The Photoelectric Effect - an Inelastic Scattering Process

$$A + \gamma_{k\lambda} \longrightarrow A^+ + e^- \; . \qquad \hat{H}(t) = \underset{\substack{\uparrow \\ \text{neutral atom (e.g. Hydrogen)}}}{\hat{H}_0} + \hat{H}_1(t)$$

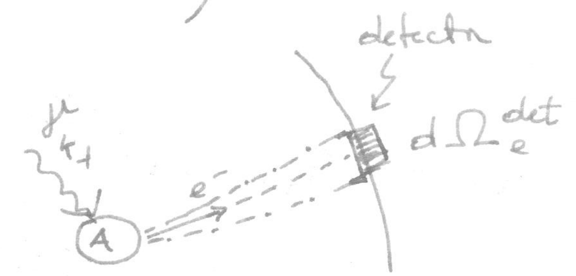
$$\hat{H}_1(t) = -(e/m)\, \underset{\substack{\uparrow \\ \text{rad.}}}{\hat{\vec{A}}} \cdot \underset{\substack{\uparrow \\ \text{atom}}}{\hat{\vec{p}}} + (e/m)^2 \underbrace{\cancel{\vec{A}\cdot\vec{A}}}_{=0 \text{ (single photon process)}}$$

$\hat{\vec{A}}$ - ops. on photon (radiation) states

$\hat{\vec{p}}$ - op. on electron (atomic) states

$$\hat{\vec{A}}(\vec{r},t) = \sum_{k',\lambda'} \left(\frac{\hbar}{2\varepsilon_0 \omega_{k'} V}\right)^{1/2} \left(\hat{a}_{k'\lambda'}\, e^{i(\vec{k}'\cdot\vec{r} - \omega_{k'} t)}\, \vec{\varepsilon}_{k'\lambda'} + \hat{a}^+_{k'\lambda'}\, e^{-i(\vec{k}'\cdot\vec{r} - \omega_{k'} t)}\, \vec{\varepsilon}^{\,*}_{k'\lambda'} \right)$$

FGR for photoelectron :



$$d\Gamma_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \underbrace{\rho_e(E_e)}_{dE_e} d\Omega_e\, \delta\left[\underset{\substack{\uparrow \\ \text{ionized atom}}}{E_{A^+}} + \underset{\substack{\uparrow \\ \text{emitted free } e^-}}{E_e} - \left(\underset{\substack{\uparrow \\ \text{initial neutral atom}}}{E_A} + \underset{\substack{\uparrow \\ \text{absorbed photon}}}{\hbar\omega_k} \right) \right] \quad (1)$$

> Density of (final) states :

$$\rho_e(E_e) = \frac{V}{(2\pi\hbar)^3} p_e^2 \left(\frac{dp_e}{dE_e}\right) = \frac{V p_e^2}{(2\pi\hbar)^3} \frac{1}{\left(\frac{dE_e}{dp_e}\right)} = \frac{V p_e^2}{(2\pi\hbar)^3} \frac{1}{\frac{d}{dp}\left(\frac{p^2}{2m_e}\right)} = \frac{V p_e^2}{(2\pi\hbar)^3 \frac{p_e}{m_e}}$$

$$= \frac{V}{(2\pi\hbar)^3} m_e p_e \quad (2)$$

> Transition matrix element:

$$V_{fi} \equiv \langle \phi_f | \hat{H}_1 | \phi_i \rangle$$

$$|\phi_i\rangle \equiv |A\rangle \otimes |1_{\vec{k}\lambda}\rangle = |A^+\rangle \otimes |\psi_{bound}\rangle \otimes |1_{k\lambda}\rangle \equiv |A^+;\psi_{bound}\rangle |1_{k\lambda}\rangle$$

$$\equiv |A\rangle |1_{k\lambda}\rangle$$

$$|\phi_f\rangle \equiv |A^+\rangle \otimes |\psi_{free}\rangle \otimes |0_{\vec{k}\lambda}\rangle \equiv |A^+;\psi_{free}\rangle |0_{k\lambda}\rangle$$

$|\psi_{bound}\rangle$ $\underbrace{-}_{\text{initial}}$ state of electron in atom i.e. $|nlm\rangle$

$|\psi_{free}\rangle = |p_e^2/2m_e\rangle$ - final state of free electron

$$V_{fi} \overset{\dots}{=} (-e/m)\sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_k}} \langle \phi_f | \hat{a}_{k\lambda} e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\varepsilon}_{k\lambda} \cdot \hat{\vec{p}} |\phi_i\rangle e^{-i\omega_k t} \quad (3)$$

↳ surviving term from $\sum_{k'\lambda'}$

$$C_{k\lambda} \equiv \langle \phi_f | \hat{a}_{k\lambda} e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\varepsilon}_{k\lambda} \cdot \hat{\vec{p}} |\phi_i\rangle$$

$$= \langle A^+;\psi_{free}| \langle 0_{k\lambda}| \hat{a}_{k\lambda} e^{i\vec{k}\cdot\hat{\vec{r}}} \vec{\varepsilon}_{k\lambda} \cdot \hat{\vec{p}} |A\rangle |1_{k\lambda}\rangle$$

$$= \vec{\varepsilon}_{k\lambda} \cdot \langle A^+;\psi_{free}| \langle 0_{k\lambda}| \hat{a}_{k\lambda} e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\vec{p}} |A\rangle |1_{k\lambda}\rangle$$

~~Need $\hat{\vec{p}}|\psi_{free}\rangle = ?$~~

$$= \vec{\varepsilon}_{k\lambda} \cdot \underbrace{\langle A^+;\psi_{free}| e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\vec{p}} |A\rangle}_{\equiv \langle \vec{atom} \rangle} \underbrace{\langle 0_{k\lambda}| \hat{a}_{k\lambda} |1_{k\lambda}\rangle}_{\equiv \langle rad \rangle = \langle 0_{k\lambda}|0_{k\lambda}\rangle = 1}$$

Need ~~$e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\vec{p}} |\psi_{free}\rangle = ?$~~ $\langle \psi_{free}| \vec{\epsilon}_{k\lambda} \cdot e^{i\vec{k}\cdot\hat{\vec{r}}} \hat{\vec{p}} = ?$

Drop $\vec{k}\lambda$ subscript:

$$\vec{\varepsilon}\cdot[\hat{\vec{p}}, e^{i\vec{k}\cdot\vec{r}}]\psi(\vec{r}) = \vec{\varepsilon}\cdot[\hat{\vec{p}}(e^{i\vec{k}\cdot\vec{r}}\psi) - e^{i\vec{k}\cdot\vec{r}}\hat{\vec{p}}\psi]$$

$$= \vec{\varepsilon}\cdot[-i\hbar\nabla(e^{i\vec{k}\cdot\hat{\vec{r}}}\psi) - (-i\hbar)e^{i\vec{k}\cdot\vec{r}}\nabla\psi]$$

Using
$\hat{p}\psi(\vec{r}) = -i\hbar\nabla\psi(\vec{r})$
$f(\hat{\vec{r}})\psi(\vec{r}) = f(\vec{r})\psi(\vec{r})$

$$= -i\hbar\vec{\varepsilon}\cdot(i\vec{k}e^{i\vec{k}\cdot\vec{r}}\psi + \cancel{e^{i\vec{k}\cdot\vec{r}}\nabla\psi} - \cancel{e^{i\vec{k}\cdot\vec{r}}\nabla\psi})$$

$$= \hbar\underbrace{\vec{\varepsilon}\cdot\vec{k}}_{=0}e^{i\vec{k}\cdot\vec{r}}\psi(\vec{r})$$

$=0$ Coulomb Gauge $\left(\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow i\vec{k}\cdot\vec{A} = 0 \Rightarrow \vec{k}\cdot\vec{\varepsilon} = 0\right)$

$= 0$

$$\Rightarrow \cancel{(\vec{\varepsilon}\cdot e^{i\vec{k}\cdot\hat{\vec{r}}}\hat{\vec{p}})|\psi_{free}\rangle}$$

$$\langle\psi_{free}|\vec{\varepsilon}_{k\lambda}\cdot e^{i\vec{k}\cdot\hat{\vec{r}}}\hat{\vec{p}} = \langle\psi_{free}|\vec{\varepsilon}_{k\lambda}\cdot\hat{\vec{p}}\,e^{i\vec{k}\cdot\hat{\vec{r}}}$$

$$= \vec{\varepsilon}_{k\lambda}\cdot\langle\psi_{free}|\hat{\vec{p}}\,e^{i\vec{k}\cdot\hat{\vec{r}}} = \vec{\varepsilon}_{k\lambda}\cdot\langle\tfrac{p_e^2}{2m}|\hat{\vec{p}}\,e^{i\vec{k}\cdot\hat{\vec{r}}}$$

$$= \vec{\varepsilon}_{k\lambda}\cdot\vec{p}_e\langle\tfrac{p_e^2}{2m}|e^{i\vec{k}\cdot\hat{\vec{r}}} = \vec{\varepsilon}_{k\lambda}\cdot\vec{p}_e\langle\psi_{free}|e^{i\vec{k}\cdot\hat{\vec{r}}}$$

acts on bound electron in $|A\rangle$ i.e. on $|nlm\rangle$

$$\Rightarrow C_{k\lambda} = \vec{\varepsilon}_{k\lambda}\cdot\langle\vec{atom}\rangle\cdot 1$$

$$\cancel{\vec{\varepsilon}_{k\lambda}\cdot\langle A^+;\psi_{free}|} = \vec{\varepsilon}_{k\lambda}\cdot\vec{p}_e\langle A^+;\psi_{free}|e^{i\vec{k}\cdot\hat{\vec{r}}}|A\rangle$$

$$= \vec{\varepsilon}_{k\lambda}\cdot\vec{p}_e\langle A^+;\psi_{free}|e^{i\vec{k}\cdot\hat{\vec{r}}}|A^+;\psi_{bound}\rangle$$

$$= \vec{\varepsilon}_{k\lambda}\cdot\vec{p}_e\langle\psi_{free}|e^{i\vec{k}\cdot\vec{r}}|\psi_{bound}\rangle\underbrace{\langle A^+|A^+\rangle}_{=1}$$

$$\langle \psi_{free} | e^{i\vec{k}\cdot\vec{r}} | \psi_{bound} \rangle = \langle \psi_{free} | \underbrace{\,}_{\hat{1}_r} e^{i\vec{k}\cdot\hat{\vec{r}}} | n l m \rangle$$

$$= \int d^3r \, \underbrace{\langle \psi_{free} | \vec{r}}\rangle\langle \vec{r} | e^{i\vec{k}\cdot\hat{\vec{r}}} | n l m \rangle$$

$$= \int d^3r \, \psi^*_{free}(\vec{r}) \, \psi_{nlm}(\vec{r}) \, e^{i\vec{k}\cdot\vec{r}}$$

$$\Rightarrow \quad c_{k\lambda} = (\vec{\varepsilon}_{k\lambda} \cdot \vec{p}_e) \int d^3r \, \psi^*_{free}(\vec{r}) \, \psi_{nlm}(\vec{r}) \, e^{i\vec{k}\cdot\vec{r}}$$

$\Rightarrow$ (3) :

$$V_{fi} = \frac{-e}{m}\left(\frac{\hbar}{2\varepsilon_0 V \omega_k}\right)^{1/2} \int d^3r \, \underset{\text{final}}{\psi^*_{free}(\vec{r})} \, \underset{\text{initial}}{\psi_{nlm}(\vec{r})} \, e^{i\vec{k}\cdot\vec{r}} (\vec{\varepsilon}_{k\lambda} \cdot \vec{p}_e) \, e^{-i\omega_k t}$$

Let $\psi_{nlm}(\vec{r}) = \psi_{100}(\vec{r})$ i.e. atom is initially in grnd state
hydrogenic

initial :

$$\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-r/a_0} \quad // \quad \text{initial} \qquad (4)$$

final :

$$\psi_{free}(\vec{r}) = \frac{e^{i\vec{p}_e\cdot\vec{r}/\hbar}}{\sqrt{V}} \quad // \quad \text{final free electron}$$

↳ assume $E_{photon} = \hbar\omega \gg E_{ionization}$

$$\Rightarrow \quad |V_{fi}|^2 = \left(\frac{e}{m}\right)^2 \frac{\hbar}{2\varepsilon_0 V \omega_k} \frac{Z^3}{\pi a_0^3} (\vec{\varepsilon}_{k\lambda} \cdot \vec{p}_e)^2 \left| \int d^3r \, e^{-Zr/a_0} e^{i(\vec{k} - \vec{p}_e/\hbar)\cdot\vec{r}} \right|^2 \qquad (5)$$

$$\underset{(2)}{\Rightarrow} \quad d\Gamma_{fi} = \frac{2\pi}{\hbar}\left(\frac{e}{m}\right)^2 \frac{\hbar Z^3}{2\varepsilon_0 \pi a_0^3} \frac{m_e p_e \, d\epsilon_e}{(2\pi\hbar)^3 V\omega} (\vec{\varepsilon}_{k\lambda} \cdot \vec{p}_e)^2 \cdot \left| \int d^3r \, e^{-Zr/a_0} e^{i(\vec{k} - \vec{p}_e/\hbar)\cdot\vec{r}} \right|^2 \qquad (5')$$

$$\cdot \, d\Omega_e \, \delta\left[E_{A^+} + E_e - (E_A + \hbar\omega)\right]$$

$$d\Gamma'_{fi} = \frac{2\pi}{\hbar} d\Omega_e \int d\epsilon_e |V_{fi}|^2 \rho(\epsilon_e)\, \delta\left(E_e + E_{A+} - E_A - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar} d\Omega_e \left\{ |V_{fi}|^2 \rho(E_e) \right\}_{E_e = p_e^2/2m_e \,\stackrel{!}{=}\, -(\overbrace{E_{A+} - E_A}^{\epsilon_{\text{ionization}} = \epsilon_{\text{binding}}} - \hbar\omega)}$$

$$= \frac{2\pi}{\hbar} d\Omega_e \frac{\hbar (e/m_e)^2}{2\varepsilon_0 \pi a_0^3} \frac{m_e Z^3}{(2\pi\hbar)^3 \omega V} \left\{ p_e \left(\vec{\varepsilon}\cdot\vec{p}_e\right)^2 |\dot{I}|^2 \right\}_{p_e \stackrel{!}{=} \sqrt{2m_e(\hbar\omega - E_{\text{ioniz}})}}$$

$$= d\Omega_e \frac{e^2/m_e}{\varepsilon_0 a_0^3 V} \frac{Z^3}{(2\pi\hbar)^3 \omega} \left\{ p_e \left(\vec{\varepsilon}\cdot\vec{p}_e\right)^2 |\dot{I}|^2 \right\} \quad (6)$$

where $\dot{I} = \int d^3r\, e^{-Zr/a_0} e^{i(\vec{k} - \vec{p}_e/\hbar)\cdot\vec{r}}$

The dependence on the arbitrary "interaction volume" V is reconciled by resorting to the <u>differential cross-section</u> for the PE effect:

$$\left(\frac{d\sigma}{d\Omega_e}\right)_{\hbar\omega \gg E_{\text{ioniz}}} \simeq \frac{V}{c} \frac{d\Gamma'_{fi}}{d\Omega_e}$$

Total cross-section:

$$\sigma = \int_{\text{Det}} \left(\frac{d\sigma}{d\Omega_e}\right) d\Omega_e$$

$$= \frac{e^2/m_e}{c\varepsilon_0 a_0^3} \frac{Z^3}{(2\pi\hbar)^3\omega} \left\{ p_e \left(\vec{\varepsilon}\cdot\vec{p}_e\right)^2 |\dot{I}|^2 \right\}_{p_e \stackrel{!}{=} \sqrt{2m_e(\hbar\omega - E_{\text{ioniz}})}} \quad (7)$$

$$= \cdots = 32 Z^5 a_0^2 \left\{ \left(\frac{p_e c}{\hbar\omega}\right) \left(\frac{\vec{\varepsilon}\cdot\vec{p}_e}{m_e c}\right)^2 \frac{1}{(Z^2 + a_0^2 q^2)^4} \right\}_{p_e \stackrel{!}{=} \sqrt{}}$$

~~fr~~

For <u>hydrogenic</u> atoms:

$$\boxed{\left(\frac{d\sigma}{d\Omega_e}\right) = 32 Z^5 a_0^2 \left\{ \left(\frac{p_e c}{\hbar\omega}\right) \left(\frac{\vec{\varepsilon}\cdot\vec{p}_e}{m_e c}\right)^2 \frac{1}{(Z^2 + a_0^2 q^2)^4} \right\}_{p_e \stackrel{!}{=} \sqrt{}} \quad (8)}$$

For (8), I used the following:

$$a_0 = \frac{\hbar}{Z\alpha m_e c}, \quad \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}, \quad \dot{I} = \frac{8\pi a_0^3 Z}{(Z^2 + a_0^2 q^2)^2}$$

$q^2 \equiv |\vec{k} - \vec{p}_e/\hbar|^2$

(see next page)

Evaluate the integral in (5)

- Let $\vec{k} - \vec{p}_e/\hbar \equiv \vec{q}$; $\beta \equiv Z/a_0$

$$I \equiv \int d^3r\, e^{-r/a_0} e^{i\vec{q}\cdot\vec{r}} = \int d^3r\, e^{-\beta r} e^{i\vec{q}\cdot\vec{r}}$$

$$= -\frac{d}{d\beta}\left(\int d^3r\, \frac{e^{-\beta r}}{r} e^{i\vec{q}\cdot\vec{r}}\right) = -\frac{d}{d\beta}\left(\frac{4\pi}{\beta^2+q^2}\right) = \frac{8\pi\beta}{(\beta^2+q^2)^2}$$

$$= \frac{8\pi}{a_0}\,\frac{Z}{\left(\frac{Z^2}{a_0^2}+\left|\vec{k}-\vec{p}_e/\hbar\right|^2\right)^2} = \frac{8\pi a_0^3 Z}{\left(Z^2+a_0^2\left|\vec{k}-\vec{p}_e/\hbar\right|^2\right)^2} \qquad (9)$$

$$q^2 = \left|\vec{k}-\vec{p}_e/\hbar\right|^2 = \frac{\left|\hbar\vec{k}-\vec{p}_e\right|^2}{\hbar^2} = \frac{1}{\hbar^2}\left[\hbar^2k^2 + p_e^2 - 2\hbar\vec{k}\cdot\vec{p}_e\right]$$

$$= \frac{\hbar^2k^2 + p_e^2 - 2\hbar k\, p_e\cos\theta}{\hbar^2} \equiv \frac{p_\gamma^2 + p_e^2 - 2p_\gamma p_e\cos\theta}{\hbar^2}$$

$$= \cancel{\frac{p_\gamma^2}{\hbar^2}\left(1 + \frac{p_e^2}{p_\gamma^2} - 2\frac{p_e}{p_\gamma}\cos\theta\right)}$$

Photon momentum: $\hbar k \equiv p_\gamma = \frac{\hbar\omega}{c}$ (a)

($\omega_k \equiv \omega$, dropping k)

Energy conservation:

$E_{photon} = E_{ioniz} + E_{free}$

$\hbar\omega$; Binding energy (13.6 eV for H atom) ; $\frac{p_e^2}{2m_e}$

$\hbar\omega = \epsilon_{ioniz} + p_e^2/2m \simeq p_e^2/2m_e$ (b)

(assume $\hbar\omega \gg \epsilon_{ioniz}$)

(a), (b) : $\boxed{p_\gamma \simeq \frac{p_e^2}{2m_e c}}$ (c)

(c) $\Rightarrow$

$$\simeq \frac{1}{\hbar^2}\left(\underbrace{\frac{p_e^4}{4m_e^2c^2}}_{\to 0} + p_e^2 - 2\frac{p_e^3}{2m_e c}\cos\theta\right)$$

for $p_e \ll m_e c$ i.e. non-relativistic electrons

($p_e = m_e v_e$)

$$\simeq \frac{1}{\hbar^2}\left(p_e^2 - \frac{p_e^3}{m_e c}\cos\theta\right)$$

$$= \left(\frac{p_e}{\hbar}\right)^2\left(1 - \frac{p_e}{m_e c}\cos\theta\right)$$

$$= \left(\frac{p_e}{\hbar}\right)^2\left(1 - \frac{v_e}{c}\cos\theta\right) \qquad (10)$$

(9), (10) $\Rightarrow$

$$I = \frac{8\pi a_0^3 Z}{\left[Z^2 + \left(a_0\frac{p_e}{\hbar}\right)^2\left(1 - \frac{v_e}{c}\cos\theta\right)\right]^2} \qquad (7')$$

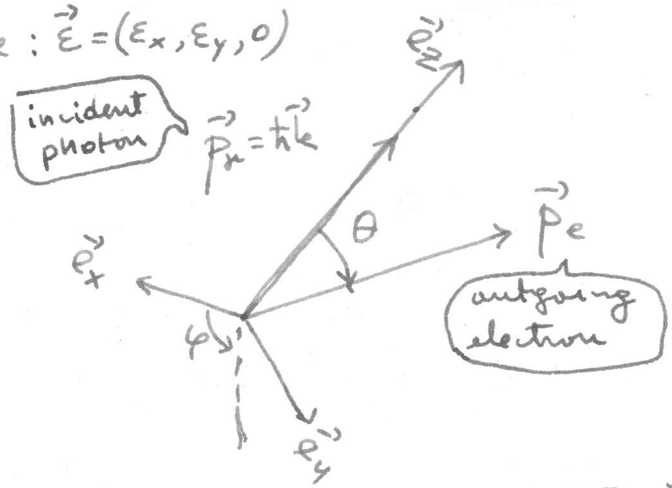
Evaluate "$\vec{\varepsilon}_{\vec{k}\lambda} \cdot \vec{p}_e$" from (5):

(Drop "$\vec{k}\lambda$" subscript $\vec{\varepsilon}_{k\lambda} \equiv \vec{\varepsilon}$). Let photon direction be $\vec{e}_z$ i.e. $\vec{k} = k\,\vec{e}_z$.

Then polarization vector $\vec{\varepsilon}$ is in xy plane: $\vec{\varepsilon} = (\varepsilon_x, \varepsilon_y, 0)$

$$\vec{p}_e = p_e(\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta)$$

$$\underline{\vec{\varepsilon}\cdot\vec{p}_e = \varepsilon_x \sin\theta\cos\varphi + \varepsilon_y \sin\theta\sin\varphi}$$



* Linearly polarized incident photon:

$$\vec{\varepsilon} = \vec{e}_x \Rightarrow \vec{\varepsilon}\cdot\vec{p}_e = (\sin\theta\cos\varphi)\,p_e$$

$$|V_{fi}|^2 = \frac{(e/m)^2}{\pi a_0^3 V}\frac{\hbar}{2\varepsilon_0\omega}(\sin^2\theta\cos^2\varphi)\left[\frac{8\pi a_0^3 p_e^2 Z}{\left[Z^2 + \left(a_0\frac{p_e}{\hbar}\right)^2\left(1-\frac{v_e}{c}\cos\theta\right)\right]^2}\right] \qquad \left(p_e = \sqrt{2m_e E_e}\right)$$

$$\Rightarrow \left[\frac{d\sigma}{d\Omega_e} = \frac{V}{c}\frac{d\Gamma'_{fi}}{d\Omega_e} = \frac{2\pi}{\hbar}\frac{V}{c}\left\{|V_{fi}|^2\rho(p_e^2/2m)\right\}_{p_e \doteq \sqrt{2m(\hbar\omega - E_{ioniz})}}\right.$$

$$= \dots$$

* Circularly polarized incident photon (i.e. unpolarized):

$$\vec{\varepsilon} = \vec{\varepsilon}_1 = 1/\sqrt{2}(\vec{e}_x + i\vec{e}_y) \Rightarrow \vec{\varepsilon}\cdot\vec{p}_e = 1/\sqrt{2}(\sin\theta\cos\varphi + i\sin\theta\sin\varphi)p_e$$

$$= \frac{\sin\theta}{\sqrt{2}}(\cos\varphi + i\sin\varphi)p_e$$

$$= \frac{p_e}{\sqrt{2}}\sin\theta\, e^{i\varphi}$$

$$|V_{fi}|^2 = \frac{(e/m)^2\hbar}{\pi a_0^3 V\varepsilon_0\omega}\frac{p_e^2\sin^2\theta}{4}|I|^2$$

$$\Rightarrow \left[\frac{d\sigma}{d\Omega_e} = \frac{V}{c}\frac{d\Gamma'_{fi}}{d\Omega_e} \simeq \dots Z^7\, 2\sqrt{2}\,\alpha^8 \frac{a_0^2}{Z^2}\left(\frac{m_e c^2}{E_e}\right)^{7/2}\frac{\sin^2\theta}{\left(1-\frac{v_e}{c}\cos\theta\right)^4}\right.$$

Premise:

$$\underbrace{\hbar\omega \gg E_{ioniz}\ (= E_{A^+} - E_A)}\ \Longleftrightarrow\ \underbrace{E_e \gg \alpha^2\frac{m_e c^2}{2}}$$