Liberation of electron using a photon
photoelectric effect/photoemission
Science By The Slice

Xiaoshan Xu
July 22, 2016
The complete absorption of a photon by a solid with the emission of an electron. (Handbook of chemistry and physics, David Lide, 87th edition, Boca Raton, FL : CRC Press, 2006)
Photoelectric effect

$I$: light intensity

$\nu$: light frequency

$E_K$: kinetic energy of emitted electron

$I_E$: photoelectric current

https://phet.colorado.edu/en/simulation/photoelectric
Properties of the photoelectric effect

- $I_E \propto I$ (The intensity of light is proportional to the induced photocurrent.)

- There is an **threshold** for the light frequency to generate photocurrent.

- The maximum kinetic energy increases with the light frequency.

http://hyperphysics.phy-astr.gsu.edu/hbase/mod2.html
Quantization of light: photon

- The energy of the light propagates in discrete wave packets (photons):
  - $E_p = h\nu$, $h$ is the Plank constant

- Conservation of energy:
  - $E_{kmax} = E_p - \phi = h\nu - \phi$

Light ($I, \nu$) → Metal

Vacuum level

$\phi$: work function
Measurement of Planck constant

Robert Millikan

\[ h = \frac{\Delta E}{\Delta \nu} = 4.1 \times 10^{-15} \text{eV} \cdot \text{s} \]

\[ \Delta E = 1.25 \text{eV} \]

\[ \Delta \nu = 3 \times 10^{14} \text{Hz} \]

The linear increase in electron kinetic energy shows that whatever is ejecting them has energy proportional to frequency.

\[ E_{kmax} = E_p - \phi = h \nu - \phi \]

\[ h = 6.6 \times 10^{-34} \text{ Js} \]

http://hyperphysics.phy-astr.gsu.edu/hbase/mod2.html
## Work functions of metals (eV)

<table>
<thead>
<tr>
<th>Element</th>
<th>Work Function Range (eV)</th>
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<tbody>
<tr>
<td>Ag</td>
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<tr>
<td>Au</td>
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<tr>
<td>Be</td>
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<td>Co</td>
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<td>Hg</td>
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<td>K</td>
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<tr>
<td>Lu</td>
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<tr>
<td>Mo</td>
<td>4.36 – 4.95</td>
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<td>Pb</td>
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<tr>
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<td>V</td>
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<tr>
<td>Yb</td>
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<tr>
<td>In</td>
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<tr>
<td>Th</td>
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<tr>
<td>U</td>
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<tr>
<td>Y</td>
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<tr>
<td>Zr</td>
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</table>

Visible light: 1.6-3.1 eV
Light: Wave and particle

- Klein–Gordon equation (Relativistic)

\[-\hbar^2 \frac{\partial^2}{\partial t^2} \psi = (-\hbar^2 c^2 \nabla^2 + m^2 c^4)\psi = E^2\]

For photon: \( m=0 \)

\[-\hbar^2 \frac{\partial^2}{\partial t^2} \psi = -\hbar^2 c^2 \nabla^2 \psi = E^2\]

\[\psi = Ae^{i\left(\frac{2\pi}{\lambda}x - \omega t\right)}, \quad E = \hbar \omega = h \nu\]

\[\omega \equiv 2\pi \nu, \quad \hbar \equiv \frac{h}{2\pi}\]
Light Induced Quantum Transitions

- Transition matrix

\[ H_{12} = \langle \psi_1 | \overrightarrow{E_0} e^{-i \omega t} | \psi_2 \rangle \]

\[ = \langle \psi_1^0 | \overrightarrow{E_0} | \psi_2^0 \rangle e^{-i \frac{(E_2 - E_1 - \omega)t}{\hbar}} \]

Transition probability

\[ P(t) \propto \left| \int_0^t H_{12} dt \right|^2 \propto \left| \int_0^t e^{-i \frac{(E_2 - E_1 - \omega)t}{\hbar}} dt \right|^2 \]

\[ \propto \left| \langle \psi_1^0 | \overrightarrow{E_0} | \psi_2^0 \rangle \right|^2 \delta \left( \frac{E_2 - E_1}{\hbar} - \omega \right) \]
Application of photoelectric effect

- Photoelectric cell for light sensing
- Photomultiplier tube for single-photon detection
Excitation in an insulator (semiconductor)

- Light $(I, \nu)$
- Vacuum level
  - *Conduction band*
  - $E_g$: band gap
  - *Valence band*
- Metal
- Vacuum level
  - $\phi$: work function
Light induced electron-hole pair

Photovoltaic effect

Photodetector: charge coupled device (CCD)
PHOTOEMISSION

Light \((I, \nu)\)

Electron \((E_k, I_E)\)

Metal and insulators
Photoemission

Binding energy: $E_B = h\nu - E_k$

- Binding energy of valence electron
  - $< 100 \text{ eV} \rightarrow$ ultraviolet light
- Binding energy of core electron:
  - $> \text{keV} \rightarrow$ x-ray

Ultraviolet photoelectron spectroscopy (UPS)

- Fix photon energy
- Measure kinetic energy

- Surface sensitive due to small kinetic energy
- Must be in UHV (typically $<10^{-9}$ Torr)

X-ray photoelectron spectroscopy (XPS)

\[ h\text{-LuFeO}_3 \]
Auger effect (Secondary photoemission)

1st, x-ray excites electron to conduction band and generate a core hole

2nd, electron recombine with the hole; the emitted energy expels another electron

X-ray absorption

Electron-hole recombination and emission of another electron
\[ \psi_2 = \psi_2^0 e^{-i\frac{E_2}{\hbar}t} \]

\[ \psi_1 = \psi_1^0 e^{-i\frac{E_1}{\hbar}t} \]

\[ P(t) \propto |\langle \psi_1^0 | E_0 | \psi_2^0 \rangle|^2 \delta\left(\frac{E_2 - E_1}{\hbar} - \omega\right) \]
Optical absorption spectroscopy

\[ \alpha (\text{cm}^{-1}) \]

Energy (eV)

300 K
4 K

\[ {^6A_{1g}} \rightarrow {^4T_{2g}} \]

\[ {^6A_{1g}} \rightarrow {^4T_{1g}} \]

BiFeO\textsubscript{3}

PHYSICAL REVIEW B 79, 134425 2009
Color of BiFeO$_3$ comes from the absorption

Fe$^{3+}$ 3d$^5$

<table>
<thead>
<tr>
<th></th>
<th>Spin</th>
<th>Parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>5/2</td>
<td>Even</td>
</tr>
<tr>
<td>Final</td>
<td>3/2</td>
<td>Even</td>
</tr>
</tbody>
</table>

Photon

$$\begin{align*}
\text{e}_g & \quad \text{Exciton} \\
\text{t}_{2g} & \quad \text{Exciton}
\end{align*}$$

$s = 5/2$

$^6A_{1g}$

$s = 3/2$

$^4T_{1g}$
X-ray absorption spectroscopy (XAS)

Transmission is normally difficult to measure, especially for thin films.

Fluorescence spectra is often distorted by self absorption.

Photoemission is often used for its surface sensitivity, especially for thin films.
XAS using synchrotron x-ray

- Unlike XPS, UPS, the x-ray energy is canned, which requires synchrotron source
- UHV is also necessary

XAS at Canadian Light Source
Electronic structures by XAS

- **Hexagonal**
- **Orthorhombic**

LuFeO$_3$
X-ray magnetic circular dichroism (XMCD)

Photoemission electron microscopy (PEEM)

Fe magnetic domains

Magnetic domains
Thank you for your attention !