Photoelectric effect in hydrogen

Consider a hydrogen atom in its ground state $|100\rangle$, centered at the origin, exposed to an incident electromagnetic wave in Coulomb gauge $(\vec{\nabla}\cdot\vec{A}=0)$

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

If ω is large enough, this can ionize the atom.

Let's try to calculate the ionization rate using Fermi's golden rule:

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

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

The final state is a position 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 Bethe and Salpeter, The Theory of One- and 2-electron atoms", Plenum 1977), for excitation from s-states (but not from p-states!) we can replace the the Coulomb wave by a plane wave, $|\vec{p}_f\rangle \leftrightarrow \dfrac{e^{-i\vec{p}_f\cdot\vec{r}}}{(2\pi\hbar)^{3/2}}$.

We write the interaction Hamiltonian in Coulomb gauge as (remember $\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}$)

$$\hat{H}'(t) = -\left(\frac{-e}{c}\right)\frac{1}{2m}\left(\vec{A}\cdot\hat{\vec{P}} + \hat{\vec{P}}\cdot\vec{A}\right)$$

(ignore term $\sim|\vec{A}|^2$ which is second order in $\vec{A}$)

$(\vec{\nabla}\cdot A = 0)$

$$= \frac{e}{mc}\vec{A}\cdot\hat{\vec{P}} = \frac{e}{mc}\cos(\vec{k}\cdot\hat{\vec{r}} - \omega t)\,\vec{A}_0\cdot\hat{\vec{P}}$$

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

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

$$\longrightarrow \frac{e}{2mc}e^{i\vec{k}\cdot\hat{\vec{r}}}\,\vec{A}_0\cdot\hat{\vec{P}}\,e^{-i\omega t} \equiv \hat{H}'(\hat{\vec{r}})\,e^{-i\omega t}$$

$$\Rightarrow \langle f^0|\hat{H}'|i^0\rangle = \frac{e}{2mc}\frac{1}{(2\pi\hbar)^{3/2}}\sqrt{\frac{1}{\pi a_0^3}}\int d^3r\, e^{-i\vec{p}_f\cdot\vec{r}/\hbar}\,e^{i\vec{k}\cdot\vec{r}}$$
$$\times\,\vec{A}_0\cdot(-i\hbar\vec{\nabla})\,e^{-r/a_0}$$

The factor $e^{i\vec{k}\cdot\vec{r}}$ adds a momentum $\hbar k$ to the atom $\to$ the electromagnetic wave imparts momentum on the atom. How does this affect the energetics?

To ionize the atom, we must transfer an energy of order $1\,Ry$: $\quad \hbar\omega \sim \frac{e^2}{a_0} \Rightarrow \hbar k = \hbar\frac{\omega}{c} \sim \frac{e^2}{a_0 c}$

In the ground state, the electron has a typical momentum (from the uncertainty relation)

$$p \sim \frac{\hbar}{a_0}$$

$$\Rightarrow \frac{\hbar k}{p} \cong \frac{e^2}{a_0 c} \cdot \frac{a_0}{\hbar} = \frac{e^2}{\hbar c} = \alpha = \frac{1}{137}$$

So $\frac{\hbar k}{p} \ll 1$ unless we give the final state electron an energy of $O(137\ Ry)$. So let's work in this energy domain where we can use $\hbar k \ll p$.

In principle we should also account for the interaction of the electron spin with the B-field associated with the incident $\vec{A}(\vec{r},t)$:

$$\frac{\left\langle \frac{e}{2mc} \vec{S} \cdot \vec{B} \right\rangle}{\left\langle \frac{e}{mc} \vec{A} \cdot \vec{P} \right\rangle} \simeq \frac{1}{4} \frac{\langle \hbar \vec{\sigma} \cdot (\vec{\nabla} \times \vec{A}) \rangle}{\langle \vec{A} \cdot \vec{P} \rangle} \simeq \frac{1}{4} \frac{\hbar k}{p} \ll 1$$

So we can ignore the $\vec{\mu}_s \cdot \vec{B}$ interaction for the same reason.

Since $\hbar k \ll p \sim \frac{\hbar}{a_0} \Rightarrow \boxed{k a_0 \ll 1}$

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

$\rightarrow$ $\vec{A}$ is basically $\vec{r}$-independent over the range of the atom in its initial state.

$\rightarrow$ we may approximate $e^{i\vec{k}\cdot\vec{r}} \approx 1$ under the integral ("dipole approximation")

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

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

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

Let's integrate first by parts:

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

$$= \vec{p}_f\cdot\vec{A}_0\int d^3r\, e^{-i\vec{p}_f\cdot\vec{r}/\hbar}e^{-r/a_0} =$$

$$= \vec{p}_f\cdot\vec{A}_0\int_0^{2\pi} d\varphi\int_0^{\infty} r^2 dr\, e^{-r/a_0}\underbrace{\int_{-1}^{1} d(\cos\vartheta)\, e^{-ip_f r\cos\vartheta/\hbar}}_{\frac{e^{-ip_f r/\hbar}-e^{ip_f r/\hbar}}{-ip_f r/\hbar}}$$

$$= 2\pi\hbar\frac{\vec{p}_f\cdot\vec{A}_0}{p_f}\, i\left(-\frac{\partial}{\partial(1/a_0)}\right)\int_0^{\infty} dr\left(e^{-\left(\frac{1}{a_0}+i\frac{p_f}{\hbar}\right)r} - e^{-\left(\frac{1}{a_0}-\frac{ip_f}{\hbar}\right)r}\right)$$

$$= \frac{8\pi/a_0}{\left[1/a_0^2 + (p_f/\hbar)^2\right]^2}\,\vec{p}_f\cdot\vec{A}_0$$

Putting this together with the normalization factors and squaring it we finally get

$$\boxed{R_{i\to f} = \frac{2\pi}{\hbar}\left(\frac{e}{2mc}\right)^2 \frac{1}{(2\pi\hbar)^3}\frac{1}{\pi a_0^3}\frac{|\vec{A}_0\cdot\vec{p}_f|^2\, 64\pi^2 a_0^6}{\left[1+\left(\frac{p_f a_0}{\hbar}\right)^2\right]^4}\delta(E_f^\circ - E_i^\circ - \hbar\omega)}$$

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 δ-function which is peaked at

$$\frac{p_f^2}{2m} = E_i^\circ + \hbar\omega \quad \rightarrow \quad p_f = \sqrt{2m(E_i^\circ + \hbar\omega)}$$

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

$$\underset{\sim\sim\sim}{R_{i\to d\Omega}} = \int_{p_f-\varepsilon}^{p_f+\varepsilon} p^2\,dp\,d\Omega\,\frac{4e^2a_0^3}{m^2\hbar^4c^2}\frac{\vec{A}_0\cdot\vec{p}_f}{[1+(p_f a_0/\hbar)^2]^4}\underbrace{\delta\left(\frac{p^2}{2m}-\frac{p_f^2}{2m}\right)}_{\frac{m}{p_f}\delta(p-p_f)}$$

$$= \frac{4e^2a_0^3}{mc^2\hbar^4}\frac{p_f\,|\vec{p}_f\cdot\vec{A}_0|^2}{\left[1+\left(\frac{p_f a_0}{\hbar}\right)^2\right]^4}\cdot d\Omega$$

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 $e^{i\vec{k}\cdot\vec{r}}$ factor, we would see that there is an additional (weaker) bias towards $\vec{k}$, reflecting the momentum transfer from the light wave.

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

$$R \sim \left|\vec{A}_0\cdot(\vec{p}_f - \hbar\vec{k})\right|^2$$

This is largest when $\vec{p}_f \parallel \vec{k}$ and $\vec{p}_f \parallel \vec{E} \sim \vec{A}_0$.)

The total ionization rate is obtained by integrating over the solid angle: $\int_{-1}^{1} \cos^2\vartheta \, d\cos\vartheta = \frac{2}{3}$, $\int_0^{2\pi} d\varphi = 2\pi$

$$\boxed{R_{i\to all} = \frac{16\, a_0^3 e^2 p_f^3 |\vec{A}_0|^2}{3 m c^2 \hbar^4 \left(1+\left(p_f\frac{a_0}{\hbar}\right)^2\right)^4}}$$ total ionization rate

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

$$\frac{dE_{abs}}{dt} = \hbar\omega\, R_{i\to all}$$

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

The incoming plane wave brings in energy at a rate of $|\vec{S}| = \frac{\omega^2 |\vec{A}_0|^2}{4\pi c}\left\langle \sin^2(\vec{k}\cdot\vec{r} - \omega t)\right\rangle_t = \frac{\omega^2 |\vec{A}_0|^2}{8\pi c}$ per unit area.

If we put a perfectly black (100% absorbing) disk of area σ into that beam, it absorbs energy at the rate

$$\frac{\omega^2|\vec{A}_0|^2}{8\pi c}\cdot\sigma = \frac{dE_{abs}}{dt}$$

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)

$$\sigma_{ioniz} = \frac{8\pi c}{\omega^2|\vec{A}_0|^2}\cdot\hbar\omega\cdot R_{i\to all} = \frac{128 a_0^3\pi e^2 p_f^3}{3mc\omega\hbar^3\left[1+\left(\frac{p_f a_0}{\hbar}\right)^2\right]^4}$$

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

$$\frac{d\sigma}{d\Omega} = \frac{8\pi c}{\omega^2|\vec{A}_0|^2}\hbar\omega\frac{dR_{i\to d\Omega}}{d\Omega} = \frac{32 a_0^3 e^2 p_f^3\cos^2\vartheta}{mc\omega\hbar^3\left[1+\left(\frac{p_f a_0}{\hbar}\right)^2\right]^4}$$

For $\frac{p_f a_0}{\hbar} \gg 1$ we can ignore the 1 in the denominator:

$$\frac{d\sigma}{d\Omega}\xrightarrow[p_f a_0\gg\hbar]{}\frac{32 e^2\hbar^5\cos^2\vartheta}{mc\omega p_f^5 a_0^5}$$ (remember: $p_i a_0 \simeq \hbar$)

$$= 32\frac{\alpha^2 a_0}{\hbar\omega}\frac{\hbar c}{(p_f a_0/\hbar)^5}$$

(units of σ are barn $= 10^{-28}m^2$ or $mb = 0.1 fm^2$)

Spontaneous radiation decay of excited atoms

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