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# EEE 6212
Semiconductor Materials

Lecture 9: Bandstructure and effective mass

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Outline

- review of quantum mechanics – some stories from ~1900!
- wavefunctions
- operators
- Schrödinger equation
- band structure
- effective mass
- summary

History of the 'ultraviolet catastrophe'

- everything absorbs and emits e-m radiation
- classical physics attempted to describe the emission from a perfect black body,
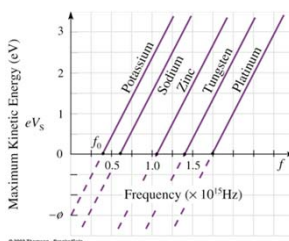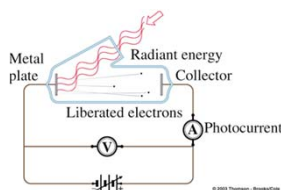- Rayleigh-Jeans Law is accurate at long wavelength – but breaks down at short wavelengths (UV)

Predicted   UV Catastrophe

Flux

$$B_\lambda(T) = \frac{2ckT}{\lambda^4}$$

Observed

λ
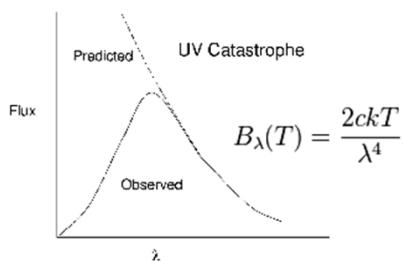
Planck solved this by hypothesising that the emission could only be in discrete "packets" or "quanta"

$$E_n = nh\nu = n\hbar\omega$$

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Photoelectric Effect

Metal plate   Radiant energy
Collector
Liberated electrons
Photocurrent

Maximum Kinetic Energy (eV)

Potassium Sodium Zinc Tungsten Platinum

eV_s

f_0

0.5   1.0   1.5 f

Frequency (× 10^{15}Hz)

$-\phi$

- many metals emit electrons when light is shone upon them (photo-electrons) – Hertz, Thomson, Lenard
- intensity of light has no influence on kinetic energy of emitted electrons – just get more photoelectrons with higher intensity
- threshold frequency of incident light for photoelectron emission

Photoelectric Effect (2)

"Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt." *Annalen der Physik. Leipzig* <u>17</u> (1905) 132

It seems to me that the observation associated with black body radiation, fluorescence, the photoelectric effect, and other related phenomena associated with the emission or transformation of light are more readily understood if one assumes that the energy of light is discontinuously distributed in space. In accordance with the assumption to be considered here, the energy of a light ray spreading out from a point is not continuously distributed over an increasing space, but consists of a finite number of energy quanta which are localized at points in space, which move without dividing, and which can only be produced and absorbed as complete units.

In the following I wish to present the line of thought and the facts which have led me to this point of view, hoping that this approach may be useful to some investigators in their research.

Einstein developed the concept of
photons as discrete wave packets

Wave-Particle Duality

- for many centuries we have argued whether light is a wave (Huygens) or a particle (Newton)
- currently held view is that you may consider a particle to have both properties
- general rule of thumb – get wave mechanical effects when physical dimensions are on a scale similar to the wavelength
- de Broglie hypothesis equates a wave to each particle, of wavelength

$$\lambda = \frac{h}{p}$$

h= Planck's constant
p= momentum

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Wavefunction – Ψ (psi)

The state of a system is described by the wavefunction which depends upon a set of physical coordinates (e.g. *x,y,z*) and time (*t*)
Ψ - often complex valued, expressed in position space here

Ψ solves the Schrödinger equation which describes how the wave-function evolves over time (here for a free electron, i.e. potential *V*=0)

$$\Psi(x, y, z, t)$$

$$i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} = H\Psi(x, y, z, t)$$

$\hbar$ = Planck's reduced constant = $h/(2\pi)$

$i^2 = -1$

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Wavefunctions & operators

Wavefunctions contain information about the state of the system

Different operators extract a measurable (physically observable) quantity from the system (via differentiation, integration, multiplication, etc.)

Physical quantity	Operator	Expectation value
x, y, z (coordinates)	x, y, z	$<x> = \int \Psi^* x \Psi dx dy dz$
p_x, p_y, p_z (momentum)	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$	$<p_x> = \int \Psi^* \frac{\hbar}{i}\frac{\partial \Psi}{\partial x} dx dy dz$
E (kinetic energy)	$i\hbar \frac{\partial}{\partial t}$	$<E> = \int \Psi^* i\hbar \frac{\partial \Psi}{\partial t} dx dy dz$

Schrödinger Equation

The Hamiltonian "*H*" in the time dependent Schrödinger equation represents the total energy of the system in terms of operators.

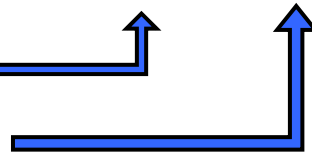$$i\hbar \frac{\partial \Psi(x,y,z,t)}{\partial t} = H\Psi(x,y,z,t)$$

Simple system – sum of potential and kinetic energy operators

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(x,y,z,t)$$

(*m*= mass)

kinetic energy

U(x, y, z, t) – describes a 3D potential energy varying in time

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Schrödinger Equation (2)

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(x,y,z,t)$$

Kinetic energy term written in orthonormal coordinates in terms of the Laplacian

$$\nabla^2\Psi(x,y,z) = \frac{\partial^2\Psi(x,y,z)}{\partial x^2} + \frac{\partial^2\Psi(x,y,z)}{\partial y^2} + \frac{\partial^2\Psi(x,y,z)}{\partial z^2}$$

$$|\Psi(x,y,z,t)|^2 \, dxdydz$$

$$\int |\Psi(x,y,z,t)|^2 \, dxdydz = 1$$

probability density function

The sum of the probabilities of all possible values of spatial coordinates

Wavefunctions

Ψ, dΨ/dx, dΨ/dy, dΨ/dz must be finite, continuous and single-valued – even if discontinuous change in $U(x,y,z)$
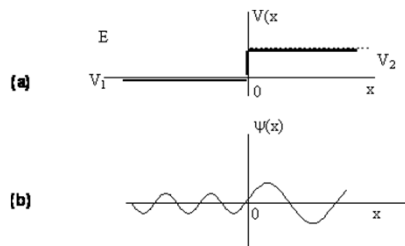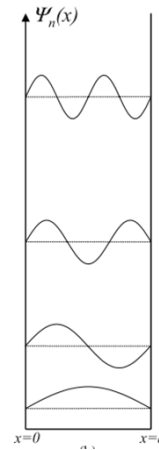(except if U(x,y,z) becomes infinite)

Fig. 1 Potential Energy Step

Heisenberg's uncertainty principle

- In classical physics one can measure e.g. momentum and position with arbitrarily high precision.
- Heisenberg's uncertainty principle denies this ability within quantum mechanics.
- Certain operators/observables are complimentary – such as linear position and momentum, energy and time
- These pairs of observables are "simultaneously unknowable".
- useful for atomic physics and nanotechnology:

$$\Delta x \cdot \Delta p \geq \hbar/2 \ , \qquad \Delta E \cdot \Delta t \geq \hbar/2$$

Slide 13:

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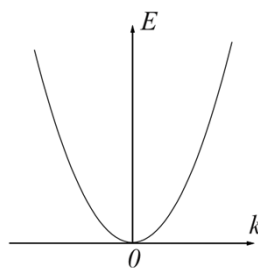# Free particle

Schrödinger equation

$$\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + E\Psi(x) = 0$$

planar standing wave

$$\Psi(x) = Ae^{ikx}$$

so

$$-\frac{\hbar^2 k^2}{2m}\Psi(x) + E\Psi(x) = 0$$

cancel & rearrange

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{8\pi^2 m}$$

(graph of E vs k, parabola)

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Electrons in crystals

potential energy

$U(x)$ (periodic potential graph)

1. Band structure of semiconductors

1.1. The crystal Hamiltonian

FOR an assembly of atoms the classical energy is the sum of the following:
(a) the kinetic energy of the nuclei;
(b) the potential energy of the nuclei in one another's electrostatic field;
(c) the kinetic energy of the electrons;
(d) the potential energy of the electrons in the field of the nuclei;
(e) the potential energy of the electrons in one another's field;
(f) the magnetic energy associated with the spin and the orbit.

Dividing the electrons into core and valence electrons and leaving out magnetic effects leads to the following expression for the crystal Hamiltonian:

$$H = \sum_l \frac{\mathbf{p}_l^2}{2M_l} + \sum_{l,m} U(\mathbf{R}_l - \mathbf{R}_m) + \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i,l} V(\mathbf{r}_i - \mathbf{R}_l) + \sum_{i,j} \frac{e^2/4\pi\epsilon_0}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.1)$$
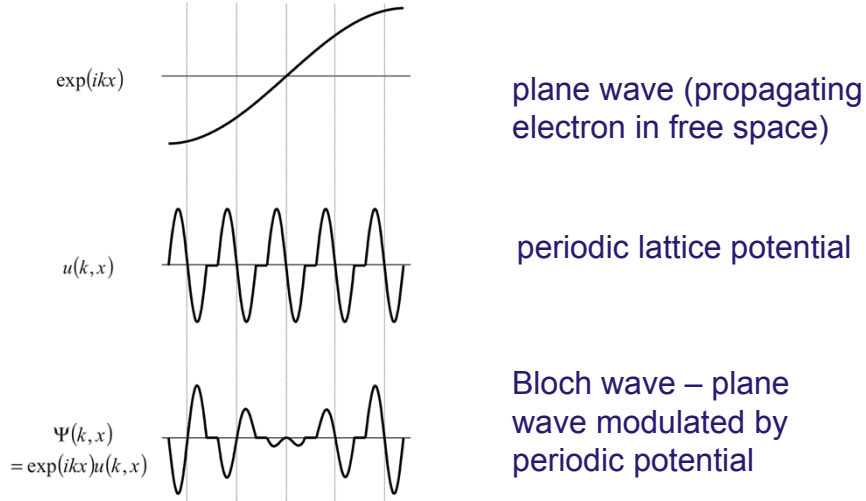
where l and m label the ions, i and j label the electrons, $\mathbf{p}$ is the momentum, M is the ionic mass, m is the mass of the electron, $U(\mathbf{R}_l - \mathbf{R}_m)$ is the interionic potential, and $V(\mathbf{r}_i - \mathbf{R}_l)$ is the valence–electron–ion potential.

The Schrödinger equation determines the time-independent energies of the system:

$$H\Xi = E\Xi \quad (1.2)$$

where H is now the Hamiltonian operator.

Approximations–Bloch Theorem

$\exp(ikx)$

plane wave (propagating electron in free space)

$u(k,x)$

periodic lattice potential

$\Psi(k,x)$
$= \exp(ikx)u(k,x)$

Bloch wave – plane wave modulated by periodic potential

Bloch Theorem

Bloch wave

$$\Psi\!\left(\vec{k},\vec{r}\right) = \exp\!\left(i\vec{k}.\vec{r}\right)u\!\left(\vec{k},\vec{r}\right)$$

space-dependent amplitude function – reflects periodicity of the lattice

$$u\!\left(\vec{k},\vec{r}+\vec{R}\right) = u\!\left(\vec{k},\vec{r}\right)$$

so -

$$\Psi\!\left(\vec{k},\vec{r}+\vec{R}\right) = \exp\!\left(i\vec{k}.\vec{R}\right)\Psi\!\left(\vec{k},\vec{r}\right)$$

$-\dfrac{\pi}{d} < k \le \dfrac{\pi}{d}$. (within the Brillouin zone)

$$\Psi(k,x+d) = \exp(ikd)\Psi(k,x)$$

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Kroenig-Penney

- Bloch theorem simplifies the wavefunction
- Kroenig-Penney simplifies the periodic potential – much of the physics remains
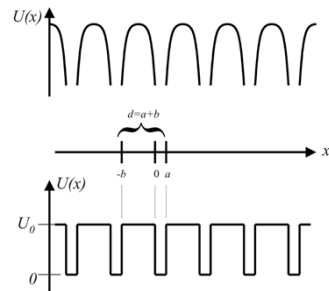
energy spectrum, dispersion, band diagram, band structure…

Band 4

Band 3

Band 2

Band 1

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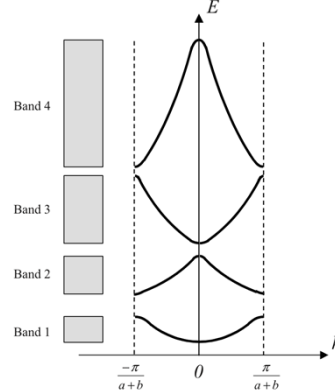
Semiconductor bandstructure

- energy is a periodic function of $\underline{k}$…..All information contained within the 1st Brillouin zone
- $\hbar\underline{k}$ is the quasi momentum or crystal momentum – includes interaction with the crystal
- E-k plot approximates to parabolic function at $k \approx 0$
- dE/dk = 0 at k=0 and edge of Brillouin zone
- nearly free electron model….
- tight binding model…..
- As computer power increases, more complex simulations become possible.
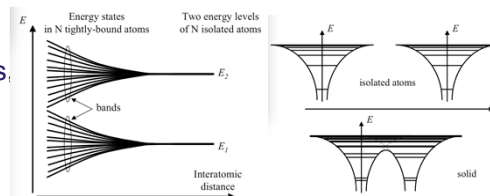
Example bandstructure
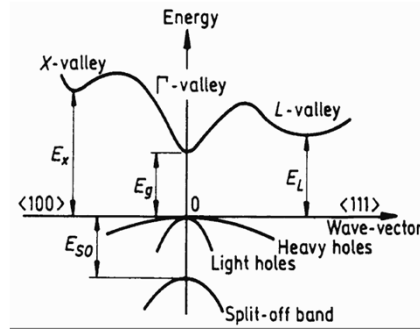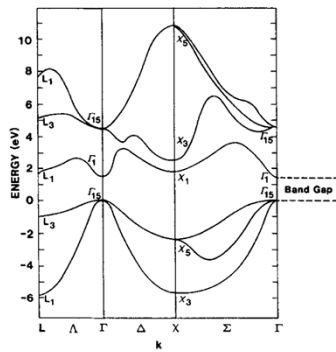
Note that the band-structure shows parabola around points of high symmetry: Γ-point, L-point, X-point where we have global and local minima/maxima

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Electron as a wavepacket

Electron has energy E and wavenumber $\underline{\textbf{k}}$, so group velocity, v_g

$$v_g = \frac{d\omega}{dk}$$

$E=\hbar\omega$, so

$$v_g = \frac{1}{\hbar}\frac{dE}{dk}$$

Force $\underline{\textbf{F}}$ changes energy by dE

$$dE = Fdx = Fv_g dt$$

or

$$F = \frac{1}{v_g}\frac{dE}{dt} = \frac{1}{v_g}\frac{dE}{dk}\frac{dk}{dt}$$

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Electron as a wavepacket (2)

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

differentiating w.r.t. time: $\quad \frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}$

or $\quad \frac{dv_g}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \frac{d(\hbar k)}{dt}$

F=d*p*/d*t*=d(ℏ*k*)/d*t*, so $\quad F = \left(\cfrac{1}{\frac{1}{\hbar^2} \frac{d^2 E}{dk^2}} \right) \frac{dv_g}{dt}$
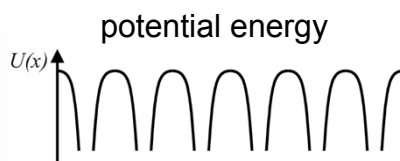

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Electron as a wavepacket (3)

remember Newton's Law of Motion $\qquad F = m^* \frac{dv_g}{dt}$

where *m** is the effective mass $\qquad m^* = \frac{\hbar^2}{d^2 E / dk^2}$

potential energy

$U(x)$

classical laws of dynamics apply if mass of electron is changed so it follows the curvature of the *E-k* plots

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Effective mass approximation
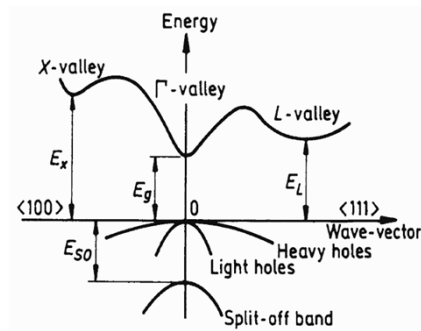
Most important region of interest are the states near the band-gap.

May describe these states as free electrons with an effective mass – given by the curvature of the *E-k* plot

Semiconductor	Energy gap (eV) at 273 K	Effective mass m*/m	
		Electrons	Holes
Ge	0.67	0.2	0.3
Si	1.14	0.33	0.5
InSb	0.16	0.013	0.6
InAs	0.33	0.02	0.4
InP	1.29	0.07	0.4
GaSb	0.67	0.047	0.5
GaAs	1.39	0.072	0.5

Summary

- briefly described development of quantum mechanics
- introduced wavefunctions and Schrödinger equation
- mentioned Heisenberg Uncertainty Principle
- explored electrons in crystals – simplifications to solving Schrödinger equation
- effective mass approximation in region of band edges as a useful way to described electrons (and holes) in semi-conductors

Tutorial Questions

Estimate the de Broglie wavelength of

- a 200keV electron
- a carbon atom at room temperature ($k_{B}T$)
- a human sprinter