Photoelectric effect

Let $\psi_a(\mathbf{r})$ be the ground state for hydrogen.

$$\psi_a(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}} \exp(-r/a)$$

Let $\psi_b(\mathbf{r})$ be the wave function for a free electron.

$$\psi_b(\mathbf{r}) = \frac{1}{\sqrt{l^3}} \exp(i\mathbf{k} \cdot \mathbf{r}) = \frac{1}{\sqrt{l^3}} \exp(ikr\cos\theta)$$

Find the transition rate $R_{a\to b}$ using Fermi's golden rule

$$R_{a\to b} = \frac{2\pi}{\hbar} \left|\langle\psi_b|H_1|\psi_a\rangle\right|^2 \rho(E_b)$$

§1

Start by finding the perturbing Hamiltonian H_1.

We have for a particle with charge q

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A}) \cdot (\mathbf{p} - q\mathbf{A})$$

Expand the inner product.

$$H = \frac{1}{2m}(\mathbf{p}^2 - \mathbf{p} \cdot q\mathbf{A} - q\mathbf{A} \cdot \mathbf{p} + q^2\mathbf{A}^2)$$

Hence the first-order perturbation is

$$H_1 = -\frac{q}{2m}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})$$

For an electron we have $q = -e$.

$$H_1 = \frac{e}{2m}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})$$

For any wave function $\psi(\mathbf{r}, t)$

$$(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})\psi(\mathbf{r}, t) = 2\mathbf{A} \cdot \mathbf{p}\psi(\mathbf{r}, t) - i\hbar\psi(\mathbf{r}, t)\nabla \cdot \mathbf{A} \tag{1}$$

Hence for the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$ we have the identity

$$\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} = 2\mathbf{A} \cdot \mathbf{p}$$

Hence

$$H_1 = \frac{e}{m}\mathbf{A} \cdot \mathbf{p}$$

§2

Let $\mathbf{E}$ be the electric field

$$\mathbf{E} = E_0 \sin(\mathbf{k}\cdot\mathbf{r} - \omega t)\,\boldsymbol{\epsilon}$$

where $\boldsymbol{\epsilon}$ is a polarization vector such that $|\boldsymbol{\epsilon}| = 1$ and $\mathbf{k}\cdot\boldsymbol{\epsilon} = 0$.

Then the magnetic vector potential $\mathbf{A}$ is

$$\mathbf{A} = -\frac{E_0}{\omega}\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)\,\boldsymbol{\epsilon}$$

so that in SI units

$$\mathbf{E} = -\frac{\partial}{\partial t}\mathbf{A} \tag{2}$$

Hence

$$H_1 = \frac{e}{m}\mathbf{A}\cdot\mathbf{p} = -\frac{eE_0}{m\omega}\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p}$$

In exponential form

$$H_1 = -\frac{eE_0}{2m\omega}\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p} - \frac{eE_0}{2m\omega}\exp(-i\mathbf{k}\cdot\mathbf{r} + i\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p}$$

Use the dipole approximation $\exp(i\mathbf{k}\cdot\mathbf{r}) \approx 1$.

$$H_1 = -\frac{eE_0}{2m\omega}\exp(-i\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p} - \frac{eE_0}{2m\omega}\exp(i\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p}$$

Go back to cosine form.

$$H_1 = -\frac{eE_0}{m\omega}\cos(\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{p}$$

By the identity

$$\mathbf{p} = \frac{im}{\hbar}(H_0\mathbf{r} - \mathbf{r}H_0)$$

we have

$$\langle\psi_b|\mathbf{p}|\psi_a\rangle = \frac{im}{\hbar}(E_b - E_a)\langle\psi_b|\mathbf{r}|\psi_a\rangle$$

Hence

$$H_1 = -ieE_0\frac{\omega_0}{\omega}\cos(\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{r}$$

where

$$\omega_0 = \frac{E_b - E_a}{\hbar}$$

For the photoelectric effect we have $\omega_0 = \omega$ hence

$$H_1 = -ieE_0\cos(\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{r}$$

Rotate the lab frame so that $\boldsymbol{\epsilon}\cdot\mathbf{r} = z$.

$$H_1 = -ieE_0\cos(\omega t)\,z$$

§3

For perturbing Hamiltonians of the form

$$H_1 = V(\mathbf{r})\cos(\omega t)$$

we have

$$|\langle\psi_b|H_1|\psi_a\rangle|^2 = |H_{ba}|^2$$

where H_{ba} is the transition amplitude

$$H_{ba} = \frac{1}{2}\int \psi_b^* V(\mathbf{r})\psi_a \, d\mathbf{r}$$

Hence for

$$V(\mathbf{r}) = -ieE_0 z$$

we have in polar coordinates

$$H_{ba} = -\frac{ieE_0}{2}\frac{1}{\sqrt{\pi a^3 l^3}}\int_0^\infty \int_0^\pi \int_0^{2\pi} \exp(ikr\cos\theta - r/a)\, zr^2 \sin\theta \, dr\, d\theta\, d\phi$$

Integrate over ϕ (multiply by 2π).

$$H_{ba} = -i\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\int_0^\infty \int_0^\pi \exp(ikr\cos\theta - r/a)\, zr^2 \sin\theta \, dr\, d\theta$$

Change of variable $u = \cos\theta$.

$$H_{ba} = -i\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\int_0^\infty \int_{-1}^1 \exp(ikru - r/a)\, zr^2 \, dr\, du$$

Solve the integral over u.

$$H_{ba} = -i\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\int_0^\infty \frac{1}{ikr}\left[\exp(ikr - r/a) - \exp(-ikr - r/a)\right] zr^2 \, dr \tag{3}$$

Cancel i and r.

$$H_{ba} = -\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\frac{1}{k}\int_0^\infty \left[\exp(ikr - r/a) - \exp(-ikr - r/a)\right] zr \, dr$$

Substitute $z = r\cos\theta$. This θ is different from θ in $\mathbf{k}\cdot\mathbf{r} = kr\cos\theta$.

$$H_{ba} = -\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\frac{\cos\theta}{k}\int_0^\infty \left[\exp(ikr - r/a) - \exp(-ikr - r/a)\right] r^2 \, dr$$

Solve the integral.

$$H_{ba} = -\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\frac{\cos\theta}{k}\left[-\frac{2}{(ik - 1/a)^3} + \frac{2}{(-ik - 1/a)^3}\right] \tag{4}$$

Rewrite as

$$H_{ba} = -\pi eE_0 \frac{1}{\sqrt{\pi a^3 l^3}}\cos\theta\, ia^4\left[\frac{16}{(a^2k^2+1)^3} - \frac{4}{(a^2k^2+1)^2}\right] \tag{5}$$

§4

For the transition density we have

$$|\langle\psi_b|H_1|\psi_a\rangle|^2 = |H_{ba}|^2 = \pi e^2 E_0^2 \frac{a^5}{l^3}\cos^2\theta \left[\frac{16}{(a^2k^2+1)^3} - \frac{4}{(a^2k^2+1)^2}\right]^2 \tag{6}$$

Hence by Fermi's golden rule

$$\begin{aligned} R_{a\to b} &= \frac{2\pi}{\hbar}\,|\langle\psi_b|H_1|\psi_a\rangle|^2\,\rho(E_b) \\ &= \frac{2\pi^2}{\hbar}e^2E_0^2\frac{a^5}{l^3}\cos^2\theta\left[\frac{16}{(a^2k^2+1)^3} - \frac{4}{(a^2k^2+1)^2}\right]^2\rho(E_b) \end{aligned}$$

The density of states for a free electron is

$$\rho(E_b) = \left(\frac{l}{2\pi}\right)^3\frac{\sqrt{2m^3E_b}}{\hbar^3} = \left(\frac{l}{2\pi}\right)^3\frac{k}{a\alpha\hbar c} \tag{7}$$

Hence

$$R_{a\to b} = \frac{ka^4}{4\pi\alpha\hbar^2 c}e^2E_0^2\cos^2\theta\left[\frac{16}{(a^2k^2+1)^3} - \frac{4}{(a^2k^2+1)^2}\right]^2 \tag{8}$$

§5

Verify dimensions.

$$\begin{aligned} \alpha &= [1] \\ a &= [\mathrm{m}] \\ k &= [\mathrm{m}^{-1}] \\ \omega &= [\mathrm{s}^{-1}] \\ e &= [\mathrm{C}] \\ E_0 &= [\mathrm{N\,C}^{-1}] = [\mathrm{kg\,m\,s}^{-2}\,\mathrm{C}^{-1}] \\ \hbar &= [\mathrm{J\,s}] = [\mathrm{kg\,m}^2\,\mathrm{s}^{-1}] \end{aligned}$$

$$\frac{k}{a\alpha\hbar c} = \frac{[\mathrm{m}^{-1}]}{[\mathrm{m}]\,[\mathrm{J\,s}]\,[\mathrm{m\,s}^{-1}]} = \frac{1}{[\mathrm{J}]\,[\mathrm{m}^3]}$$

$$R_{a\to b} = \frac{[\mathrm{m}^{-1}]\,[\mathrm{m}]^4}{[\mathrm{J\,s}]^2\,[\mathrm{m\,s}^{-1}]}\,[\mathrm{N}]^2 = [\mathrm{s}^{-1}] \tag{9}$$

Eigenmath script