-field associated with the incident \( A' \):

\[ \frac{\langle \frac{e}{2mc} \vec{S} \cdot \vec{B} \rangle}{\langle \frac{e}{mc} \vec{A}' \cdot \vec{p} \rangle} = \frac{\frac{\text{thc}}{4} \langle \hat{\sigma} \cdot (\nabla \times \vec{A}') \rangle}{\langle \vec{A}' \cdot \vec{p} \rangle} \ll 1 \]

so we can ignore the \( \vec{B} \) interaction for the same reason.

Since \( \text{thc} < p \sim \frac{h}{a_0} \Rightarrow k a_0 \ll 1 \)

So for ionization into final states with \( E_f \sim O(\text{few Ry}) \), the wavelength of the light is much larger than
The Bohr radius of the 1s electron

$\bar{A}$ is basically $r^2$ independent over the range of the atom in its initial state.

We may approximate $e^{i \frac{2\pi}{\hbar} \cdot} \approx 1$ make the integral ("dipole approximation")

The atom sees effectively a spatially constant electric field whose magnitude oscillates in time with frequency $\omega$:

$$E = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\frac{1}{c} \frac{\partial}{\partial t} \left( \frac{\mathbf{A}_0}{2} e^{-i \omega t} \right) = \frac{i\omega \mathbf{A}_0}{2c} e^{-i \omega t}$$

Now let's work out the matrix element in dipole approximation.

Let's integrate first by path:

$$\int d^3r \ e^{-i \mathbf{p}_f \cdot \mathbf{r}} \mathbf{A}_0 \cdot (-i \hbar \nabla) e^{-\frac{i}{\hbar} \xi_0} = \int d^3r \ (i \hbar \nabla e^{-i \mathbf{p}_f \cdot \mathbf{r}}) \mathbf{A}_0 e^{-\frac{i}{\hbar} \xi_0}$$

$$= \mathbf{p}_f \cdot \mathbf{A}_0 \int d^3r \ e^{-i \mathbf{p}_f \cdot \mathbf{r}} e^{-\frac{i}{\hbar} \xi_0}$$

$$= \mathbf{p}_f \cdot \mathbf{A}_0 \int dp \int_0^\infty r^2 dr \ e^{-\frac{i}{\hbar} \xi_0} \int d(\cos \theta) \left[ e^{-i \mathbf{p}_f \cos \theta / \lambda} - e^{-i \mathbf{p}_f / \lambda} \right]$$

$$= 2\pi \ h \ \mathbf{p}_f \cdot \mathbf{A}_0 \ i \left( -\frac{\partial}{\partial (\mathbf{p}_f \cdot \mathbf{A}_0)} \right) \int_0^\infty dr \left( e^{-\frac{\mathbf{p}_f + i \mathbf{p}_f \cdot \mathbf{r}}{\lambda} r} - e^{-\frac{\mathbf{p}_f - i \mathbf{p}_f \cdot \mathbf{r}}{\lambda} r} \right)$$

$$= \frac{8\pi / \lambda_0}{\sqrt{\lambda_0^2 + (\mathbf{p}_f / k)^2}} \mathbf{p}_f \cdot \mathbf{A}_0$$
Putting this together with the normalization factors and squaring it we finally get

\[ R_{\text{eff}} = \frac{2\pi}{\hbar} \left( \frac{e}{2mc} \right)^2 \frac{1}{(2\pi\hbar)^3} \frac{1}{1 + (\frac{P_f^0 a_o}{\hbar})^2} \frac{|\vec{A}_0 \cdot \vec{P}_f|^2}{\left[ 1 + (\frac{P_f a_o}{\hbar})^2 \right]^4} \delta(E_f^0 - E_i^0 - \hbar\omega) \]

Experimentally, we can't measure $E_f$ with infinite accuracy, so we must integrate this rate over the finite energy resolution. This means we are only interested in the area under the $\delta$-function which is peaked at

\[ P_f^2 = E_i^0 + \hbar\omega \implies P_f = \sqrt{2m(E_i^0 + \hbar\omega)} \]

So let's count the number of electrons per unit time emitted into solid angle $d\Omega$:

\[ R_{\text{em}} d\Omega = \int_{P_f - \delta}^{P_f + \delta} p^2 dp d\Omega = \frac{4e^2 a_o^3}{m^2 c^4} \frac{\vec{A}_0 \cdot \vec{P}_f}{[1 + (\frac{P_f a_o}{\hbar})^2]^4} \delta(\frac{P_f^2 - \frac{m^2 c^4}{2m})}{P_f} \delta(p^2 - P_f^2) \]

\[ = \frac{4e^2 a_o^3}{m^2 c^4} \frac{P_f |\vec{P}_f \cdot \vec{A}_0|^2}{[1 + (\frac{P_f a_o}{\hbar})^2]^4} d\Omega \]

The $\vec{P}_f \cdot \vec{A}_0$ factor tells us that the emission is biased towards the direction of $\vec{A}_0$, which is also the direction of the electric field of the light that rips out the electron from its bound state.
If we had kept the $e^{i\mathbf{k} \cdot \mathbf{r}}$ factor, we would see that there is an additional (weaker) bias towards $\mathbf{k}$ reflecting the momentum transfer from the light wave.

(We can actually do this calculation exactly by simply combining $e^{-i\mathbf{p}_f \cdot \mathbf{r}}$ under the integral and replacing $\mathbf{p}_f \rightarrow \mathbf{p}_f - \hbar \mathbf{k}$ in the result:

$$R \sim |\tilde{A}_0^* (\mathbf{p}_f - h\mathbf{k})|^2$$

This is largest when $\mathbf{p}_f || \mathbf{k}$ and $\mathbf{p}_f || (\mathbf{E}^\omega - \mathbf{k})$.)

The total ionization rate is obtained by integrating over the solid angle:

$$\int \cos^2 \theta \, d\cos \theta = \frac{2}{3}, \quad \int dp = 2\pi$$

$$R_{i\rightarrow all} = \frac{16 \alpha_0^2 e^2 p_f^3 |A_0|^2}{3 m c^2 \hbar^4 (1 + (p_f^2 / \hbar^2)^2)^2}$$

The amount of energy absorbed from the incoming light per unit time is

$$\frac{dE_{abs}}{dt} = \text{two } R_{i\rightarrow all}$$

How does this compare with the energy contained in the incoming light wave?

The incoming plane wave brings in energy at a rate of $|S|^2 = \frac{\omega^2 |A_0|^2}{4\pi c} < \sin^2 \left( k_z \cdot \mathbf{r} - \omega t \right) > = \frac{\omega^2 |A_0|^2}{8\pi c}$ per unit area.
If we put a perfectly black (100% absorbing) disk of area \( A \) into that beam, it absorbs energy at the rate

\[ \frac{\omega^2 A_0^2}{8\pi c} \cdot \sigma = \frac{\dd E_{abs}}{dt} \]

We can compare this with the energy absorbed by the hydrogen atom and assign to it an effective black disk area, called the "photoelectric cross section" (or ionization cross section)

\[ \sigma_{ioniz} = \frac{8\pi c}{\omega^2 A_0^2} \cdot \text{h} \omega \cdot R_{i \rightarrow e} \cdot c = \frac{128 a_0^3 \pi e^2 p_f^3}{3 m_c c \omega h^3 \left[ 1 + \left( \frac{p_f a_0}{\hbar} \right)^2 \right]^4} \]

The differential cross section \( \frac{d\sigma}{d\Omega} \) is defined correspondingly as

\[ \frac{d\sigma}{d\Omega} = \frac{8\pi c}{\omega^2 A_0^2} \tan \text{h} \omega \, dR_{i \rightarrow e} \cdot d\Omega = \frac{32 a_0^3 e^2 p_f^3 \cos^2 \theta}{m_c c \omega h^3 \left[ 1 + \left( \frac{p_f a_0}{\hbar} \right)^2 \right]^4} \]

For \( \frac{p_f a_0}{\hbar} \ll 1 \), we can ignore the 1 in the denominator:

\[ \frac{d\sigma}{d\Omega} \overset{p_f a_0 \ll \hbar}{\longrightarrow} \frac{32 e^2 h^5 \cos^2 \theta}{m_c c \omega p_f a_0^5} \]  

(remember: \( p_f a_0 \ll \hbar \))

\[ = 32 \frac{a^2 a_0}{\hbar \omega} \frac{\hbar c}{(p_f a_0 / \hbar)^5} \]

(Uits of \( \sigma \) are barn = \( 10^{-28} \text{m}^2 \) or \( 1 \text{mb} = 0.1 \text{ barn} \))
Spontaneous radiation decay of excited atoms

This requires treating the electromagnetic field as a quantum system ("field quantisation"), leading into quantum field theory. I will leave this for an advanced quantum theory course.