

Density functional theory in solid state physics


Lecture 1

- Problem with quantum-mechanical approaches for condensed matter systems
- Introduction of Density Functional Theory
- Kohn-Sham ansatz and alternatives
- Exchange-correlation approximations
- Practical considerations for DFT: parameters, basis sets, pseudopotentials
- Application of DFT to the properties of 1D, 2D and 3D crystalline materials: electronic structure, phonons, magnetism, transport properties etc.
- Time-dependent DFT
- Highly accurate predictions from many-body perturbation theory: optical properties and quasiparticles

- Venue and dates: Technically every Tuesday, 15:00-17:00, room HF

Due to Corona: Prerecorded video will be uploaded every Tuesday to the FAU video portal

- Contact: E-mail to roland.gillen@fau.de, alternatively over Zoom
- Exercises: Start in the second half of the semester, (text-)guided tutorials using the Quantum Espresso code that can be done at home or in the CIP pool (if allowed)

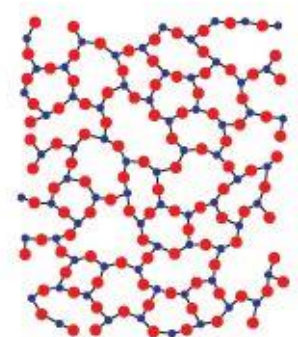
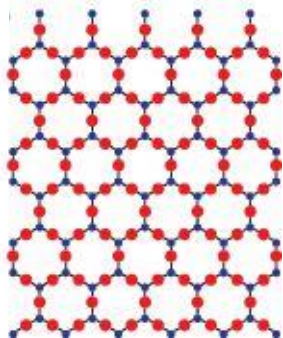
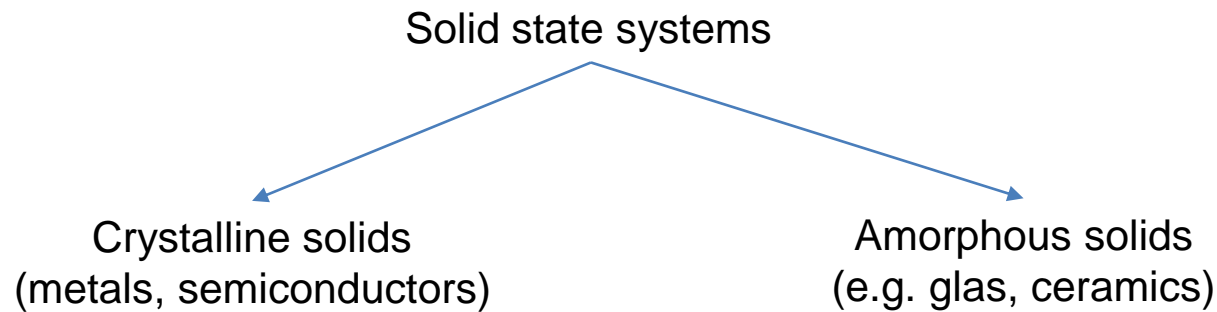
I suggest using  **QUANTUM MOBILE**, which can be downloaded from <https://www.materialscloud.org/work/quantum-mobile>

Alternatively, Quantum Espresso can be downloaded from <https://www.quantum-espresso.org/download>

- Exam: Probably written exam at the end of the summer holidays

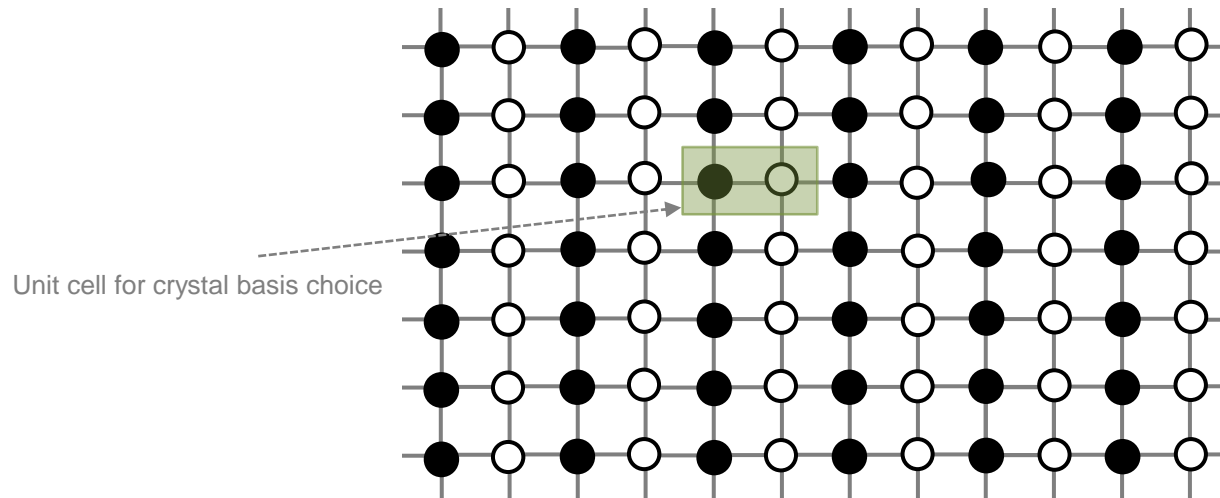
- *Electronic Structure: Basic Theory and Practical Methods*, by Richard Martin
- *Density Functional Theory: A Practical Introduction*, by David Sholl
- *The ABC of DFT*, by Kieron Burke
- *A Primer in Density Functional Theory*, edited by MAL Marques

Solid state physics: Physics that arises from interactions of a large number (on order 10^{23}) of atoms in a solid aggregate state



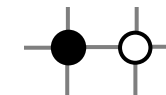
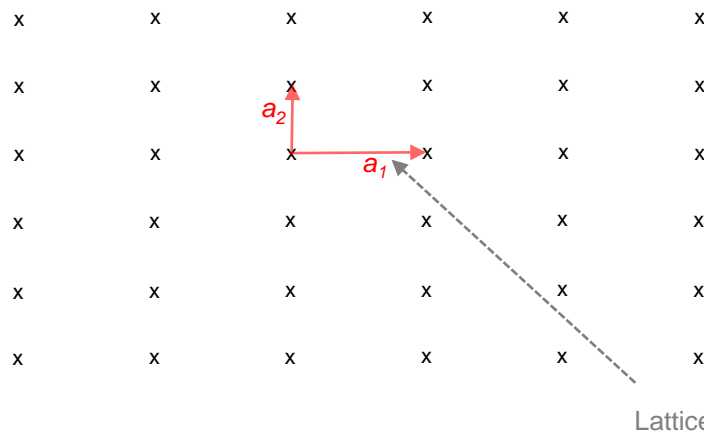
Ideal crystals

- (Ideal) Crystal: an infinite repetition of identical structural elements



- Crystal structure:

Lattice + crystal basis

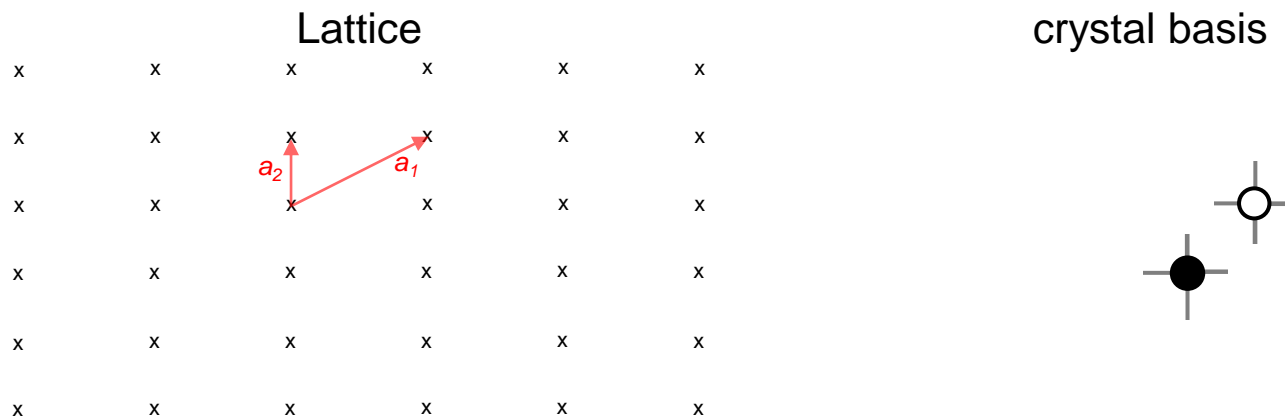
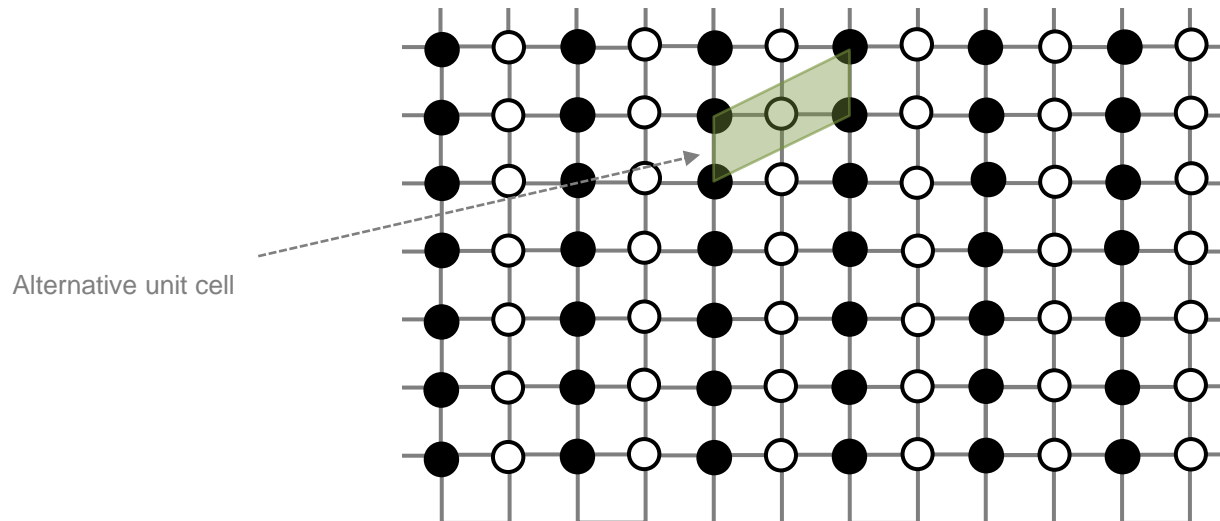


Translational invariance of „Bravais“ lattice:

Shift of the lattice by $\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + \dots$
leaves the lattice invariant

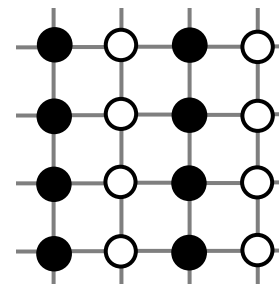
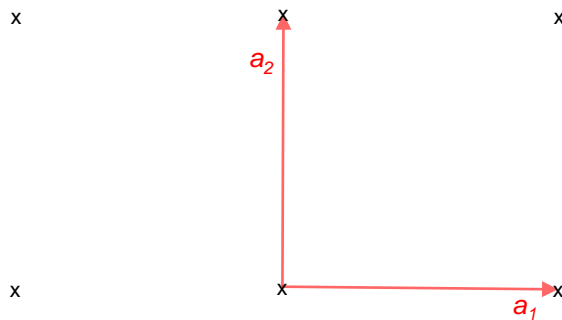
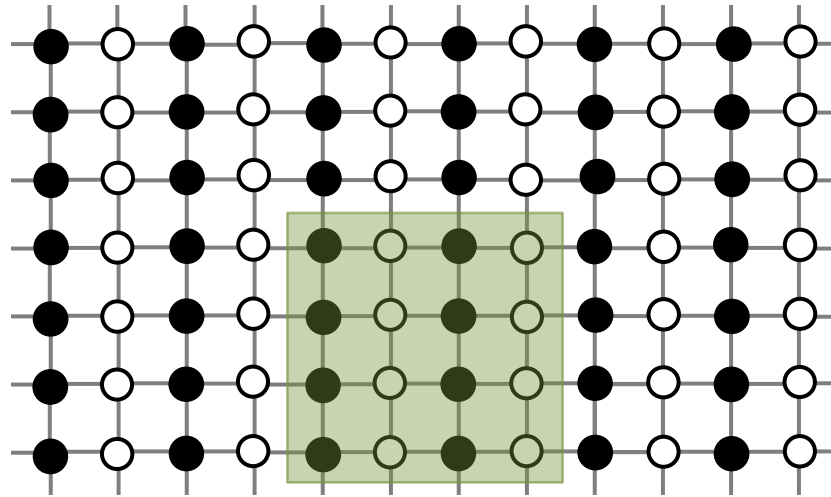
Ideal crystals

- Crystal basis choice is relatively arbitrary. Alternative unit cell:



Ideal crystals

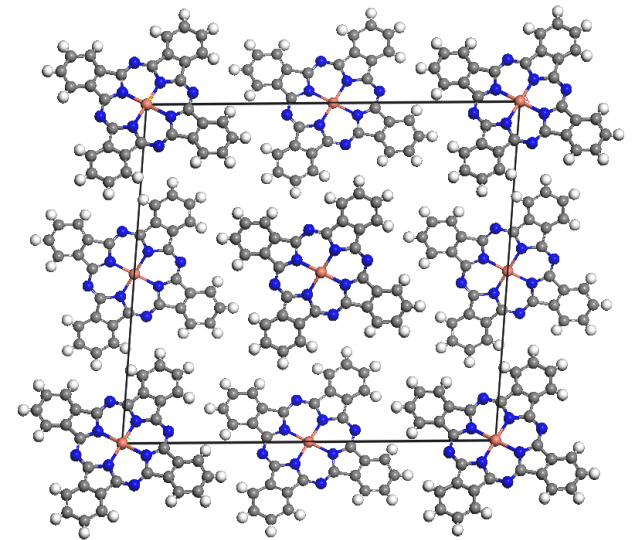
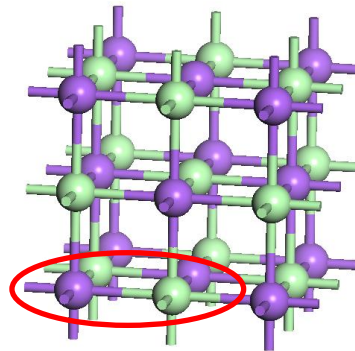
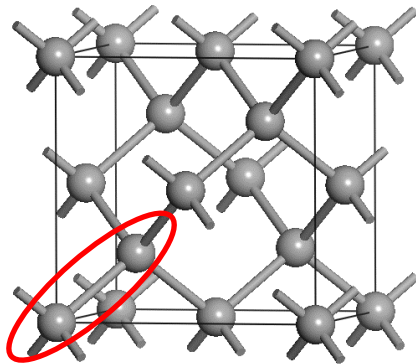
- Another possible choice:



- Unit cell choice(s) with smallest (minimal) volume: „primitive cell“

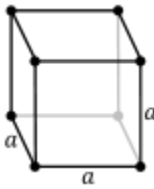
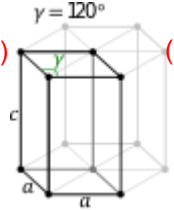
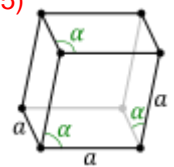
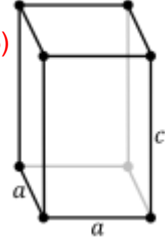
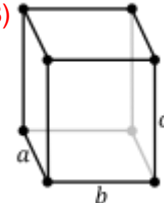
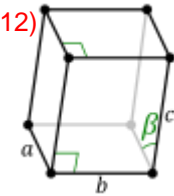
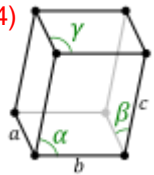
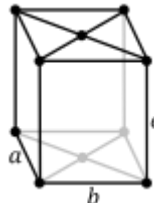
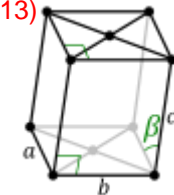
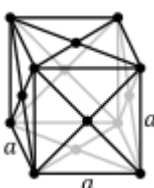
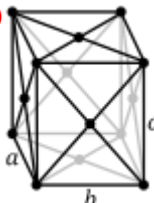
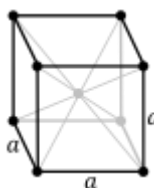
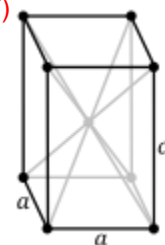
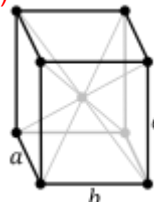
Ideal crystals

- Basis can, in principle, be anything (atom-related). Atom groups, ions, molecules etc.
- Different bonding conditions: covalent, metallic, ionic, hydrogen bridges



Bravais lattices

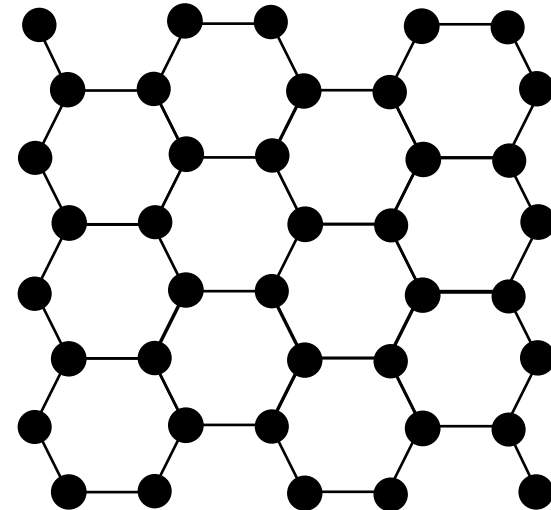
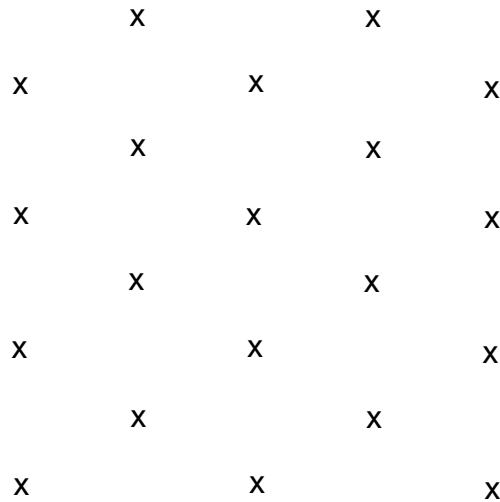
Classification: 7 Crystal systems, 14 Bravais lattices (in 3D)

	Cubic	Hexagonal	Rhombohedral	Tetragonal	Orthorhombic	Monoclinic	Triclinic
	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	$a=b$ $\alpha=\beta=90^\circ$	$a=b=c$ $\alpha=\beta=\gamma$	$a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$	$a \neq b \neq c$ $\alpha=\gamma=90^\circ \neq \beta$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
simple	(1) 	(4) 	(5) 	(6) 	(8) 	(12) 	(14) 
base-centered					(9) 	(13) 	
face-centered	(2) 				(10) 		
body-centered	(3) 			(7) 	(11) 		

Bravais lattice and symmetry

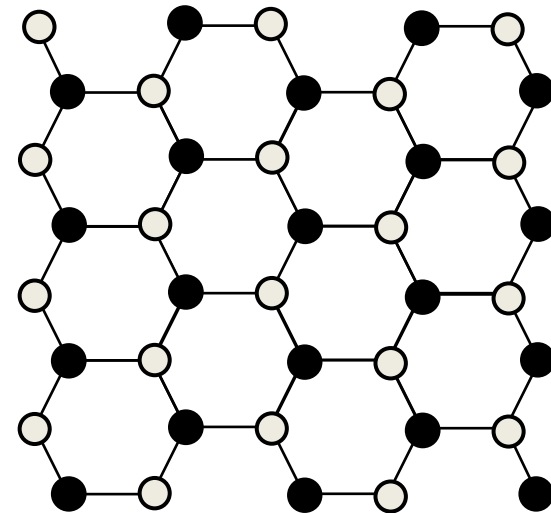
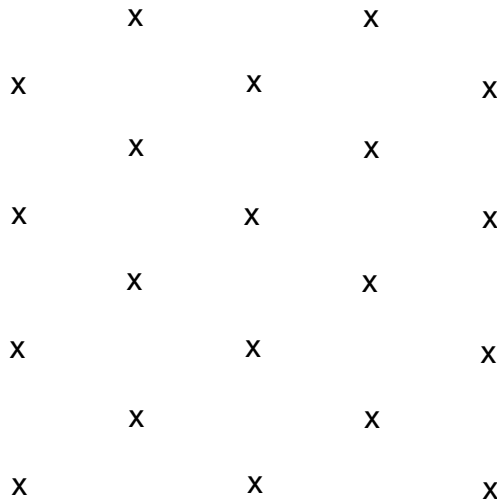
- Bravais lattice dictates the symmetry elements that the crystal can possess
- The crystal basis can remove some of these symmetries

Example: hexagonal lattice



- Bravais lattice dictates the symmetry elements that the crystal can possess
- The crystal basis can remove some of these symmetries

Example: hexagonal lattice

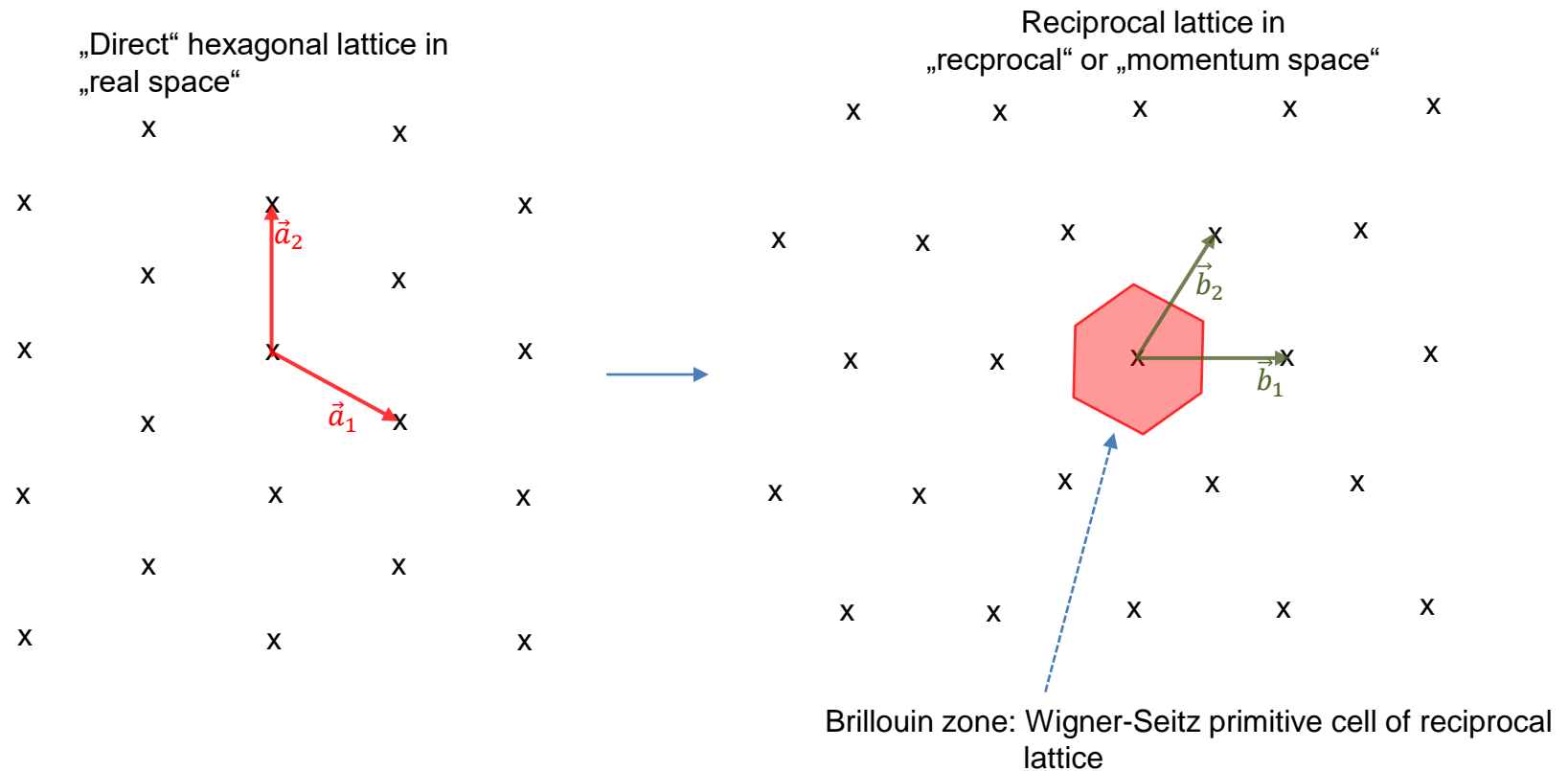


Lowered symmetry compared to lattice

Reciprocal lattice

- Fourier transformation of „direct“ lattice: „reciprocal lattice“

$$\vec{b}_1 = \frac{2\pi}{V}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{V}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{V}(\vec{a}_1 \times \vec{a}_2), \quad \vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

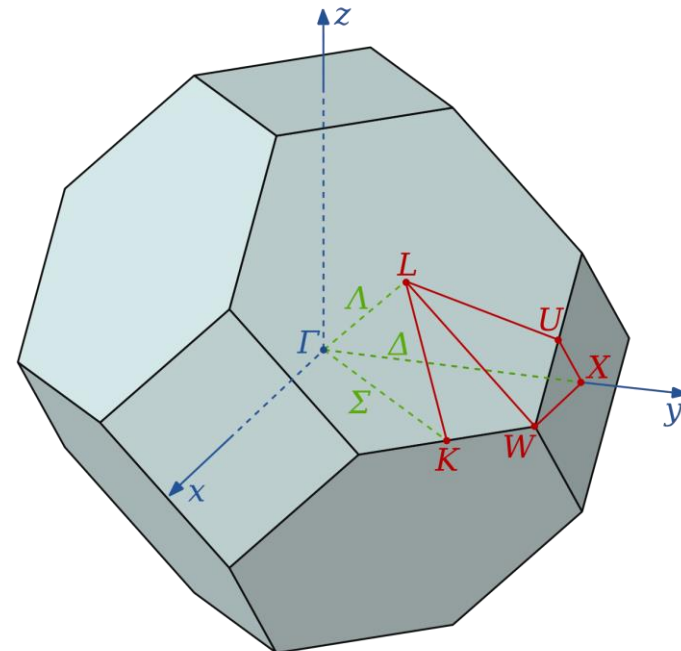
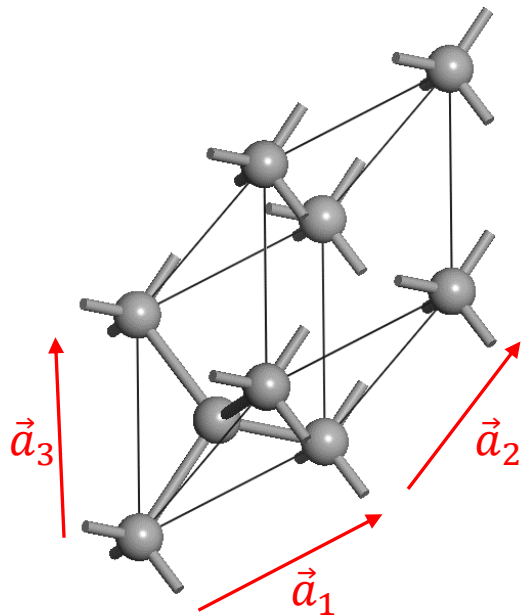


Vector connecting two reciprocal lattice points: $\vec{G} = l\vec{b}_1 + m\vec{b}_2 + \dots$

FCC Brillouin zone

- Brillouin zones of 3D crystals can be relatively complex

Example: Primitive cell and (1st) Brillouin zone of a face-centered cubic crystal (e.g. silicon)

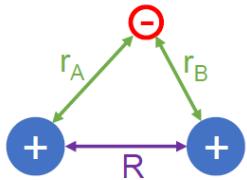


- Focus typically lies on high-symmetry points and paths

Orbital hybridization

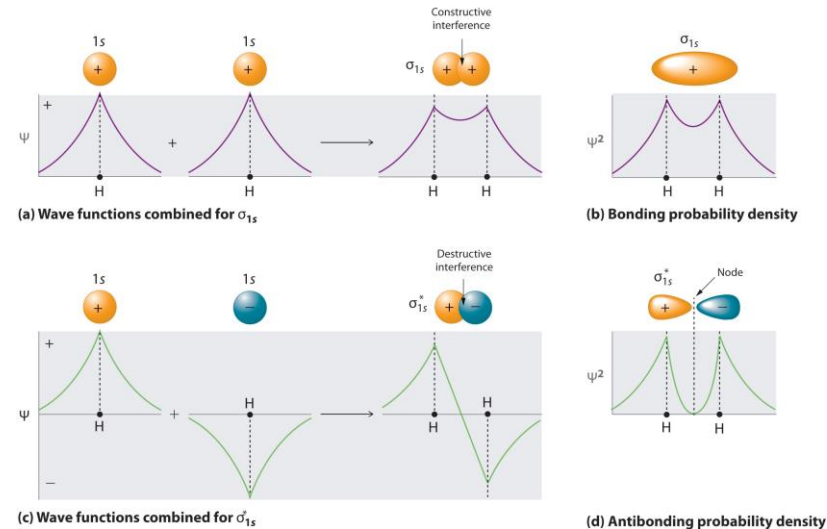
- Electronic properties of solids arise from hybridization of atomic orbitals

LCAO of H_2^+ molecule:

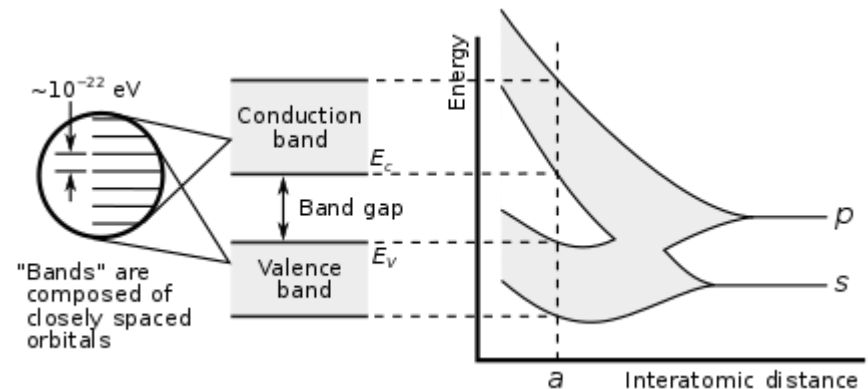
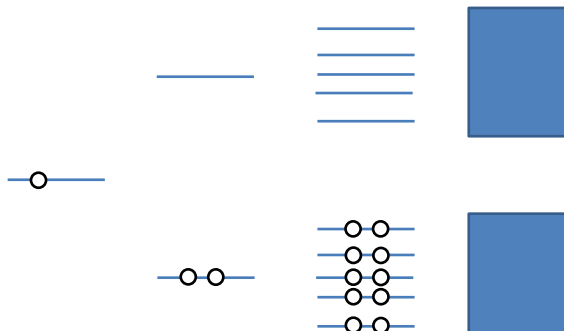


$$\psi = c_A \psi_A + c_B \psi_B$$

$$E_{\pm} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$



1 atom 2 atoms 10 atoms Many atoms



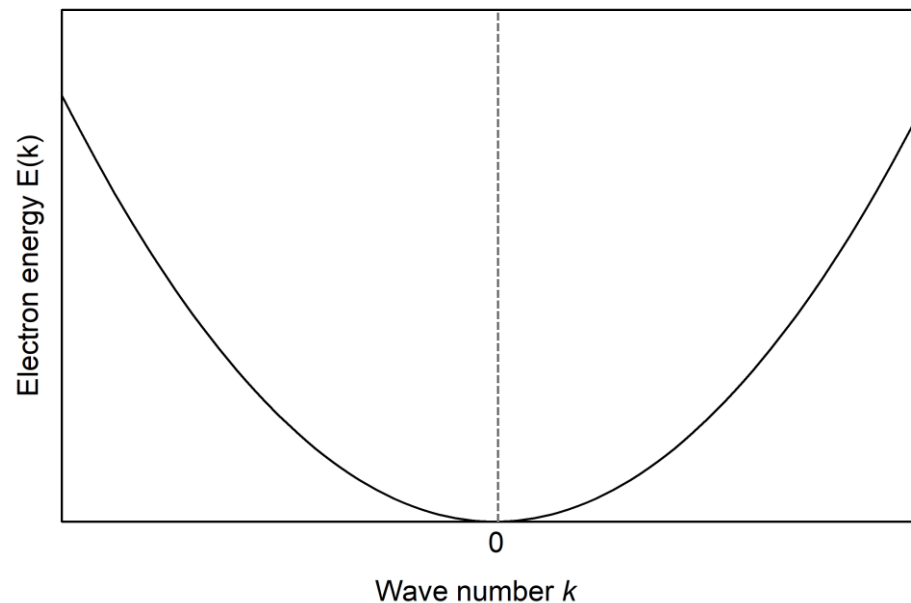
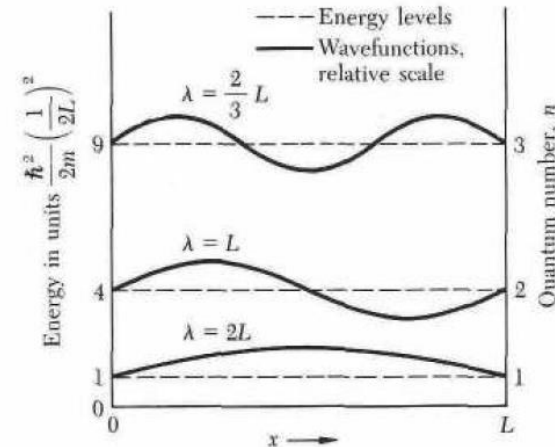
Free electron approximation

- „Free“ electrons confined to a volume V : plane waves with wave number k

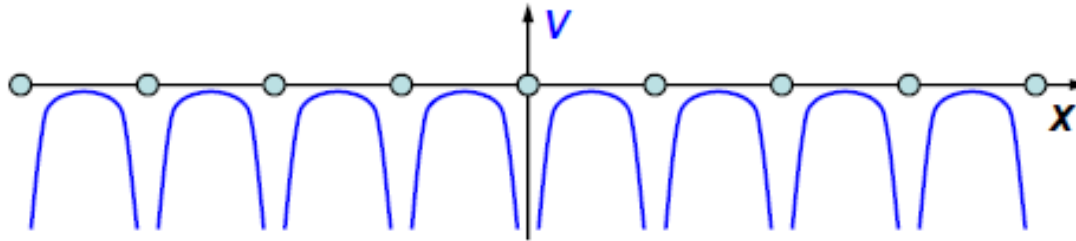
$$\varphi_k(r) = u e^{i k r}, \quad E(k) = \frac{\hbar^2 k^2}{2m}$$

$$k_{x,y,z} = n \frac{2\pi}{L_{x,y,z}}$$

(n is a quantum number such that φ_k satisfies the boundary conditions, $\hbar k$ is the electron momentum)



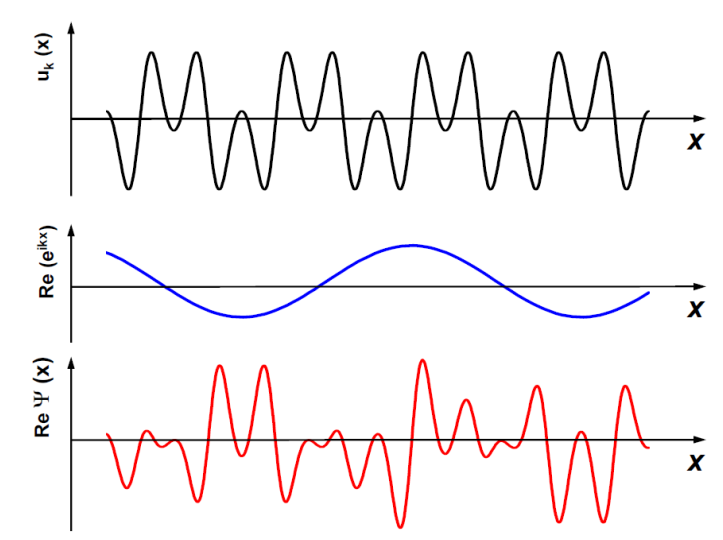
- Electron in a perfect crystal: translation symmetry affects electron wavefunctions



Gross: Festkörperphysik

Electrons can be described by Bloch waves: $\varphi_k(r) = u_k(r)e^{ikr}$

u is not uniquely defined: $u_k(r + T) = u_k(r)$, form is determined by external potential.



Gross: Festkörperphysik

Bloch waves

k is not uniquely defined either:

„crystal momentum“

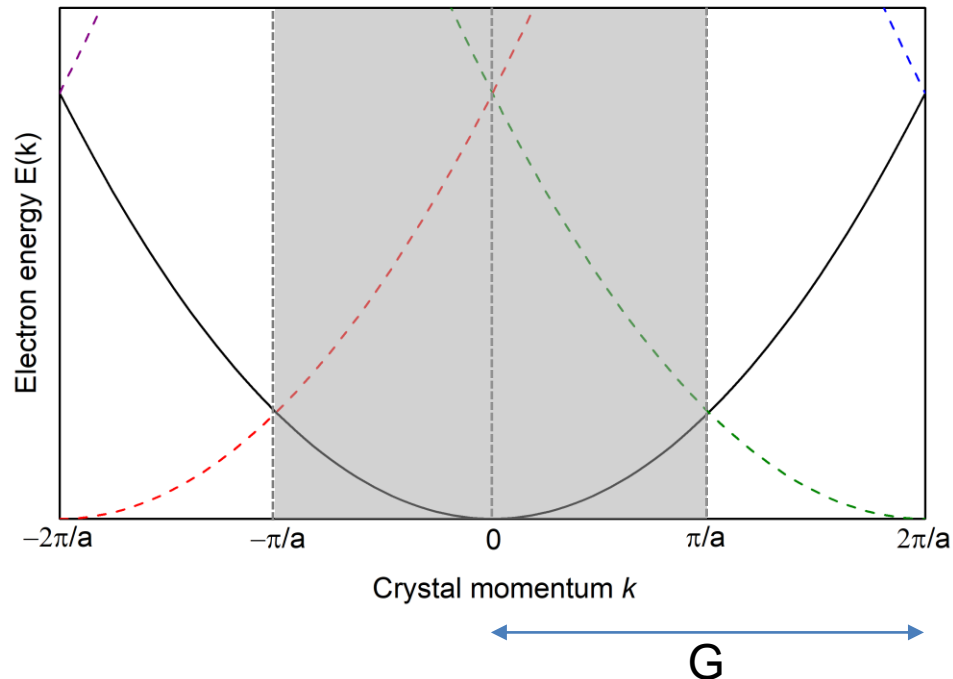
$$E(k + G) = E(k), \varphi_{k+G}(r) = \varphi_k(r)$$

$$\text{with } G = l\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3$$

→ First Brillouin zone contains all physical information, band index n , states φ_{nk} , $E_n(k)$

„Bandstructure“

Vanishing external potential:



Bloch waves

k is not uniquely defined either:

„crystal momentum“

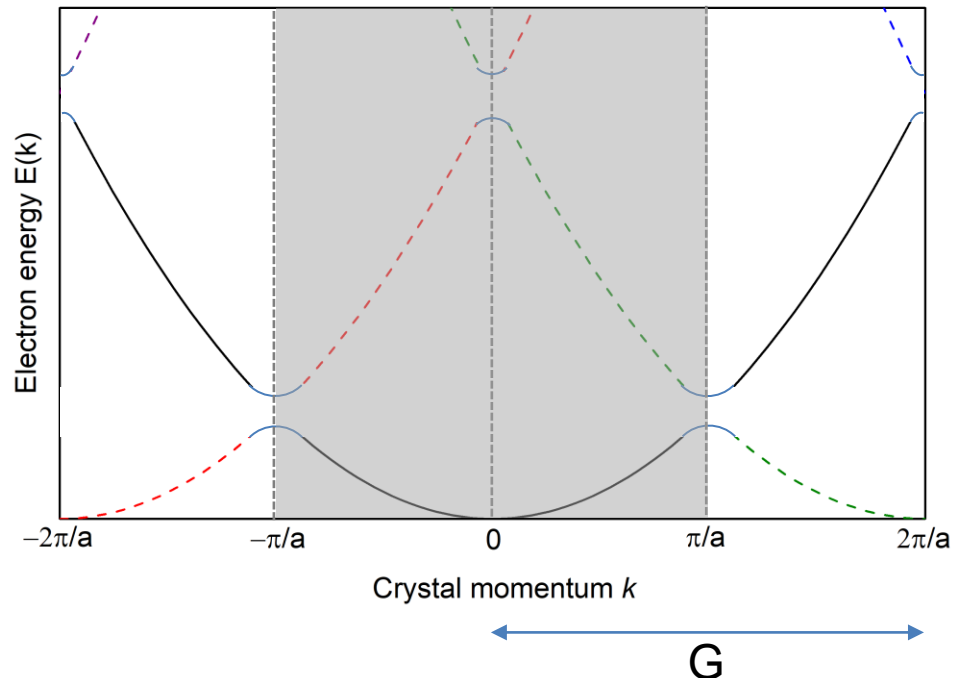
$$E(k + G) = E(k), \varphi_{k+G}(r) = \varphi_k(r)$$

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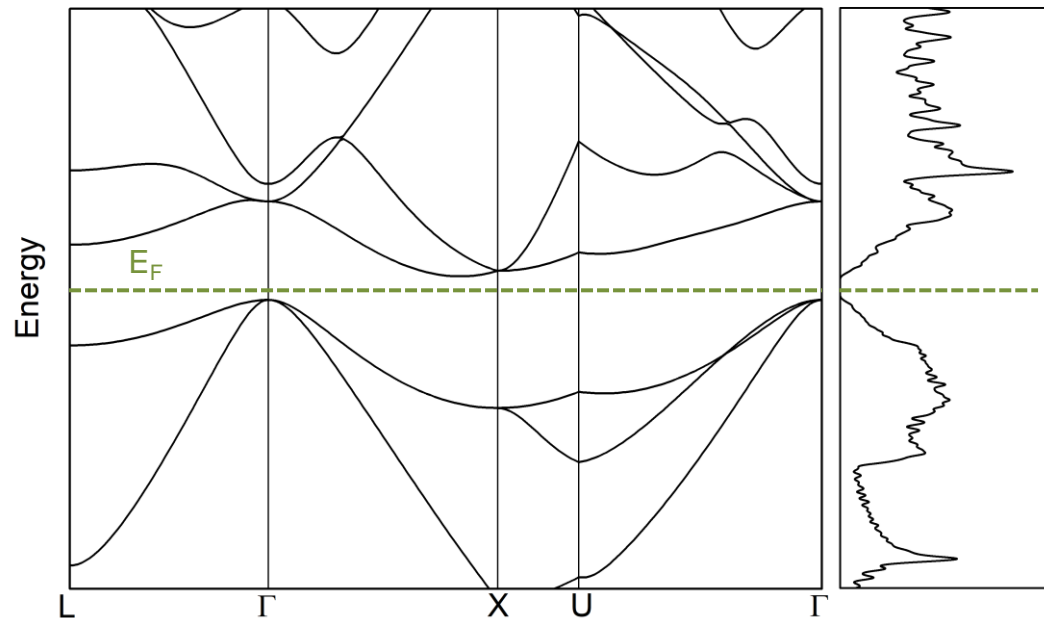
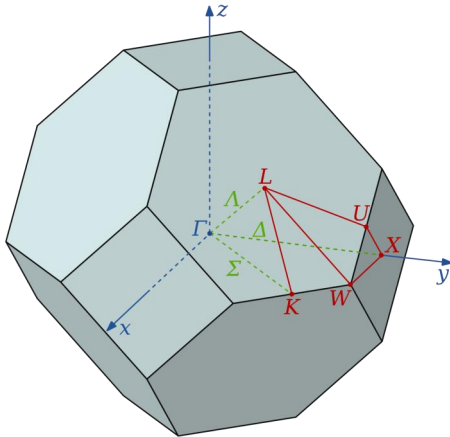
→ First Brillouin zone contains all physical information, band index n , states φ_{nk} , $E_n(k)$

„Bandstructure“

Non-vanishing atomic
potential:



Silicon



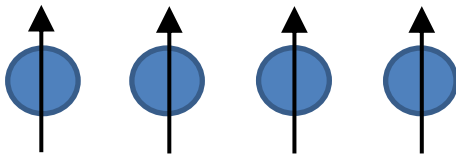
- Bandstructure of 2D and 3D crystals is more complex: high-symmetry paths
- Band occupation at temperature T: Fermi-Dirac Distribution $f_{F-D} = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$
- Fermi energy E_F decides whether material is insulating or metallic

$$N = \int_{-\infty}^{E_F} DOS(E) dE \quad (\text{N: number of electrons per unit cell})$$

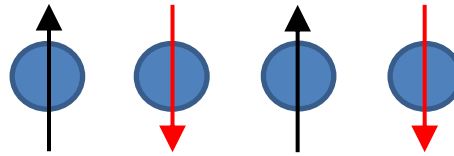
- Band structure is a very useful concept, but (in the end) a mean field theory

- Electron energies affected by electron-electron repulsion, screening of electrons from surrounding electron cloud in a 'real' material etc. to properties of a material
- Magnetism: electron-electron interaction can cause long-range alignment of electron spins

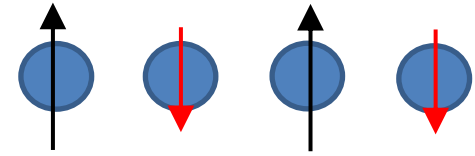
Ferromagnetism



Antiferromagnetism



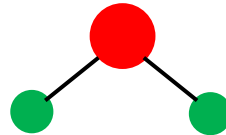
Ferrimagnetism



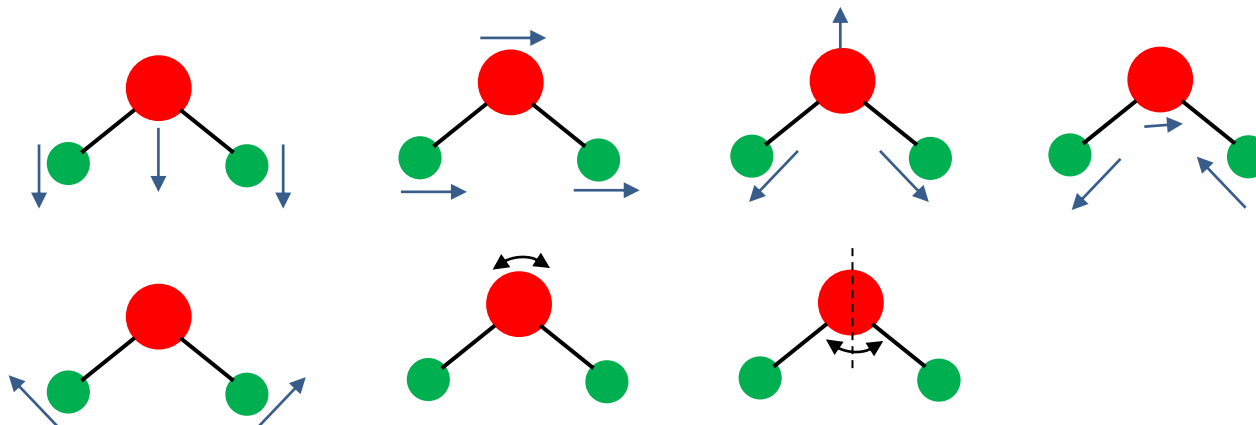
- Strongly-correlated systems: electrons couple strongly through Coulomb interaction, mean-field theory does not apply anymore

e.g. Mott insulator, metal-insulator transition,
high-temperature superconductivity

- Temperature (or other external effects) induces oscillations of the atoms around their equilibrium positions
- Oscillations can be described by means of normal vibrational modes, similar to coupled-spring-mass systems in classical mechanics
- Example: water molecule



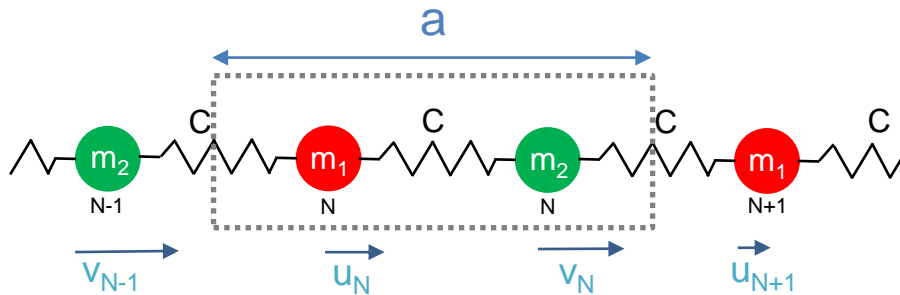
Normal modes:



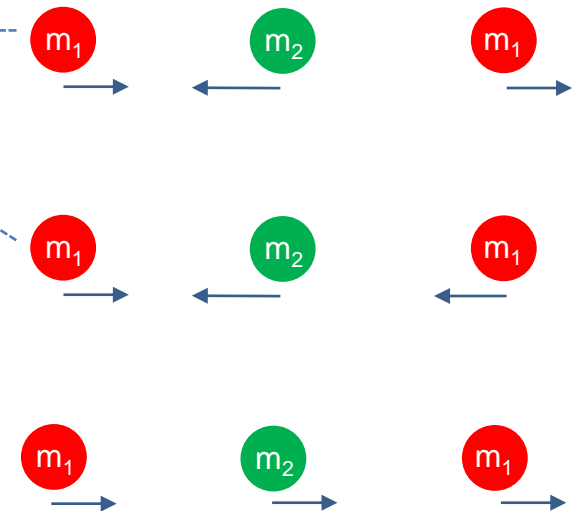
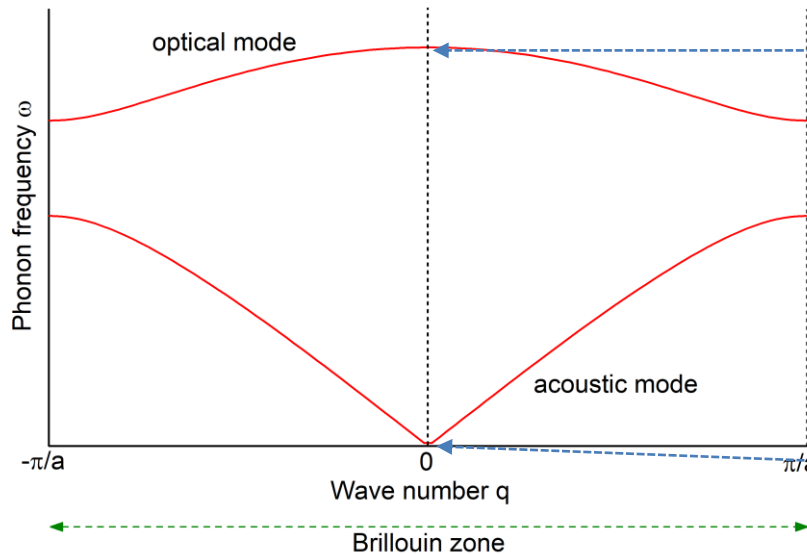
(+corresponding
mode with
out-of-plane
vibration)

Phonons

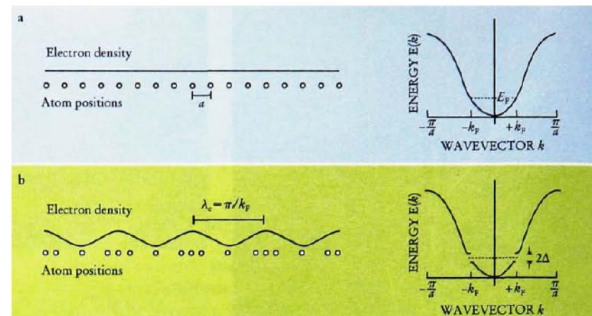
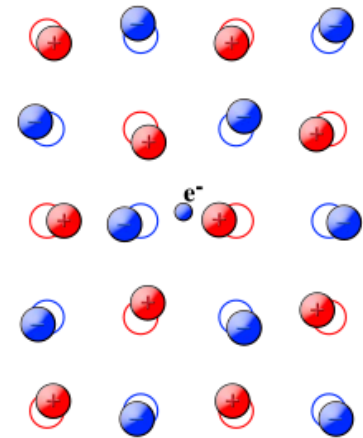
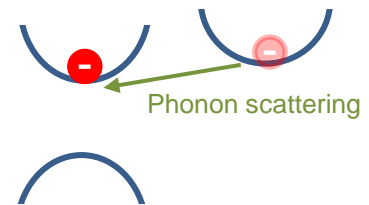
- Phonons: collective excitations of crystal atoms
- Vibrational spectra of solids offer a wealth of information
- Important effect on, e.g., thermal properties of solids, heat transport, anharmonicity



$$\text{Ansatz: } u_n = A e^{-iq(na)}$$



- Phonons modify the potential energy landscape felt by electrons
→ electrons-phonon coupling
- Electron scattering on phonons
 - phonons act as sources for crystal momentum
 - Important mechanism limiting charge transport in materials
- Polarons: quasiparticle of an electron and a surrounding „phonon“ cloud
- Superconductivity in metals from phonon-mediated coupling (and condensation) of electron pairs
- Charge-density waves in 1D and 2D metals

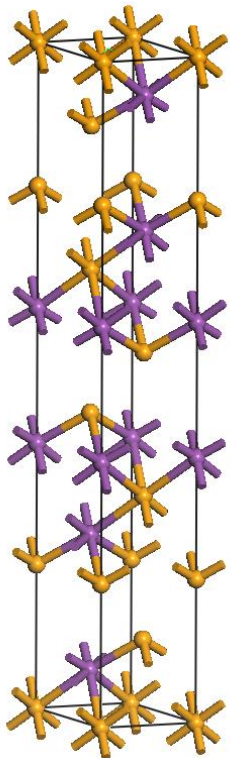


- Experiments are the primary way of studying properties of materials
- Wealth of experimental probing techniques available:
 - Diffraction (elastic and inelastic)
 - X-ray
 - Neutron
 - Electron
 - Spectroscopy
 - Photoelectron
 - Optical (Absorption, luminescence, Raman, etc.)
 - NMR
 - Etc.
 - Microscopy (STM, AFM, TEM, etc.)
 - Transport
- Always there: additional effects from environment, non-ideal crystal samples, impurities, etc.

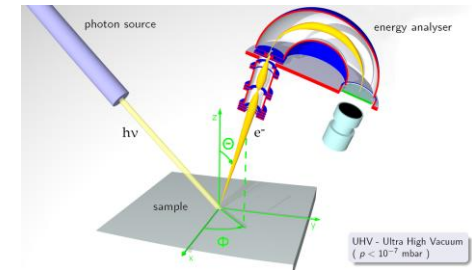
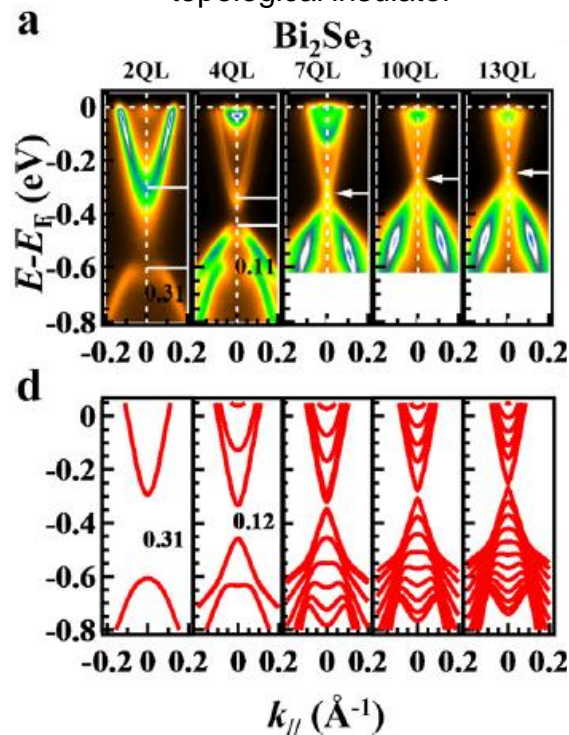
- Simulations offer an alternative route for the study of material properties
- Steady increase of available computation power allows more sophisticated models
- Well-defined systems allow investigation of intrinsic properties
- But: Detailed inclusion of environmental effects can be difficult
→ Complementing instead of substitution of experiment
- Modern approach: Combination of experiments and computational investigations to arrive at thorough picture about the investigated material.

Bandstructures of solids

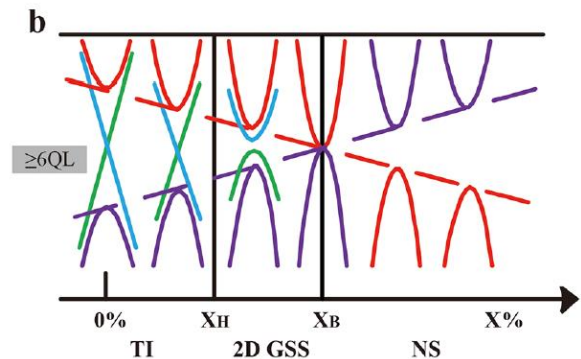
Band gap engineering of Bi_2Se_3 by thickness and In substitution



Transition 2D→3D
topological insulator



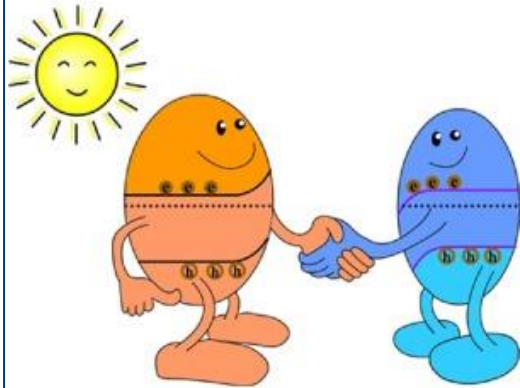
Transition topological
to normal insulator



Nano Lett. 19, 4627 (2019)

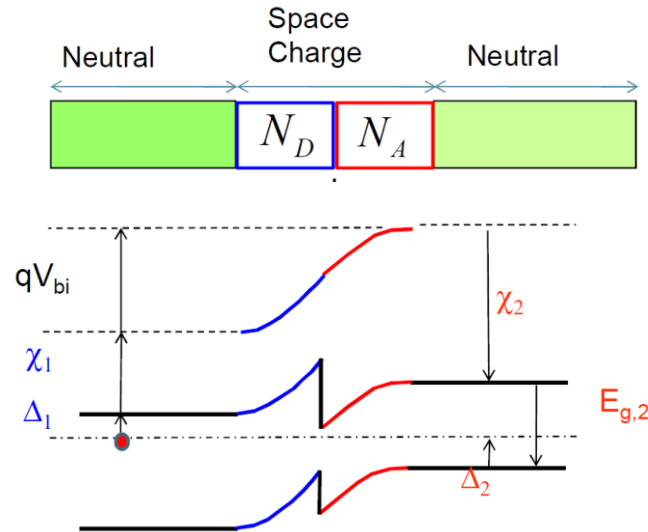
Simulations reproduce experimental data and provide fine-structure of the valence and conduction bands

Band alignments in heterostructures

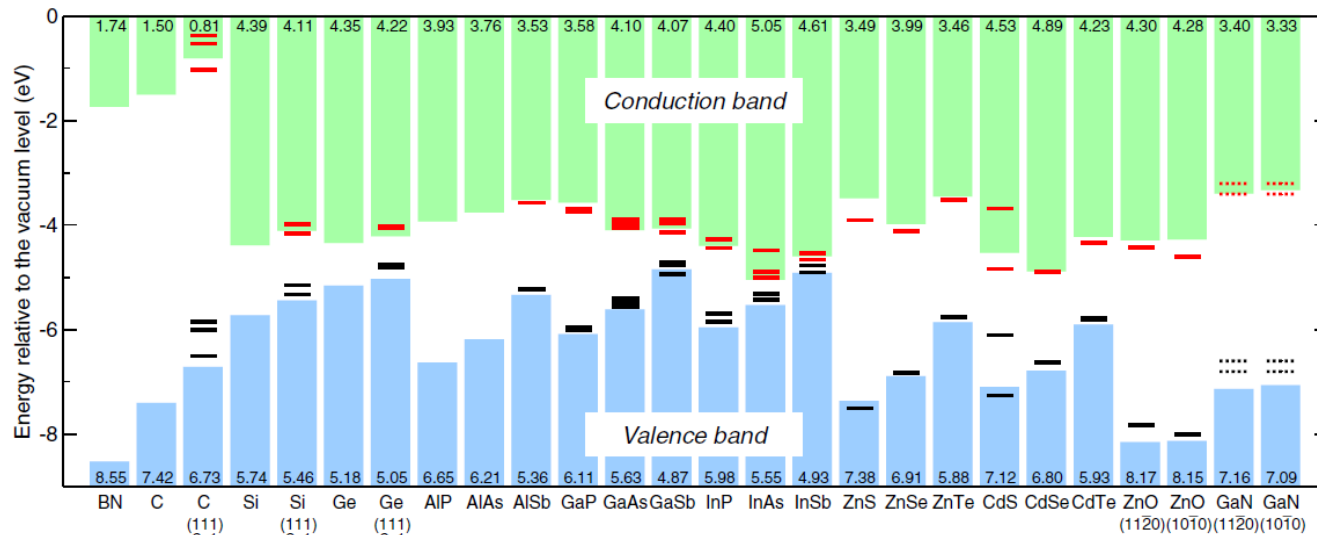
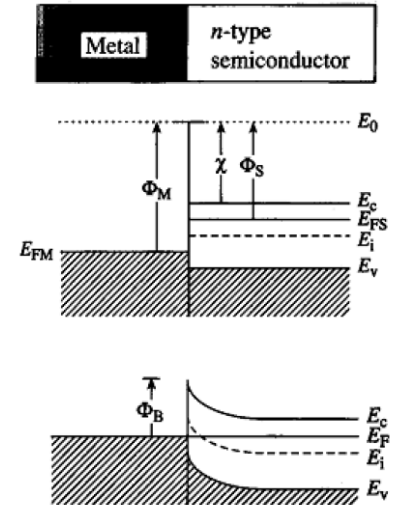


Applied Surface Science 430, 2 (2018)

Between two semiconductors

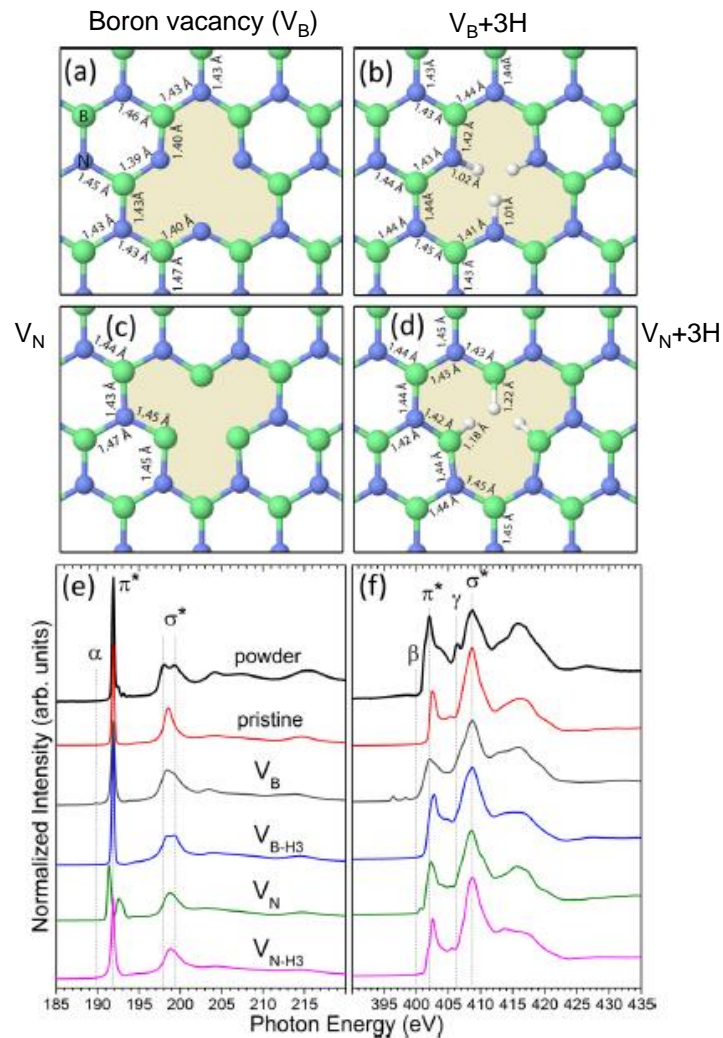


Metal-semiconductor contact



Phys. Rev. B 90, 155405 (2014)

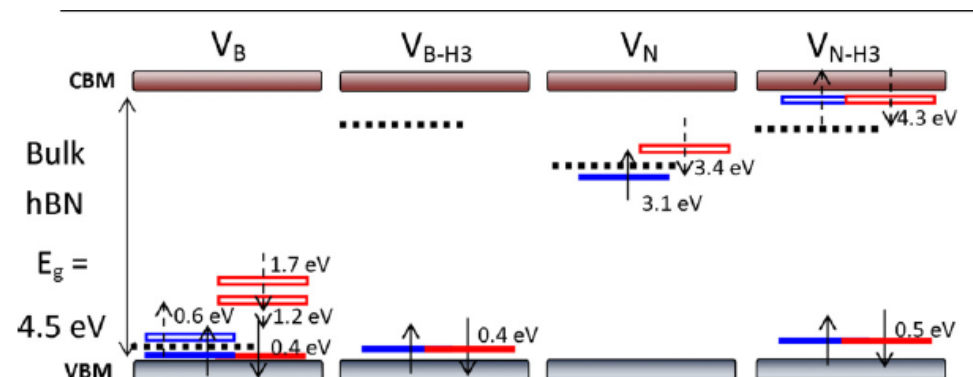
Intrinsic defects in BN



Phys. Rev. B 96, 144106 (2017)

Signatures of energetically favourable intrinsic defects and impurities in BN from x-ray absorption near edge (XANES) measurements

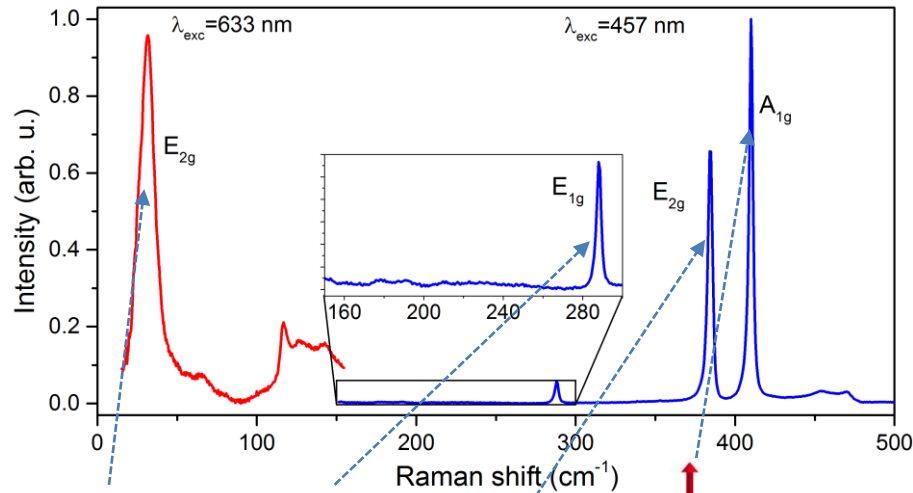
Comparison with simulations allows to draw conclusions about the defect nature, the atomic structure surrounding the defect and the energetics.



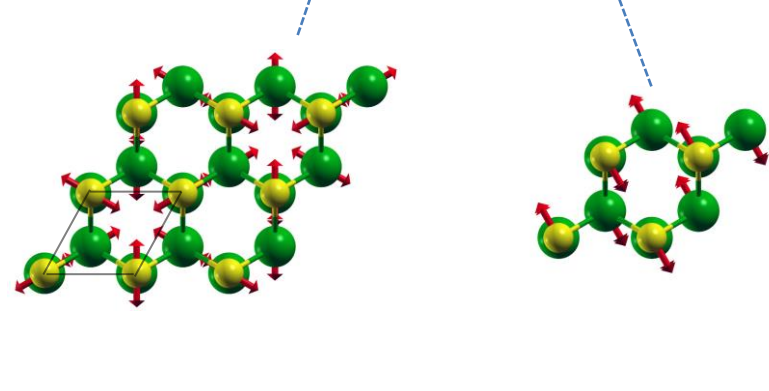
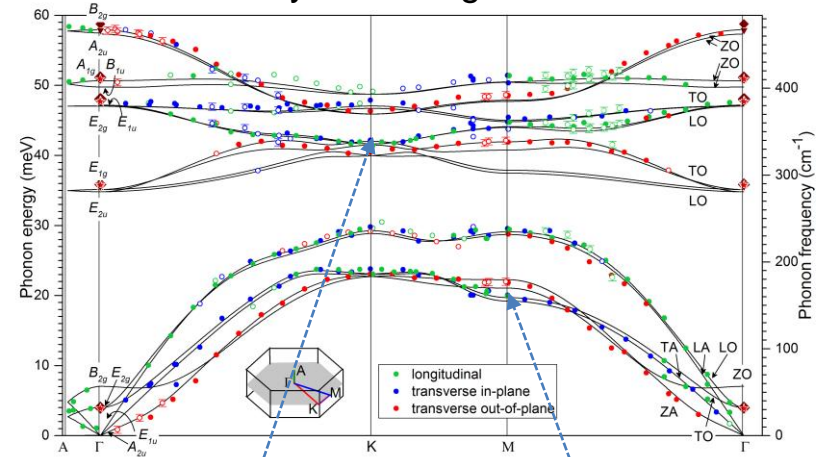
Characterization of vibrational spectra

For example MoS₂

Raman

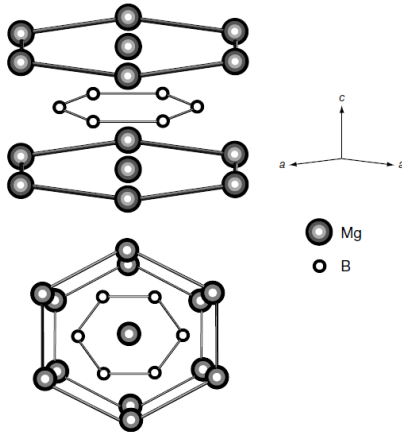


Inelastic x-ray scattering

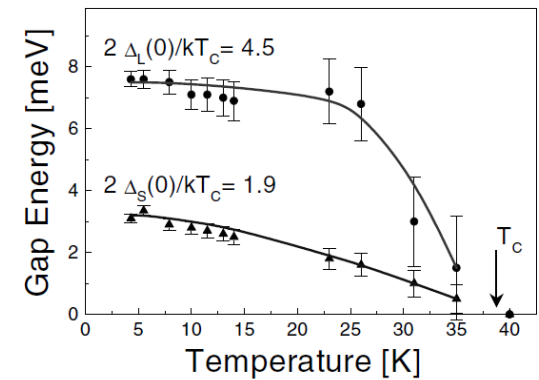
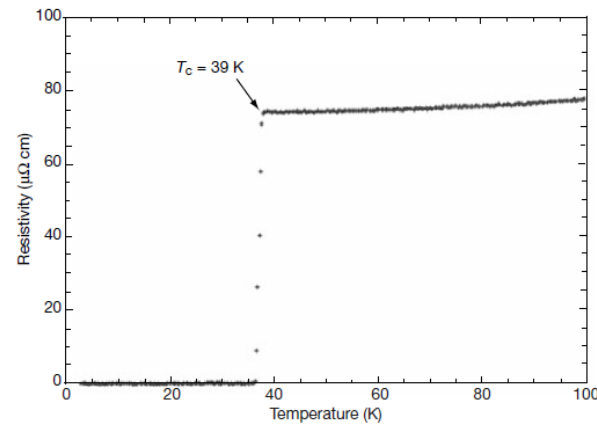


Phys. Rev. B 99, 144309 (2019)

Superconductivity in MgB_2

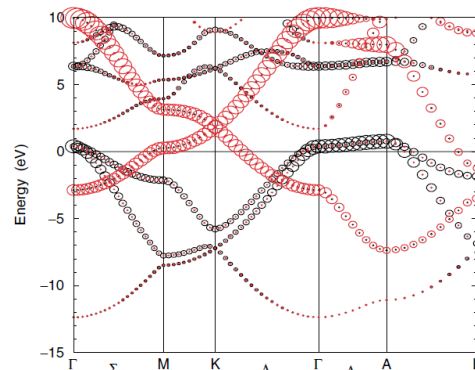


Nature 410, 63 (2001)

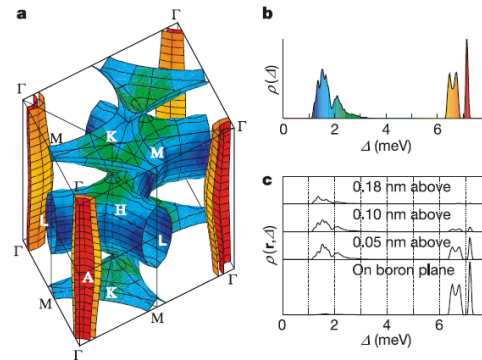


Phys. Rev. Lett. 87, 177008 (2001)

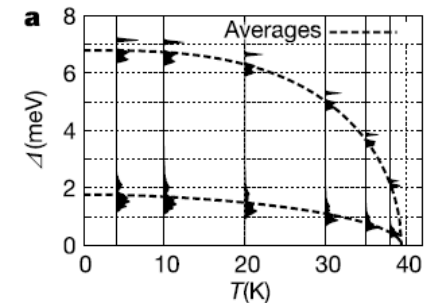
Theory:



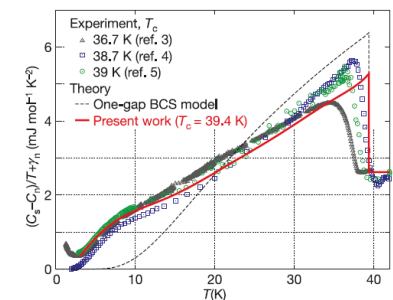
Phys. Rev. Lett. 86, 4656 (2001)



Nature 418, 760 (2002)

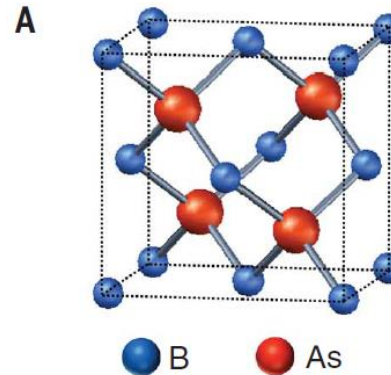


- Obtain T_c and superconducting gaps from ab initio calculations of (an)harmonic phonon frequencies and electron-phonon coupling strengths

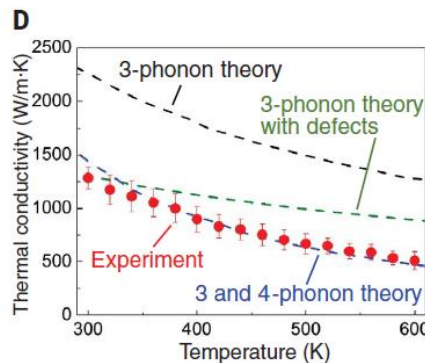
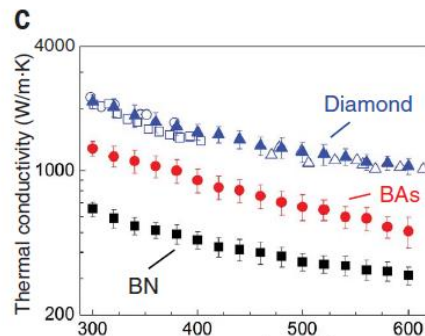
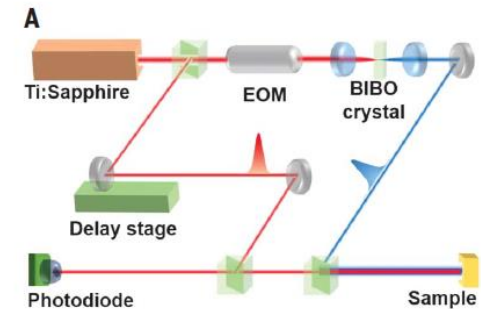


Thermal conductivity in boron arsenides

Materials with high thermal conductivity are highly desirable for heat dissipation in devices



TDTR setup



Boltzmann Transport Equation

$$v_{\lambda} \cdot \nabla T \frac{\partial n_{\lambda}}{\partial T} = \left(\frac{\partial n_{\lambda}}{\partial t} \right)_{ph-ph} + \left(\frac{\partial n_{\lambda}}{\partial t} \right)_{ph-defect}$$

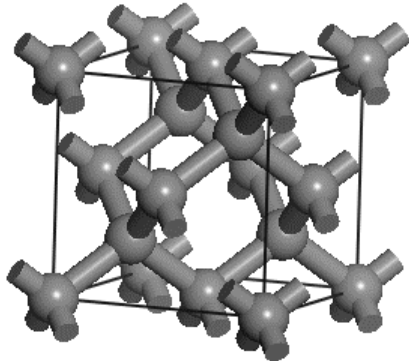
Three-phonon- and four-phonon terms, can be obtained from ab initio simulations

Obtained from ab initio simulations

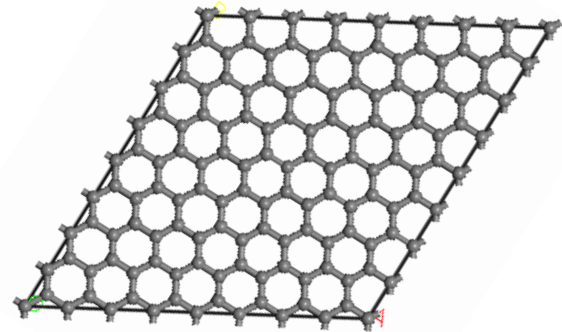
Science 361, 575 (2018)

- Simulations can be used to go beyond experiments: study materials that are very difficult or not not accessible for experiments.
- Example: The search for new carbon allotropes

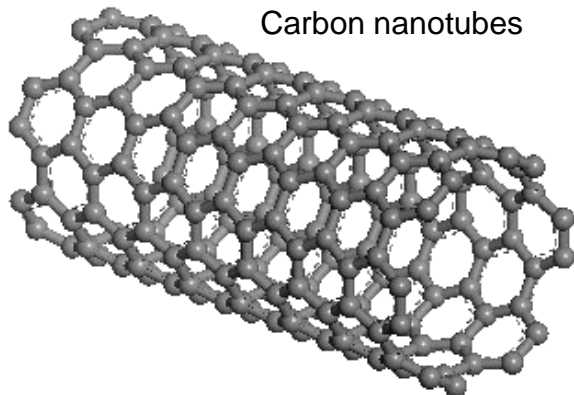
Diamond



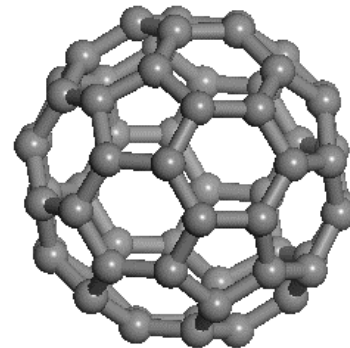
Graphene/Graphite



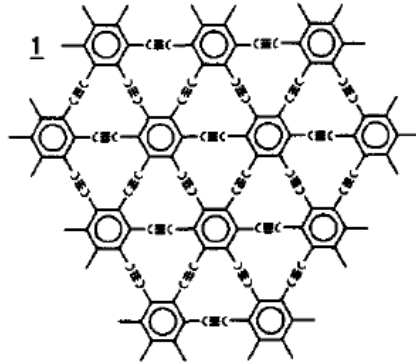
Carbon nanotubes



Fullerenes

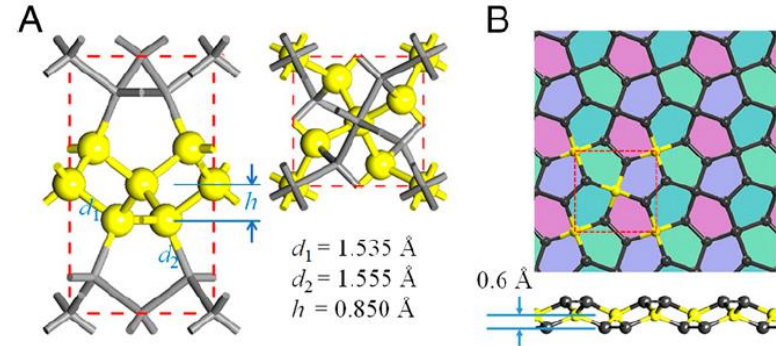


Graphyne



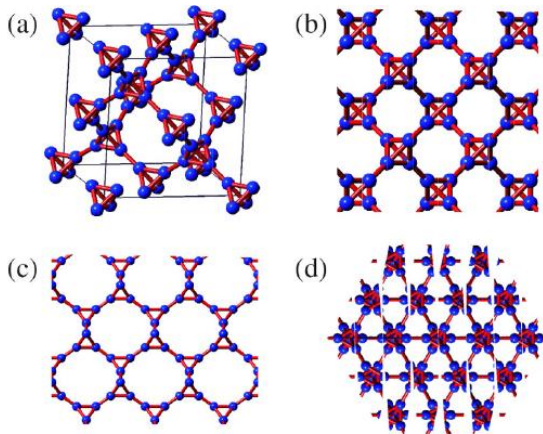
J. Chem. Phys. 87, 6687 (1987)

Pentagraphene



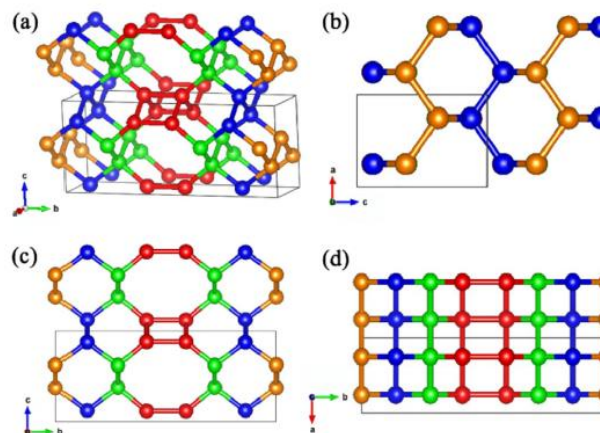
PNAS 112, 2372 (2015)

T-carbon



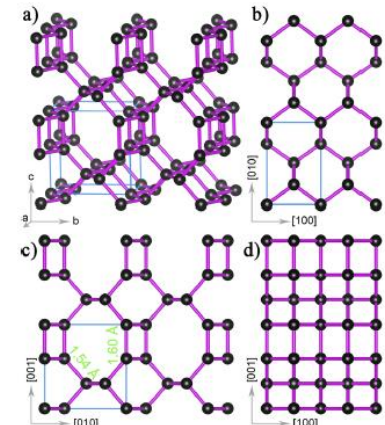
Phys. Rev. Lett. 106, 155703 (2011)

Orthorhombic C14 carbon



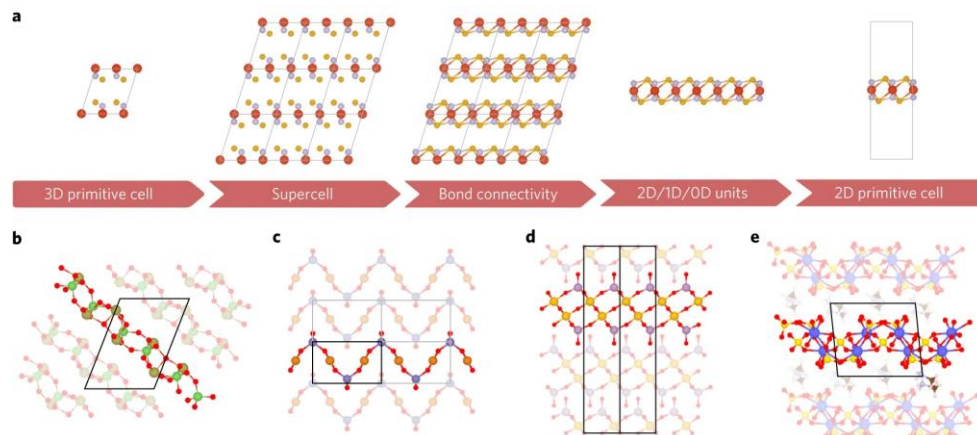
Carbon 156, 309 (2020)

D-carbon



J. Chem. Phys 149, 114702 (2018)

- Example: How many layered materials exist?
- High-throughput screening of material databases containing >50000 known crystal structures to identify exfoliable layered materials:



Nature Nanotechnology 13, 246 (2018)

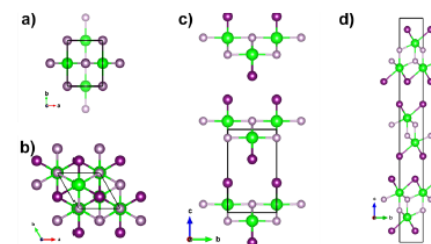
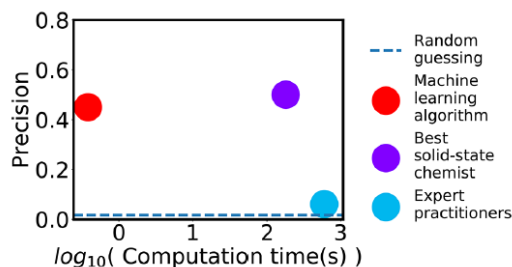
- Superhuman prediction of yet unsynthesized layered materials

Machine learning model based on existing material databases

Predict crystal structure and chemical composition of novel materials

Model predicts possibility of ~3000 binary and ternary layered materials

Comparison with Human Experts



J. Phys. Chem. Lett. 9, 6967 (2018)

- Properties in solid materials are determined by quantum mechanical interactions
- Exact quantum-mechanical treatment in principle known:

Time-independent Schrödinger equation of a system of M atoms and N electrons:

$$\hat{H}\psi(\vec{R}_1, \dots, \vec{R}_M; \vec{r}_1, \dots, \vec{r}_N) = E_{tot}\psi(\vec{R}_1, \dots, \vec{R}_M; \vec{r}_1, \dots, \vec{r}_N)$$

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Hamiltonian

Many-body wavefunction

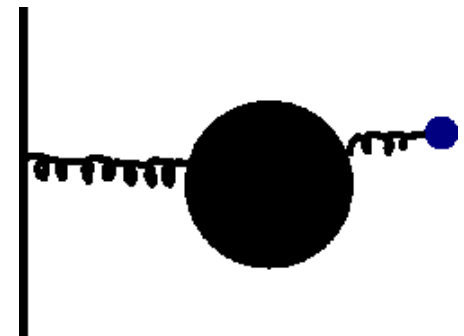
Total energy of the system

Many-body Hamiltonian

General Hamiltonian:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}}_{\text{Nuclei contribution}} \underbrace{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{Electronic contribution}} + \underbrace{\sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}}_{\text{Coulomb coupling between electrons and nuclei}}$$

- Complex function of 3(M+N) coupled spatial coordinates.
- $\frac{1}{M_I}$ term is small, as always $M_I \gg m_e$
- „backreaction“ of electronic motion on nuclei is slow and nuclei „feel“ only an averaged interaction with electrons
- Electronic and nucleic degrees-of-freedom in the wavefunction can be treated as decoupled,



Simplification: Born-Oppenheimer (or adiabatic) approximation:

- The kinetic energy contribution and the uncertainty in the position of the nuclei is neglected
- Focus on the quantum-mechanical system of electrons for an instantaneous set of positions of nuclei $[\vec{R}_I]$

$$\hat{H} \approx \underbrace{-\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2}_{\hat{T}} + \underbrace{\sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}}_{\hat{V}_{ext}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}_{e-e}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}}_{E_{nucl}}$$

$$\hat{H} \psi_e(\vec{r}_1, \dots, \vec{r}_N; [\vec{R}_I]) = (E_{tot,el} + E_{nucl}) \psi_e(\vec{r}_1, \dots, \vec{r}_N; [\vec{R}_I])$$

- Positions of nuclei are treated as parameters, for each set $[\vec{R}_I]$ we get different energy levels
- B-O approximation works very well for most materials
- Additional external interactions (electric fields etc) can be included in V_{ext}
- Nominal ground state: $E_{tot,el}([\vec{R}_I]) + E_{nucl}([\vec{R}_I])$ is minimal

Example: Hydrogen atom

$$\hat{H} \approx -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{|\vec{r} - \vec{R}|} \quad (\text{can as origin use } \vec{R} \text{ as origin})$$

- Analytical solution possible, see introductory quantum-mechanical textbooks
- Spherical symmetric problem: Use Ansatz $\psi(r, \phi, \theta) = R(r) \underbrace{Y(\phi, \theta)}_{\Phi(\phi)\Theta(\theta)}$
- Three coupled differential equations in polar coordinates

$$\begin{aligned} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_e r^2}{\hbar^2} \left(E + \left(\frac{e^2}{4\pi\epsilon_0 r} \right)^2 \right) R - AR &= 0 \\ \frac{\sin(\theta)}{\theta} \frac{d}{d\theta} \left(\sin(\theta) \frac{d\Theta}{d\theta} \right) + A \sin^2(\theta) - B &= 0 \\ \frac{d^2 \Phi}{d\phi^2} + B &= 0 \end{aligned}$$

- After (slightly tedious) algebra: $E_n = -R_\infty \frac{1}{n^2}$, $\psi(r, \phi, \theta) \propto R_{n,l}(r) \Theta_l^m(\theta) e^{im\phi}$

Unfeasible problems

- Helium atom

$$\hat{H} \approx -\frac{\hbar^2}{2m_e} \sum_i^2 \nabla_i^2 + \sum_i^2 \frac{e^2}{|\vec{r}_i - \vec{R}|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

- Lithium atom

$$\hat{H} \approx -\frac{\hbar^2}{2m_e} \sum_i^3 \nabla_i^2 + \sum_{i,I}^3 \frac{e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j \neq i}^2 \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

- Not possible to solve analytically because of electron correlation terms.
Solution in principle possible numerically using a grid with d discrete points
- Electron correlation couples all electronic $3N$ degrees-of-freedom
 - Computational effort and memory cost increase with $O(d^{3N})$
 - Intractable, except for very simple systems

How can we treat more complex systems?

- Neglect electron correlation effects:

$$\hat{H} \approx -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 + \sum_{i,I}^N \frac{e^2}{|\vec{r}_i - \vec{R}_I|}$$

→ Decoupled system of N differential equations

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→ Decoupled system of N differential equations

→ Ansatz: *Hartree product* of orthogonal one-electron functions (neglecting spin here),

$$\psi_e(\vec{r}_1, \dots, \vec{r}_N) = \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\dots\varphi_N(\vec{r}_N)$$

→ Much easier to solve the Schrödinger equation due to reduced complexity of the many-body wavefunction.

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→ Much easier to solve the Schrödinger equation due to reduced complexity of the many-body wavefunction.

Problem: electron-electron interaction is a considerable effect in almost all systems of interest.

- Hartree approximation
 - We again assume that the many-body wavefunction can be expressed through

$$\psi_e(\vec{r}_1, \dots, \vec{r}_N) = \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\dots\varphi_N(\vec{r}_N)$$

leading to a set of one-electron Schrödinger equations

$$\left(-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

Hartree approximation

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- Here, the electron-electron interaction is approximated with the *Hartree potential*,

$$V_H(\vec{r}) = -e \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}',$$

where $n(\vec{r}) = \sum_i f_i |\varphi_i(\vec{r})|^2$ is the *electron density* of the system.

← Fermi-Dirac distribution

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← Fermi-Dirac distribution

- Similarly: Total energy $E = \sum_i f_i \varepsilon_i$

- The Hartree approximation is computationally feasible, could solve equations iteratively by assuming initial electron density distribution
- But: Two problems
 - 1. The electron-electron interaction is calculated from the whole electron density, i.e. an electron would interact with itself through V_H .

This can be corrected by adding the potential

$$V_{SIC}(\vec{r}) = -e \int \frac{|\varphi_i(\vec{r})|^2}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

that correct for the self-interaction for orbital j .

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2. No electron spin, i.e. no Pauli exclusion