Physics of Condensed Matter I

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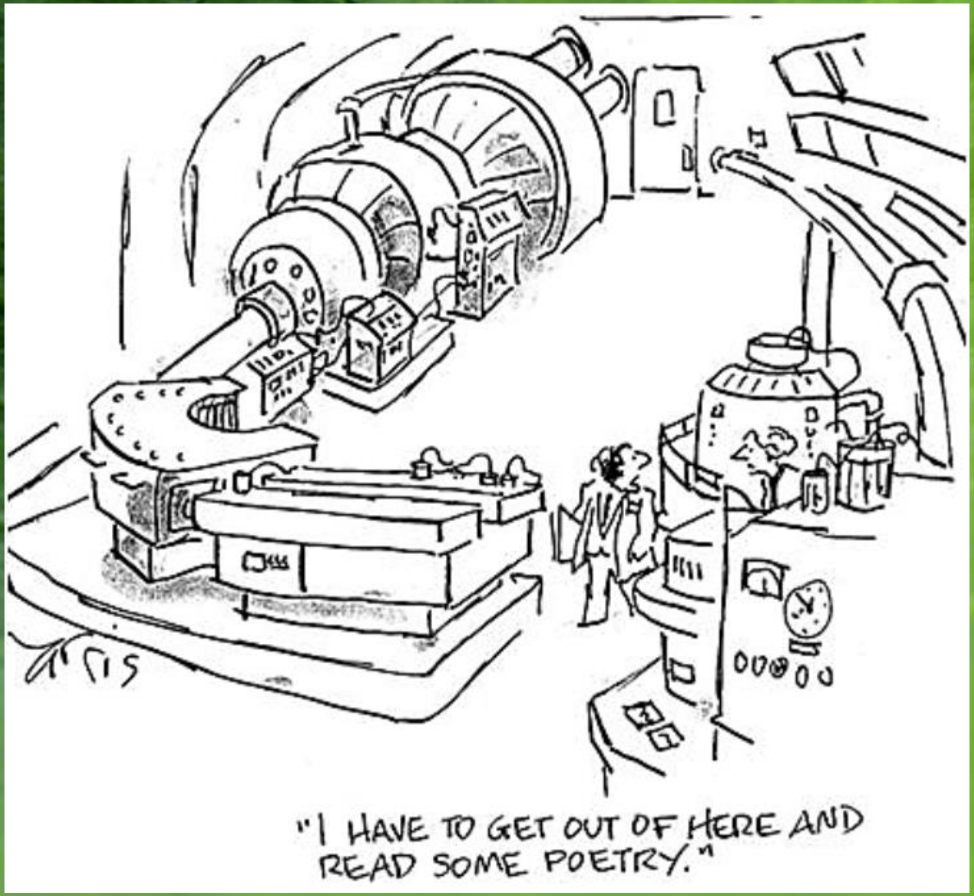

Solid state 3

Faculty of Physics UW

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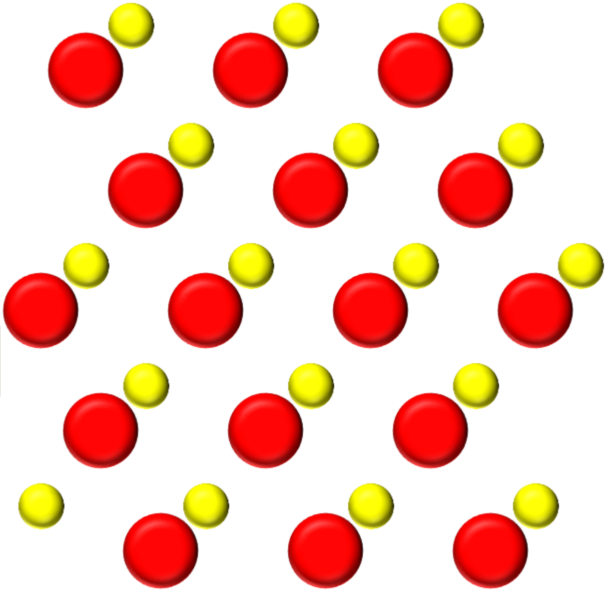
inżynieria nanostruktur

Crystalography

Maximal value of the intensity

$$\left[\sum_{n_1} e^{-i\Delta\vec{k}(n_1\vec{t}_1)}\right]\left[\sum_{n_2} e^{-i\Delta\vec{k}(n_2\vec{t}_2)}\right]\left[\sum_{n_3} e^{-i\Delta\vec{k}(n_3\vec{t}_3)}\right]$$



When $e^{-i\Delta\vec{k}(n_1\vec{t}_1)} = 1$

$$\boxed{\vec{T} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3}$$

$$\boxed{\begin{array}{c}\Delta\vec{k}\vec{t}_1 = 2\pi h \\ \Delta\vec{k}\vec{t}_2 = 2\pi k \\ \Delta\vec{k}\vec{t}_3 = 2\pi l\end{array}}$$

Laue conditions

$$\Delta\vec{k} \equiv G = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$$

$$\boxed{\vec{g}_i\vec{t}_j = 2\pi\delta_{ij}}$$

$$|\vec{g}_i| = \frac{2\pi}{a_i} \qquad \vec{g}_i = 2\pi\,\frac{\vec{t}_j \times \vec{t}_k}{\vec{t}_i(\vec{t}_j \times \vec{t}_k)}$$

reciprocal lattice

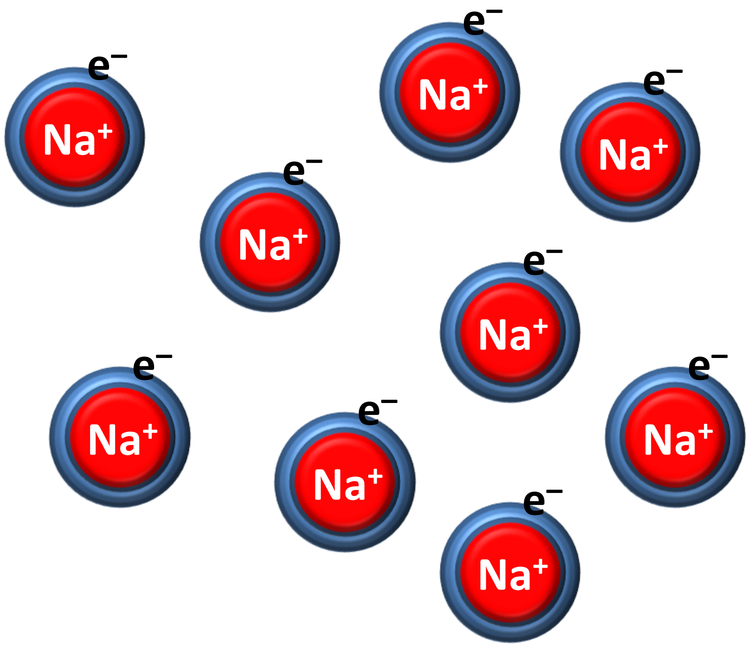
Structure factor S_G

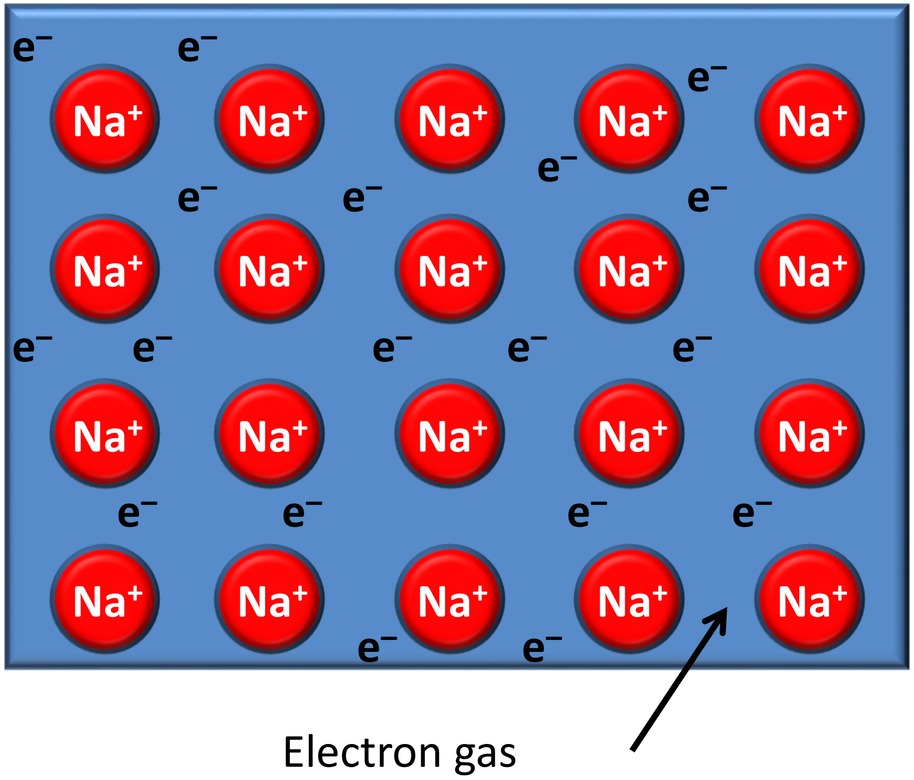
$$S_G = \int_{cell} dV\rho(\vec{R})e^{-i\vec{G}\vec{R}}$$

Types of chemical bonds

Metalic bonding

The chemical bond in metals, formed by the electrodynamic interaction between the positively charged atom cores, which are located in nodes of the lattice, and negatively charged **plasma electrons** (**delocalized electrons**, **electron gas**). Similar to a covalent bond, but electrons forming a bond are common to a large number of atoms.





Electrons in crystal

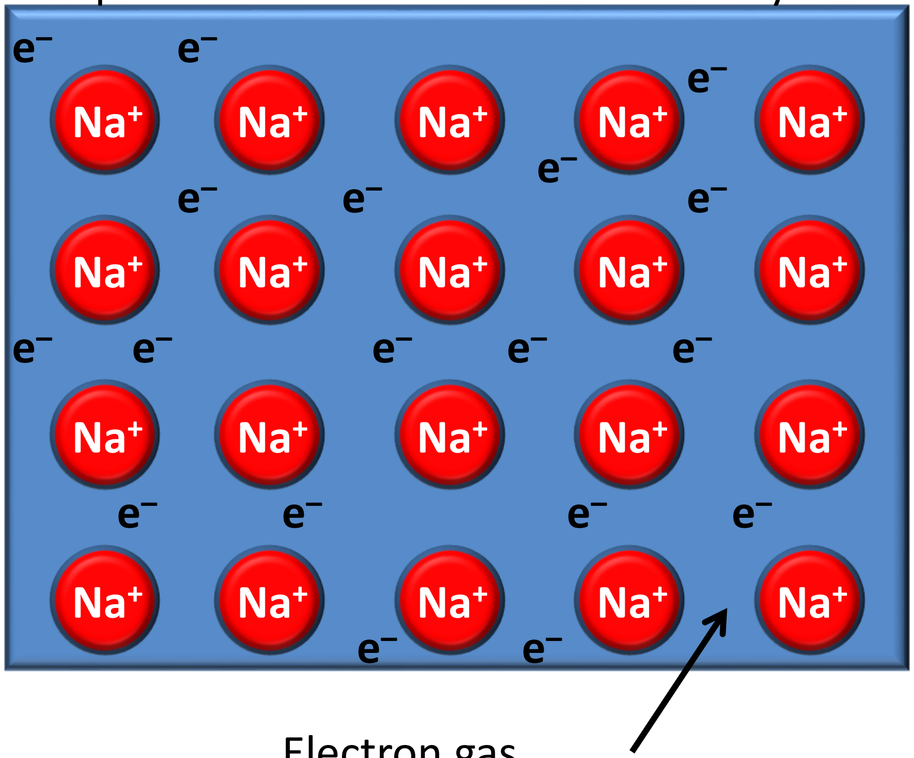
Metalic bonding

- Strict mathematical description is impossible – these systems are too complicated, (typically 1 cm^3 → $2,2\times10^{22}$ atoms (GaAs)).
- Nuclei + closed electrons shells→ atomic cores or ions
- Valence electrons - relatively weakly bound
- As a result of interaction electrons detach from the parent core and move almost freely throughout the crystal volume.
- Crystal bound through electrostatic interaction between negative cloud of electrons and positive ions.

Features:

a) high electrical conductivity

b) ductility (*ciągliwość*) ↔ Hardening (*hartowanie*)



Classical theory for the index of refraction

The wave in the media (different):

$$\frac{d^2\vec{x}}{dt^2}+\gamma\frac{d\vec{x}}{dt}+\omega_0^2\vec{x}=\frac{q}{m}\vec{E}e^{i\omega t}$$

Lorentz model

$$\frac{d^2\vec{x}}{dt^2}+\gamma\frac{d\vec{x}}{dt}+\omega_0^2\vec{x}=0$$

Emission spectrum

$$\frac{d^2\vec{x}}{dt^2}+0+0=\frac{q}{m}\vec{E}e^{i\omega t}$$

Plasma waves

the steady state solution:

$$\vec{x}(t)=\vec{x}_0e^{i\omega t}$$

Classical theory for the index of refraction

$$\frac{d^2\vec{x}}{dt^2} + 0 + 0 = \frac{q}{m}\vec{E}e^{i\omega t}$$

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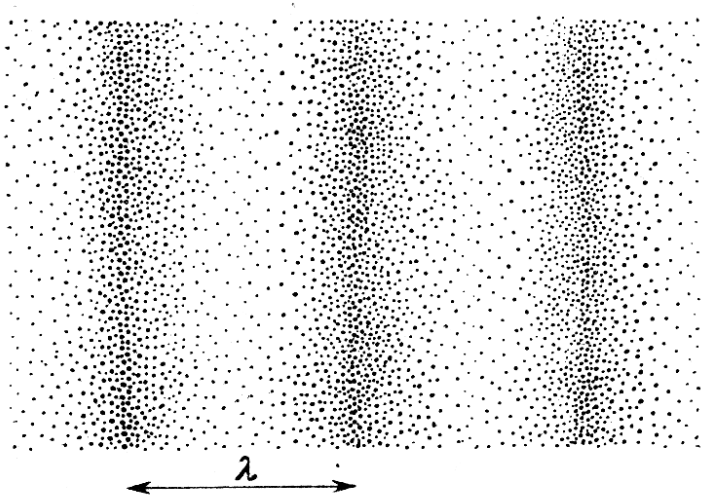
the steady state solution:
$\vec{x}(t) = \vec{x}_0 e^{i\omega t}$



Free carriers: $\vec{j} = \sigma\,\vec{E}$

$$-\vec{k}\left(\vec{E}_0\vec{k}\right) + k^2\vec{E}_0 = \frac{\omega^2}{c^2}\left(\varepsilon_L - \frac{Nq^2}{\varepsilon_0 m\omega^2}\right)\vec{E}$$

- ionized gases (eg. in gas lamps, ionosphere in the atmospheres of stars and planets),
- plasma,
- plasma in a solid - the gas free carriers in metals or semiconductors,
- liquids - as electrolytes or molten conductors.

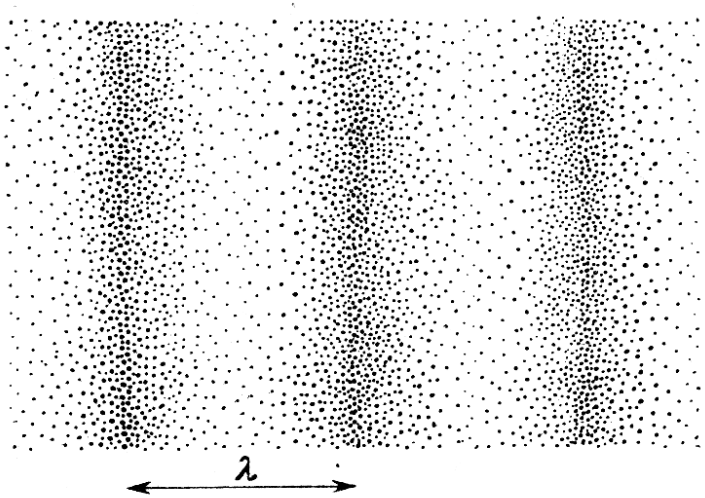
Plasma waves

$$\frac{d^2\vec{x}}{dt^2} + 0 + 0 = \frac{q}{m}\vec{E}e^{i\omega t}$$

Plasma waves

the steady state solution:
$\vec{x}(t) = \vec{x}_0 e^{i\omega t}$

$$-\vec{k}(\vec{E}_0\vec{k}) + k^2\vec{E}_0 = -\frac{\omega^2}{c^2}\left(\varepsilon_L - \frac{Nq^2}{\varepsilon_0 m\omega^2}\right)\vec{E}$$



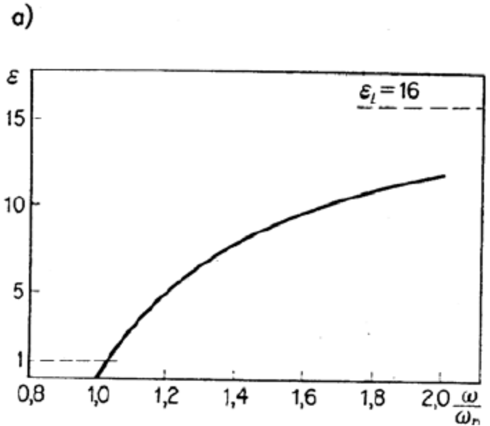
Longitudinal wave (*fala podłużna*): $\vec{k} \parallel \vec{E}$

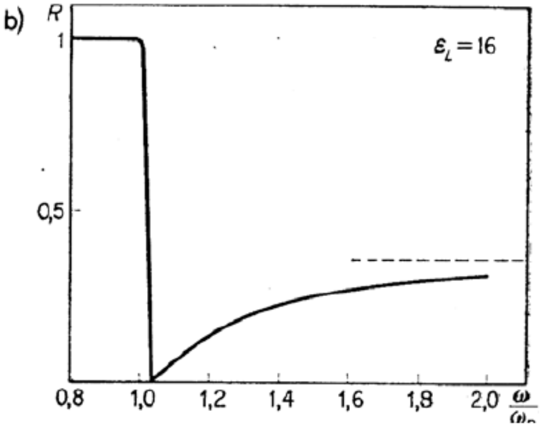
$$-\vec{k}(\vec{E}_0\vec{k}) + k^2\vec{E}_0 = 0 \qquad \omega_p^2 = \frac{Nq^2}{\varepsilon_0\varepsilon_L m}$$

The transverse wave (*fala poprzeczna*): $\vec{k} \perp \vec{E}$

$$-\vec{k}(\vec{E}_0\vec{k}) + k^2\vec{E}_0 = \frac{\omega^2}{c^2}\varepsilon_L\left(1 - \frac{\omega_p^2}{\omega^2}\right)\vec{E} = \frac{\omega^2}{c^2}\varepsilon_L\varepsilon(\omega)$$

$$R = \left|\frac{n-1}{n+1}\right|^2 = \left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2$$





Plasma waves

$$\frac{d^2\vec{x}}{dt^2} + 0 + 0 = \frac{q}{m}\vec{E}e^{i\omega t}$$

$$-\vec{k}\left(\vec{E}_0\vec{k}\right) + k^2\vec{E}_0 = -\frac{\omega^2}{c^2}\left(\varepsilon_L - \frac{Nq^2}{\varepsilon_0 m\omega^2}\right)\vec{E}$$

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$$R = \left|\frac{n-1}{n+1}\right|^2 = \left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2$$

$$R = \left|\frac{\tilde{n}-1}{\tilde{n}+1}\right|^2 = \frac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2}$$ (with damping)

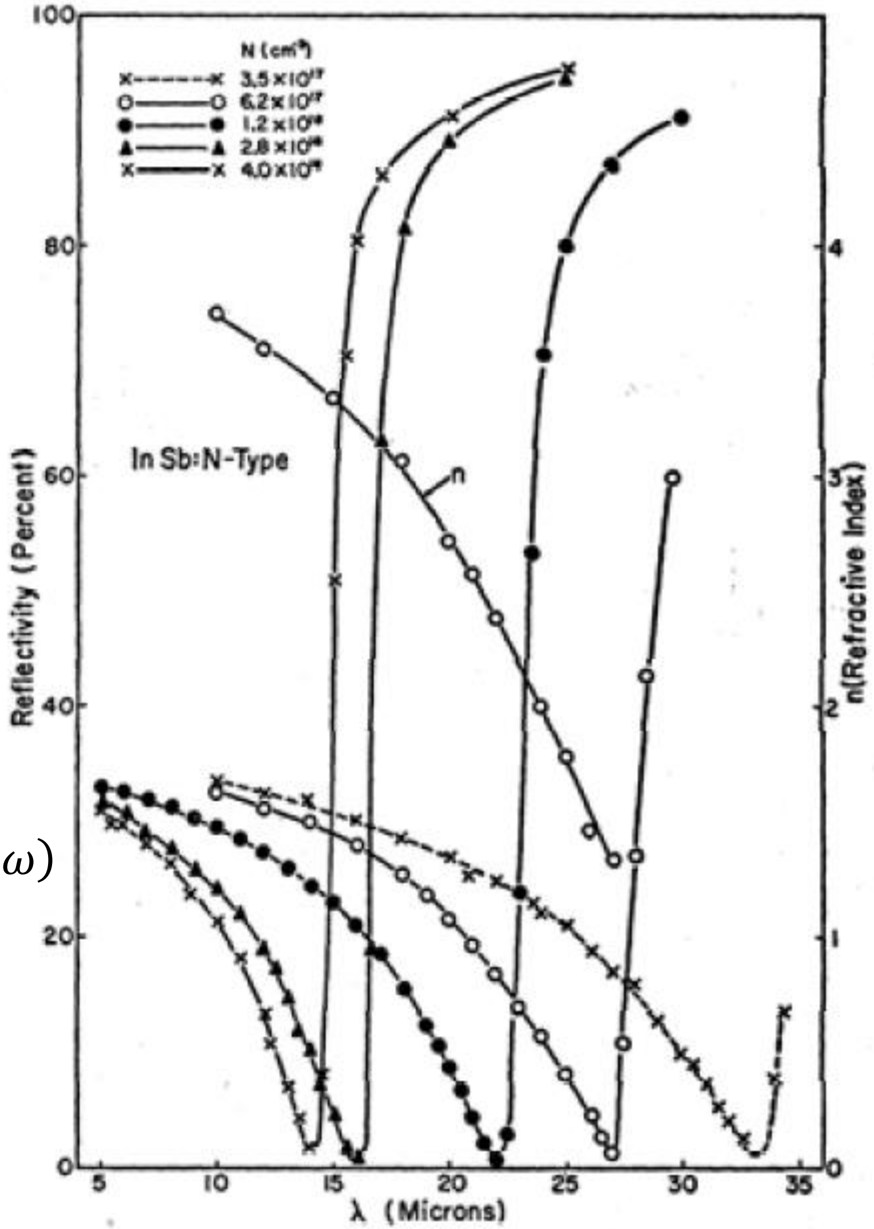
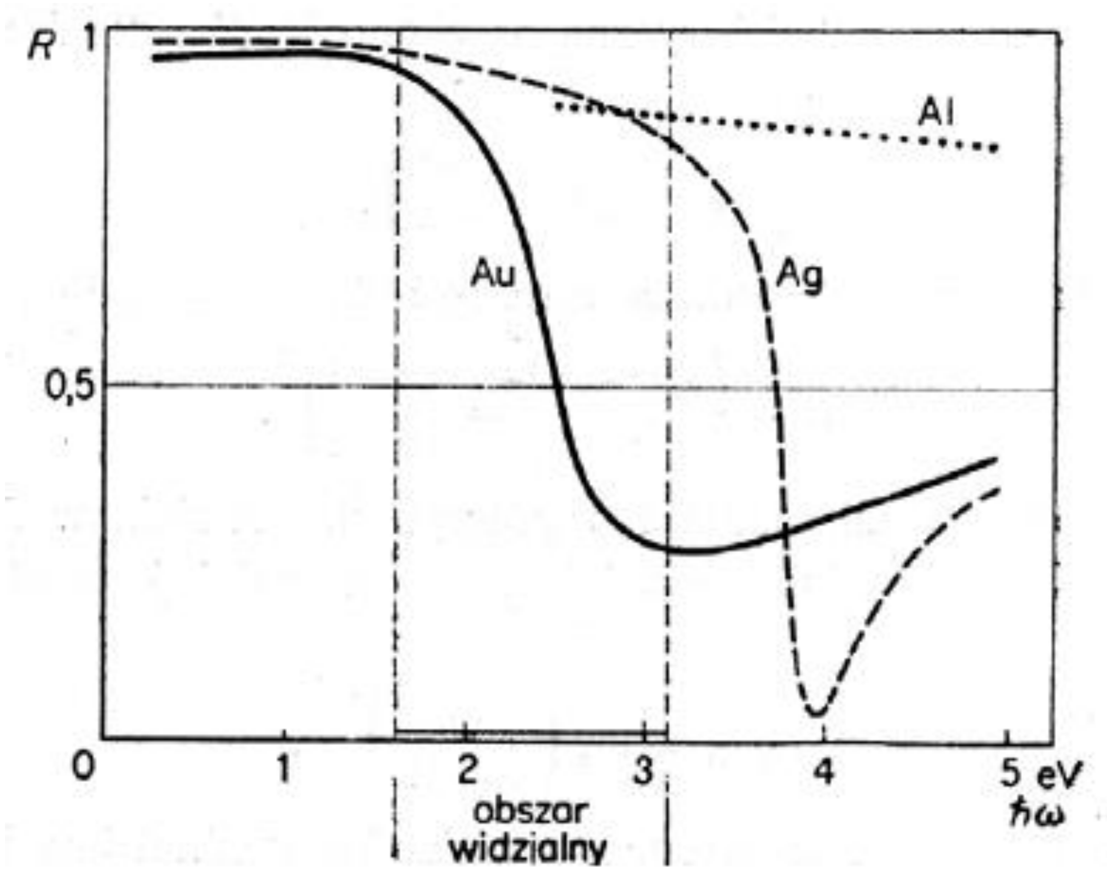
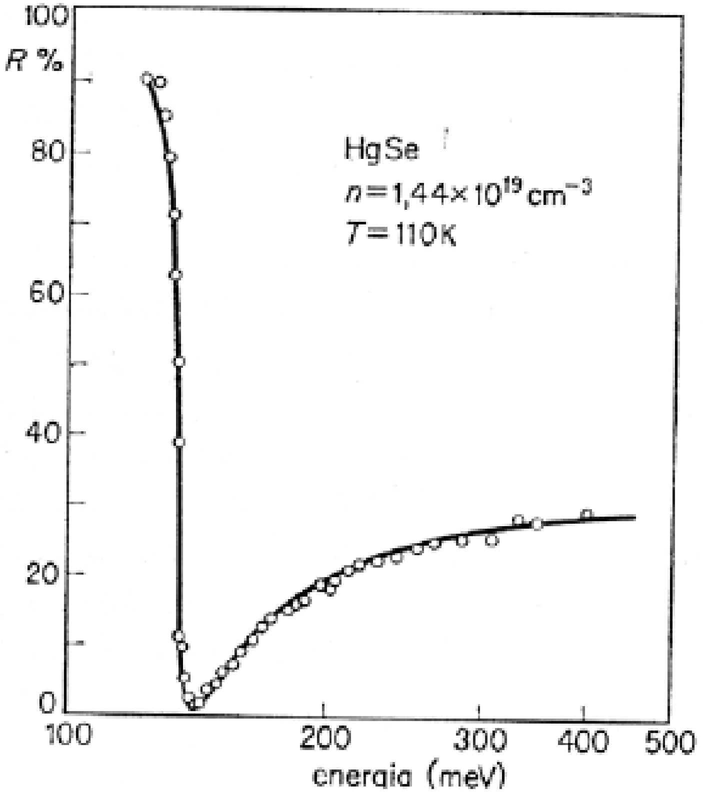


FIG. 8. Reflectivity *vs* wavelength for five *n*-type indium anti-monide samples. The refractive index curve labeled *n* is for the sample with $N = 6.2\times10^{17}$ cm^{-3}.

Plasma waves

$$\frac{d^2\vec{x}}{dt^2} + 0 + 0 = \frac{q}{m}\vec{E}e^{i\omega t}$$

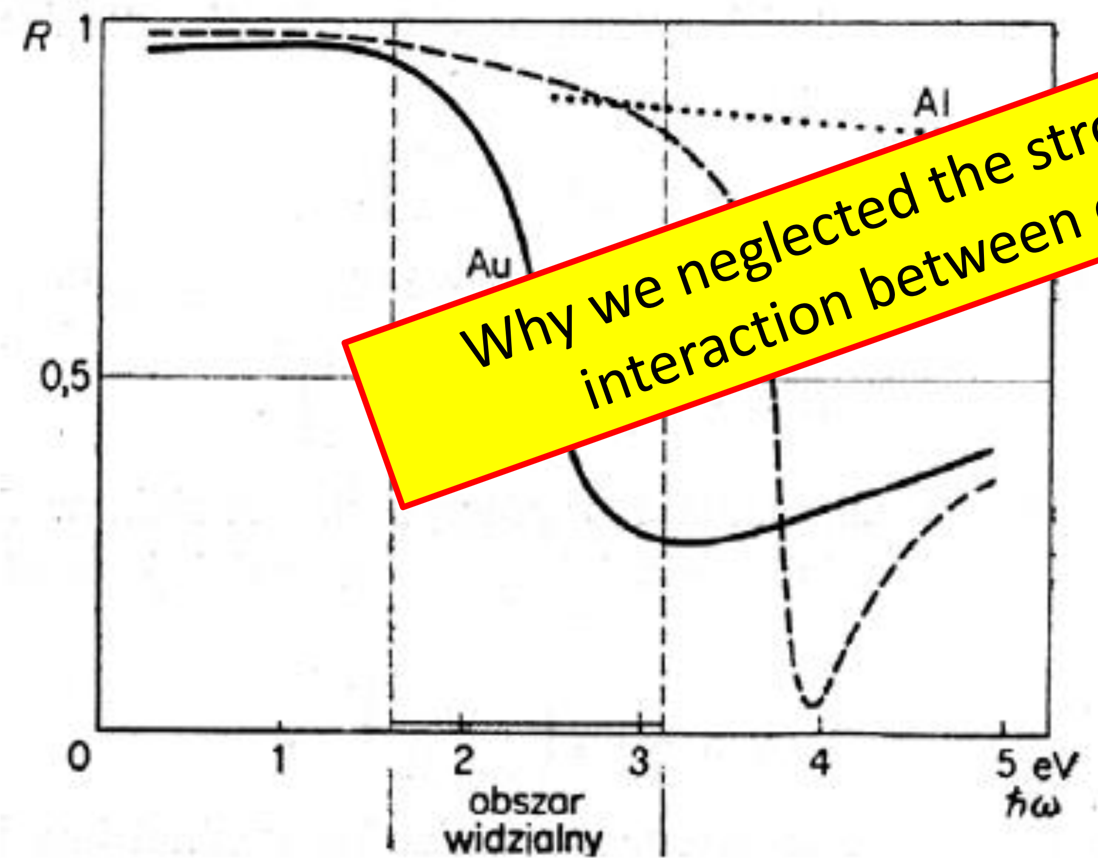


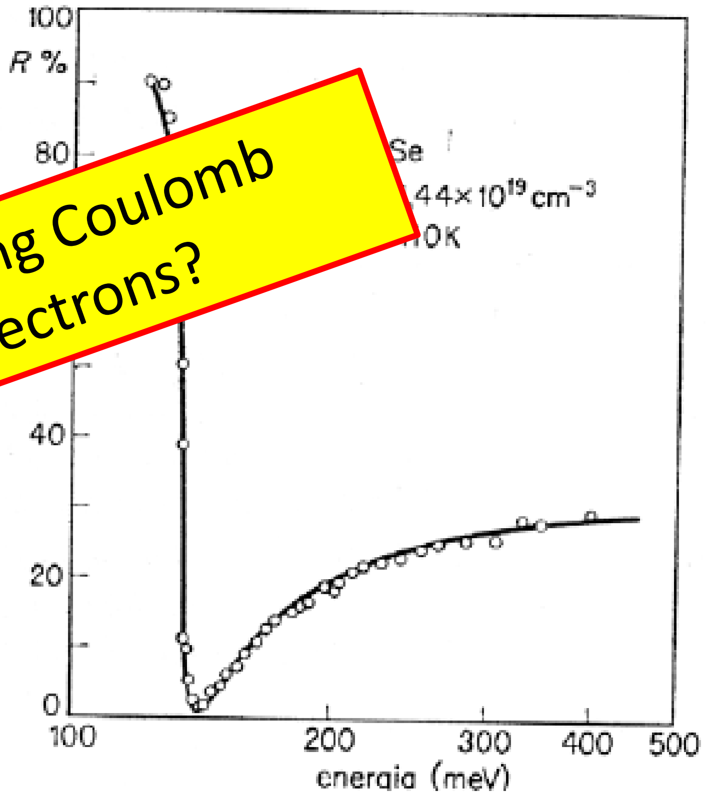


$$R = \left|\frac{n-1}{n+1}\right|^2 = \left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2$$

Plasma waves

$$\frac{d^2\vec{x}}{dt^2} + 0 + 0 = \frac{q}{m}\vec{E}e^{i\omega t}$$





Why we neglected the strong Coulomb interaction between electrons?

$$R = \left|\frac{n-1}{n+1}\right|^2 = \left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2$$

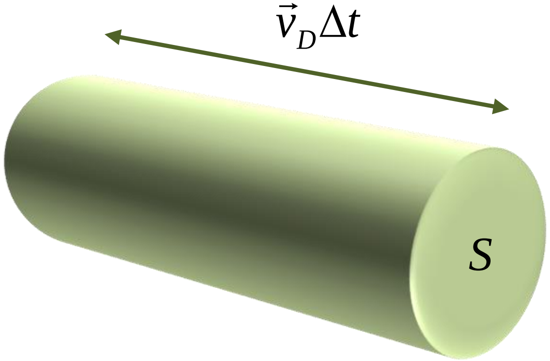
The classical model of electrical conduction

Electrical conductivity of plasma:

Paul Karl Ludwig Drude
1863-1906

Current density:

$$\vec{j} = \frac{1}{S}\frac{\Delta Q}{\Delta t} = \frac{1}{S}\frac{\Delta(-enV)}{\Delta t} = \frac{ne}{S}\frac{S\vec{v}_D\Delta t}{\Delta t}$$



$$\vec{j} = -en\vec{v}_D$$

Drift velocity $\vec{v}_D = \vec{v} - \vec{v}_{therm}$

Drude model. Model of the conductivity of metals proposed by Drude approx. 1900, soon after the discovery of the electron.

$$m\frac{d\vec{v}}{dt} + \frac{m}{\tau}\vec{v}_D = -e\vec{E}$$

After switching off the electric field $\vec{v}$ returns to thermal velocity (exponentially: τ)

For the stationary case: $\frac{d\vec{v}}{dt} = 0 \Rightarrow \vec{v}_D = -\frac{e\tau}{m}\vec{E}$

Mobility: $\mu = \frac{e\tau}{m}$

The classical model of electrical conduction

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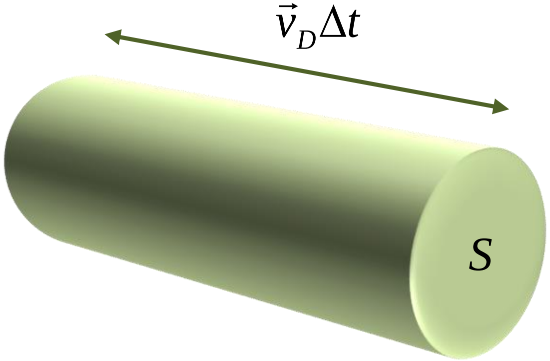


$$\vec{j} = -en\vec{v}_D$$

Drift velocity $\vec{v}_D = \vec{v} - \vec{v}_{therm}$

$$\sigma = ne\mu = \frac{ne^2}{m}\tau \approx \frac{ne^2}{m}\frac{l}{\langle v\rangle}$$

How can we calculate the average speed of electrons?

The classical model of electrical conduction

Electrical conductivity of plasma:

Paul Karl Ludwig Drude
1863-1906

How can we calculate the average speed of electrons?

Drude: Ideal gas, Boltzman distribution

$$\frac{1}{2}\,m\langle v\rangle^2 = \frac{3}{2}k_BT$$

$$\langle v\rangle = \sqrt{\frac{3k_BT}{m}} = \ \ldots 300K \ldots = 1{,}2\cdot 10^5\,\frac{m}{s}$$

Pure metals at T = 300 K $\langle l\rangle \approx 5 \times 10^{-6}$ m,
at T = 4 K $\langle l\rangle \approx$1cm

Arnold Johannes
Wilhelm Sommerfeld
(1868 –1951)

Sommerfeld: degenerated Fermi gas (Fermi-Dirac distribution):

$$\langle v\rangle = \sqrt{\frac{2E_F}{m}} = \ 1{,}6\cdot 10^6\,\frac{m}{s}$$

$$\langle l\rangle \approx 40\,nm$$

The classical model of electrical conduction

Electrical conductivity of plasma:

How can we calculate the average speed of electrons?

Drude: Ideal gas, Boltzman distri $= \frac{3}{2} k_B T$

P

At low temperatures and pure metals ⟨*l*⟩ may be even larger
(in the order of millimeters)!
Based on classical mechanics the "transparency" of metals
cannot be explained!
End of classical models.

Som degenerated Fermi gas (Fermi-Dirac distribution):

$$\langle v \rangle = \sqrt{\frac{2E_F}{m}} = 1{,}6 \cdot 10^6 \frac{m}{s} \qquad \langle l \rangle \approx 40\ nm$$

Arnold Johannes
Wilhelm Sommerfeld
(1868 –1951)

The classical model of electrical conduction

Electrical conductivity of plasma:

Paul Karl Ludwi

186

How can we calculate the average speed of electrons?

Drude: Ideal gas, Boltzman distribution

$\frac{1}{2}m\langle \qquad \frac{3}{2}k_BT$

$$\langle v\rangle = \sqrt{\frac{3k_BT}{m}} = \ldots 300K \ldots =$$

Pure metals m,

at T

Digression: Drude, Sommerfeld

Which classical model is better?

Sommerfeld: degenerated Fermi gas (Fermi-Dirac distribution):

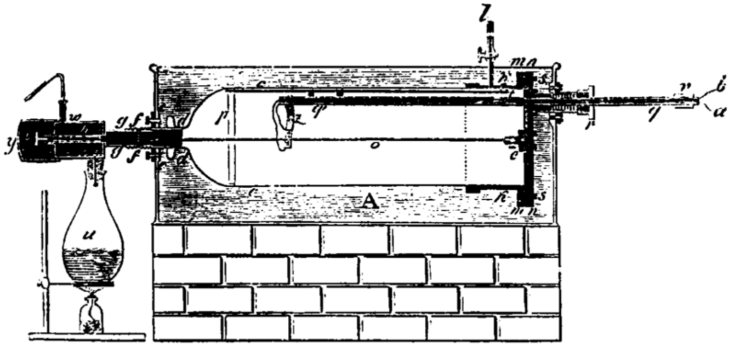
$$\langle v\rangle = \sqrt{\frac{2E_F}{m}} = 1{,}6\cdot 10^6\,\frac{m}{s} \qquad \langle l\rangle \approx 40\,nm$$

Arnold Johannes
Wilhelm Sommerfeld
(1868 –1951)

The classical model of electrical conduction

Wiedemann-Franz law: the ratio of the thermal conductivity κ and electrical conductivity σ in any metal is directly proportional to the temperature (L - constant Lorentz)

$$\boxed{\frac{\kappa}{\sigma} = LT}$$

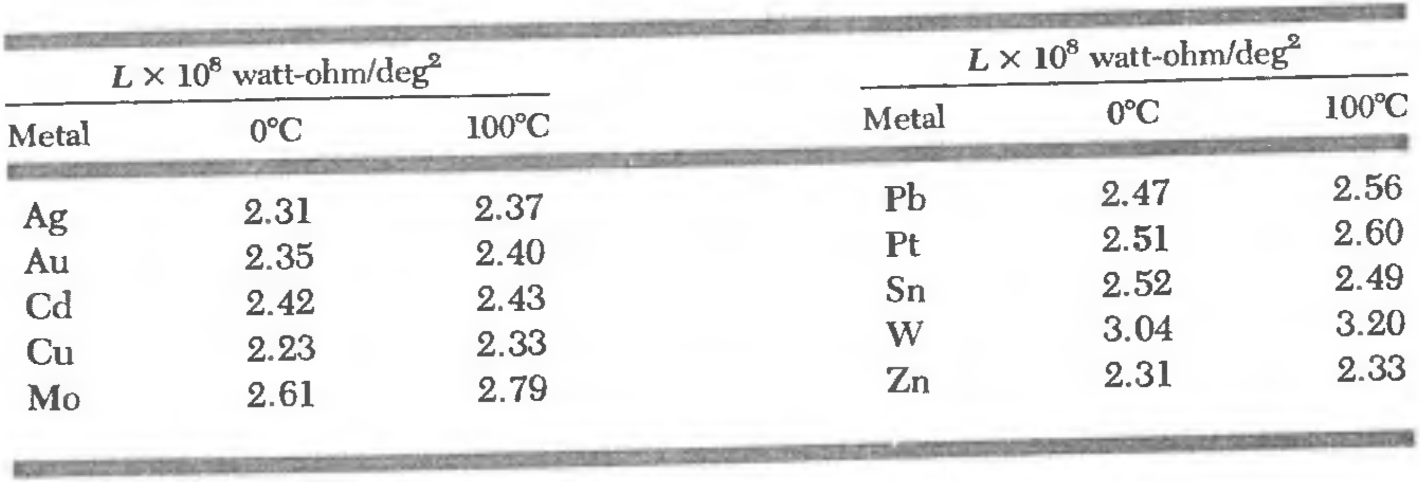


$$L_{Drude} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1{,}11 \cdot 10^{-8}\,\frac{W\Omega}{K^2}$$

$$L_{Sommerfeld} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2{,}44 \cdot 10^{-8}\,\frac{W\Omega}{K^2}$$

Better result!

Table 5 Experimental Lorenz numbers



	$L \times 10^8$ watt-ohm/deg^2			$L \times 10^8$ watt-ohm/deg^2	
Metal	0°C	100°C	Metal	0°C	100°C
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Sn	2.52	2.49
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

Ch. Kittel

Theoretical description of condensed matter

Born – Oppenheimer approximation

Full non-relativistic Hamiltonian of the system of nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$\begin{aligned}
&H(\vec{r},\vec{R})\\
&= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_N \frac{\hbar^2}{2M_N}\nabla_N^2 - -\frac{1}{4\pi\varepsilon_0}\sum_{N,i}\frac{Z_N e^2}{|\vec{r}_i - \vec{R}_N|} +\\
&+ \frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|} + \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} =\\
&= \hat{T}_e + \hat{T}_N + V(\vec{r},\vec{R}) + V_e(\vec{r}) + G(\vec{R})
\end{aligned}$$

Electron and nuclear (ions) subsystems coordinates are intermixed, separation of electronic and nuclear variables is impossible

Assumption: motion of atomic nuclei and electrons in a molecule can be separated

Born-Oppenheimer adiabatic approximation

Theoretical description of condensed matter

LCAO method

The solution of the equation of electron states requires numerical methods

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

One of methods: LCAO-MO with Hartree-Fock approximation – **self-consistent field method** (iterative method), n-electron wave function as Slater determinant, trivially satisfies the antisymmetric property of the exact solution:

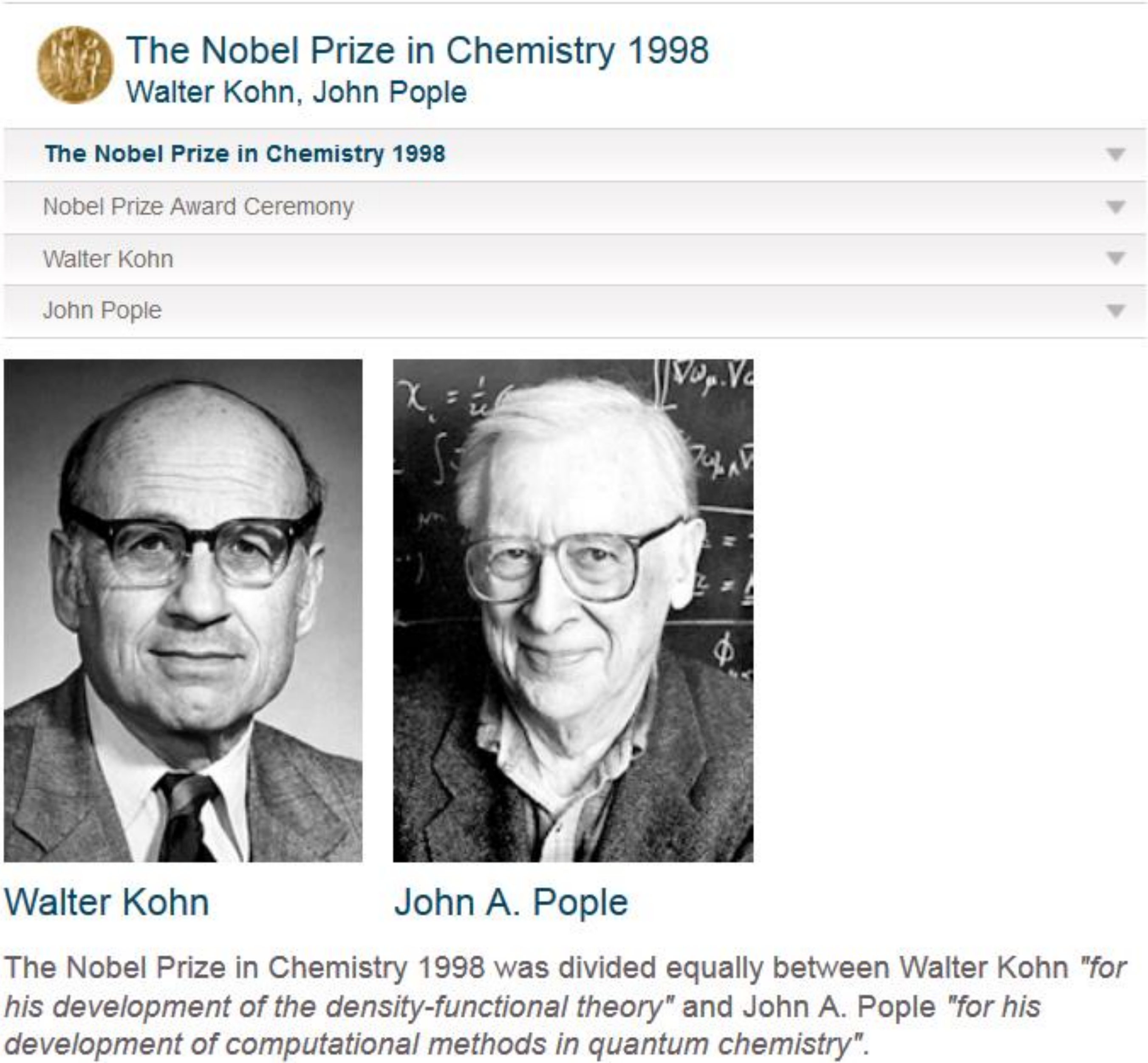
$$\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots s_1,s_2,s_3,\dots) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1^{sp}(\vec{r}_1,s_1) & \varphi_1^{sp}(\vec{r}_2,s_2) & \dots & \varphi_1^{sp}(\vec{r}_n,s_n) \\ \varphi_2^{sp}(\vec{r}_1,s_1) & \varphi_2^{sp}(\vec{r}_2,s_2) & \dots & \varphi_2^{sp}(\vec{r}_n,s_2) \\ \dots & \dots & & \dots \\ \varphi_n^{sp}(\vec{r}_1,s_1) & \varphi_n^{sp}(\vec{r}_2,s_2) & \dots & \varphi_n^{sp}(\vec{r}_n,s_n) \end{vmatrix}$$

Each of the single-electron spin-orbital $\varphi_n^{sp}(\vec{r}_n,s_n)$ must be different – two spin-orbital can for instance share the same orbital function, but then theirs spins are different

$$\varphi_n^{sp}(\vec{r}_n,s_n) = \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}0\\1\end{bmatrix} \text{ or } \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}1\\0\end{bmatrix}$$

Theoretical description of condensed matter

DFT method



The Nobel Prize in Chemistry 1998
Walter Kohn, John Pople

Walter Kohn
John A. Pople

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn *"for his development of the density-functional theory"* and John A. Pople *"for his development of computational methods in quantum chemistry"*.

Theoretical description of condensed matter

Hartree approximation (one-electron)

$$\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots) = \varphi_1(\vec{r}_1)\cdot\varphi_2(\vec{r}_2)\cdot\varphi_3(\vec{r}_3)\cdot\dots\cdot\varphi_n(\vec{r}_n)$$

We assume that an average potential from other ions and electrons acts on each electron:

$$\left(\sum_i \frac{p_i^2}{2m} + \sum_i V_i(\vec{r}_i)\right)\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots) = E_{tot}^{k}\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots)$$

Thus

$$\left(\frac{p_i^2}{2m} + V_i(\vec{r}_i)\right)\varphi_i(\vec{r}_i) = E_i\varphi_i(\vec{r}_i)$$

If every potential is the same $V_1(\vec{r}_1) \approx V_2(\vec{r}_2) \approx \cdots \approx V_n(\vec{r}_n) \approx V(\vec{r})$ we get $\sum_i E_i = E_{tot}$

One-electron Schrödinger equation:

$$\left(\frac{p^2}{2m} + V(\vec{r})\right)\varphi_i(\vec{r}_i) = E_i\varphi_i(\vec{r}_i)$$

This time i is the set of quantum numbers of one-electron quantum states $\varphi_i(\vec{r}_i)$ of energies E_i.

One-electron states are subject to the Pauli exclusion principle.

A significant change in the number of electrons in a given band, leads to the change of $V(\vec{r})$ and of the one –particle spectra! (for instance energy gap renormalization)

Periodic potential

Bloch theorem

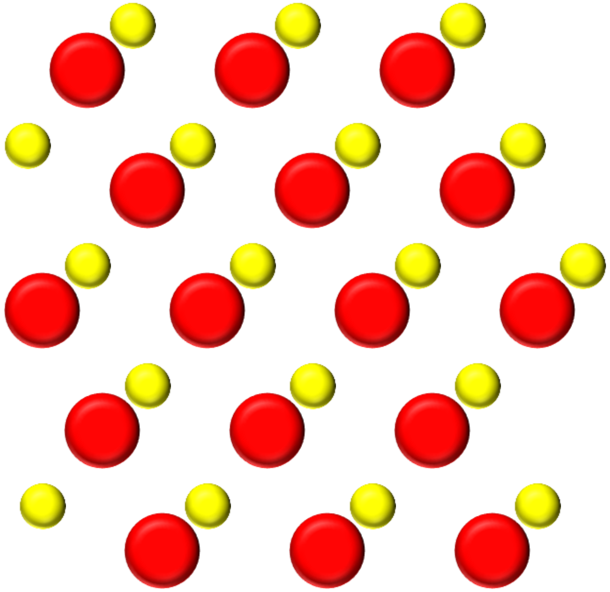
Assumptions:

Motionless atoms, crystal (periodic) lattice .

One-electron Hartree approximation

$$\Psi_{el}^{k}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots) = \varphi_1(\vec{r}_1) \cdot \varphi_2(\vec{r}_2) \cdot \varphi_3(\vec{r}_3) \cdot \dots \cdot \varphi_n(\vec{r}_n)$$

or Hartree-Fock approximation (Slater determinant).



Self-consistent field method – the multi-electron issue is reduced to the solution of one-electron problem in a potential of all other electrons and atoms

$$\left(\frac{p^2}{2m} + V(\vec{r})\right)\varphi_n(\vec{r}_n) = E_n\varphi_n(\vec{r}_n)$$

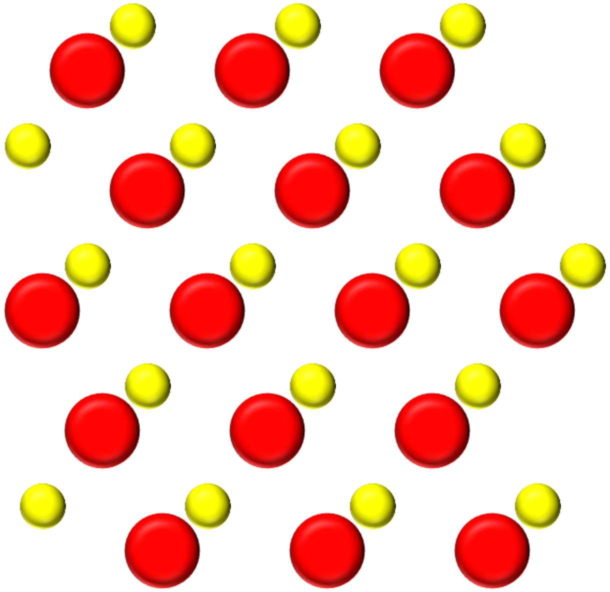
„One-electron” Schrödinger equation

Effective potential, periodic potential of the crystal lattice, the same for all electrons.

$$\boxed{V(\vec{r}) = V\left(\vec{r} + \vec{R}\right)}$$

Periodic potential

Bloch theorem



For every periodic potential $\boxed{V(\vec{r}) = V(\vec{r} + \vec{R})}$

The solutions of the Schrodinger equation:

$$\left(\frac{p^2}{2m} + V(\vec{r})\right)\psi_n(\vec{r}_n) = E_n\psi_n(\vec{r}_n)$$

have a form: $\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r})\, e^{i\vec{k}\vec{r}}$

Bloch wave,
Bloch function

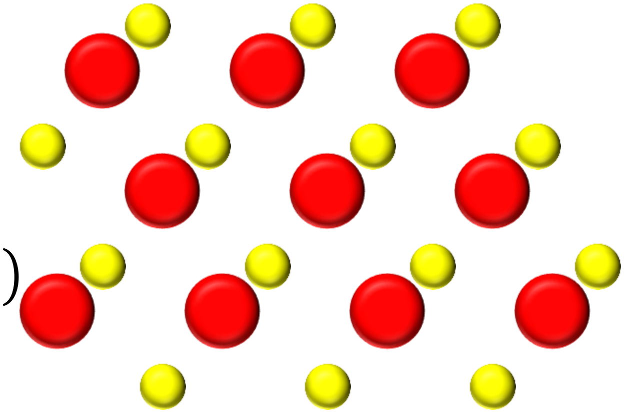
Bloch amplitude,
Bloch envelope

The solution of the one-electron Schrödinger equation for a periodic potential has a form of modulated plane wave:

$$u_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r} + \vec{R})$$

Periodic potential

Bloch theorem



Proof:

Translation operator $\hat{T}_{\vec{R}}$ $\hat{T}_{\vec{R}}\left(f(\vec{r})\right) = f\left(\vec{r}+\vec{R}\right)$

Perodic potential of the crystal lattice: $\hat{T}_{\vec{R}}\left(V(\vec{r})\right) = V\left(\vec{r}+\vec{R}\right)$

Hamiltonian with periodic potential

$$\hat{T}_{\vec{R}}\left(\hat{H}(\vec{r})\,\psi(\vec{r})\right) = \hat{H}\left(\vec{r}+\vec{R}\right)\psi\left(\vec{r}+\vec{R}\right) = \hat{H}(\vec{r})\,\psi\left(\vec{r}+\vec{R}\right) = \hat{H}(\vec{r})\hat{T}_{\vec{R}}\left(\psi(\vec{r})\right)$$

$$\hat{T}_{\vec{R}}\hat{T}_{\vec{R}'}\psi(\vec{r}) = \psi\left(\vec{r}+\vec{R}+\vec{R}'\right) = \hat{T}_{\vec{R}'}\hat{T}_{\vec{R}}\psi(\vec{r})$$

operators are commutative!

Eigenfunctions $\psi_{n,\vec{k}}(\vec{r})$ of the translation operator $\hat{T}_{\vec{R}}$:

$$\hat{T}_{\vec{R}}\psi_{n,\vec{k}}(\vec{r}) = C\left(\vec{R}\right)\psi_{n,\vec{k}}(\vec{r}) = e^{if\left(\vec{R}\right)}\psi_{n,\vec{k}}(\vec{r}) \qquad \left|C\left(\vec{R}\right)\right|^2 = 1$$

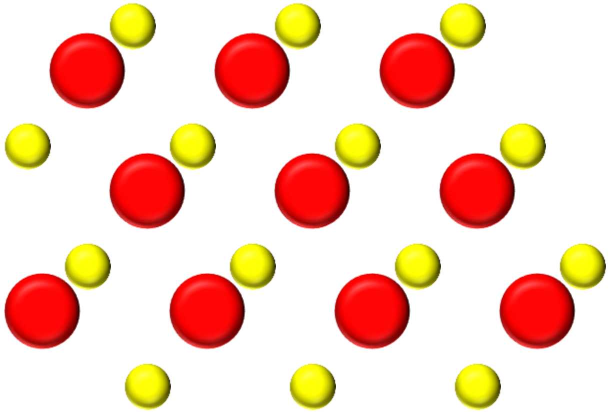
where $f\left(\vec{R}+\vec{R}'\right) = f\left(\vec{R}\right) + f\left(\vec{R}'\right)$

$f(0) = 0$

$\Rightarrow\ f\left(\vec{R}\right) = \vec{k}\vec{R}$

Periodic potential

Bloch theorem



Proof:

Translation operator $\hat{T}_{\vec{R}}$ $\quad \hat{T}_{\vec{R}}\left(f(\vec{r})\right) = f(\vec{r}+\vec{R})$

Eigenfunctions $\psi_{n,\vec{k}}(\vec{r})$ of the operator $\hat{T}_{\vec{R}}$

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = C(\vec{R})\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{R}}\psi_{n,\vec{k}}(\vec{r})$$

We denote our eigenfunction $\psi_{n,\vec{k}}(\vec{r})$ where n distinguishes the different functions of the same $\vec{k}$. Let us define:

$$u_{n,\vec{k}} = \psi_{n,\vec{k}}(\vec{r})e^{-i\vec{k}\vec{r}}$$

periodic function

$$\hat{T}_{\vec{R}}\left(u_{n,\vec{k}}\right) = \hat{T}_{\vec{R}}\left(\psi_{n,\vec{k}}(\vec{r})e^{-i\vec{k}\vec{r}}\right) = e^{i\vec{k}\vec{R}}\psi_{n,\vec{k}}(\vec{r})e^{-i\vec{k}(\vec{r}+\vec{R})} = \psi_{n,\vec{k}}(\vec{r})e^{-i\vec{k}\vec{r}} = u_{n,\vec{k}}$$

Thus:

$$\boxed{\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}e^{i\vec{k}\vec{r}}}$$

The eigenstates of the electron in a periodic potential are characterized by two quantum numbers $\vec{k}$ and n

$\vec{k}$ – wave vector

n – describes the energy bands (for a moment!)

Periodic potential

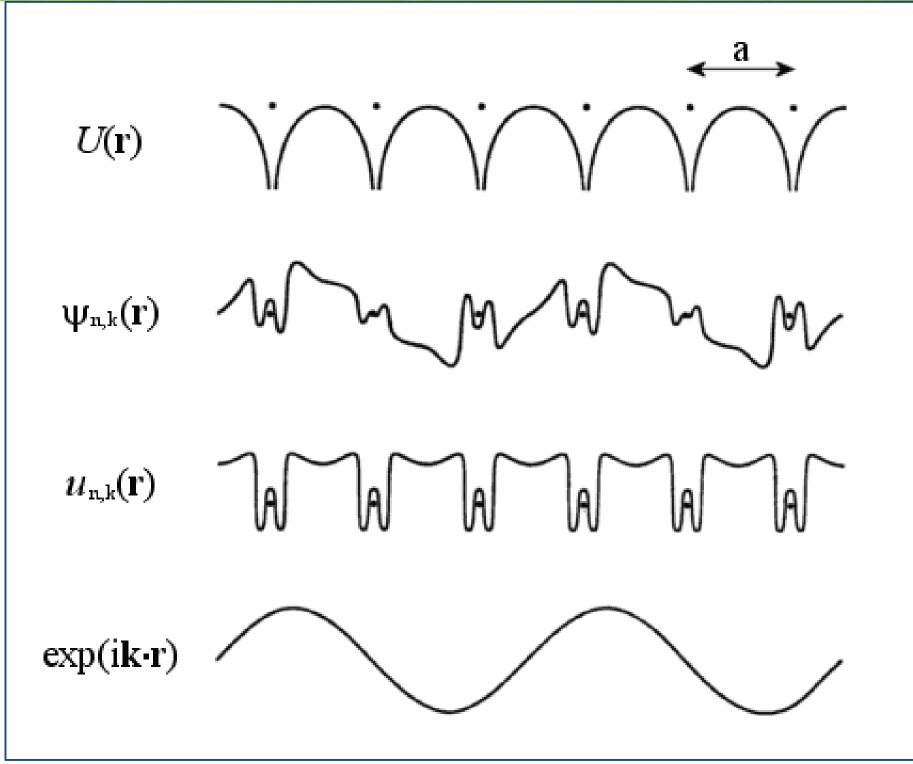
Bloch theorem

Bloch function:

$$\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r})\, e^{i\vec{k}\vec{r}}$$

Bloch wave,
Bloch function

Bloch amplitude,
Bloch envelope



Example:
Motion of the electron in a constant potential

$$\hat{H} = \frac{\hat{p}^2}{2m} + V = -\frac{\hbar^2}{2m}\Delta + V$$

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} \qquad \Rightarrow \quad E = -\frac{\hbar^2 k^2}{2m} + V$$

Momentum operator $\hat{p} = -i\hbar\nabla$ we get: $\hat{p}\psi_{n,\vec{k}}(\vec{r}) = \hbar\vec{k}\,\psi_{n,\vec{k}}(\vec{r})$

The solutions of the Schrödinger equation are eigenfunctions of the momentum operator $\hat{p}$. The momentum is well defined, the eigenvalues of the operator are $\hbar\vec{k}$ (the physical meaning of the wave vector $\vec{k}$)

Periodic potential

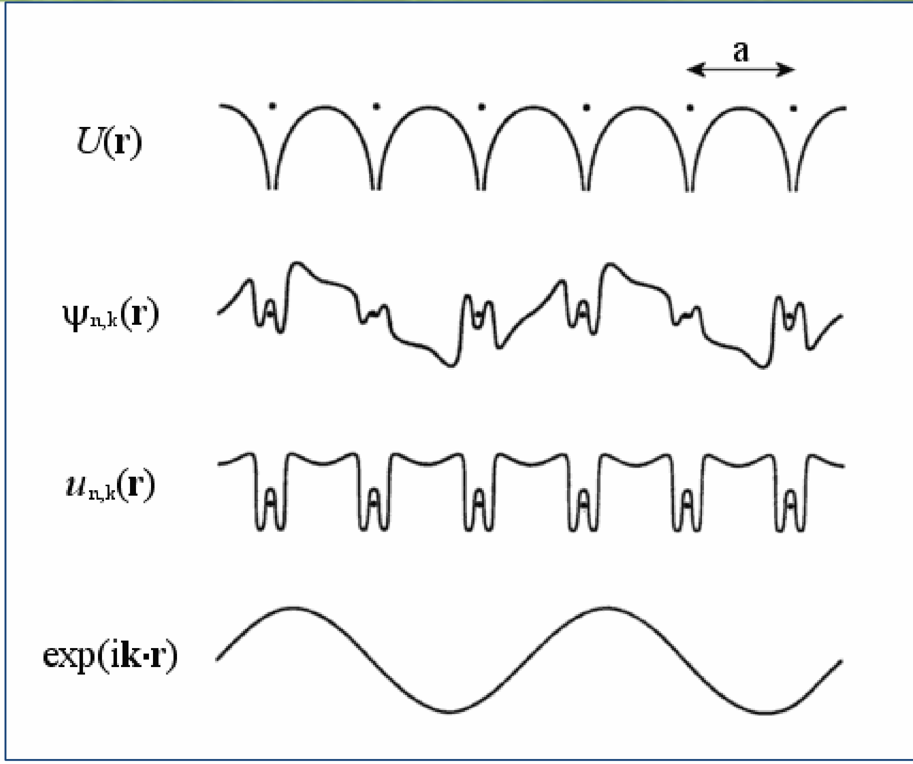
Bloch theorem

Bloch function:

$$\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r})\, e^{i\vec{k}\vec{r}}$$

Bloch wave,
Bloch function

Bloch amplitude,
Bloch envelope



Example:
Motion of the electron in a periodic potential

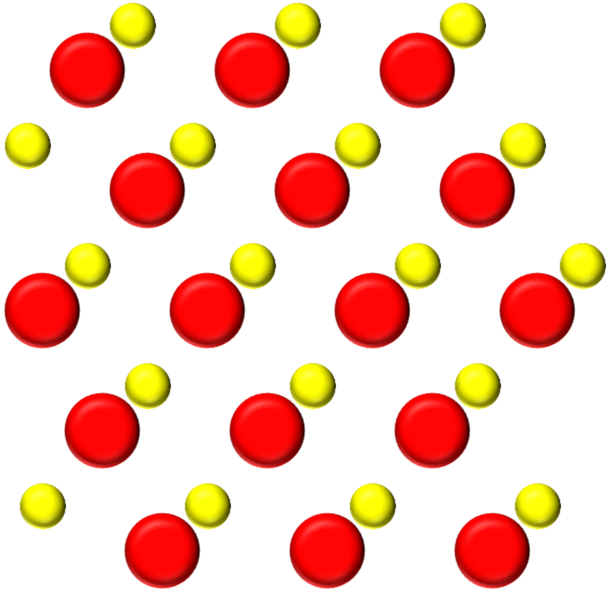
$$V(\vec{r}) = V\left(\vec{r} + \vec{R}\right)$$

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} \exp\left(i\vec{G}\vec{r}\right)$$

the Fourier series expansion

Periodic potential

Bloch theorem



Crystal lattice:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, \qquad n_i \in \mathbb{Z}$$

For periodic functions with the lattice period $\vec{R}$

$f(\vec{r}) = f(\vec{r} + \vec{R})$ a good base in the Fourier series expansion are functions $g(\vec{r}) = \exp(i\vec{G}\vec{r})$ which depend on the reciprocal lattice vectors:

$$\vec{G} = m_1\vec{a}_1^* + m_2\vec{a}_2^* + m_3\vec{a}_3^*, \qquad m_i \in \mathbb{Z}$$

$$\boxed{\vec{a}_i\vec{a}_j^* = 2\pi\delta_{ij}}$$

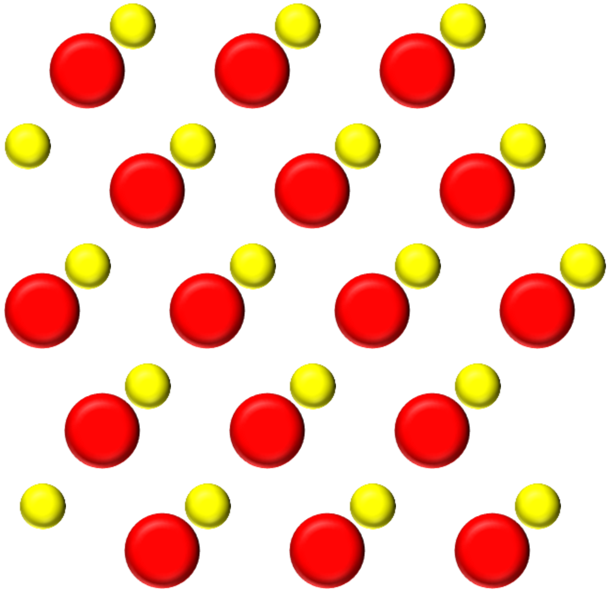
$$\exp\left[i\vec{G}\left(\vec{r} + \vec{R}\right)\right] =$$
$$= \exp\left[i\vec{G}\vec{r}\right] \cdot \exp\left[i\vec{G}\vec{R}\right] = \exp\left[i\vec{G}\vec{r}\right] \exp[2\pi\,(n_1m_1 + n_2m_2 + n_3m_3)] = \exp\left(i\vec{G}\vec{r}\right)$$

therefore $g(\vec{r}) = g\left(\vec{r} + \vec{R}\right)$ and finally we get:

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} \exp\left(i\vec{G}\vec{r}\right)$$

Periodic potential

Bloch theorem



Periodic potenetial we can expand as a Fourier series:

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} \exp\left(i\vec{G}\vec{r}\right)$$

The wavefunction can be represented as a sum of plane waves of different wavelengths satisfying periodic boundary conditions :

$$\varphi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right)$$

Schrödinger equation:

$$\left(\frac{\hat{p}^2}{2m} + V(\vec{r})\right)\varphi(\vec{r}) = E\,\varphi(\vec{r})$$

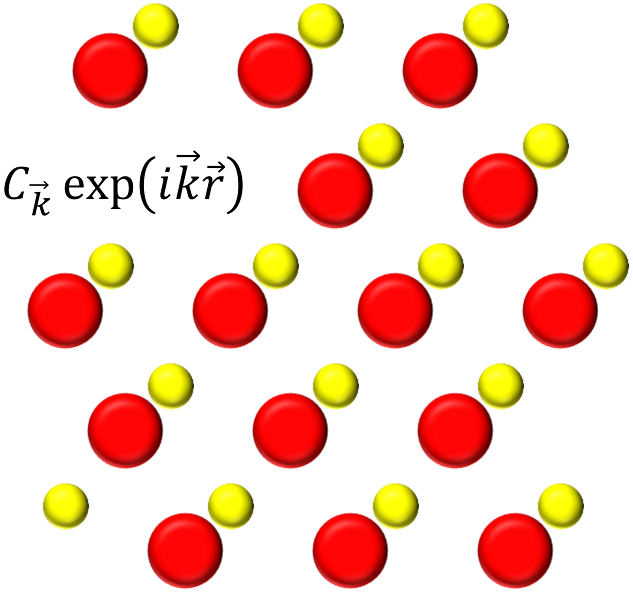
$$\sum_{\vec{k}} \frac{\hbar^2\vec{k}^2}{2m} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right) + \sum_{\vec{k},\vec{G}} C_{\vec{k}}\, V_{\vec{G}} \exp\left[i\left(\vec{k}+\vec{G}\right)\vec{r}\right] = E \sum_{\vec{k}} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right)$$

This is an equation for E and $C_{\vec{k}}$ for all vectors $\vec{k}, \vec{r}$ and $\vec{G}$.

See also: Ibach, Luth „Solid State Physics”

Periodic potential

Bloch theorem



$$\sum_{\vec{k}} \frac{\hbar^2\vec{k}^2}{2m} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right) + \sum_{\vec{k},\vec{G}} C_{\vec{k}}\, V_{\vec{G}} \exp\left[i\left(\vec{k}+\vec{G}\right)\vec{r}\right] = E\sum_{\vec{k}} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right)$$

The sum is over all $\vec{k}, \vec{G}$,therefore:

$$\sum_{\vec{k},\vec{G}} C_{\vec{k}}\, V_{\vec{G}} \exp\left[i\left(\vec{k}+\vec{G}\right)\vec{r}\right] = \;\ldots\; \vec{k}+\vec{G} \to \vec{k} \;\ldots$$

$$= \sum_{\vec{k},\vec{G}} C_{\vec{k}-\vec{G}}\, V_{\vec{G}} \exp\left[i\vec{k}\vec{r}\right]$$

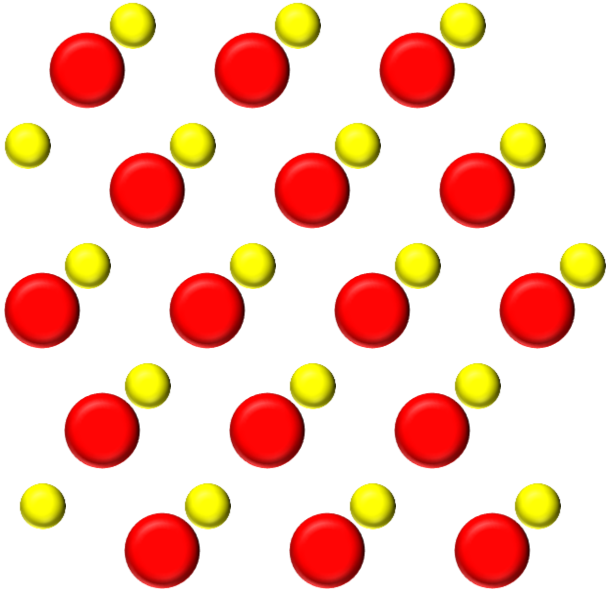
We get Schrödinger equation in a form:

$$\sum_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right)\left[\left(\frac{\hbar^2\vec{k}^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} C_{\vec{k}-\vec{G}} V_{\vec{G}}\right] = 0$$

That must be met for each vector $\vec{r}$.

Periodic potential

Bloch theorem



$$\sum_{\vec{k}} \exp(i\vec{k}\vec{r}) \left[\left(\frac{\hbar^2 \vec{k}^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} C_{\vec{k}-\vec{G}} V_{\vec{G}} \right] = 0$$

for each vector $\vec{r}$.

Thus, for each vector $\vec{k}$ we got equation for coefficients $C_{\vec{k}}$ and E:

$$\left(\frac{\hbar^2 \vec{k}^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} C_{\vec{k}-\vec{G}} V_{\vec{G}} = 0$$

In this equation for $C_{\vec{k}}$ also coefficients shifted by $\vec{G}$ like $C_{\vec{k}-\vec{G}_1}, C_{\vec{k}-\vec{G}_2}, C_{\vec{k}-\vec{G}_3}$ appear (but others do not, even when we started for any $\vec{k}$!).

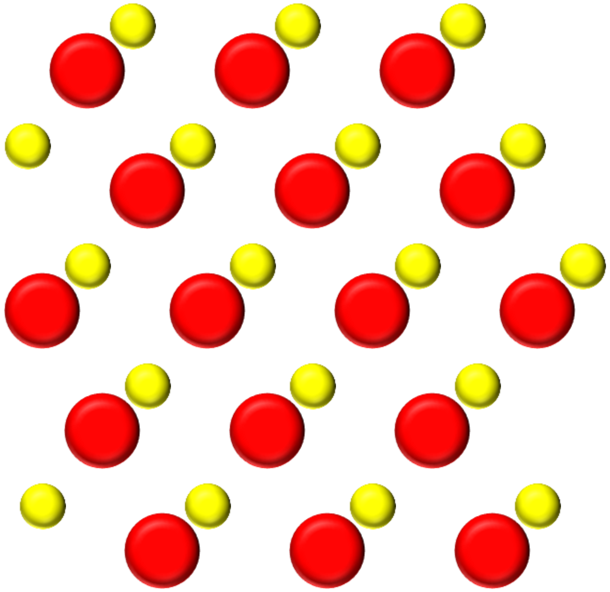
This equation couples those expansion coefficients $\varphi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k}\vec{r})$, whose $\vec{k}$ - values differ from one another by a reciprocal lattice vector $\vec{G}$.

Conclusion?

Try to plot the mattrix of this equation $\begin{bmatrix} C_{k_1} \\ C_{k_2} \\ C_{k_2} \\ \dots \\ C_{k_n} \end{bmatrix}$

Periodic potential

Bloch theorem



$$\left(\frac{\hbar^2\vec{k}^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} C_{\vec{k}-\vec{G}} V_{\vec{G}} = 0$$

We do not need to solve these equations for all vectors $\vec{G}$ – we can find a solution in **one** unit cell of the reciprocal lattice and copy it N times (N – number of unit cells)!

Thus we can find eigenvalues $E \rightarrow E_{\vec{k}} \rightarrow E(\vec{k})$ corresponding to the wave-function $\varphi_{\vec{k}}(\vec{r})$ represented as a superposition of plane waves whose wave vectors $\vec{k}$ differ only by reciprocal lattice vectors $\vec{G}$.

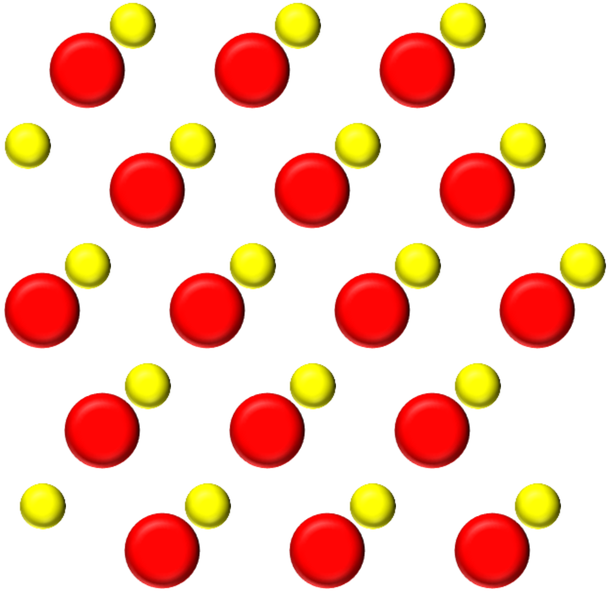
Wave vector $\vec{k}$ is a good quantum number according to which the energy eigenvalues and quantum states may be indexed. Thus the function $\varphi(\vec{r})$ is the superposition of $\varphi_{\vec{k}}(\vec{r})$ of energies $E(\vec{k})$

$$\varphi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} \exp\left(i\vec{k}\vec{r}\right) = \cdots = \sum_{\vec{k}} \varphi_{\vec{k}}(\vec{r})$$

(later on we introduce coefficient n for different solutions of $E_{\vec{k}}$ corresponding to the same $\vec{k}$)

Periodic potential

Bloch theorem



Wave-function which is the solution of the Schrodinger equation $\varphi_{\vec{k}}(\vec{r})$ is represented as a superposition of plane waves whose wave vectors $\vec{k}$ differ only by reciprocal lattice vectors $\vec{G}$ and it has energies $E_{\vec{k}} = E(\vec{k})$:

$$\varphi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} \exp[i(\vec{k}-\vec{G})\vec{r}]$$

Each vector $\vec{k}-\vec{G}$ can enumerate states; it is convenient to choose the shortest vector (which belongs to the first Brillouin zone).

$$\varphi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}}\, e^{i(\vec{k}-\vec{G})\vec{r}} = \sum_{\vec{G}} C_{\vec{k}-\vec{G}}\, e^{-i\vec{G}\vec{r}} \; e^{i\vec{k}\vec{r}} = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}}$$

The function $u_{\vec{k}}(\vec{r})$ is a Fourier series over reciprocal lattice points $\vec{G}$, and thus has the periodicity of the lattice.

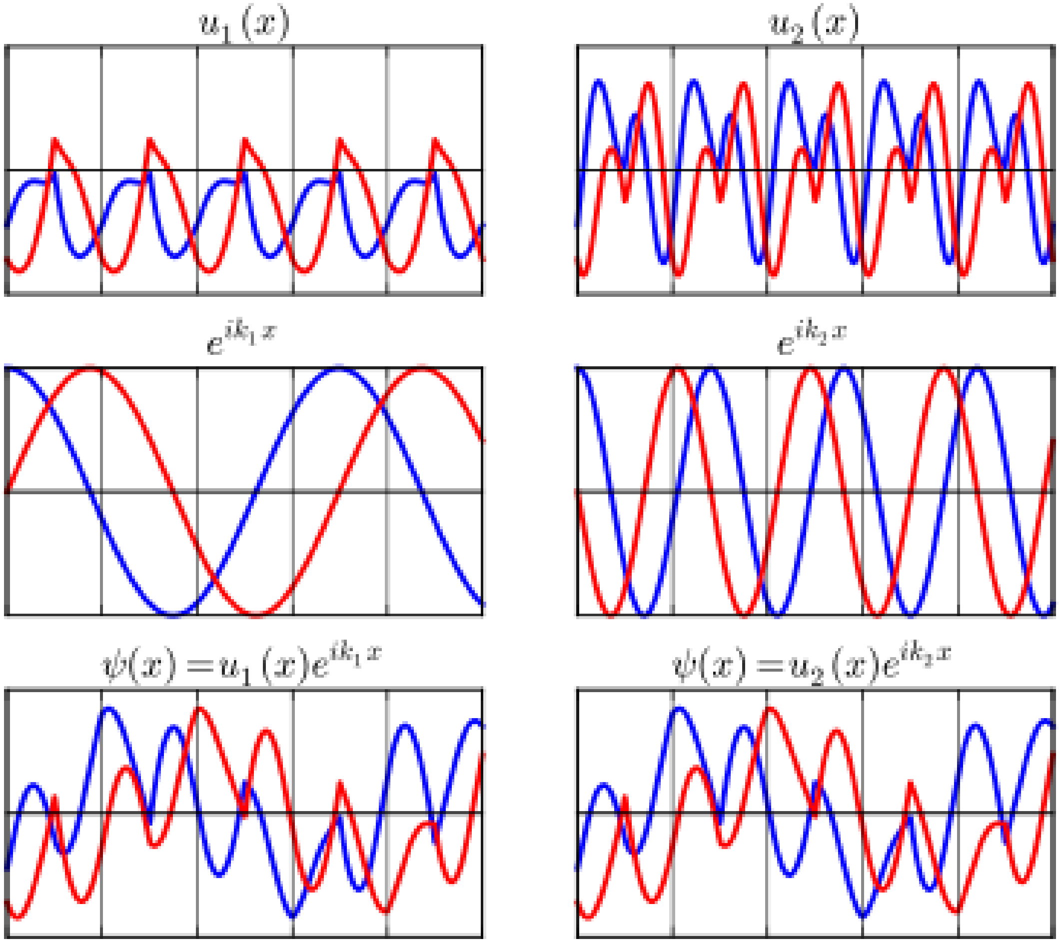
Conclusion?

Periodic potential

Bloch theorem

$$\varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}$$

Bloch waves whose wave vectors differ by a reciprocal lattice vector are IDENTICAL!



$$\vec{k}_1 - \vec{k}_2 = \vec{G}$$