# Photoelectric effect <br> Masatsugu Sei Suzuki <br> Department of Physics, SUNY at Binghamton 

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## 1. Sinusoidal perturbation

We consider the case of interaction between photon and electron. The perturbation can be given by

$$
\begin{aligned}
\hat{H}_{1} & \left.=\frac{e}{m c} \right\rvert\, \boldsymbol{A}_{0}\left[e^{i(\boldsymbol{k} \cdot \boldsymbol{r}-\omega t)}+e^{-i(\boldsymbol{k} \cdot \boldsymbol{r}-\omega t)}\right](\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}) \\
& =\hat{V}^{+} e^{-i \omega t}+\hat{V} e^{i \omega t}
\end{aligned}
$$

with

$$
\hat{V}^{+}=\frac{e}{m c}\left|\boldsymbol{A}_{0}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}}(\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}) .
$$

where $\boldsymbol{A}_{0}$ is the vector potential. The matrix element is given by

$$
\left\langle\varphi_{f}\right| \hat{V}^{+}\left|\varphi_{i}\right\rangle=\left\langle\varphi_{i}\right| \hat{V}\left|\varphi_{f}\right\rangle^{*}=\frac{e}{m c}\left|\boldsymbol{A}_{0}\right|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot r}(\varepsilon \cdot \hat{\boldsymbol{p}})\left|\varphi_{i}\right\rangle
$$

In conclusion, the transition probability is proportional to

$$
\left.\frac{e^{2}}{m^{2} c^{2}}\left|\boldsymbol{A}_{0}\right|^{2}\left|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}}(\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}})\right| \varphi_{i}\right\rangle\left.\right|^{2}
$$

The absorption cross section $\sigma_{\text {abs }}$ is

$$
\begin{aligned}
\sigma_{\mathrm{abs}} & =\frac{\left.\hbar \omega \frac{2 \pi}{\hbar} \frac{e^{2}}{m^{2} c^{2}}\left|\boldsymbol{A}_{0}\right|^{2}\left|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| \varphi_{i}\right\rangle\left.\right|^{2} \delta\left(E_{f}-E_{i}-\hbar \omega\right)}{\frac{1}{2 \pi} \frac{\omega^{2}}{c}\left|\boldsymbol{A}_{0}\right|^{2}} \\
& \left.=\frac{4 \pi^{2} \hbar}{m^{2} \omega}\left(\frac{e^{2}}{\hbar c}\right)\left|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| \varphi_{i}\right\rangle\left.\right|^{2} \delta\left(E_{f}-E_{i}-\hbar \omega\right)
\end{aligned}
$$

Note that the energy flux (energy per area per unit time) is given by

$$
c u=\frac{1}{2 \pi} \frac{\omega^{2}}{c}\left|\boldsymbol{A}_{0}\right|^{2}
$$

The fine structure constant is defined by

$$
\alpha=\frac{e^{2}}{\hbar c} .
$$

## 2. Photoelectric effect

In the photoelectric effect, electrons are emitted from metals when they absorb energy from light. Electrons emitted in this manner may be called photoelectrons.


Fig. Electron potential energy across the metal surface. An electron with the highest energy in the metal absorps a photon of energy $h f$. Conservation of energy requires that its kinetic energy after leaving the surface be $h_{\mathrm{f}}-. \phi$.

## ((Note))

The energy conservation:

$$
\hbar \omega=\frac{1}{2} m v_{f}^{2}+E_{B} \frac{1}{2} m c^{2}(Z \alpha)^{2}
$$

where $\hbar \omega$ is the photon energy, $\frac{1}{2} m v_{f}{ }^{2}$ is the kinetic energy of free electron, and $E_{B}=\frac{1}{2} m c^{2}(Z \alpha)^{2}$ is the bound energy.

Ejection of an electron when an atom us placed in the radiation field.
$|i\rangle$ : atomic (bound) state
$|n\rangle:$ continum state $(E>0)$

Plane-wave state $\left|\boldsymbol{k}_{f}\right\rangle$, an approximation that is valid if the final electron is not too slow.

$$
\left\langle\boldsymbol{r} \mid \boldsymbol{k}_{f}\right\rangle=\frac{1}{L^{3 / 2}} e^{i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}
$$

with the periodic boundary condition

$$
\begin{aligned}
k_{x} & =\frac{2 \pi}{L} n_{x}, k_{y}=\frac{2 \pi}{L} n_{y}, k_{z}=\frac{2 \pi}{L} n_{z} . \\
E & =\frac{\hbar^{2}}{2 m}\left(k_{x}^{2}+k_{y}^{2}+k_{z}^{2}\right) \\
& =\frac{\hbar^{2}}{2 m}\left(\frac{2 \pi}{L}\right)^{2}\left(n_{x}^{2}+n_{y}^{2}+n_{z}^{2}\right)=\frac{\hbar^{2}}{2 m}\left(\frac{2 \pi}{L}\right)^{2} n^{2}
\end{aligned}
$$

where

$$
\begin{aligned}
& \left(\begin{array}{l}
n_{x}=0, \pm 1, \pm 2, \cdots \\
n_{y}=0, \pm 1, \pm 2, \cdots \\
n_{z}=0, \pm 1, \pm 2, \cdots
\end{array}\right. \\
& n^{2}=n_{x}^{2}+n_{y}^{2}+n_{z}^{2}=\left(\frac{L}{2 \pi}\right)^{2} k_{f}^{2}
\end{aligned}
$$



Fig. Density of states in the 3D $\boldsymbol{k}$-space. There is one state per $(2 \pi / L)^{3}$.
The number of states for $k_{f} \sim k_{f}+d k_{f}$ and solid angle element $d \Omega$

$$
\begin{aligned}
& \begin{aligned}
& \frac{k_{f}^{2} d k_{f} d \Omega}{\left(\frac{L}{2 \pi}\right)^{3}}=\left(\frac{L}{2 \pi}\right)^{3} k_{f}^{2} d k_{f} d \Omega \\
&=\left(\frac{L}{2 \pi}\right)^{3} \frac{m k_{f}}{\hbar^{2}} d E d \Omega \\
&\left(\because d E=\frac{\hbar^{2}}{2 m} 2 k_{f} d k_{f}=\frac{\hbar^{2}}{m} k_{f} d k_{f}\right)
\end{aligned}
\end{aligned}
$$

## 3. Fermi's golden rule

Using the Fermi’s golden rule, we have the differential cross section as

$$
\left.d \sigma=\frac{4 \pi^{2} \hbar}{m^{2} \omega}\left(\frac{e^{2}}{\hbar c}\right)\left|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| \varphi_{i}\right\rangle\left.\right|^{2} \frac{m k_{f}}{\hbar^{2}} \frac{L^{3} d \Omega}{(2 \pi)^{3}}
$$

or

$$
\begin{aligned}
\frac{d \sigma}{d \Omega} & \left.=\frac{4 \pi^{2} \alpha \hbar}{m^{2} \omega}\left|\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| i\right\rangle\left.\right|^{2} \frac{m k_{f}}{\hbar^{2}} \frac{L^{3}}{(2 \pi)^{3}} \\
& \left.=\frac{4 \pi^{2} \alpha k_{f}}{m \hbar \omega}\left|\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| i\right\rangle\left.\right|^{2} \frac{L^{3}}{(2 \pi)^{3}}
\end{aligned}
$$

where $\alpha$ is the fine structure constant,

$$
\alpha=\frac{e^{2}}{\hbar c}
$$

To be specific, let us consider the ejection of a $K$-shell (the innermost shell) electron caused by absorption of light. $|i\rangle$ : essentially the same as the ground state hydrogen atom wave function except that the Bohr radius $a_{0}$ is replaced by $a_{0} / Z$;

$$
\langle\boldsymbol{r} \mid i\rangle=R_{10}(r) Y_{0}^{0}(\theta, \phi)=\frac{2}{\sqrt{4 \pi}} e^{-Z r / a_{0}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}
$$

The matrix element is given by

$$
\begin{aligned}
\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}|i\rangle & =\boldsymbol{\varepsilon} \cdot \int d^{3} \boldsymbol{r} \frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}} e^{i \boldsymbol{k} \cdot \boldsymbol{r}}\left(\frac{\hbar}{i} \nabla\right)\left[\frac{2}{\sqrt{4 \pi}} e^{-Z r / a_{0}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}\right] \\
& =(i \hbar) \int d^{3} \boldsymbol{r} \boldsymbol{\varepsilon} \cdot \nabla\left[\frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}} e^{i \boldsymbol{k} \cdot \boldsymbol{r}}\right] \frac{2}{\sqrt{4 \pi}} e^{-Z r / a_{0}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}
\end{aligned}
$$

Here note that

$$
\begin{aligned}
I_{1} & =\boldsymbol{\varepsilon} \cdot \nabla\left[\frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}} e^{i \boldsymbol{k} \cdot \boldsymbol{r}}\right] \\
& =\boldsymbol{\varepsilon} \cdot \nabla\left(\frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}}\right) e^{i \boldsymbol{k} \cdot \boldsymbol{r}}+\boldsymbol{\varepsilon} \cdot \nabla\left(e^{i \boldsymbol{k} \cdot \boldsymbol{r}}\right) \frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}}
\end{aligned}
$$

We have

$$
\boldsymbol{\varepsilon} \cdot\left[\nabla\left(e^{i k \cdot r}\right)\right]=0
$$

because

$$
\varepsilon \cdot \boldsymbol{k}=0
$$

Using

$$
\nabla\left(e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}\right)=e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}\left(-i \boldsymbol{k}_{f}\right)
$$

we get

$$
I_{1}=-i \boldsymbol{k}_{f} \cdot \varepsilon \frac{e^{-i \boldsymbol{k}_{f} \cdot \boldsymbol{r}}}{L^{3 / 2}} e^{i \boldsymbol{k} \cdot \boldsymbol{r}}=-i \boldsymbol{k}_{f} \cdot \varepsilon \frac{1}{L^{3 / 2}} e^{-i \boldsymbol{q} \cdot \boldsymbol{r}}
$$

with

$$
\boldsymbol{q}=\boldsymbol{k}_{\mathrm{f}}-\boldsymbol{k}
$$

All we need to do is to take the Fourier transform of the atomic wave function.

$$
\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}|i\rangle=i \hbar\left(-i \boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}\right) \frac{1}{L^{3 / 2}} \int d^{3} \boldsymbol{r} e^{-i \boldsymbol{q} \cdot \boldsymbol{r}}\left[\frac{2}{\sqrt{4 \pi}} e^{-Z r / a_{0}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}\right]
$$

Here we calculate

$$
\begin{aligned}
I_{2} & \equiv \int d^{3} \boldsymbol{r} e^{-i q \cdot \cdot}\left[\frac{2}{\sqrt{4 \pi}} e^{-Z r / a_{0}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}\right] \\
& =\frac{2}{\sqrt{4 \pi}}\left(\frac{Z}{a_{0}}\right)^{3 / 2} \int_{0}^{\infty} 2 \pi r^{2} d r \int_{0}^{\pi} \sin \theta d \theta e^{-i q r \cos \theta} e^{-Z r / a_{0}}
\end{aligned}
$$

Using the Mathematica, we get

$$
\int_{0}^{\infty} 2 \pi r^{2} d r \int_{0}^{\pi} \sin \theta d \theta e^{-i q r \cos \theta} e^{-Z r / a_{0}}=\frac{8 \pi \frac{Z}{a_{0}}}{\left(q^{2}+\frac{Z^{2}}{a_{0}{ }^{2}}\right)^{2}}
$$

((Mathematica))

$$
\begin{aligned}
& \text { Clear ["Global`*"]; } \\
& \text { f1 }=2 \pi r^{2} \operatorname{Sin}[\theta] \operatorname{Exp}[-\dot{\text { i } q} \operatorname{r} \operatorname{Cos}[\theta]] \operatorname{Exp}\left[-\frac{\mathrm{Zr}}{\mathrm{a} 0}\right] ; \\
& \text { Integrate[Integrate[f1, }\{\theta, 0, \pi\}],\{r, 0, \infty\}] / / \\
& \text { Simplify }\left[\#,\left\{\operatorname{Abs}[\operatorname{Im}[q]] \leq \operatorname{Re}\left[\frac{Z}{a 0}\right] \& \& \operatorname{Re}\left[\frac{\mathrm{Z}}{\mathrm{a} 0}\right]>0\right\}\right] \& \\
& \frac{8 \mathrm{a} 0^{3} \pi \mathrm{Z}}{\left(\mathrm{a} 0^{2} \mathrm{q}^{2}+\mathrm{Z}^{2}\right)^{2}}
\end{aligned}
$$

Thus we get

$$
\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}|i\rangle=\hbar\left(\boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}\right) \frac{1}{L^{3 / 2}} \frac{16 \pi i}{\sqrt{4 \pi}}\left(\frac{Z}{a_{0}}\right)^{5 / 2} \frac{1}{\left[\left(\frac{Z}{a_{0}}\right)^{2}+q^{2}\right]^{2}}
$$

Since

$$
\left.\frac{d \sigma}{d \Omega}=\frac{4 \pi^{2} \alpha k_{f}}{m \hbar \omega}\left|\left\langle\boldsymbol{k}_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| i\right\rangle\left.\right|^{2} \frac{L^{3}}{(2 \pi)^{3}}
$$

the differential cross section is obtained as

$$
\begin{aligned}
\frac{d \sigma}{d \Omega} & =\frac{4 \pi^{2} \alpha k_{f}}{m \hbar \omega} \frac{L^{3}}{(2 \pi)^{3}} \hbar^{2}\left(\boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}\right)^{2} \frac{1}{L^{3}} \frac{16^{2} \pi^{2}}{4 \pi}\left(\frac{Z}{a_{0}}\right)^{5} \frac{1}{\left[\left(\frac{Z}{a_{0}}\right)^{2}+q^{2}\right]^{4}} \\
& =32 e^{2} k_{f} \frac{\left(\boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}\right)^{2}}{m c \omega}\left(\frac{Z}{a_{0}}\right)^{5} \frac{1}{\left[\left(\frac{Z}{a_{0}}\right)^{2}+q^{2}\right]^{4}}
\end{aligned}
$$

where

$$
q^{2}=k_{f}^{2}-2 k_{f} \frac{\omega}{c} \cos \theta+\frac{\omega^{2}}{c^{2}}
$$

and

$$
\boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}=k_{f} \sin \theta \cos \phi
$$



Fig. Experimental configuration for the photoelectric effect. $\varepsilon$ is the polarization vector. $\boldsymbol{n}$ is the unit vector of incident photon. $\boldsymbol{k}_{\mathrm{f}}$ is the wavevector of the outgoing electron.

## 2. Energy conservation in the photoelectric effect

Energy is conserved in the system,

$$
\begin{aligned}
& \hbar c k=E_{B}+\frac{\hbar^{2} k_{f}^{2}}{2 m} \\
& q^{2}=k^{2}+k_{f}^{2}-2 k k_{f} \cos \theta
\end{aligned}
$$

We use the following approximation, for simplicity,

$$
\hbar c k \gg E_{B} \quad \text { or } \quad \frac{2 m c k}{\hbar} \gg\left(\frac{Z}{a_{0}}\right)^{2}
$$

$$
\begin{aligned}
& \hbar c k \approx \frac{\hbar^{2} k_{f}^{2}}{2 m} \gg E_{B}=\frac{\hbar^{2}}{2 m}\left(\frac{Z}{a_{0}}\right)^{2} \\
& k_{f}^{2} \gg\left(\frac{Z}{a_{0}}\right)^{2}
\end{aligned}
$$

where the binding energy is given by

$$
E_{B}=\frac{1}{2} m c^{2}(Z \alpha)^{2}=\frac{1}{2} m c^{2} Z^{2} \frac{\hbar^{2}}{m^{2} c^{2} a_{0}{ }^{2}}=\frac{\hbar^{2}}{2 m}\left(\frac{Z}{a_{0}}\right)^{2}
$$

$\alpha$ is the fine structure constant:

$$
\alpha=\frac{e^{2}}{\hbar c}=\frac{\hbar^{2}}{m a_{B}} \frac{1}{\hbar c}=\frac{\hbar}{m c a_{B}}
$$

The Bohr radius is

$$
a_{B}=\frac{\hbar^{2}}{m e^{2}}
$$

In nonrelativistic theory:

$$
E_{e}^{2}=m^{2} c^{4}+c^{2} p_{e}^{2}, \quad m^{2} c^{2} \gg p_{e}^{2}=\hbar^{2} k_{f}^{2}=2 m c k \hbar^{2}
$$

or

$$
m c^{2} \gg 2 c \hbar k
$$

Since

$$
k_{f}^{2}=\frac{p_{e}^{2}}{\hbar^{2}}=\frac{2 m \hbar c k}{\hbar^{2}}=\frac{2 m c k}{\hbar}=\frac{2 m c^{2}}{\hbar c k} k^{2} \gg 4 k^{2}>k^{2}
$$

and

$$
k_{f}^{2} \gg\left(\frac{Z}{a_{B}}\right)^{2}
$$

we get

$$
\begin{aligned}
q^{2}+\left(\frac{Z}{a_{B}}\right)^{2} & \approx\left(\frac{Z}{a_{B}}\right)^{2}+k^{2}+k_{f}^{2}-2 k k_{f} \cos \theta \\
& \approx k_{f}^{2}-2 k k_{f} \cos \theta \\
& =\frac{2 m c k}{\hbar}-2 k k_{f} \cos \theta \\
& =\frac{2 m c k}{\hbar}\left(1-\frac{2 \hbar k k_{f}}{2 m c k} \cos \theta\right) \\
& =\frac{2 m c k}{\hbar}\left(1-\frac{\hbar k_{f}}{m c} \cos \theta\right) \\
& =\frac{2 m c k}{\hbar}\left(1-\frac{v_{f}}{c} \cos \theta\right)
\end{aligned}
$$

Then we have

$$
\frac{d \sigma}{d \Omega} \approx \frac{32 e^{2} k_{f}^{3}}{m c \omega}\left(\frac{Z}{a_{B}}\right)^{5}\left(\frac{\hbar}{2 m c k}\right)^{4} \frac{\sin \theta^{2} \cos ^{2} \phi}{\left(1-\frac{v_{f}}{c} \cos \theta\right)^{4}}
$$

When $\phi=0$ (in the $z-x$ plane), we put

$$
f(\theta)=\frac{\sin \theta^{2}}{\left(1-\frac{v_{f}}{c} \cos \theta\right)^{4}}
$$

The derivative of $f(\theta)$ with respect to $\theta$ is

$$
f^{\prime}(\theta)=\frac{\sin \theta}{\left(1-\frac{v_{f}}{c} \cos \theta\right)^{5}}\left[2 \cos \theta+\frac{v_{f}}{c}(-3+\cos (2 \theta)]\right.
$$

In the limit of small $\frac{v_{f}}{c}, f(\theta)$ has a local maximum when

$$
\cos \theta=\frac{\sqrt{1+8 \frac{v_{f}^{2}}{c^{2}}}-1}{2 \frac{v_{f}}{c}} \approx 2 \frac{v_{f}}{c}
$$

or

$$
\theta=\arccos \left[2 \frac{v_{f}}{c}\right]
$$

When $\frac{v_{f}}{c} \ll 1, \cos \theta=0$, or $\theta=\pi / 2$. As $\frac{v_{f}}{c}$ increases, $\theta$ decreases.

## 3. Angular dependence of $\frac{d \sigma}{d \Omega}$

((Mathematica)) We make a plot of a part of $\frac{d \sigma}{d \Omega}$ using the SphericalPlot3D
The cross section vanishes in the forward direction. This is a consequence of the fact that photons are transversely polarized. The matrix element is proportional to $\left(\boldsymbol{k}_{f} \cdot \boldsymbol{\varepsilon}\right)^{2}$. When $\boldsymbol{k}_{\mathrm{f}}$ is parallel to the photon momentum $\boldsymbol{k}=\boldsymbol{k} \boldsymbol{n}$, this factor vanishes.


Fig. $\quad v / c=0$. Angular distribution of photoelectric electrons. The green line (the direction of photon). The red line (the direction of polarization vector for photon).


Fig. $\quad$ The case of $v / c=0.6$.


Fig. The case of $v / c=0.8$.


Fig. The case of $v / c=0.95$.

## REFERENCES

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Eugen Merzbacher, Quantum Mechanics, third edition (John Wiley \& Sons, New York, 1998).

## APPENDIX

## A1. Free electron gas in three dimensions

We consider the Schrödinger equation of an electron confined to a cube of edge $L$.

$$
H \psi_{\mathbf{k}}=\frac{\mathbf{p}^{2}}{2 m} \psi_{\mathbf{k}}=-\frac{\hbar^{2}}{2 m} \nabla^{2} \psi_{\mathbf{k}}=\varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}
$$

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions.
Boundary condition (Born-von Karman boundary conditions).

$$
\begin{aligned}
& \psi_{\mathbf{k}}(x+L, y, z)=\psi_{\mathbf{k}}(x, y, z), \\
& \psi_{\mathbf{k}}(x, y+L, z)=\psi_{\mathbf{k}}(x, y, z), \\
& \psi_{\mathbf{k}}(x, y, z+L)=\psi_{\mathbf{k}}(x, y, z) .
\end{aligned}
$$

The wavefunctions are of the form of a traveling plane wave.

$$
\psi_{\mathbf{k}}(\mathbf{r})=e^{i \mathbf{k} \cdot \mathbf{r}}
$$

with

$$
\begin{aligned}
& k_{\mathrm{x}}=(2 \pi / L) n_{\mathrm{x}},\left(n_{\mathrm{x}}=0, \pm 1, \pm 2, \pm 3, \ldots \ldots\right), \\
& k_{\mathrm{y}}=(2 \pi / L) n_{\mathrm{y}},\left(n_{\mathrm{y}}=0, \pm 1, \pm 2, \pm 3, \ldots \ldots .\right), \\
& k_{\mathrm{z}}=(2 \pi / L) n_{\mathrm{z}},\left(n_{\mathrm{z}}=0, \pm 1, \pm 2, \pm 3, \ldots \ldots\right) .
\end{aligned}
$$

The components of the wavevector $\boldsymbol{k}$ are the quantum numbers, along with the quantum number $m_{\mathrm{s}}$ of the spin direction. The energy eigenvalue is

$$
\varepsilon(\mathbf{k})=\frac{\hbar^{2}}{2 m}\left(k_{x}^{2}+k_{y}^{2}+k_{z}^{2}\right)=\frac{\hbar^{2}}{2 m} \mathbf{k}^{2} .
$$

Here

$$
\mathbf{p} \psi_{k}(\mathbf{r})=\frac{\hbar}{i} \nabla_{\mathbf{k}} \psi_{k}(\mathbf{r})=\hbar \mathbf{k} \psi_{k}(\mathbf{r})
$$

So that the plane wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenfunction of $\boldsymbol{p}$ with the eigenvalue $\hbar \mathbf{k}$. The ground state of a system of $N$ electrons, the occupied orbitals are represented as a point inside a sphere in $\boldsymbol{k}$-space.

Because we assume that the electrons are noninteracting, we can build up the N electron ground state by placing electrons into the allowed one-electron levels we have just found.

## A2. The Pauli's exclusion principle

The one-electron levels are specified by the wavevectors $\boldsymbol{k}$ and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\pm \hbar / 2$. Therefore associated with each allowed wave vector k are two levels:

$$
|\boldsymbol{k}, \uparrow\rangle,|\boldsymbol{k}, \downarrow\rangle .
$$

In building up the $N$-electron ground state, we begin by placing two electrons in the oneelectron level $k=0$, which has the lowest possible one-electron energy $\varepsilon=0$. We have

$$
N=2 \frac{L^{3}}{(2 \pi)^{3}} \frac{4 \pi}{3} k_{F}^{3}=\frac{V}{3 \pi^{2}} k_{F}^{3},
$$

## A3 Density of states

There is one state per volume of $\boldsymbol{k}$-space $(2 \pi / L)^{3}$. We consider the number of oneelectron levels in the energy range from $\varepsilon$ to $\varepsilon+\mathrm{d} \varepsilon, D(\varepsilon) \mathrm{d} \varepsilon$

$$
D(\varepsilon) d \varepsilon=2 \frac{L^{3}}{(2 \pi)^{3}} 4 \pi k^{2} d k
$$

where $D(\varepsilon)$ is called a density of states. Since $k=\left(2 m / \hbar^{2}\right)^{1 / 2} \sqrt{\varepsilon}$, we have $d k=\left(2 m / \hbar^{2}\right)^{1 / 2} d \varepsilon /(2 \sqrt{\varepsilon})$. Then we get the density of states

$$
\begin{equation*}
D(\varepsilon)=\frac{V}{2 \pi^{2}}\left(\frac{2 m}{\hbar^{2}}\right)^{3 / 2} \sqrt{\varepsilon} \tag{14}
\end{equation*}
$$

## B. Pythagorean relationship (relativistic dynamics)

Relativistic dynamics

$$
\frac{E^{2}}{c^{2}}=m^{2} c^{2}+\boldsymbol{p}^{2}
$$

with

$$
\begin{aligned}
& E=\frac{m c^{2}}{\sqrt{1-\frac{v^{2}}{c^{2}}}}, \quad \boldsymbol{p}=\frac{m v}{\sqrt{1-\frac{v^{2}}{c^{2}}}} \\
& \frac{E^{2}}{c^{2}}-m^{2} c^{2}=\frac{m^{2} c^{2}}{1-\frac{v^{2}}{c^{2}}}-m^{2} c^{2}=m^{2} c^{2}\left(\frac{1}{1-\frac{v^{2}}{c^{2}}}-1\right)=\frac{m^{2} v^{2}}{1-\frac{v^{2}}{c^{2}}}=\boldsymbol{p}^{2}
\end{aligned}
$$

Kinetic energy $K$ is defined by

$$
K=E-m c^{2}=\frac{E^{2}-m^{2} c^{4}}{E+m c^{2}}=\frac{c^{2}}{E+m c^{2}} \boldsymbol{p}^{2}
$$

When $E \approx m c^{2}, K$ is equal to

$$
K \approx \frac{\boldsymbol{p}^{2}}{2 m}
$$

## Pythagorean relationship



Fig. Pythagorean relationship. $\frac{E^{2}}{c^{2}}=m^{2} c^{2}+\boldsymbol{p}^{2}$

## C. Application - interaction with the classical radiation field

We consider the absorption and emission of light which is caused through the interaction between atoms and electromagnetic fields. The light is the electromagnetic field which periodically varies with time. Here we discuss the absorption and stimulated emission, where the electromagnetic field is semi-classically treated and the atoms are quantum-mechanically treated. There is another emission, so-called the spontaneous emission, where the electromagnetic field should be quantum-mechanically treated.

Classical radiation field
$\Rightarrow$ electric or magnetic field derivable from a classical radiation field as opposed to quantized field

$$
\hat{H}=\frac{1}{2 m} \hat{\boldsymbol{p}}^{2}+e \phi(\hat{\boldsymbol{r}})+\frac{e}{m c} \boldsymbol{A} \cdot \hat{\boldsymbol{p}}
$$

which is justified if

$$
\nabla \cdot \boldsymbol{A}=0 . \quad \text { (Coulomb gauge) }
$$

We work with a monochromatic field of the plane wave

$$
\begin{aligned}
& \boldsymbol{A}=2\left|\boldsymbol{A}_{0}\right| \boldsymbol{\varepsilon} \cos (\boldsymbol{k} \cdot \boldsymbol{r}-\omega t) \\
& \boldsymbol{k}=\frac{\omega}{c} \boldsymbol{n}, \quad \boldsymbol{\varepsilon} \cdot \boldsymbol{k}=0
\end{aligned}
$$

( $\boldsymbol{\varepsilon}$ and $\boldsymbol{n}$ are the (linear) polarization and propagation directions.)
or

$$
\boldsymbol{A}=\left|\boldsymbol{A}_{0}\right| \varepsilon\left[e^{i(\boldsymbol{k} \cdot \boldsymbol{r}-\omega t)}+e^{-i(\boldsymbol{k} \cdot \boldsymbol{r}-\omega t)}\right]
$$

The Hamiltonian is given by

$$
\hat{H}=\hat{H}_{0}+\hat{H}_{1}
$$

where $\hat{H}_{1}$ is the time dependent perturbation

$$
\begin{aligned}
\hat{H}_{1} & \left.=\frac{e}{m c} \right\rvert\, \boldsymbol{A}_{0}\left[e^{i(k \cdot r-\omega t)}+e^{-i(k \cdot r-\omega t)}\right](\varepsilon \cdot \hat{\boldsymbol{p}}) \\
& =\hat{H}_{1}^{+} e^{-i \omega t}+\hat{H}_{1} e^{i \omega t}
\end{aligned}
$$

The first term: responsible for stimulated emission, The second term: responsible for absorption

$$
\left(\hat{H}_{1}^{+}\right)_{f i}=\frac{e\left|\boldsymbol{A}_{0}\right|}{m c}\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\left|\varphi_{i}\right\rangle
$$

and

$$
\left.W_{i \rightarrow f}=\frac{2 \pi}{\hbar} \frac{e^{2}}{m^{2} c^{2}}\left|\boldsymbol{A}_{0}\right|^{2}\left|\left\langle\varphi_{f}\right| e^{i \boldsymbol{k} \cdot \boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{p}}\right| \varphi_{i}\right\rangle\left.\right|^{2} \delta\left(E_{f}-E_{i}-\hbar \omega\right)
$$

## ((Fermi's golden rule))

where the energy is conserved during the process; $E_{f}-E_{i}=\hbar \omega$


