Magnetism and Matter

MM-1: Electronic Properties

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Outline

- Introductory remarks
  - Quantum mechanical description of solid
  - Adiabatic approximation
  - Born-Oppenheimer approximation
  - Adiabatic spin wave theory
- Independent electrons
  - lattice periodicity: real and reciprocal lattice
  - Bloch functions and band structure
  - symmetry in periodic crystals
- Interacting electrons
  - Hartree- and Hartree-Fock approximation
  - density functional theory
- Relativistic effects
  - spin-orbit coupling
  - Rashba & Dresselhaus effect
  - topological insulators

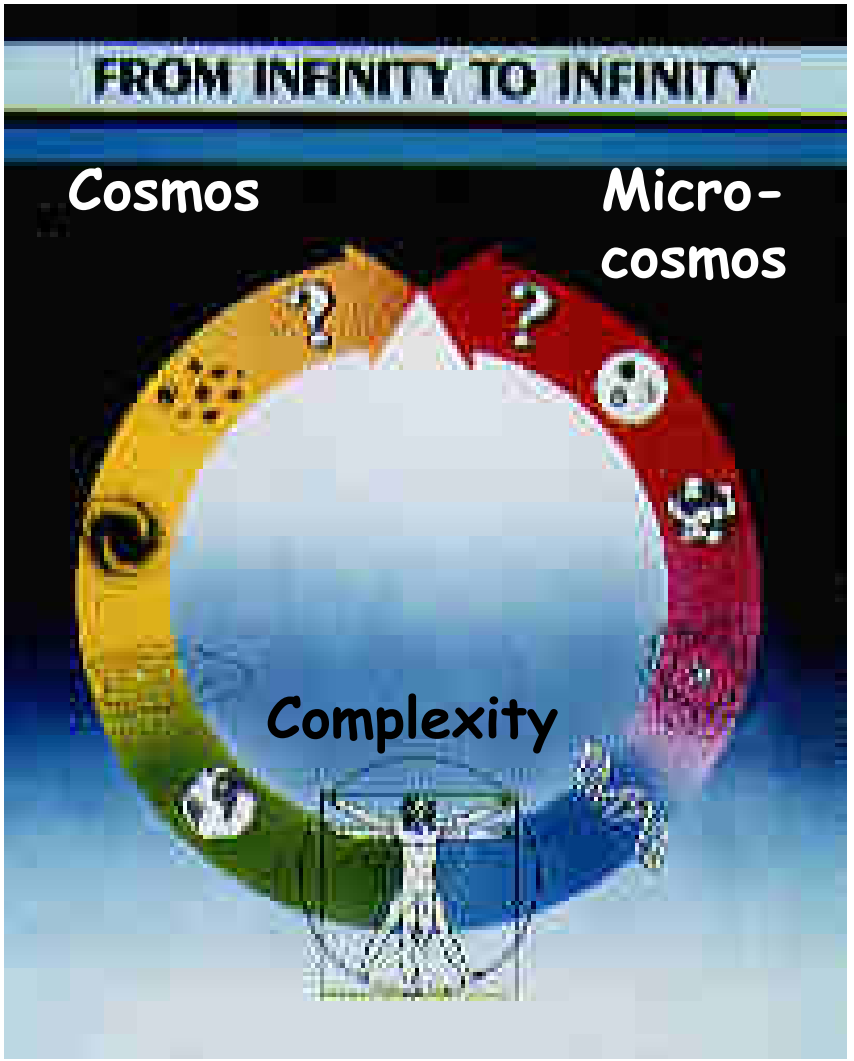
Solid State Physics

„From
the infinitely small via
the infinitely complex
to the infinitely big“

Huge complexity

- Large configuration space
- Large Hilbert space
- Hierarchy of interactions

It is the electron *!*



Quantum Mechanics

- In Solid State Physics we have only
  Electrons & Nuclei
- All described by wavefunction based theory

$$\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x)$$

E. Schrödinger (1926), Annalen der Physik, 361-377

Entire space of properties

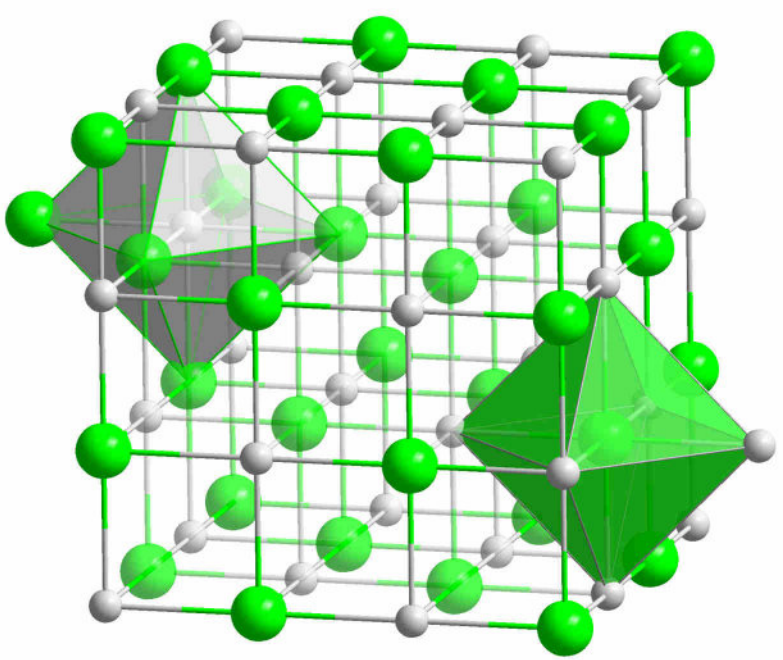
It is all in the

N electron wave-function: $\Psi(r_1,...r_N)$

$$\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x)$$

- Dzyaloshinskii Moriya interaction
- collective phenomena
- multiferroicity
- structural stability
- van der Waals
- phase diagrams
- orbital ordering
- magnetism & magnetic order
- workfunction
- Elliot Yafet damping
- chemical reactivity
- superconductivty & BEC
- electrical polarization
- Kondo physics
- ferroelectricity
- heavy fermion systems
- chemical reactivity
- Mott transition
- ionization energies
- topological insulator
- compressibilities
- quantum Hall effect
- elastic modules
- Dresselhaus effect
- giant & colossal magneto resistance

Solid – Property Relation



$$\mathcal{H}\Psi = E\Psi$$

- Dzyaloshinskii Moriya interaction
- vibrational properties
- multiferroicity
- structural stability
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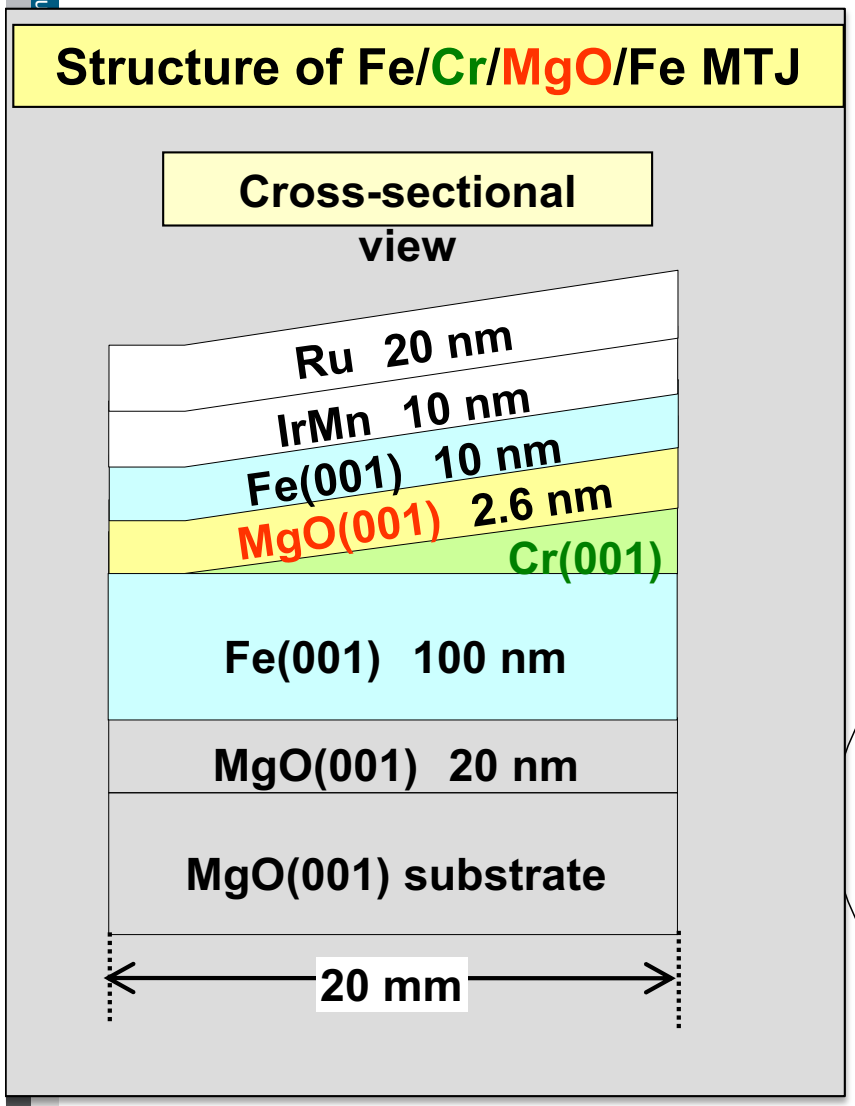
Inverse relation: Property - Materials



$\mathcal{H}\psi = E\psi$

- Dzyaloshinskii Moriya interaction
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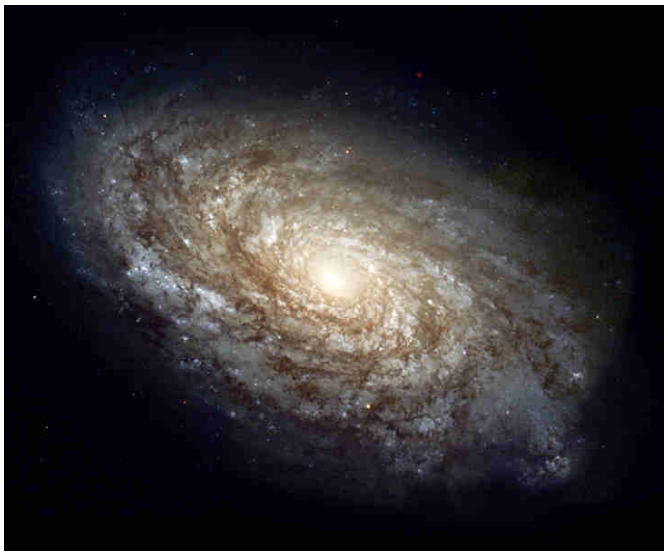
High Tc
Magnetoresistivity
High sensitivity

The Quantum Many-Body Problem

$$H\Psi = E\Psi, \quad \Psi(x_1, x_2, \cdots, x_n)$$



Example: Expressing the wavefunction:

1) Hydrogen H : n=1, exact or num. : 10^3 grid points $\Longrightarrow$ 16 KB
2) Helium He: n=2, exact or num. : 10^6 grid points $\Longrightarrow$ 16 MB < 1 DVD
3) Lithium Li : n=3, num. : 10^9 grid points $\Longrightarrow$ 16 GB ~ 2 DVD

• • •
• • •
• • •

6) Carbon C : n=6, num. : 10^{18} grid points $\Longrightarrow$ ~ 32.000T DVD
800 Trucks

• • •

27) Iron Fe: n=26, Galaxy:

Models, Approximations, Physics

P.M.A. Dirac

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.M.A. Dirac, Proceedings of the Royal Society **A 123**, 714(1929)

Describing Crystalline Solid *qualitatively* by Models

- Hubbard Model for correlated electrons

$$H = -t \sum_{\langle ij \rangle} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{j\downarrow}$$

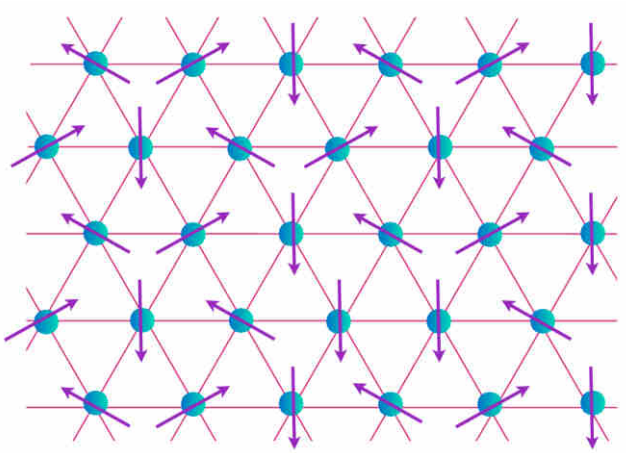
- Effective Spin Models

$$H = -\sum_{i,j} J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,j} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) + \sum_{i} K_i (S_i^z)^2$$

exchange interaction

Dzyaloshinskii-Moriya interaction

magnetic anisotropy



$$-\sum_{ij} B_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)^2 - \sum_{ijkl} K_{ijkl} \left[(\mathbf{S}_i \mathbf{S}_j)(\mathbf{S}_k \mathbf{S}_l) + (\mathbf{S}_j \mathbf{S}_k)(\mathbf{S}_l \mathbf{S}_i) - (\mathbf{S}_i \mathbf{S}_k)(\mathbf{S}_j \mathbf{S}_l) \right]$$

biquadratic interaction

4-spin interaction

Describing Crystalline Solid *quantitatively* by excellent approximations

- Born-Oppenheimer Approximation
- Hartree-Fock Approximation
- Approximation to Exchange-Correlation Energy in Density Functional Theory (DFT)
- Linear spin-wave theory
- Mean-Field Theory for Curie-Temperatures
- Boltzmann Equation for diffusive transport
- Linear-Response Theories for Transport Properties

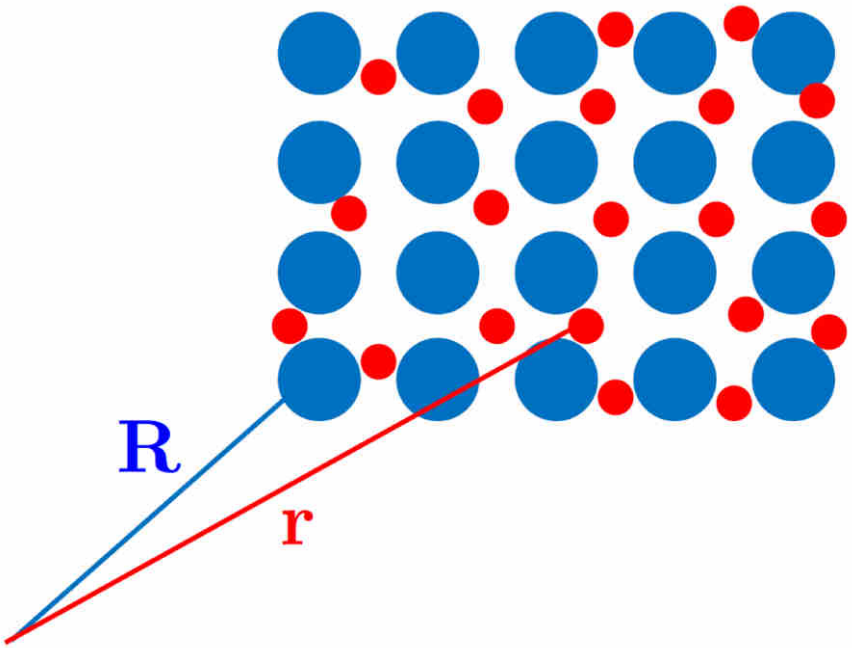
Quantum mechanical description of solids

Electron coordinates:

$$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots\}$$

Ion coordinates:

$$\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots\}$$



In principle, all the properties of crystalline solids are determined by the many-body Hamiltonian of the electrons and nuclei, which, in the non-relativistic limit, reads :

$$H = -\sum_n \frac{\hbar^2}{2M^n}\Delta^n - \sum_i \frac{\hbar^2}{2m}\Delta_i + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{n\neq n'}\frac{Z^n Z^{n'} e^2}{|\vec{R}^n - \vec{R}^{n'}|} - \sum_{n,i}\frac{Z^n e^2}{|\vec{R}^n - \vec{r}_i|}$$

in atomic units

- Distances: Bohr radius $a_0 = \hbar^2/(me^2) = 0.529\ 10^{-8}$ cm
- Energy: Hartree energy $= me^4/\hbar^2 = 2$ Ry $= 27.2$ eV

Quantum mechanical description of solids

- Hamiltonian between electrons and nuclei:

$$H = -\frac{1}{2}\sum_n \frac{m}{M^n}\Delta^n - \frac{1}{2}\sum_i \Delta_i + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{n\neq n'}\frac{Z^n Z^{n'}}{|\vec{R}^n - \vec{R}^{n'}|} - \sum_{n,i}\frac{Z^n}{|\vec{R}^n - \vec{r}_i|}.$$

Smallness parameter → cries for perturb. theory

- two sets of parameters cannot be eliminated by a scale transformation:
  - (1) The atomic number Z^n
  - (2) The mass-ratio m/M^n between 1/2000 and 1/500000
  - (3) The smallness of m/M^n has important consequences

Quantum mechanical description of solids

- Hamiltonian between electrons and nuclei:

$$H = -\frac{1}{2}\sum_n \frac{m}{M^n}\Delta^n - \frac{1}{2}\sum_i \Delta_i + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{n\neq n'}\frac{Z^n Z^{n'}}{|\vec{R}^n - \vec{R}^{n'}|} - \sum_{n,i}\frac{Z^n}{|\vec{R}^n - \vec{r}_i|}.$$

$$H = T^n + H_e(\{R^n\})$$

- can be divided into perturbation-free adiabatic Hamiltonian

$$H_e = -\frac{1}{2}\sum_i \Delta_i + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{n\neq n'}\frac{Z^n Z^{n'}}{|\vec{R}^n - \vec{R}^{n'}|} - \sum_{n,i}\frac{Z^n}{|\vec{R}^n - \vec{r}_i|}$$

- and into the kinetic energy of nuclei

$$T^n = -\frac{1}{2}\sum_n \frac{m}{M^n}\Delta^n$$

⇒ 0^{th} order approximation: $T^n = 0$

(1) $\vec{R}^n$ are constant of motion of H_e

(2) $|\vec{R}^n - \vec{R}^{n'}|$ solids have spatial structure

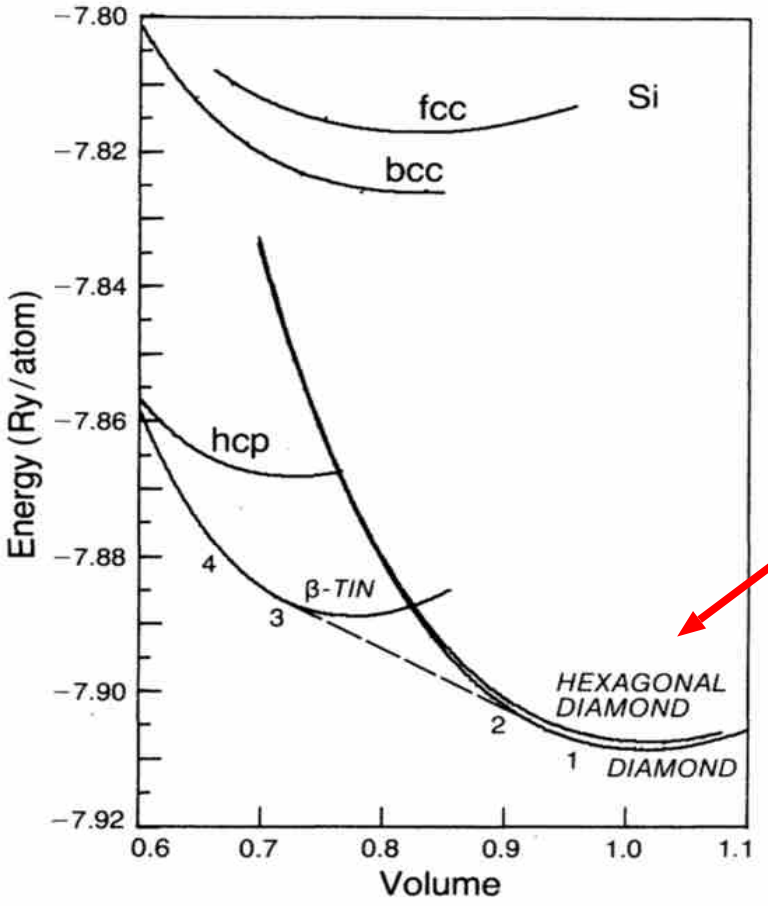
(3) structure of solid can be determined

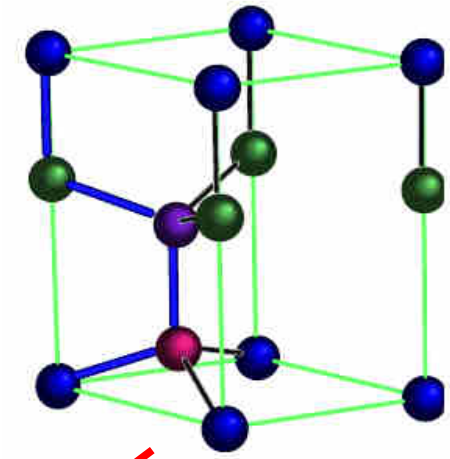
Determining structure (in zeroth order m/M)

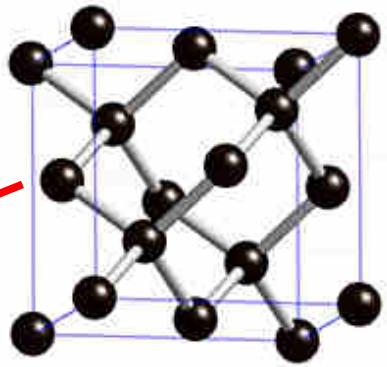
(1) Determine ground state energy of H_e for given nuclei position, e.g. Rayleigh-Ritz variation. Difficult problem, requires ground state wave function of inhomogeneous electron system (later in the lecture)

$$E_e(\{\vec{R}^n\}) = \min_{\psi} \frac{\langle\psi|H_e(\{\vec{R}^n\})|\psi\rangle}{\langle\psi|\psi\rangle}$$

Total energy of Equilibrium Structure: Silicon







- ground state structure, equilibrium volume, bulk modulus
- derived: phonon spectra, expansion coefficients, etc.

Born-Oppenheimer Approximation

- Total wave function is expanded for each set of $\{R^n\}$ into complete set of wave functions $\psi_\alpha(\{\vec{r}\})$

$$\Psi_{\text{tot}}(\{\vec{r}\},\{\vec{R}^n\}) = \sum_\alpha \chi_\alpha(\{\vec{R}^n\})\psi_\alpha(\{\vec{r}\}|\{\vec{R}^n\})$$

- which are solutions of the electronic Schrödinger equation

$$H_e(\{\vec{R}^n\})\psi_\alpha(\{\vec{r}\}|\{\vec{R}^n\}) = E_\alpha(\{\vec{R}^n\})\psi_\alpha(\{\vec{r}\}|\{\vec{R}^n\})$$

- where the expansion coefficients depend on the nuclear coordinates and are solutions of the effective nuclear Schrödinger Eq.

$$\left[T^n + E_\alpha(\{\vec{R}^n\})\right]\chi_\alpha(\{\vec{R}^n\}) = \epsilon_\alpha(\{\vec{R}^n\})\chi_\alpha(\{\vec{R}^n\})$$

↳ *Born-Oppenheimer Surface*

Born-Oppenheimer Approximation

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$$\left[T^n + E_\alpha(\{\vec{R}^n\})\right]\chi_\alpha(\{\vec{R}^n\}) = \epsilon_\alpha(\{\vec{R}^n\})\chi_\alpha(\{\vec{R}^n\})$$

To derive this effective nuclear dynamics invoke Born-Oppenheimer Approximation

Born-Oppenheimer Approximation

- Inserting expression of total wave function $\Psi_{\text{tot}}(\{\vec{r}\},\{\vec{R}^n\})$

$$\Psi_{\text{tot}}(\{\vec{r}\},\{\vec{R}^n\}) = \sum_{\alpha} \chi_\alpha(\{\vec{R}^n\})\psi_\alpha(\{\vec{r}\}|\{\vec{R}^n\})$$

- into the full Schrödinger equation

$$\left[T^n + H_e\right]\Psi_{\text{tot}} = \epsilon\,\Psi_{\text{tot}}$$

⇒ Invoke the adiabatic approximation : $\alpha = 0$

$$\Psi_{\text{tot}}(\{\vec{r}\},\{\vec{R}^n\}) \approx \chi_{\alpha=0}(\{\vec{R}^n\})\psi_{\alpha=0}(\{\vec{r}\}|\{\vec{R}^n\}) = \chi_0(\{\vec{R}^n\})\psi_{\text{GS}}(\{\vec{r}\}|\{\vec{R}^n\})$$

- multiplying from the left by ψ_{GS}, *neglecting terms* which couple different states **α** , one obtains the effective nuclear Eq.

$$\left[T^n + E_\alpha(\{\vec{R}^n\})\right]\chi_\alpha(\{\vec{R}^n\}) = \epsilon_\alpha(\{\vec{R}^n\})\chi_\alpha(\{\vec{R}^n\})$$

Born-Oppenheimer Approximation

- The *neglected terms*

(1) $$\propto \frac{1}{2}\sum_m \frac{m}{M^m}\,\chi(\{\vec{R}^n\})\left\langle \psi_0(\{\vec{R}^n\}) \left| \Delta_{\vec{R}^m} \right| \psi_0(\{\vec{R}^n\}) \right\rangle$$

(2) $$\propto \frac{1}{2}\sum_m \frac{m}{M^m}\, i\nabla_{\vec{R}^m}\,\chi(\{\vec{R}^n\}) \cdot \underbrace{i\left\langle \psi_0(\{\vec{R}^n\}) \left| \nabla_{\vec{R}^m} \right| \psi_0(\{\vec{R}^n\}) \right\rangle}_{\text{Berry Connection}}$$

- Berry connection and Berry Phase

The Hamiltonian $H_e(\{\vec{R}^n\})$ depends on a (set of) vector parameters $\{R^n\}$. Imagine they vary with time t . If the α^{th} eigenvalue E_α remains non-degenerate everywhere along the path and the variation with time t is sufficiently slow, then a system initially in the eigenstate $\psi_\alpha(\{\vec{R}^n(0)\})$ will remain in an instantaneous eigenstate $\psi_\alpha(\{\vec{R}^n(t)\})$ of the Hamiltonian, up to a phase. In the case of a cyclic evolution around a closed path C such that $\{\vec{R}^n(T)\} = \{\vec{R}^n(0)\}$ the closed-path Berry phase (= geometrical phase) is

$$\gamma_\alpha = i\oint_C d\vec{R}\left\langle \psi_\alpha(\vec{R}) \left| \nabla_{\vec{R}} \right| \psi_\alpha(\vec{R}) \right\rangle \quad \text{with} \quad \vec{R} \equiv \{\vec{R}^n\}$$

Life beyond Born-Oppenheimer Approx

- Electron - Phonon Interaction (superconductivity)
- Magnon - Phonon Interaction (Magnon - life time)
- Orbital moment – Phonon (transfer angular momentum to latti
- Spin-flip scattering (Spin-life time)

Side remark adiabaticity

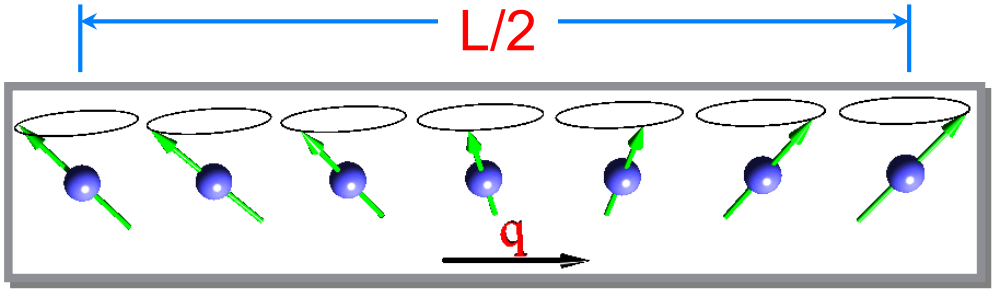
Magnetic excitations

- Thermodynamic Properties
- Magnetic fluctuations
- Spindynamics and Lifetime

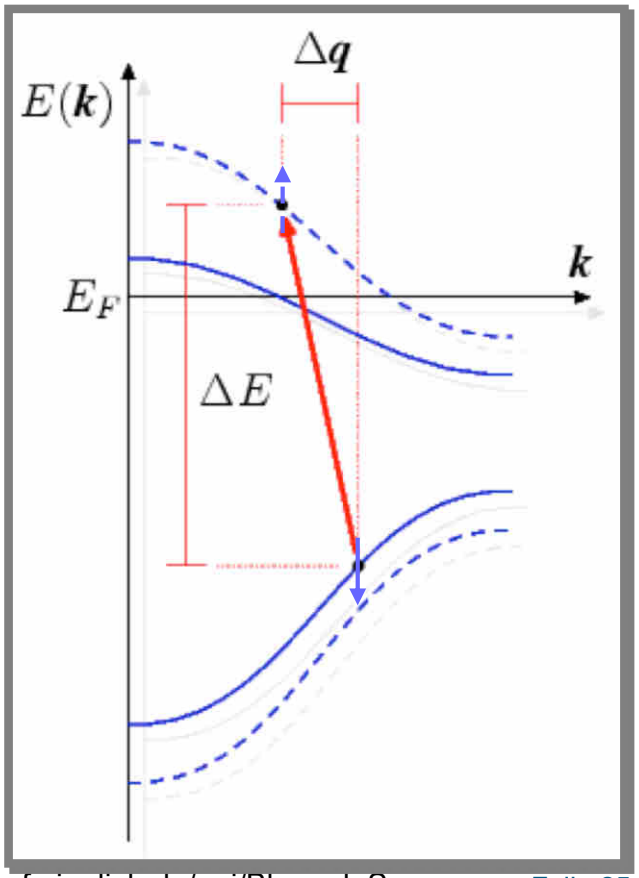
2 kinds of elementary magnetic excitations ($S_z \pm 1$):

Both can be understood as quasi-particles of momentum q and dispersion relation $\omega(q)$

Collective spin-wave (magnon) excitations



Single particle spin-flip (Stoner) Excitation

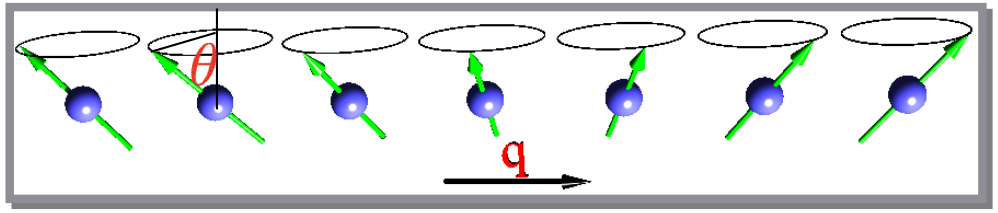


Adiabatic Approximation

Determination of magnon dispersion by DFT

- Magnon timescale << electron hopping timescale
  ≈10^{-12} sec ≈10^{-15} sec → $\langle \mathbf{M}(t) \rangle \approx \langle \mathbf{M} \rangle (t)$
- Excited state of real system ←→ Ground state of constrained system → Berry phase: Q. Niu, Xindong Wang, L. Kleinman, Wu-Ming Liu, D. M. C. Nicholson, and G. M. Stocks, PRL **83**, 207 (1999)
- Spin-spirals representing magnons (excited eigenstates in periodic crystal)

$$\mathbf{M}(\mathbf{R^n}) = M_o \left[\sin\theta \cos(\mathbf{q}\cdot\mathbf{R^n})\,\hat{e}_x + \sin\theta \sin(\mathbf{q}\cdot\mathbf{R^n})\,\hat{e}_y + \cos\theta\,\hat{e}_z \right]$$



→ $\Delta E(\mathbf{q},\theta)$ → $\omega_{\mathrm{ad}}(\mathbf{q}) = 2g\mu_B \lim_{\theta\to 0} \dfrac{\Delta E(\mathbf{q},\theta)}{\Delta M(\mathbf{q},\theta)}$

Adiabatic Approximation: Ni , q || [111]

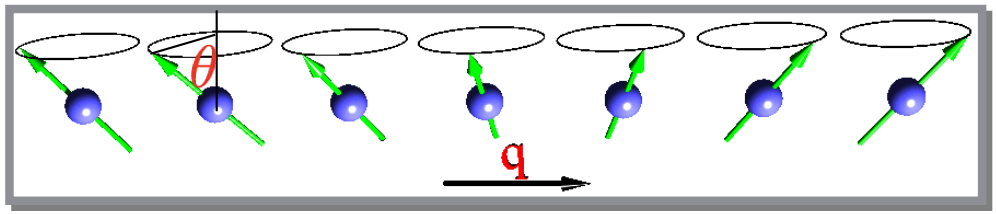
JÜLICH FORSCHUNGSZENTRUM

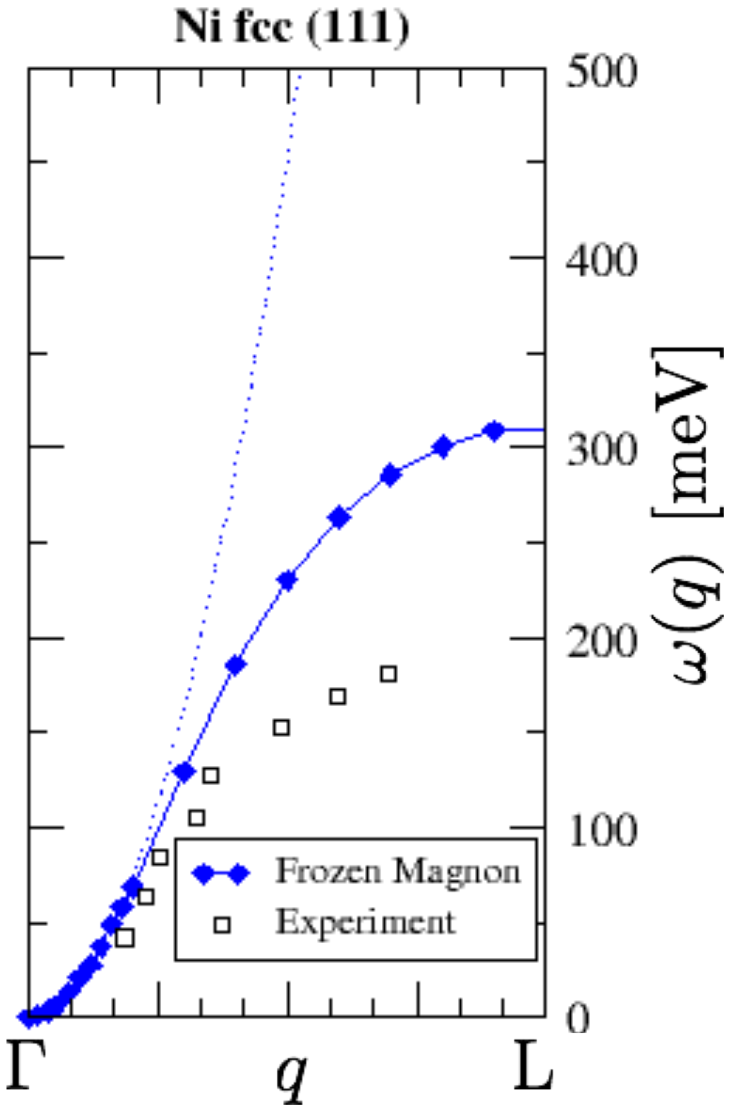
Spin stiffness D:

$$\omega(q) = Dq^2 \qquad \text{for small } q$$

$$D_{\text{Theo}} = 712\,[\text{meV}/\text{Å}^2]$$

$$D_{\text{Exp}} \simeq 550\,[\text{meV}/\text{Å}^2]$$





Theo: Marjana Lezaic, unpublished

Exp: Mook and Paul, PRL **54**, 227 (1985)

Electrons and Electronic Structure

The Many Body Problem

- Hamiltonian of N electrons in external potential (ion-cores) $V_{\text{ext}}(\vec{r})$

$$
\begin{aligned}
H &= \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{ext}}(\vec{r}_i)\right) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} \\
&= \underbrace{\sum_{i=1}^{N} h(\vec{r}_i)}_{H_0} + \underbrace{\frac{1}{2}\sum_{i\neq j}^{N} v(\vec{r}_i-\vec{r}_j)}_{U} + \frac{1}{2}\sum_{n\neq n'}\frac{Z^n Z^{n'} e^2}{|\vec{R}^n-\vec{R}^{n'}|} \\
&= H_0 + U
\end{aligned}
$$

Neglected!
for the time being

- single particle contribution H_0 and two-body interaction U
- must be approximated for large N

Independent particles in periodic potential

neglect the electron-electron interaction

$$\begin{aligned} H &= H_0 + \cancel{U} \\ &= \sum_{i=1}^{N} h(\vec{r}_i) \end{aligned}$$

solution of SchrÃ¶dinger equation

$$H\Psi = H_0\Psi = E\Psi$$

can be written as a product of solutions of the single particle equation

$$h(\vec{r})\psi(\vec{r}) = \epsilon\psi(\vec{r})$$

Independent particles in periodic potential

simplest:

$$
\begin{aligned}
H_0 \Psi(\vec{r}_1, ...\vec{r}_N) &= \sum_{i=1}^{N} h(\vec{r}_i) \left\{\psi_1(\vec{r}_1)\psi_2(\vec{r}_2).....\psi_N(\vec{r}_N)\right\} \\
&= E \left\{\psi_1(\vec{r}_1)\psi_2(\vec{r}_2).....\psi_N(\vec{r}_N)\right\}
\end{aligned}
$$

with

$$
E = \sum_{i=1}^{N} \epsilon_i
$$

electrons are Fermions: no two ϵ_i the same

but: total wavefunction must be antisymmetric! → we discuss later

Outline

- Independent electrons
  - lattice periodicity: real and reciprocal lattice
  - Bloch functions and band structure
  - symmetry in periodic crystals
- Interacting electrons
  - Hartree- and Hartree-Fock approximation
  - density functional theory
- Relativistic effects
  - spin-orbit coupling
  - Rashba & Dresselhaus effect
  - topological insulators
  - magnetism and spin-orbit coupling

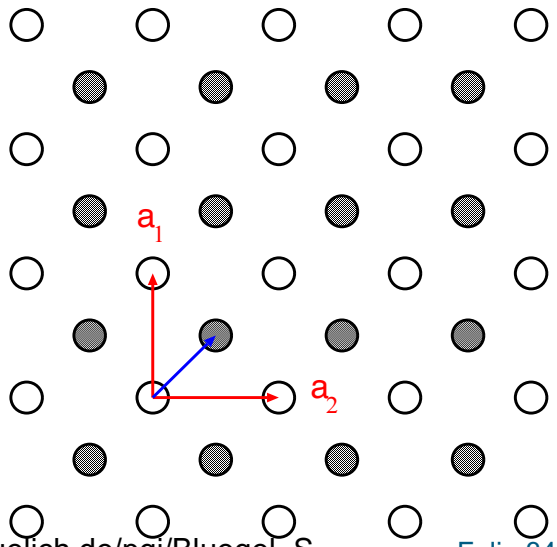
Bravais Lattice [= Crystal Lattice]

Intuitively, a Bravais lattice can also be defined as an infinite array of discrete points, such as at each point the lattice looks exactly the same (i.e. same arrangement and orientation).

A 3-dimensional (3D) Bravais lattice is defined by the set of vectors

$$\mathbf{R^n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \qquad n_1, n_2, n_3 \in \mathbb{Z}$$

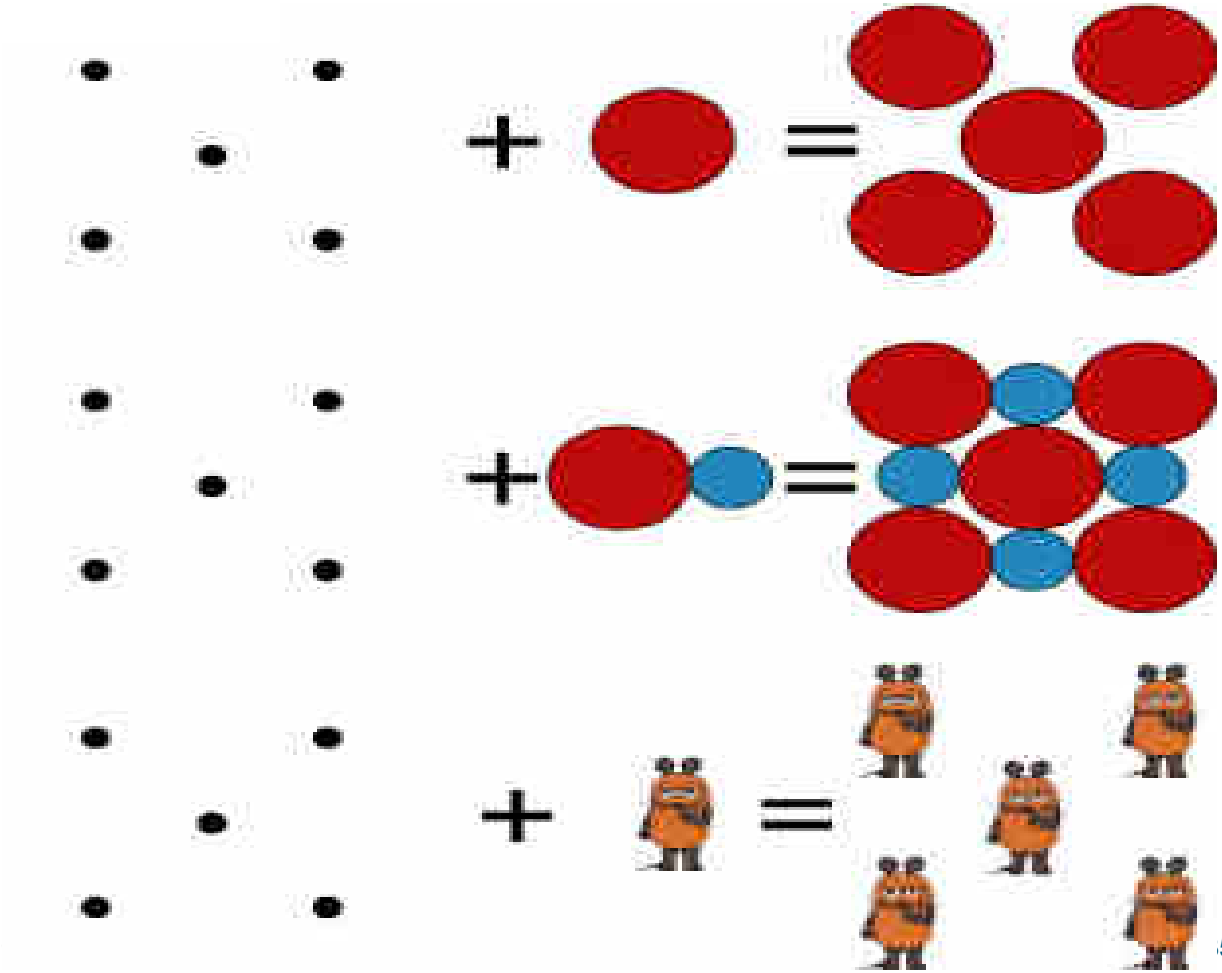
$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$: primitive lattice vectors.



Crystal Structure

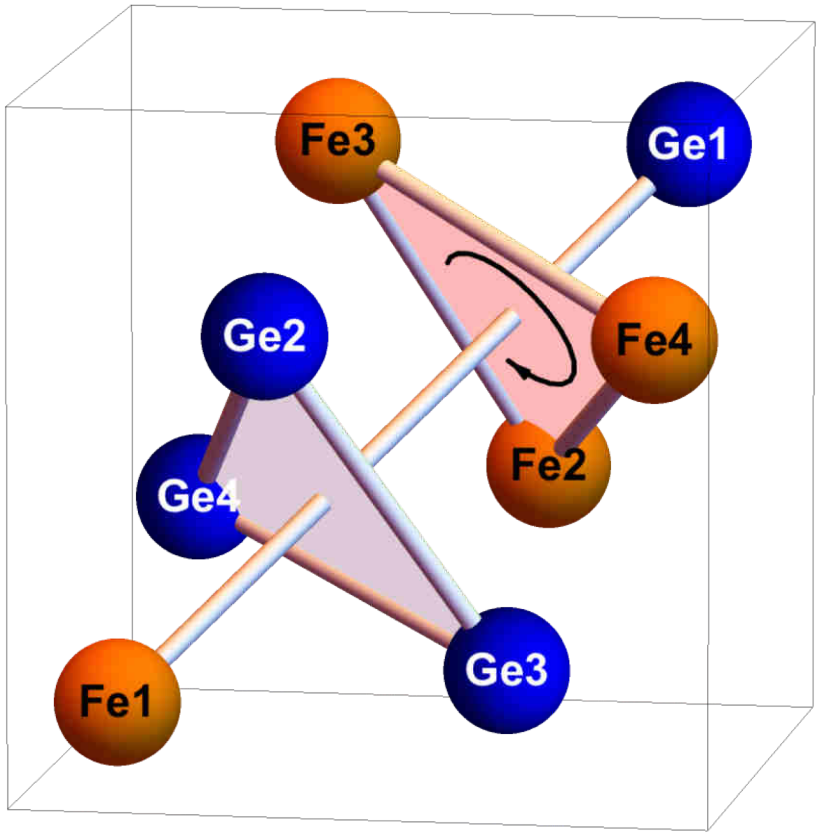
- Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sites of the lattice point.

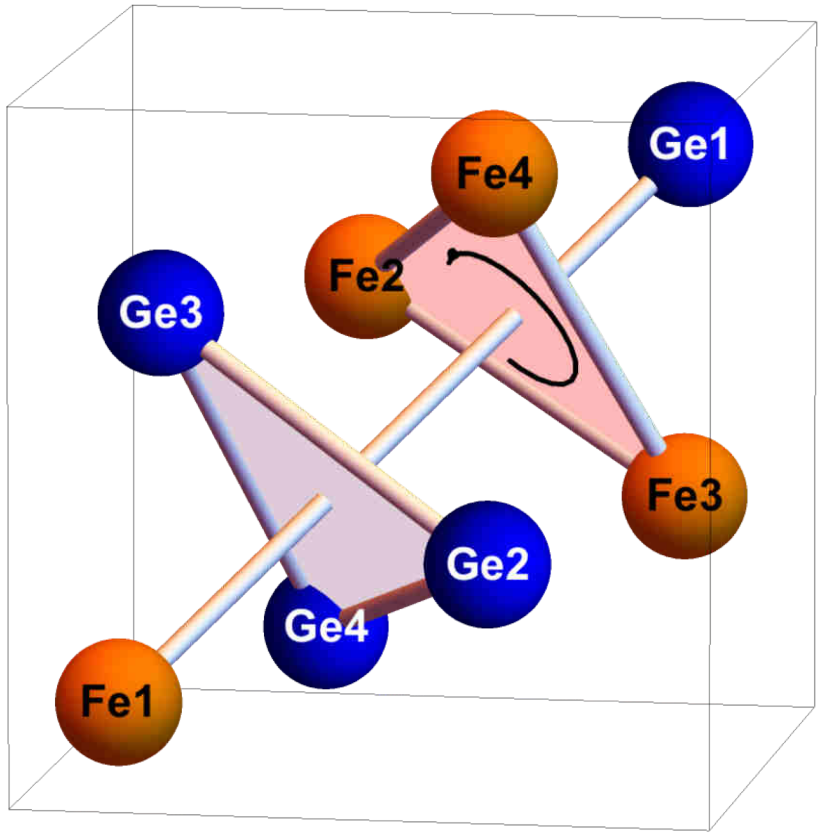
Crystal Structure = Crystal Lattice + Basis



Example B20 crystal: FeGe

Cubic, no inversion symmetry, chiral
Unit cell 4 Fe and 4 Ge atoms



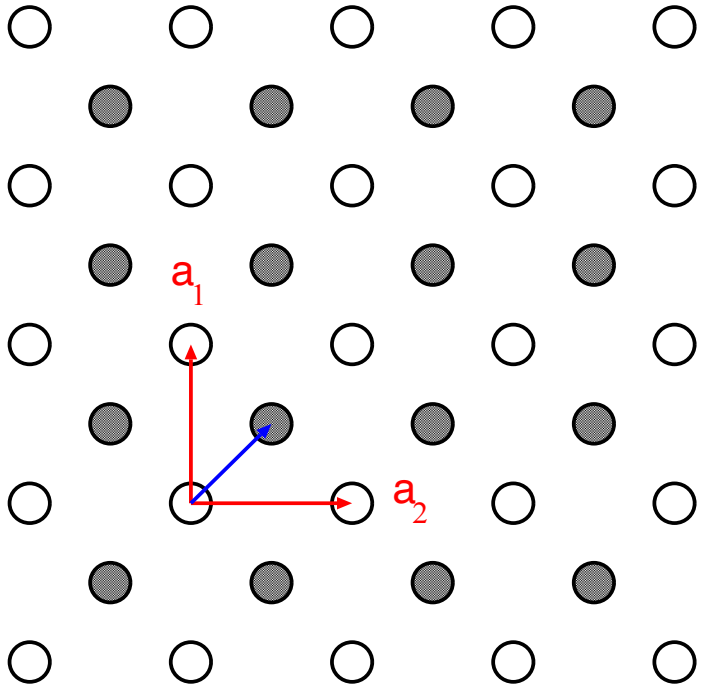


Lattice periodicity

Translation operator $\mathcal{T}$:

$$\mathcal{T}(n_1 n_2 n_3)\vec{r} = \vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$= \vec{r} + \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$$



Lattice vector $\vec{R}_{\vec{n}}$:

$$\vec{R}_{\vec{n}} = \underline{A}\vec{n} \qquad (n_i \in \mathbb{Z})$$

Potential: $\mathcal{T}_{\vec{n}} V(\vec{r}) = V(\vec{r} + \vec{R}_{\vec{n}}) = V(\vec{r})$

Hamiltonian: $\mathcal{H} = -\frac{1}{2}\boldsymbol{\nabla}^2 + V(\vec{r}) \rightarrow [\mathcal{H}, \mathcal{T}] = 0$

Translation operator - eigenvalues

Hamiltonian and translation operator commute:

$$\mathcal{T}_{\vec{n}}\mathcal{H}\phi(\vec{r}) = \mathcal{H}\mathcal{T}_{\vec{n}}\phi(\vec{r}) = \epsilon\mathcal{T}_{\vec{n}}\phi(\vec{r})$$

Eigenvalues of $\mathcal{T}_{\vec{n}}$: $\quad \mathcal{T}_{\vec{n}}\phi(\vec{r}) = \lambda_{\vec{n}}\phi(\vec{r})$

- Density $n(\vec{r}) = \phi^*(\vec{r})\phi(\vec{r})$ is lattice periodic:

$$\mathcal{T}_{\vec{n}}\phi^*(\vec{r})\phi(\vec{r}) = \lambda^*_{\vec{n}}\lambda_{\vec{n}}\phi^*(\vec{r})\phi(\vec{r}) = |\lambda_{\vec{n}}|^2 n(\vec{r}) = n(\vec{r}) \rightarrow |\lambda_{\vec{n}}|^2 = 1$$

- $\mathcal{T}_{\vec{n}}\mathcal{T}_{\vec{n}'}\phi(\vec{r}) = \lambda_{\vec{n}}\lambda_{\vec{n}'}\phi(\vec{r})$

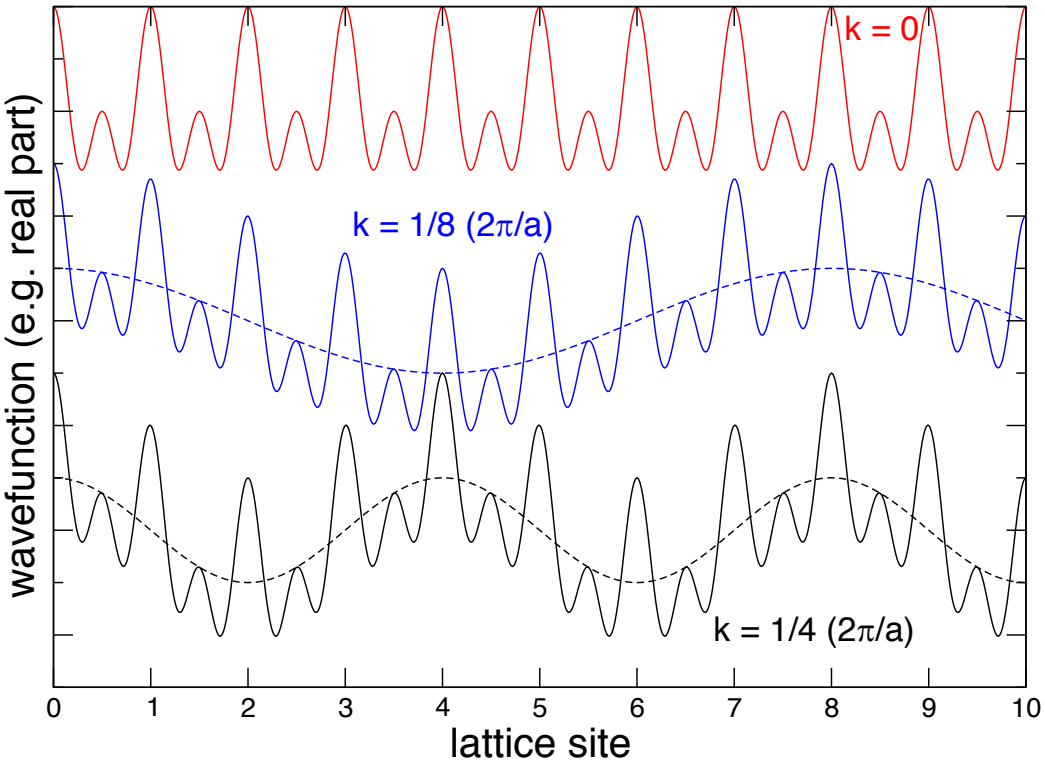
$$\mathcal{T}_{\vec{n}+\vec{n}'}\phi(\vec{r}) = \lambda_{\vec{n}+\vec{n}'}\phi(\vec{r}) \rightarrow \lambda_{\vec{n}}\lambda_{\vec{n}'} = \lambda_{\vec{n}+\vec{n}'}$$

$$\lambda_{\vec{n}} = \mathrm{e}^{i\vec{k}\cdot\vec{R}_{\vec{n}}} \quad ; \quad \mathcal{T}_{\vec{n}}\phi_{\vec{k}}(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\phi_{\vec{k}}(\vec{r})$$

Bloch functions

Translation acting on $\phi_{\vec{k}}(\vec{r})$:

$$\mathcal{T}_{\vec{n}}\phi_{\vec{k}}(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\phi_{\vec{k}}(\vec{r})$$



lattice periodic part $u_{\vec{k}}(\vec{r})$:

$$\phi_{\vec{k}}(\vec{r}) = a(\vec{r})u_{\vec{k}}(\vec{r})$$

$$\mathcal{T}_{\vec{n}}a(\vec{r})u_{\vec{k}}(\vec{r}) = a(\vec{r}+\vec{R}_{\vec{n}})u_{\vec{k}}(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot\vec{R}_{\vec{n}}}a(\vec{r})\,u_{\vec{k}}(\vec{r})$$

Bloch function: $a(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot\vec{r}} \rightarrow \phi_{\vec{k}}(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$

Gauge freedom: $\phi_{\vec{k}}(\vec{r}) \rightarrow e^{if(\vec{k})}\phi_{\vec{k}}(\vec{r})$ with $f \in \mathbb{R}$

The k-vector

Wave functions can be labeled by $\vec{k}$

Comparison with atom:

	atom	**periodic solid**
Symmetry	rotation group	translation group
Conserved quantity	angular momentum	crystal momentum
determines:		
Quantum number	(l,m)	$\vec{k}$
Wave function	$Y_{lm}(\hat{r})$	$e^{i\vec{k}\cdot\vec{r}}$
free:		
Quantum number	n	v
Wave function	$u_n(r)$	$u_{\vec{k},v}(\vec{r})$

Reciprocal lattice

Lattice periodic function $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R}_{\vec{n}})$

Fourier transform:

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} u(\vec{K}) \mathrm{e}^{i\vec{K}\cdot\vec{r}} \quad ; \quad \vec{K}\cdot\vec{R}_{\vec{n}} = \vec{K}\cdot\underline{A}\vec{n} = 2\pi N \qquad (N \in \mathbb{Z})$$

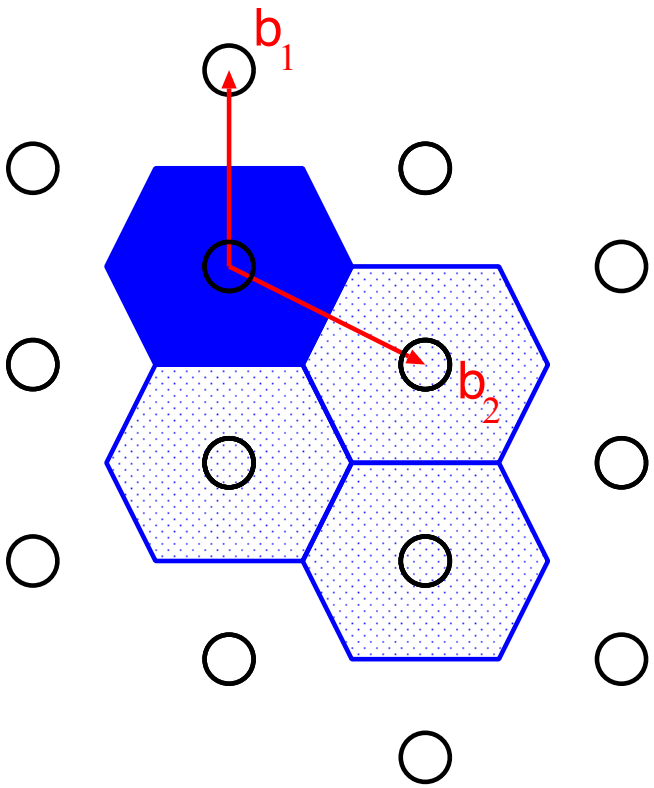
reciprocal lattice vector:

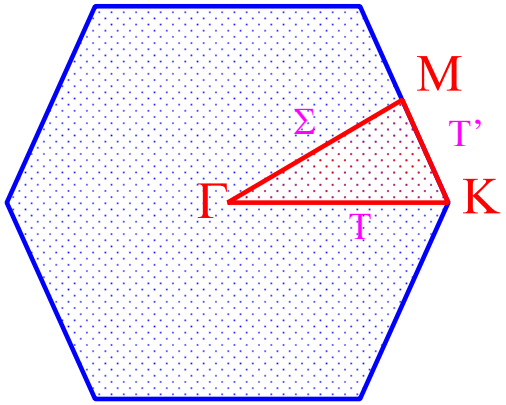
$$\vec{K}_{\vec{m}} = \vec{m}\underline{B}, \text{ so that } \quad \underline{B}\underline{A} = 2\pi\underline{1} \qquad (m_i \in \mathbb{Z})$$

Brillouin zones

Reciprocal lattice vectors $\vec{K}_{\vec{m}}$: $e^{i\vec{R}_{\vec{n}}\cdot(\vec{k}+\vec{K}_{\vec{m}})} = e^{i\vec{R}_{\vec{n}}\cdot\vec{k}}$

Restrict $\vec{k}$ to first Brillouin zone and label additionally by band index.





Band structure

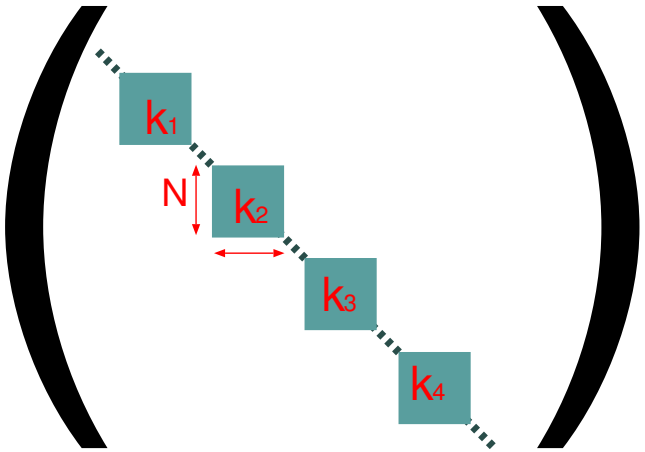
- Matrix element of two Bloch functions $\left(\vec{k}, \vec{k'}\right)$ with $\mathcal{H}$ and translate:

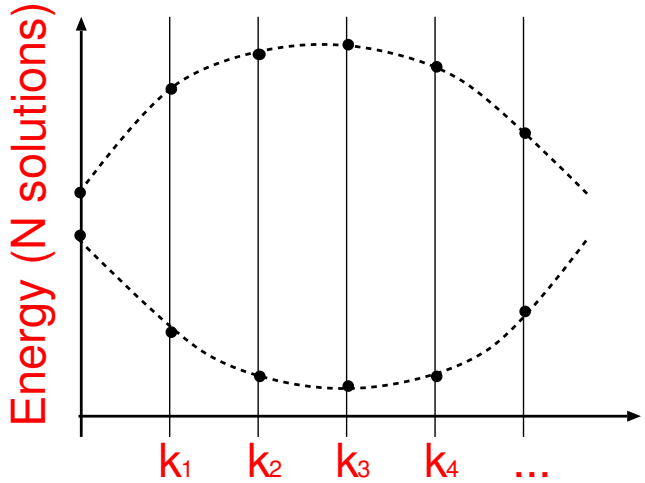
$$\left\langle \mathcal{T}_{\vec{R}_{\vec{n}}} \phi_{\vec{k}'}(\vec{r}) | \mathcal{H} | \mathcal{T}_{\vec{R}_{\vec{n}}} \phi_{\vec{k}}(\vec{r}) \right\rangle = \left\langle \mathrm{e}^{i\vec{R}_{\vec{n}}\cdot\vec{k}'} \phi_{\vec{k}'}(\vec{r}) | \mathcal{H} | \mathrm{e}^{i\vec{R}_{\vec{n}}\cdot\vec{k}} \phi_{\vec{k}}(\vec{r}) \right\rangle =$$

$$= \mathrm{e}^{i\vec{R}_{\vec{n}}\cdot\left(\vec{k}-\vec{k}'\right)} \left\langle \phi_{\vec{k}'}(\vec{r}) | \mathcal{H} | \phi_{\vec{k}}(\vec{r}) \right\rangle = \begin{cases} \left\langle \phi_{\vec{k}'}(\vec{r}) | \mathcal{H} | \phi_{\vec{k}}(\vec{r}) \right\rangle & \text{if} \quad \vec{k} - \vec{k}' = \vec{K} \\ 0 & \text{otherwise} \end{cases}$$

- Expansion of Bloch function in basis functions: $\phi_{\vec{k},\nu} = \sum_{n}^{N} c_{\vec{k},\nu}^{n} \varphi_{\vec{k}}^{n}$
- Schrödinger equation ➔ matrix equation:

$$H_{\vec{k}}^{n,n'} c_{\vec{k},\nu}^{n'} = \epsilon_{\vec{k},\nu} S_{\vec{k}}^{n,n'} c_{\vec{k},\nu}^{n'} \quad \text{with} \quad S_{\vec{k}}^{n,n'} = \left\langle \varphi_{\vec{k}}^{n} | \varphi_{\vec{k}}^{n'} \right\rangle$$





Eigenvalue problem in plane wave basis

- Plane wave representation of wave function

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{h}'} c_{\vec{h}'}(\vec{k})\, e^{i(\vec{k}+\vec{G}^{\vec{h}'})\vec{r}}$$

with

$$u_{\vec{k}\nu}(\vec{r}) = \sum_{\vec{h}'} c_{\vec{h}'\nu}(\vec{k})\, e^{i\vec{G}^{\vec{h}'}\vec{r}}$$

- Schrödinger Eq in 3D:

$$\left(-\frac{\hbar^2}{2m}\partial^2_{\vec{r}} + V(\vec{r})\right)\psi_{\vec{k}\nu}(\vec{r}) = E_{\vec{k}\nu}\psi_{\vec{k}\nu}(\vec{r})$$

- Schrödinger Eq in Matrix representation

$$\left[\sum_{\vec{h}'}\left(\frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2 - E_\nu(\vec{k})\right)\delta_{h,h'} + \tilde{V}_{\vec{h}-\vec{h}'}\right] c_{\vec{h}'}(\vec{k}) = 0$$

Eigenvalue problem in plane wave basis

- Schrödinger Eq in 3D:

$$\left(-\frac{\hbar^2}{2m}\partial_{\vec{r}}^2 + V(\vec{r})\right)\psi_{\vec{k}\nu}(\vec{r}) = E_{\vec{k}\nu}\psi_{\vec{k}\nu}(\vec{r})$$

- Schrödinger Eq in Matrix representation

$$\left[\sum_{\vec{h}'}\left(\frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2 - E_\nu(\vec{k})\right)\delta_{h,h'} + \tilde{V}_{\vec{h}-\vec{h}'}\right] c_{\vec{h}'}(\vec{k}) = 0$$

- $\langle \vec{k}+\vec{G}^{\vec{h}} | \vec{k}+\vec{G}^{\vec{h}'} \rangle = \frac{1}{V_z}\int d\vec{r}\, e^{i(-\vec{G}^{\vec{h}}+\vec{G}^{\vec{h}'})\vec{r}} = \delta_{\vec{h},\vec{h}'}$

- $\langle \vec{k}+\vec{G}^{\vec{h}} | V | \vec{k}+\vec{G}^{\vec{h}'} \rangle = \frac{1}{V_z}\int d\vec{r}\, V(\vec{r})\, e^{i(-\vec{G}^{\vec{h}}+\vec{G}^{\vec{h}'})\vec{r}} = \tilde{V}_{\vec{h},\vec{h}'}$

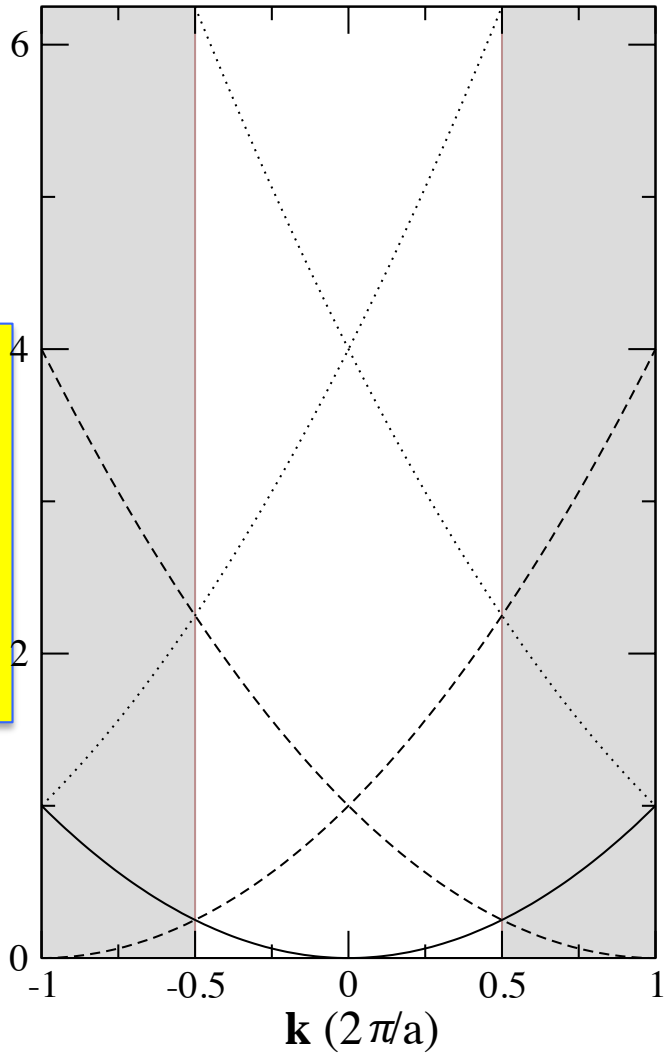
Free electron gas [= Jellum model]

- Const. potential: $\mathcal{H} = -\frac{1}{2}\nabla^2 + V_0$

- Eigenvalue problem for $V_{h,h'} = 0$, for all h

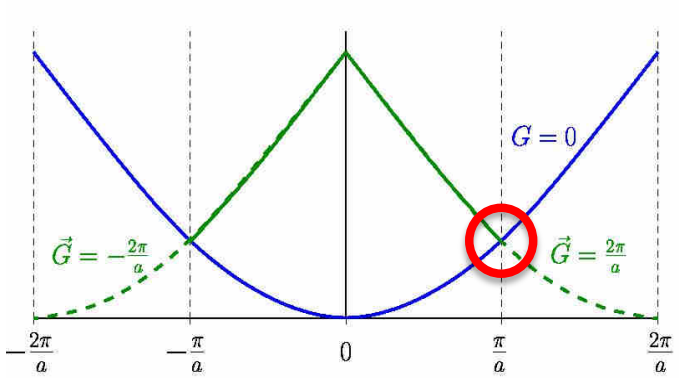
$$\det\left|\left(\frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2 - \epsilon_\nu(\vec{k})\right)\delta_{h,h'}\right| = 0$$

$$\Longrightarrow \epsilon_\nu(\vec{k}) = \frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2$$



Electrons in weak potential

- @ k-point **2** states $\nu \Leftrightarrow \vec{h} = 0 \ \wedge \ \vec{h}$
- There exists an energy $E_\nu(\vec{k})$ for which



- $\psi_{\nu,\vec{k}}(\vec{r}) = c_{\vec{h}=0}(\vec{k})e^{i\vec{k}\vec{r}} + c_{\vec{h}}(\vec{k})e^{i(\vec{k}+\vec{G}^{\vec{h}})\vec{r}} + \cdots + \underbrace{c_{\vec{l}}}_{\text{small}} e^{i(\vec{k}+\vec{G}^{\vec{l}})\vec{r}}$
- Degenerate perturbation theory

$$\left(\frac{\hbar^2}{2m}\vec{k}^2 - E + \tilde{V}_0\right) c_0 + \tilde{V}_{-\vec{h}} c_{\vec{h}} = 0$$

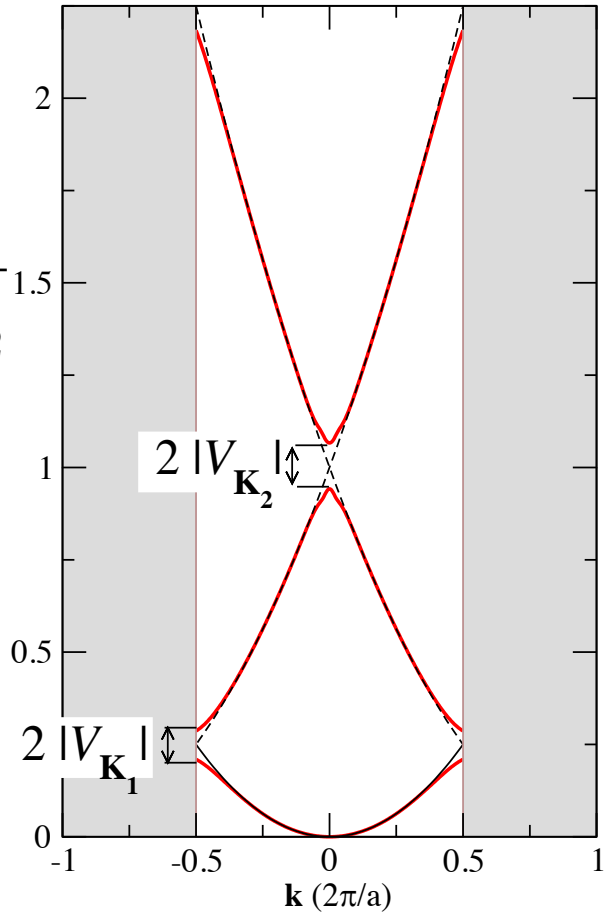
$$\tilde{V}_0 c_0 + \left(\frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2 - E + \tilde{V}_0\right) c_{\vec{h}} = 0$$

$$\Rightarrow \left(\frac{\hbar^2}{2m}\vec{k}^2 - E + \tilde{V}_0\right)\left(\frac{\hbar^2}{2m}(\vec{k}+\vec{G}^{\vec{h}})^2 - E + \tilde{V}_0\right) = |\tilde{V}_{\vec{h}}|^2, \text{ since } \tilde{V}_{-\vec{h}} = \tilde{V}_0^* \text{ if } V(\vec{r}) \text{ real}$$

Nearly free electron gas

- **2** states $\nu \Leftrightarrow \vec{h} = 0 \ \wedge \ \vec{h}$
- Eigenvalue spectrum

$$\varepsilon_{\pm\vec{k}} = \frac{\varepsilon^0_{\vec{k}} + \varepsilon^0_{\vec{k}+\vec{K}^h}}{2} \pm \sqrt{\frac{1}{4}\left(\varepsilon^0_{\vec{k}} - \varepsilon^0_{\vec{k}+\vec{K}^h}\right)^2 + |V_{\vec{K}^h}|^2}$$



- Special case Brillouin zone boundary:
  $\vec{k}^2 = (\vec{k} + \vec{G}^{\vec{h}})^2$

  Energy degeneracy is lifted

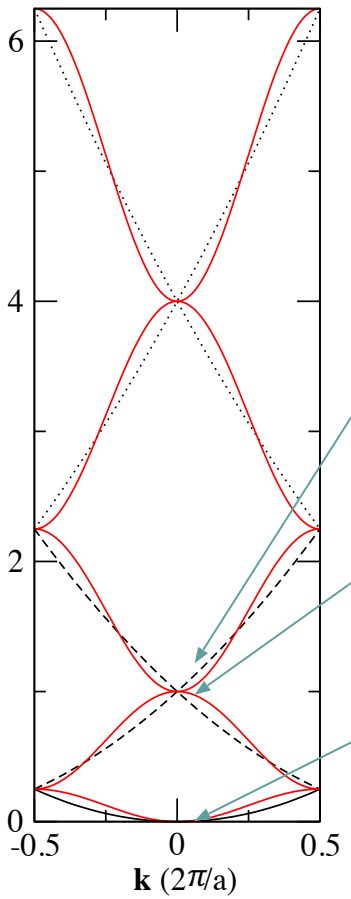
$$\Rightarrow E_{\pm} = V_0 + \frac{\hbar^2}{2m}\vec{k}^2 \pm |\tilde{V}_{\vec{h}}|$$

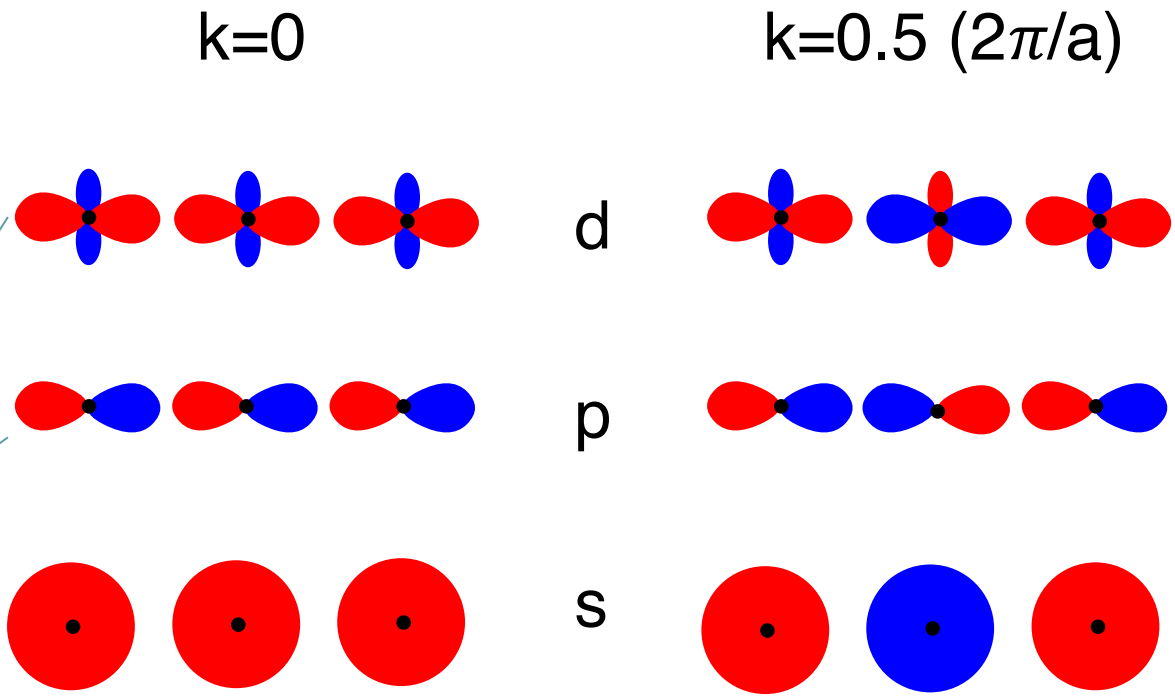
- Special case away from BZb: $\frac{\hbar^2}{2m}\left|\vec{k}^2 - (\vec{k} + \vec{G}^{\vec{h}})^2\right| \gg |\tilde{V}_{\vec{h}}|$

  back to nondegenerate results

Tight-binding representation

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{n}} e^{i\vec{k}\vec{R}_n} \chi(\vec{r} - \vec{R}_n) \quad ; \quad \varepsilon(\vec{k}) = \alpha + 2\beta \cos(ka)$$





Symmetry and band structures

Consider symmetries other than translations, e.g. inversion.

Action of inversion operator $\mathcal{I}$ on Bloch function:

$$\mathcal{T}_{\vec{R}}\mathcal{I}\phi_{\vec{k}}(\vec{r}) = \mathcal{T}_{\vec{R}}(\mathrm{e}^{-i\vec{k}\cdot\vec{r}}u_{\vec{k}}(-\vec{r})) = \mathrm{e}^{-i\vec{k}\cdot\vec{R}}\mathrm{e}^{-i\vec{k}\cdot\vec{r}}u_{\vec{k}}(-\vec{r}) = \mathrm{e}^{-i\vec{k}\cdot\vec{R}}\mathcal{I}\phi_{\vec{k}}(\vec{r})$$

gives Bloch function with wave-vector $-\vec{k}$.

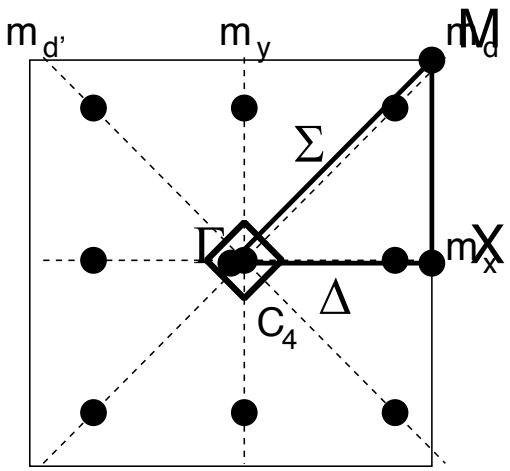
$$\mathcal{I}\mathcal{H}\phi_{\vec{k}}(\vec{r}) = \mathcal{H}\mathcal{I}\phi_{\vec{k}}(\vec{r}) = \mathcal{I}\varepsilon_{\vec{k}}\phi_{\vec{k}}(\vec{r}) \quad \text{and, therefore,} \quad \mathcal{H}\phi_{-\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}}\phi_{-\vec{k}}(\vec{r})$$

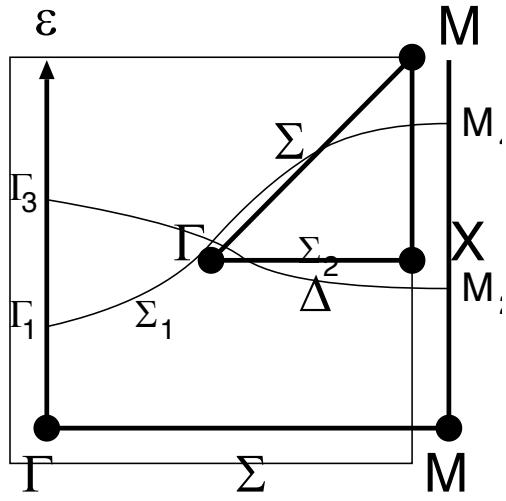
Blochfunctions with $\vec{k}$ and $-\vec{k}$ have same eigenvalues but different eigenvectors!

(Similar for other symmetry elements compatible with crystal lattice.)

Example: point group 4mm

Square lattice with full symmetry:





special high symmetry lines in Brillouin zone:

$\Delta : m_x \vec{k} = \vec{k}$

$\Sigma : m_d \vec{k} = \vec{k}$ (symmetry group m $\{\mathcal{E}, m_d\}$)

wave functions on Σ can be classified w.r.t. their transformation properties under $\{\mathcal{E}, m_d\}$: Σ_1, Σ_2

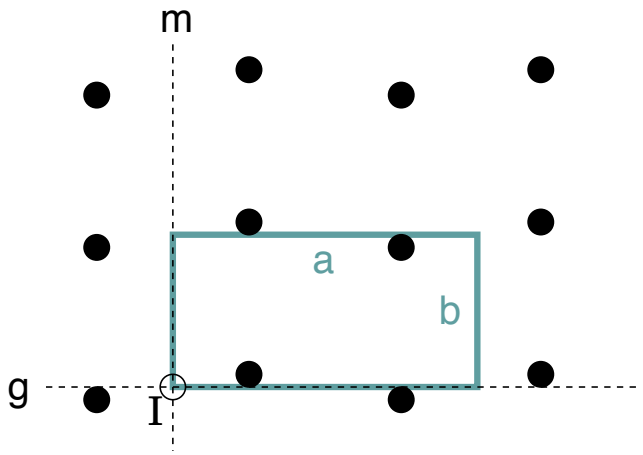
States of different symmetry are allowed to cross in the band structure

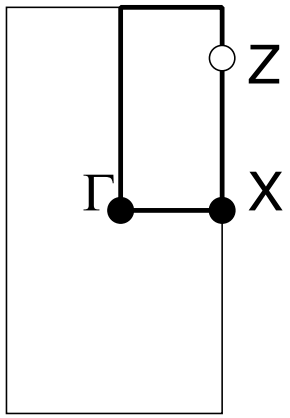
Non-symmorphic symmetries

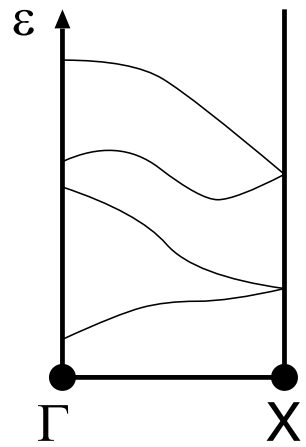
Combination of rotation/mirror operation ($\underline{R}$) with fractional translation ($\vec{\tau}$): $(\underline{R}|\ \vec{\tau})\ \vec{r} = \underline{R}\vec{r} + \vec{\tau}$

$$(\underline{R}|\vec{\tau}): \quad g = \left(\begin{array}{cc|c} 1 & 0 & 1/2 \\ 0 & -1 & 0 \end{array}\right) \quad \text{or} \quad m = \left(\begin{array}{cc|c} -1 & 0 & -1/2 \\ 0 & 1 & 0 \end{array}\right)$$

induce additional degeneracies at Brillouin zone boundaries:

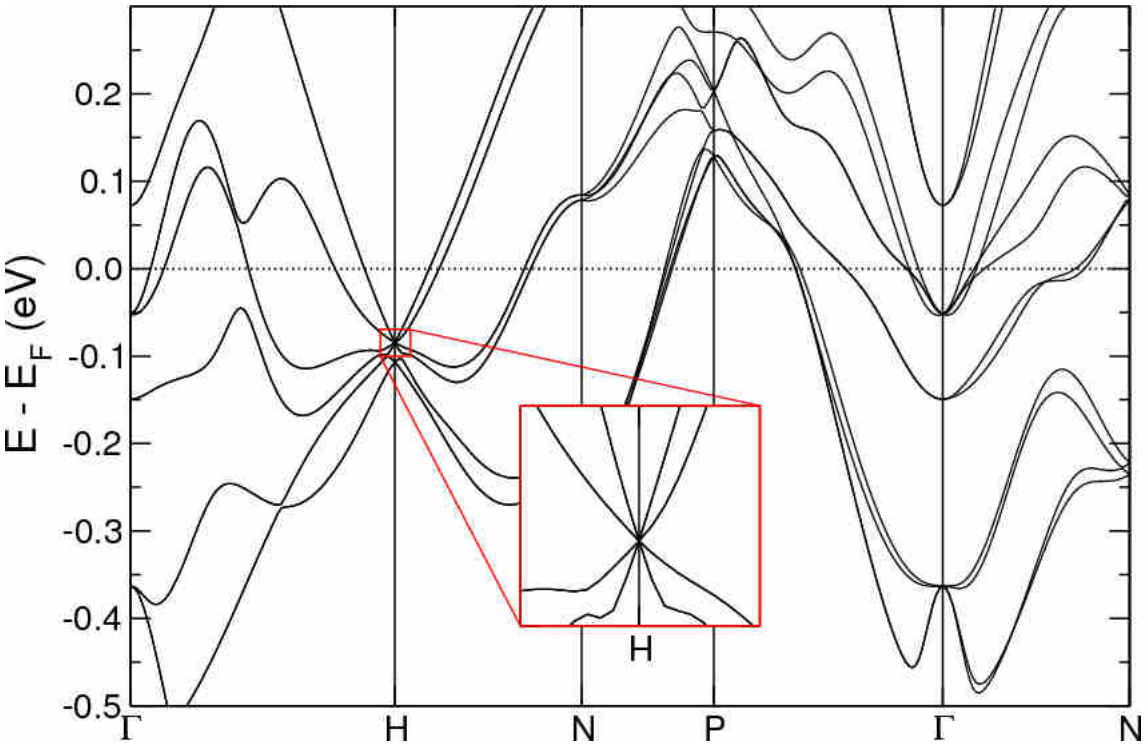


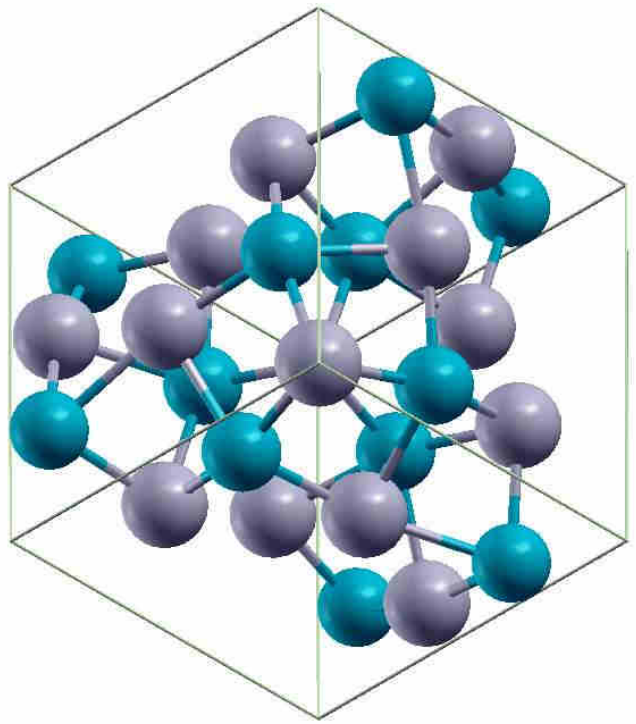




“new Fermions” in non-symmorphic crystals

Four-fold degeneracy at H-point in La_4Bi_3:





see e.g. B. Bradlyn, et al., Science 353 (6299), aaf5037 (2016)

Outline

- Independent electrons
  - lattice periodicity: real and reciprocal lattice
  - Bloch functions and band structure
  - symmetry in periodic crystals
- Interacting electrons
  - Hartree- and Hartree-Fock approximation
  - density functional theory
- Relativistic effects
  - spin-orbit coupling
  - Rashba & Dresselhaus effect
  - topological insulators
  - magnetism and spin-orbit coupling

The Many Body Problem

- Hamiltonian of N electrons in external potential (ion-cores)$V_{\text{ext}}(\vec{r})$

$$
\begin{aligned}
H &= \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{ext}}(\vec{r}_i)\right) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} \\
&= \underbrace{\sum_{i=1}^{N} h(\vec{r}_i)}_{H_0} + \underbrace{\frac{1}{2}\sum_{i\neq j}^{N} v(\vec{r}_i-\vec{r}_j)}_{U} \\
&= H_0 + U
\end{aligned}
$$

- single particle contribution H_0 and two-body interaction U
- must be approximated for large N

Hartree-Approximation

simplest:

$$\begin{aligned} H_0\Psi(\vec{r}_1,...\vec{r}_N) &= \sum_{i=1}^{N} h(\vec{r}_i)\left\{\psi_1(\vec{r}_1)\psi_2(\vec{r}_2).....\psi_N(\vec{r}_N)\right\} \\ &= E\left\{\psi_1(\vec{r}_1)\psi_2(\vec{r}_2).....\psi_N(\vec{r}_N)\right\} \end{aligned}$$

with

$$E = \sum_{i=1}^{N} \epsilon_i$$

electrons are Fermions: no two ϵ_i the same
but: total wavefunction must be antisymmetric!

Slater Determinant

simple notation for a totally antisymmetric wavefunction:

$$\Psi(\vec{r}_1,\dots\vec{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\vec{r}_1) & \dots & \psi_1(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\vec{r}_1) & \dots & \psi_N(\vec{r}_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}}\sum_P (-1)^P P\left(\psi_1(\vec{r}_1)\dots\psi_N(\vec{r}_N)\right)$$

permutation acts on index of ψ!

Example: $N = 2$

$$\frac{1}{\sqrt{2}}\sum_{P_2}(-1)^{P_2}P_2\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_2(\vec{r}_1)\psi_1(\vec{r}_2)\right)$$

Slater determinant is the solution of the free electron problem

Hartree– Fock Approximation

- Best ground state energy for interacting electron problem with Ansatz of single Slater determinant single particle states

$$\Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_1(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P\left(\psi_1(\mathbf{x}_1) \ldots \psi_N(\mathbf{x}_N)\right).$$

- Best possible ortho single particle state to obtain ground state

$$E = \min_\Psi \langle \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) | H | \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) \rangle$$

$$= \min_\Psi \sum_{\sigma_1 \ldots \sigma_N} \int \Psi^*_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) H \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N)\, dV_1 \ldots dV_N.$$

Matrix Elements

$$E = \min_{\Psi} \left\langle \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) \left| \underbrace{H_0}_{\text{single particle}} + \underbrace{U}_{\text{two particle}} \right| \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) \right\rangle$$

- Single-particle matrix elements

$$\left\langle \Psi \left| \sum_i^N h(\vec{r}_i) \right| \Psi \right\rangle = \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P'-P} \langle 1|_1 \ldots \langle N|_N P^\dagger \sum_i^N h(\vec{r}_i) P' |1\rangle_1 \ldots |N\rangle_N$$

Matrix Elements

$$E = \min_{\Psi} \left\langle \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) \left| \underbrace{H_0}_{\text{single particle}} + \underbrace{U}_{\text{two particle}} \right| \Psi_{\text{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) \right\rangle$$

- Single-particle matrix elements

$$\left\langle \Psi \left| \sum_i^N h(\vec{r}_i) \right| \Psi \right\rangle = \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P'-P} \langle 1|_1 \ldots \langle N|_N P^\dagger \sum_i^N h(\vec{r}_i) P' |1\rangle_1 \ldots |N\rangle_N$$

- $\text{Det}[N \times N] = N \times \text{Det}[(N-1) \times (N-1)]$
- $P' = P$

$$\left\langle \Psi_{j_1 \cdots j_n} \left| \sum_i^N h(\vec{r}_i) \right| \Psi_{j_1 \cdots j_n} \right\rangle = \frac{(N-1)!}{N!} \sum_{P_j} \sum_i \left\langle j_i \left| h(\vec{r}_i) \right| j_i \right\rangle$$

$$= \sum_i \sum_\sigma \int dV \, \psi_i^*(\vec{r}, \sigma) h(\vec{r}) \psi_i(\vec{r}, \sigma)$$

Hartree Fock – Two Particle Term

$$\langle \Psi | U | \Psi \rangle = \frac{1}{2} \sum_P \sum_{P'} (-1)^{P'-P} \frac{1}{2} \sum_{i \neq j} \langle 1|_1 \dots \langle N|_N P^\dagger \frac{e^2}{|\vec{r}_i - \vec{r}_j|} P' |1\rangle_1 \dots |N\rangle_N$$

$$= \frac{1}{2} \sum_{P_2} \sum_{P_2'} (-1)^{P_2'-P_2} \frac{1}{2} \sum_{i \neq j} \underbrace{\langle j|_j \langle i|_i P_2^\dagger}_{} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \underbrace{P_2' |i\rangle_i |j\rangle_j}_{}$$

permutations of 2 single particle states remain:

$$\frac{1}{\sqrt{2}} \sum_{P_2} (-1)^{P_2} P_2 |i\rangle_i |j\rangle_j = \frac{1}{\sqrt{2}} \left(|i\rangle_i |j\rangle_j - |j\rangle_i |i\rangle_j \right)$$

Product: 4-Terms

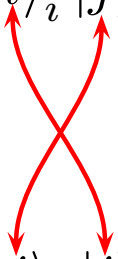
Direct and Exchange Energy

with sum over i, j two kind of terms:
direct term contains:

$$\langle i|_i \langle j|_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |i\rangle_i |j\rangle_j$$

exchange term:

$$\langle i|_i \langle j|_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |j\rangle_i |i\rangle_j$$



interaction energy: direct+exchange term

$$E_C = \langle \Psi | U | \Psi \rangle = E_{\text{dir}} + E_{\text{ex}}$$

Direct and Exchange Energy

$$E_{\text{dir}} = \frac{1}{2}\sum_{i\neq j}\frac{1}{2}\left(\langle j|_j\,\langle i|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|i\rangle_i\,|j\rangle_j + \langle i|_j\,\langle j|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|j\rangle_i\,|i\rangle_j\right)$$

$$= \frac{1}{2}\sum_{i\neq j}\langle j|_j\,\langle i|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|i\rangle_i\,|j\rangle_j$$

and

$$E_{\text{ex}} = (-1)\frac{1}{2}\sum_{i\neq j}\frac{1}{2}\left(\langle j|_j\,\langle i|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|j\rangle_i\,|i\rangle_j + \langle i|_j\,\langle j|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|i\rangle_i\,|j\rangle_j\right)$$

$$= -\frac{1}{2}\sum_{i\neq j}\langle j|_j\,\langle i|_i\,\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\,|j\rangle_i\,|i\rangle_j$$

since for $i=j$ both contributions cancel one can extend $\sum_{i\neq j}\rightarrow\sum_{i,j}$

Spin-Dependence of E_{dir}

the Hamiltonian is spin-independent: $|i\rangle_j = \psi_i(\vec{r}_j, \sigma_j) = \phi_{i\sigma}(\vec{r}_j)\chi(\sigma_j)$

$$E = \frac{1}{2}\sum_{i,j} \langle j|_j \langle i|_i \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |i\rangle_i |j\rangle_j \qquad \begin{matrix} i \to r, \sigma \\ j \to r', \sigma' \end{matrix}$$

$$= \frac{1}{2}\sum_{i,j,\sigma,\sigma'} \int dV \int dV' \phi^*_{i\sigma}(\vec{r})\phi_{i\sigma}(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} \phi^*_{j\sigma'}(\vec{r}')\phi_{j\sigma'}(\vec{r}')$$

$$\times \underbrace{\chi^*_i(\sigma)\chi_i(\sigma)}_{1} \underbrace{\chi^*_j(\sigma')\chi_j(\sigma')}_{1}$$

$$= \frac{1}{2}\int dV \int dV' n(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} n(\vec{r}')$$

Spinors:

$$\chi(\uparrow) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \chi(\downarrow) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

direct term is spin-independent
depends only on the charge density

$$n(\vec{r}) = \sum_\sigma \sum_i \phi^*_{i\sigma}(\vec{r})\phi_{i\sigma}(\vec{r})$$

Spin-Dependence of E_{ex}

$$E_{\text{ex}} = -\frac{1}{2}\sum_{i,j} \langle j|_j \langle i|_i \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |j\rangle_i |i\rangle_j$$

$$= -\frac{1}{2}\sum_{i,j}\sum_{\sigma\sigma'} \int dV \int dV' \phi^*_{i\sigma}(\vec{r})\phi_{i\sigma}(\vec{r}\,') \frac{e^2}{|\vec{r} - \vec{r}\,'|} \phi^*_{j\sigma'}(\vec{r}\,')\phi_{j\sigma'}(\vec{r})$$

$$\times \underbrace{\chi^*_i(\sigma)\chi_i(\sigma')}_{\delta_{\sigma\sigma'}} \underbrace{\chi^*_j(\sigma')\chi_j(\sigma)}_{\delta_{\sigma\sigma'}}$$

$$= -\frac{1}{2}\sum_{\sigma,\sigma'} \delta_{\sigma\sigma'} \sum_{i,j} \int dV \int dV' \phi^*_{i\sigma}(\vec{r})\phi_{i\sigma}(\vec{r}\,') \frac{e^2}{|\vec{r} - \vec{r}\,'|} \phi^*_{j\sigma'}(\vec{r}\,')\phi_{j\sigma'}(\vec{r})$$

exchange term is spin-dependent - only acts between states with $\sigma = \sigma'$!

Hartree-Fock Equations

$$E = \min_{\Psi} \langle \Psi_{\text{Slaterdet.}} | H | \Psi_{\text{Slaterdet.}} \rangle$$

minimize energy with respect to single electron wavefunctions

$$0 = \frac{\delta}{\delta \phi_i^*(\vec{r},\sigma)} \left(\langle \Psi | H_0 | \Psi \rangle + E_{\text{dir}} + E_{\text{ex}} - \underbrace{\sum_{i,\sigma} \epsilon_{i,\sigma} \left\{ \int dV \phi_{i\sigma}^*(\vec{r}) \phi_{i\sigma}(\vec{r}) - 1 \right\}}_{\text{Normalisation}} \right)$$

vary for optimal $\Psi_{\text{Slaterdet.}} \rightarrow$ find best single particle states ϕ_i

Hartree-Fock-equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_{\text{Hartree}}(\vec{r}) - \hat{V}_{\text{ex}}(\vec{r}; i\sigma) \right) \phi_{i\sigma}(\vec{r}) = \epsilon_{i\sigma} \phi_{i\sigma}(\vec{r})$$

Exchange hole:

$$V_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{\langle \phi_i^\sigma | \phi_i^\sigma \rangle} \sum_{j,\sigma'} \left\langle \phi_i^\sigma(\vec{r}) \phi_j^{\sigma'}(\vec{r}') | g_{ij} | \phi_j^\sigma(\vec{r}) \phi_i^{\sigma'}(\vec{r}') \right\rangle_{(\vec{r}')} \qquad g_{ij} = \frac{1}{2} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

is the potential produced by the **exchange pair (charge) density**:

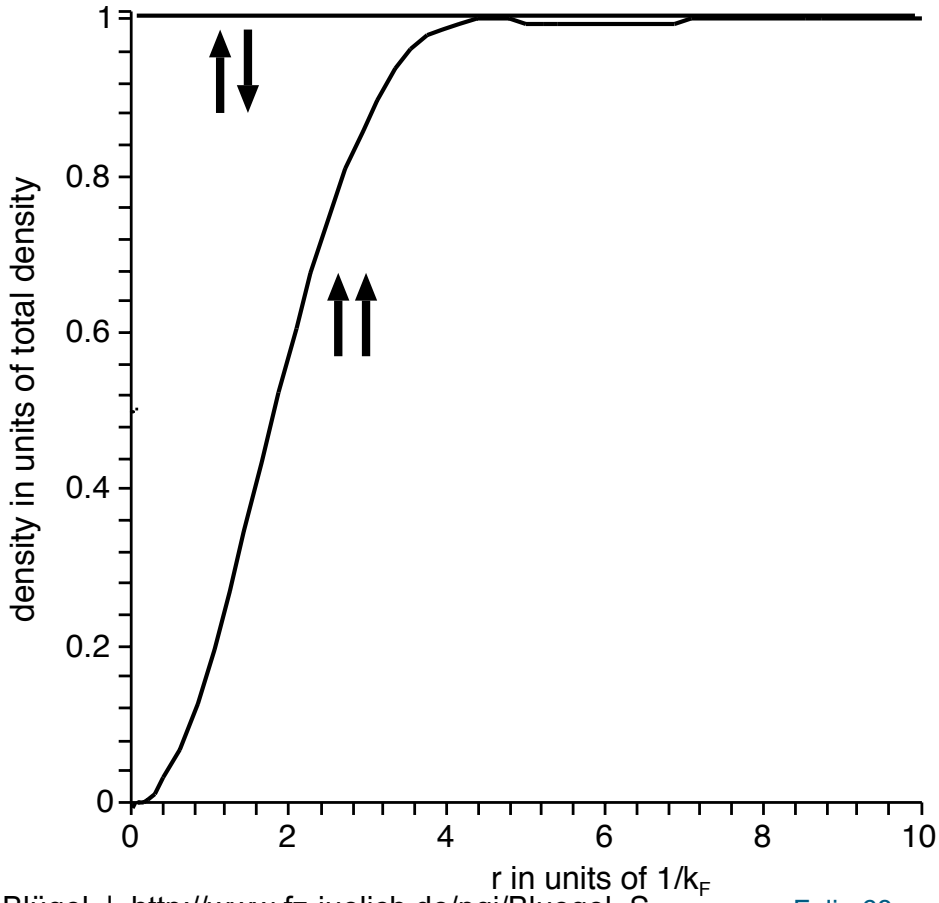
$$n_{\mathrm{x}}^\sigma(\vec{r}, \vec{r}') = -\sum_{j,\sigma'} \frac{\phi_i(\vec{r})^{\sigma *} \phi_j^{\sigma' *}(\vec{r}') \phi_j^\sigma(\vec{r}) \phi_i^{\sigma'}(\vec{r}')}{\phi_i(\vec{r})^* \phi_i(\vec{r})}$$

Properties of $n_{\mathrm{x}}^\sigma(\vec{r}, \vec{r}')$:

Charge: $\int n_{\mathrm{x}}^\sigma(\vec{r}, \vec{r}') d(\vec{r}') = -1$

Limit $(\vec{r}') \to (\vec{r})$:
$n_{\mathrm{x}}^\sigma(\vec{r}, \vec{r}) = -\sum_j \phi_j^{\sigma *}(\vec{r}) \phi_j^\sigma(\vec{r})$

J. C. Slater, Phys. Rev. **81**, 385 (1951)



Simple Picture of Two Conduction Electrons

two non-interacting electrons in the homogeneous electron gas
two-particle wavefunction is Slater determinant

$$\Psi_{12} = \phi_{12}(\vec{r}_1, \vec{r}_2)\chi_{12} = \frac{1}{\sqrt{2}} \sum_{P_2} (-1)^{P_2} P_2 \phi_1(\vec{r}_1)\chi_1(\sigma_1)\phi_2(\vec{r}_2)\chi_2(\sigma_2)$$

1) antisymmetry can be in spin-part

$$\chi_{12} = \frac{1}{\sqrt{2}} \{\chi_1(\uparrow)\chi_2(\downarrow) - \chi_2(\uparrow)\chi_1(\downarrow)\}$$

spatial wavefunction is symmetric
only one possible wavefunction $\rightarrow$singlet state
total spin zero, i.e. two electron spins are antiparallel

$$\phi_{12}(\vec{r}_1, \vec{r}_2) = \frac{1}{V} e^{i\vec{k}_1\vec{r}_1} e^{i\vec{k}_2\vec{r}_2}$$

Simple Picture of Two Conduction Electrons

two non-interacting electrons in the homogeneous electron gas
two-particle wavefunction is Slater determinant

$$\Psi_{12} = \phi_{12}(\vec{r}_1, \vec{r}_2)\chi_{12} = \frac{1}{\sqrt{2}} \sum_{P_2} (-1)^{P_2} P_2 \phi_1(\vec{r}_1)\chi_1(\sigma_1)\phi_2(\vec{r}_2)\chi_2(\sigma_2)$$

2) symmetric spin-part

$$\chi_{12} = \frac{1}{\sqrt{2}} \begin{cases} \chi_1(\uparrow)\chi_2(\uparrow) \\ \frac{1}{2}\left(\chi_1(\uparrow)\chi_2(\downarrow) + \chi_1(\downarrow)\chi_2(\uparrow)\right) \\ \chi_1(\downarrow)\chi_2(\downarrow) \end{cases}$$

three wavefunction $\rightarrow$triplet state
total spin one, i.e. two electron spins are parallel
antisymmetry is in spatial wave function part

$$\phi_{12}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}V}\left(e^{i\vec{k}_1\vec{r}_1}e^{i\vec{k}_2\vec{r}_2} - e^{i\vec{k}_1\vec{r}_2}e^{i\vec{k}_2\vec{r}_1}\right)$$

Exchange hole homogeneous e-gas

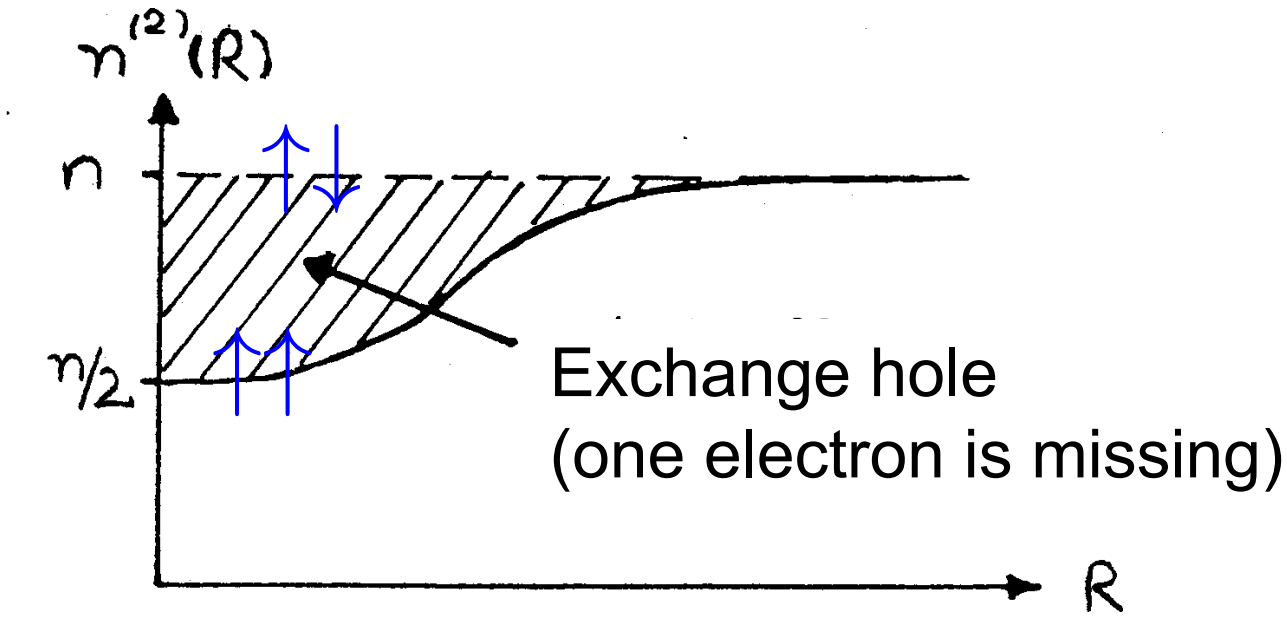
in the triplet state: pair correlation function

$$G_{\uparrow\uparrow}(\vec{r}_1,\vec{r}_2) = \left|\phi_{12}(\vec{r}_1,\vec{r}_2)\right|^2 = \frac{1}{V^2}\left(1-\cos\left(\vec{k}_1-\vec{k}_2\right)\left(\vec{r}_1-\vec{r}_2\right)\right)$$

summed over all states

$$G_{\uparrow\uparrow}(\vec{r}=\vec{r}_1-\vec{r}_2) = \sum_{|\vec{k}_1|<k_F}\sum_{|\vec{k}_2|<k_F}\frac{1}{V^2}\left(1-\cos\left(\vec{k}_1-\vec{k}_2\right)\vec{r}\right) = \frac{en}{2}\left(1-9\frac{(\sin k_F r - k_F r\cos k_F r)^2}{(k_F r)^6}\right)$$

Exchange hole homogeneous e-gas

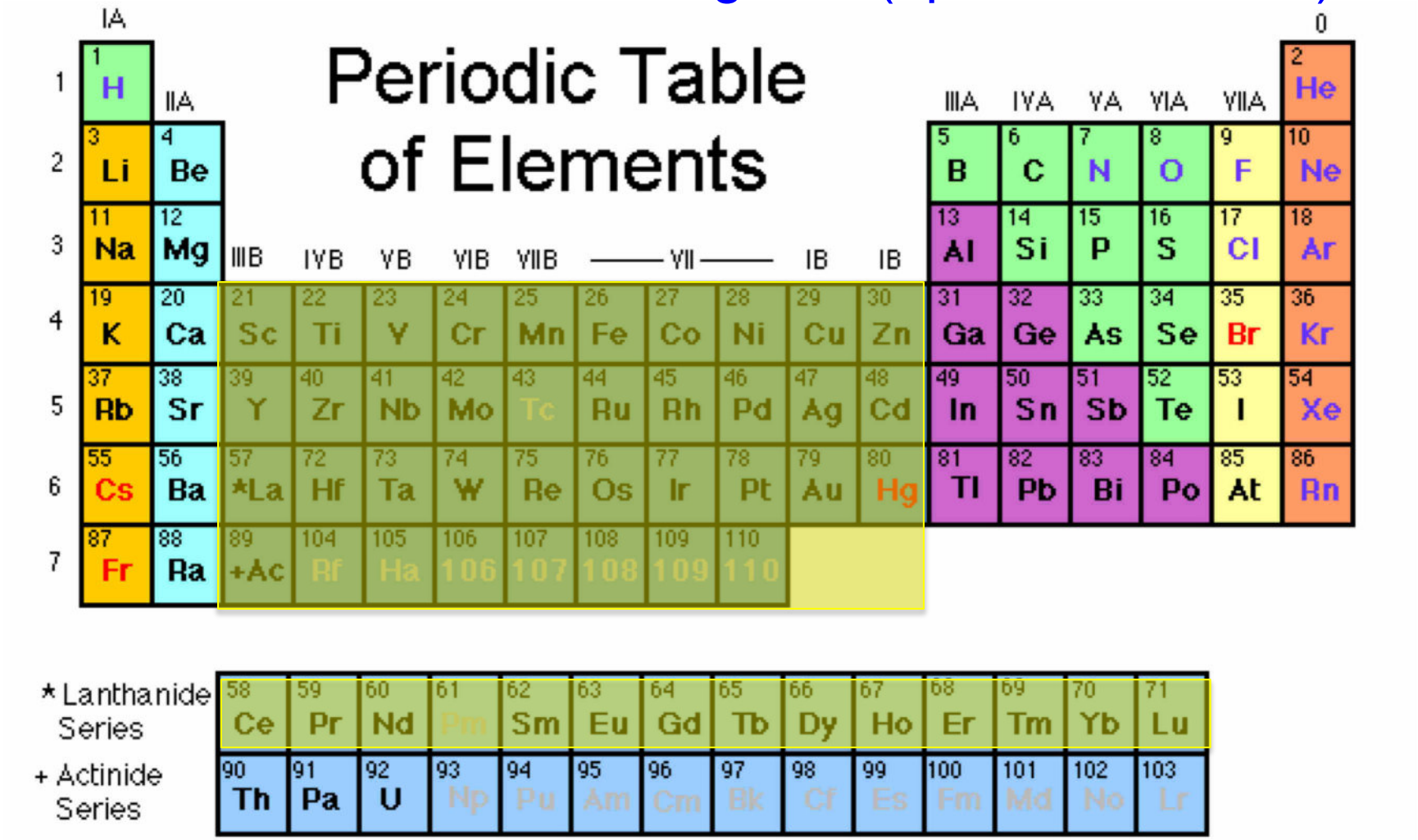


- Coulomb energy gain due to lack of electron in exchange hole

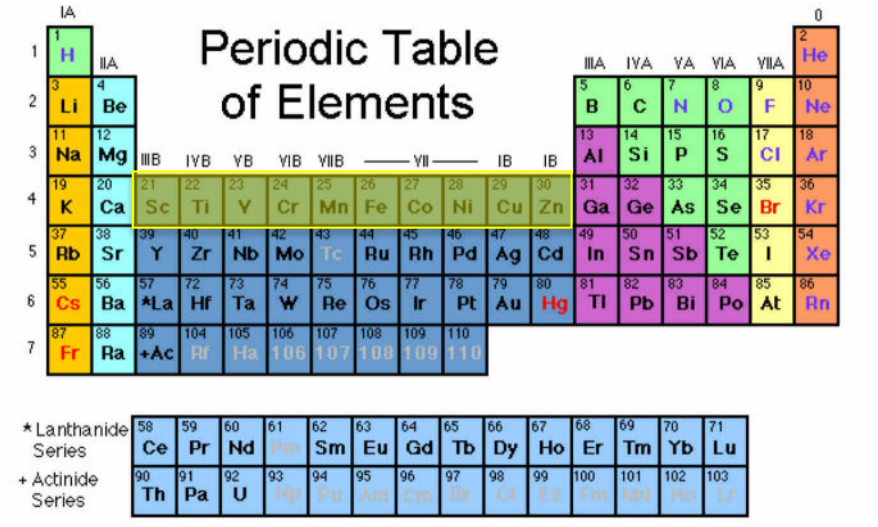
$$E_{\text{ex-hole}} = e^2 n \int d^3 r \, \frac{g(r) - 1}{r} = -\frac{6}{\pi} e^2 k_F \int_0^\infty dx \, \frac{j_1(x)^2}{x} = -\frac{3}{4} \frac{e^2}{\pi} k_F$$

Magnetism of Atoms
Transition-metals and rare earths

"almost all" atoms are magnetic (open shell atoms)



Hund's rule: Intra-atomic exchange



M=3μ$_B$

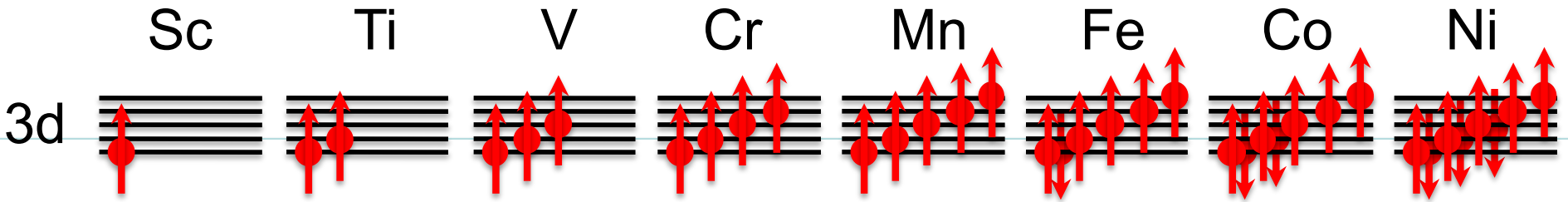
3d

4s

Possible quantum states

$$P = \binom{2(2l+1)}{N_d}$$

Hund's 1st rule: maximizes the sum of the values S for all of the electrons in the open subshell



Magnetism of Atoms

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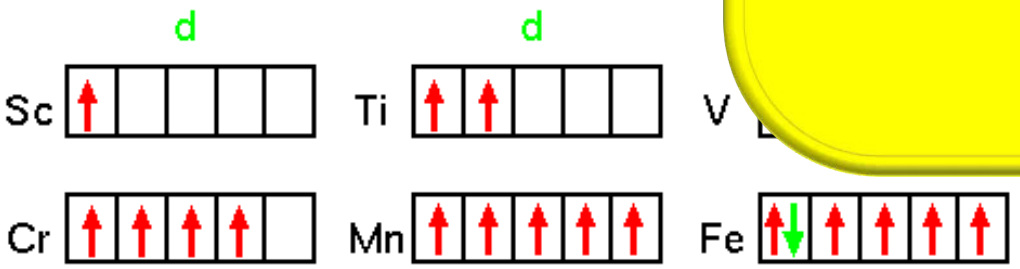
"almost all" atoms are m

1.Hund's Rule

(Exchange Interaction)

Example: 3d Transition Me

Sc	Ti	V	Cr	Mn	Fe
$4s^2$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$



Exchange Interaction

$$\Psi(\mathbf{r}_1\sigma_1,\cdots\mathbf{r}_i\sigma_i,\cdots,\mathbf{r}_j\sigma_j,\cdots\mathbf{r}_5\sigma_5) =$$
$$= -\Psi(\mathbf{r}_1\sigma_1,\cdots\mathbf{r}_j\sigma_j,\cdots,\mathbf{r}_i\sigma_i,\cdots\mathbf{r}_5\sigma_5)$$
$$= \underbrace{\Psi^{\mathrm{Mn}}(\mathbf{r}_1,\cdots,\mathbf{r}_5)}_{\text{antisymmetric}} \cdot \underbrace{\chi_{\uparrow\uparrow\uparrow\uparrow\uparrow}}_{\text{symmetric}}$$

$$\lim_{\mathbf{r}_i\to\mathbf{r}_j} \Psi^{\mathrm{Mn}}(\mathbf{r}_1,\cdots,\mathbf{r}_5) \longrightarrow 0$$

$$U(\mathbf{r}_i,\mathbf{r}_j) = \frac{1}{2}\int d\mathbf{r}_1\cdots\mathbf{r}_5 \frac{|\Psi^{\mathrm{Mn}}(\mathbf{r}_1,\cdots,\mathbf{r}_5)|^2}{|\mathbf{r}_i-\mathbf{r}_j|}$$

$$= \text{small}$$

Hartree and Hartree-Fock:

pedestrian crowd

single particle
in a mean field

dancers (Opernball)

single particle in a mean field
plus a male-depletion clowd

Hartree-Fock: summary

Advantages:

- physically transparent
- proper antisymmetric behavior of wave functions

Disadvantages:

- more demanding for “open shell systems”
- works poor for metals
- overestimated band gap for insulators

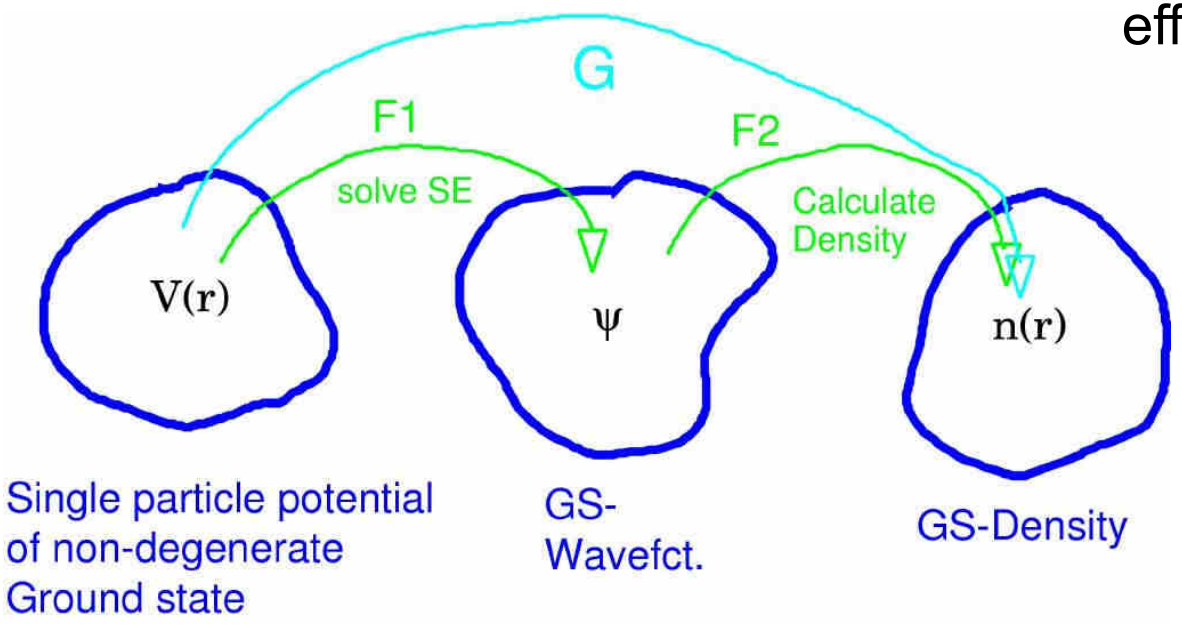
missing: electron correlation

→ more complicated wavefunction or...

Important message : Although Hamiltonian is without explicit spin-dependence, effective interaction is spin-dependent. Its all in the wavefunctions !! Antiskymmetry + Coulomb

Density Functional Theory (DFT)

Maps interacting many body problem onto noninteracting electrons in an effective Potential



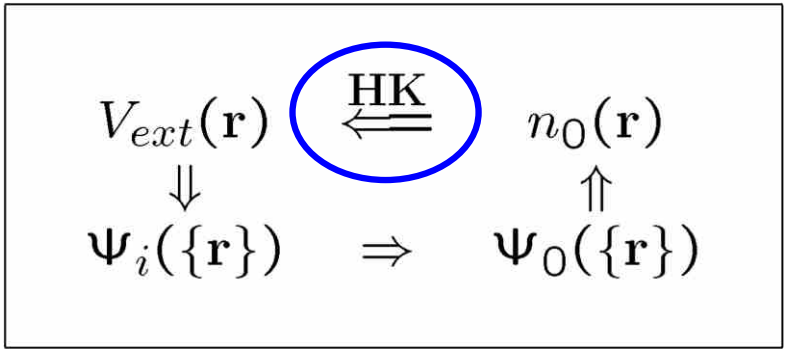
$$\left.\begin{array}{rcl} F_1 & : & V(\mathbf{r}) \longmapsto \psi \\ F_2 & : & \psi \longmapsto n(\mathbf{r}) \end{array}\right\}$$ per construction surjective

$$F_1 \circ F_2 := G \quad : \quad V(\mathbf{r}) \longmapsto n(\mathbf{r})$$

Hohenberg-Kohn-Theorem (1964): G is invertable

Density Functional Theory (DFT)

- Hohenberg-Kohn (1964)

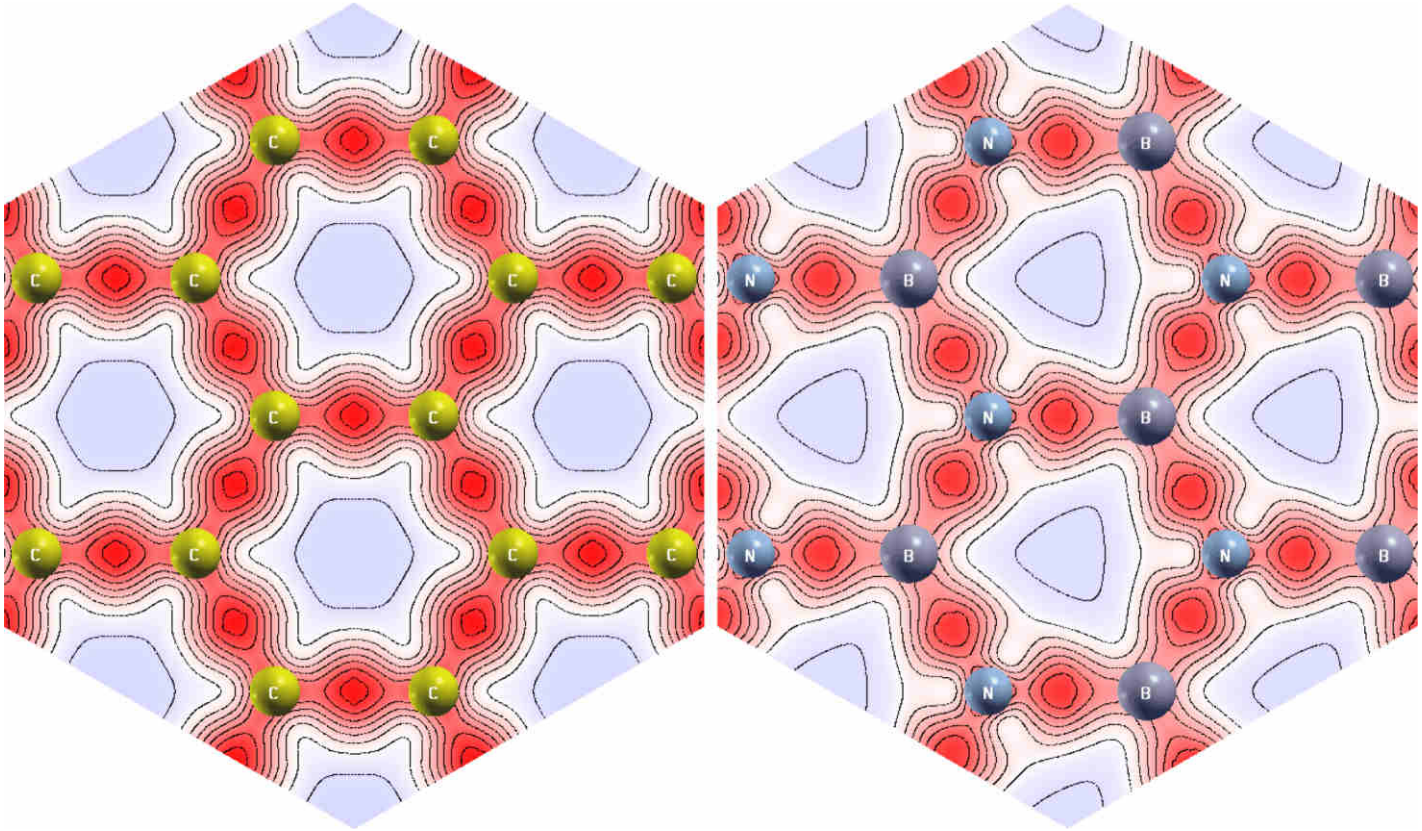


- All properties of the many-body system are determined by the ground state density $n_0(r)$

- Each property is a functional of the ground state density $n_0(r)$ which is written as $f[n_0]$

- A functional $f[n_0]$ maps a function to a result: $n_0(r) \longrightarrow f$

The density as basic variable



- access to local charges, ionicity, magnetization density etc.
- via Poisson-equation: potential, work-function, dielectric constant

The Kohn-Sham Ansatz (1)

- Kohn-Sham (1965) – Replace original many-body problem with an independent electron problem – that can be solved!
- The ground state density is required to be the same as the exact density $n_0(\mathbf{r}) = \sum_\sigma \sum_{i=1} |\psi_i^\sigma(\mathbf{r})|^2,$

$$
\begin{array}{ccccccc}
V_{ext}(\mathbf{r}) & \overset{HK}{\Longleftarrow} & n_0(\mathbf{r}) & \overset{KS}{\Longleftrightarrow} & n_0(\mathbf{r}) & \overset{HK_0}{\Longrightarrow} & V_{KS}(\mathbf{r}) \\
\Downarrow & & \Uparrow & & \Uparrow & & \Downarrow \\
\Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) & & \psi_{i=1,N_e}(\mathbf{r}) & \Leftarrow & \psi_i(\mathbf{r})
\end{array}
$$

- Only the ground state density and energy are required to be the same as in the original many-body system

The Kohn-Sham (KS) Ansatz (2)

- From Hohenberg-Kohn the ground state energy is a functional of the density $E_0[n]$, minimum at $n = n_0$
- From Kohn-Sham
  - ➢Electron Density: $$n(\mathbf{r}) = \sum_{i(occ)}^{M} |\psi_i(\mathbf{r})|^2$$
  - ➢Kohn Sham Total Energy:

$$E_{\rm KS}[n|\{\mathbf{R}\}] = E_{\rm kin}[n] + E_{\rm H}[n] + E_{\rm ext}[n|\{\mathbf{R}\},] + E_{\rm ion}[\{\mathbf{R}\}] + E_{\rm xc}[n]$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- **The new paradigm – find useful, approximate functionals**

The Kohn-Sham Standard Model

"**The** Computational Approach"

For: Physics, Chemistry, Nanoscience, Materials Science, Bio-Physics, Minerology, Geology,…

Total Energy: $E = E[n, \{R_I\}, a, \ldots]$

Energy is functional of electron density n and external parameters such as lattice constants, atoms positions, magnetization direction…

Secular Equation: $\hat{H}[n]\,\psi_i[n] = \varepsilon_i[n]\,\psi_i[n]$

Selfconsistency loop

Density:

$$n(\mathbf{r}) = \sum_{i(occ)}^{M} |\,\psi_i(\mathbf{r})\,|^2$$

CPU-Time scaling: ≈ N^3_{atom} ≈ Volume^3, ≈ Precision^3

Comparison: DFT to Hartree (Fock)

- Variation of E_{KS} with respect to density n and wave function ϕ
  Leads to Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\rm ext}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + \frac{\delta E_{\rm xc}}{\delta n(\vec{r})}\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

- With the Kohn-Sham Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + V_{\rm ext}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + V_{\rm xc}(\vec{r})$$

- To be compared to the many-body problem

$$\mathcal{H} = -\sum_i \left(\frac{1}{2}\nabla_i^2 + V_{\rm ext}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|} = \sum_i h_i + \sum_{i,j} g_{ij}$$

Hartree Approx: $[h_i + \sum_j \langle\phi_j|g_{ij}|\phi_j\rangle - \langle\phi_i|g_{ij}|\phi_i\rangle]\phi_i = \varepsilon_i\phi_i$

Hartree-Fock: $[h_i + \sum_j \langle\phi_j|g_{ij}|\phi_j\rangle]\phi_i - \underbrace{\sum_j \langle\phi_j|g_{ij}|\phi_i\rangle\,\phi_j}_{\text{corresponds to } V_X(\vec{r}) \text{ in DFT}} = \varepsilon_i\phi_i$

Exchange-correlation energy functionals

- Local-density approximation (LDA, Kohn and Sham, 1965)

$$E_{xc}[\rho] = \int \epsilon_{xc}(\rho(\mathbf{r}))\,\rho(\mathbf{r})\,d\mathbf{r}$$

- Generalized-gradient approximation (GGA, Becke, Perdew, and Wang, 1986)

$$E_{xc} = \int \rho(\mathbf{r})\,\epsilon_{GGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)\,d\mathbf{r}$$

- DFT+ U (Anisimov and others, early 90 ‘s)

$$E_{DFT+U}[\rho] = E_{DFT} + Un(n-1)$$

- Meta-GGA (Perdew and others 2003)

$$E_{mGGA} = \int \rho(\mathbf{r}) \times \epsilon_{mGGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \tau_s(\mathbf{r}))\,d\mathbf{r}$$

$$\tau_s(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla^2\psi_i(\mathbf{r})|^2$$

- Hybrid functionals (B3Lyp, PBE0, Becke 1993)

$$E_{hybr} = \alpha E^x_{HF} + (1-\alpha)E^x_{GGA} + E^c$$

- ...

exchange-correlation energy functionals
(its all about precision and computational efficiency)

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- Local-density approximation
  (LDA, Kohn and Sham, 1965)

$$E_{xc}[\rho] = \int \epsilon_{xc}(\rho(\mathbf{r}))\,\rho(\mathbf{r})\,d\mathbf{r}$$

- Generalized-gradient approximation
  (GGA, Becke, Perdew, and Wang,1986)

Materials Science

$$E_{xc} = \int \rho(\mathbf{r})\,\epsilon_{GGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)\,d\mathbf{r}$$

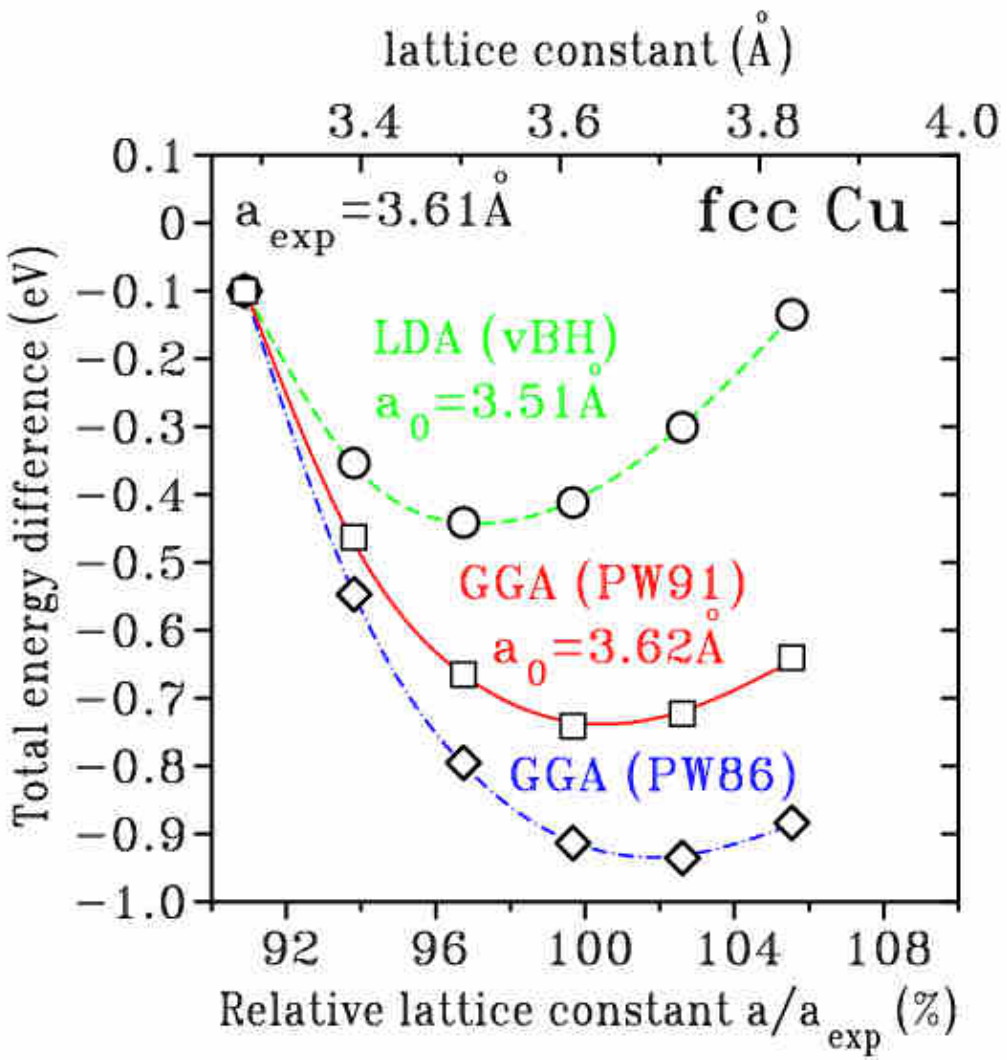
- Hybrid functionals (B3Lyp, PBE0, Becke 1993)

Chemie

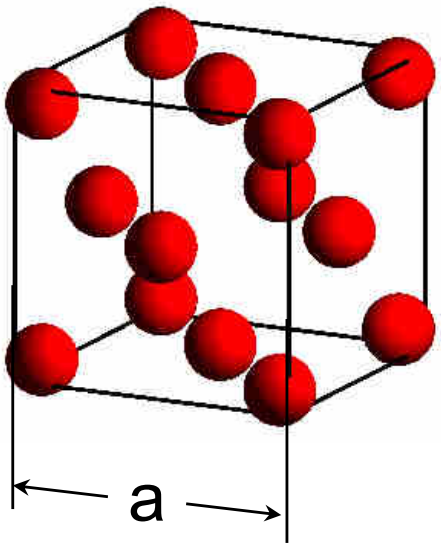
$$E_{hybr} = \alpha E_{NL}^{x} + (1-\alpha)\,E_{GGA}^{x} + E^{c}$$

$$E_{\mathrm{x}}^{\mathrm{NL}} = -\frac{1}{2}\sum_{\sigma}\sum_{n,n'}^{\mathrm{occ.}}\sum_{\mathbf{k},\mathbf{q}}^{\mathrm{BZ}}\iint \varphi_{n\mathbf{k}}^{\sigma *}(\mathbf{r})\varphi_{n'\mathbf{q}}^{\sigma}(\mathbf{r})v(\mathbf{r},\mathbf{r}')\varphi_{n'\mathbf{q}}^{\sigma *}(\mathbf{r}')\varphi_{n\mathbf{k}}^{\sigma}(\mathbf{r}')d^3r d^3r'$$

Example: Lattice Constant of Cu



$$E[\mathrm{a}, S = fcc, n_0^a]$$



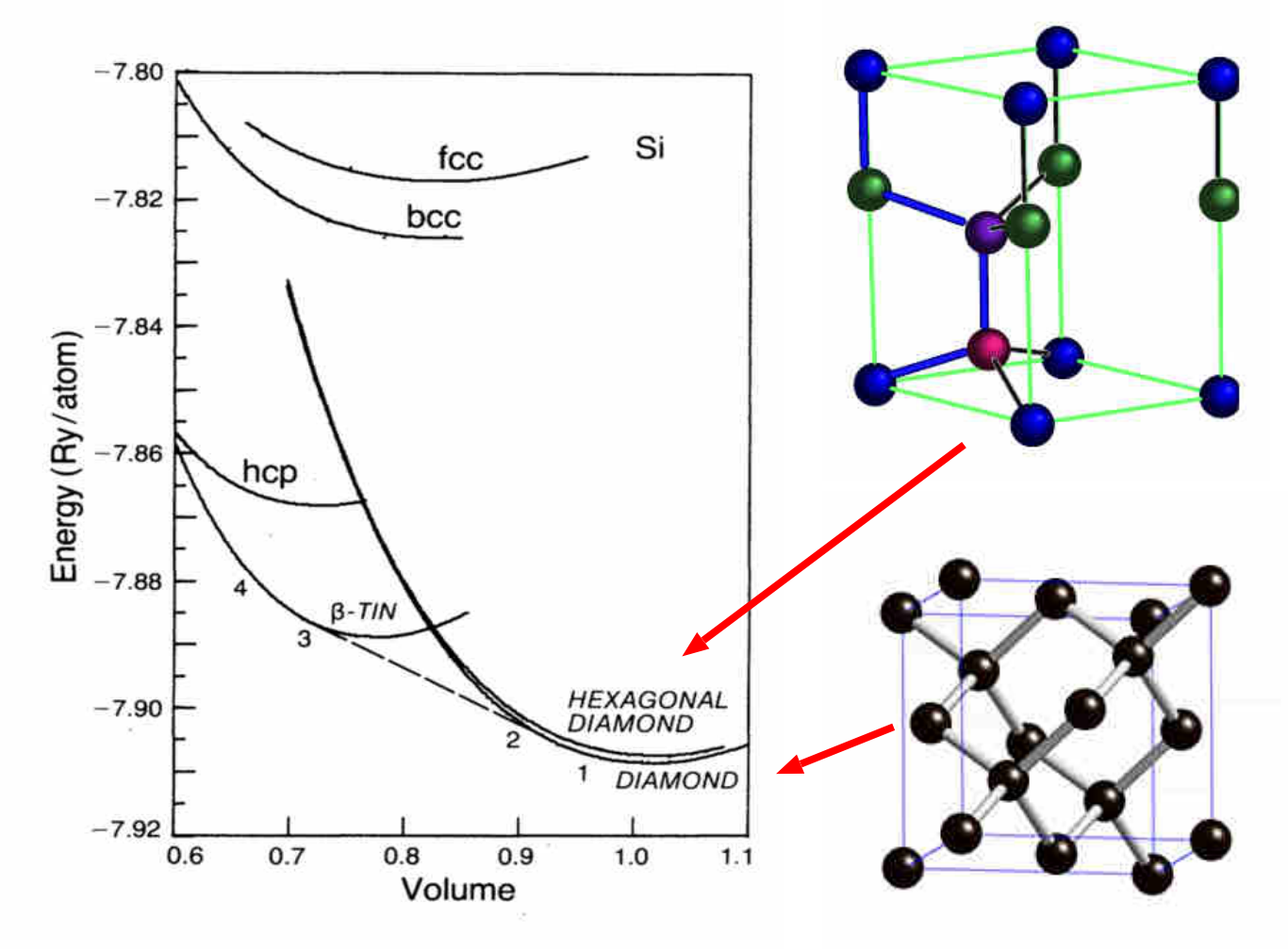
Example (2): Solids

Accuracy: lattice constants in solids.

	C	Al	Si	MgO	Pt	Ir	W
LDA	3.536	3.983	5.407	4.169	3.909	3.828	3.143
PBE	3.575	4.041	5.475	4.261	3.985	3.887	3.191
Exp.	3.544	4.019	5.415	4.186	3.913	3.831	3.160

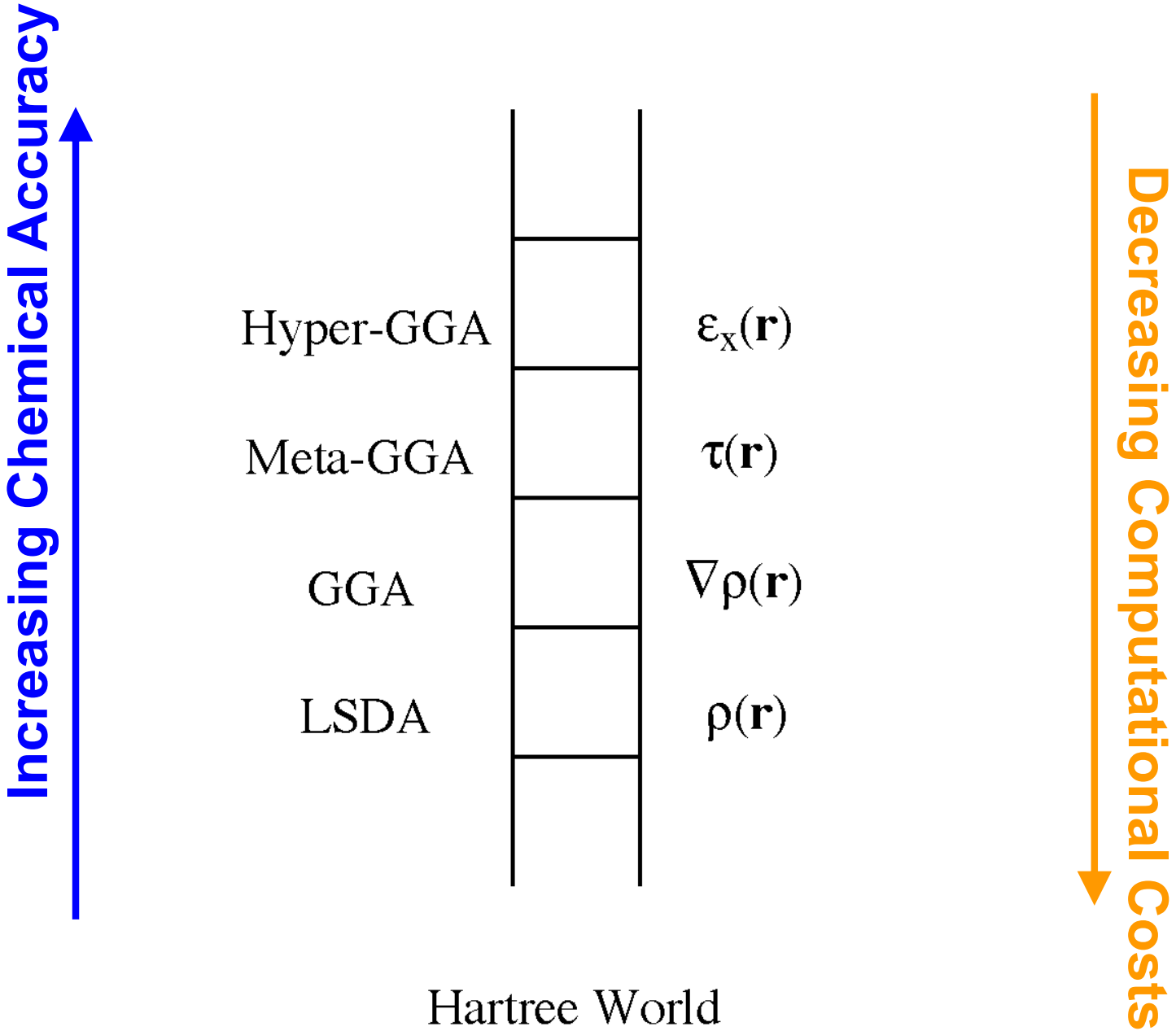
P. Haas *et al. Phys. Rev. B.* **79**, 085104 (2009)

What the total energy tells us

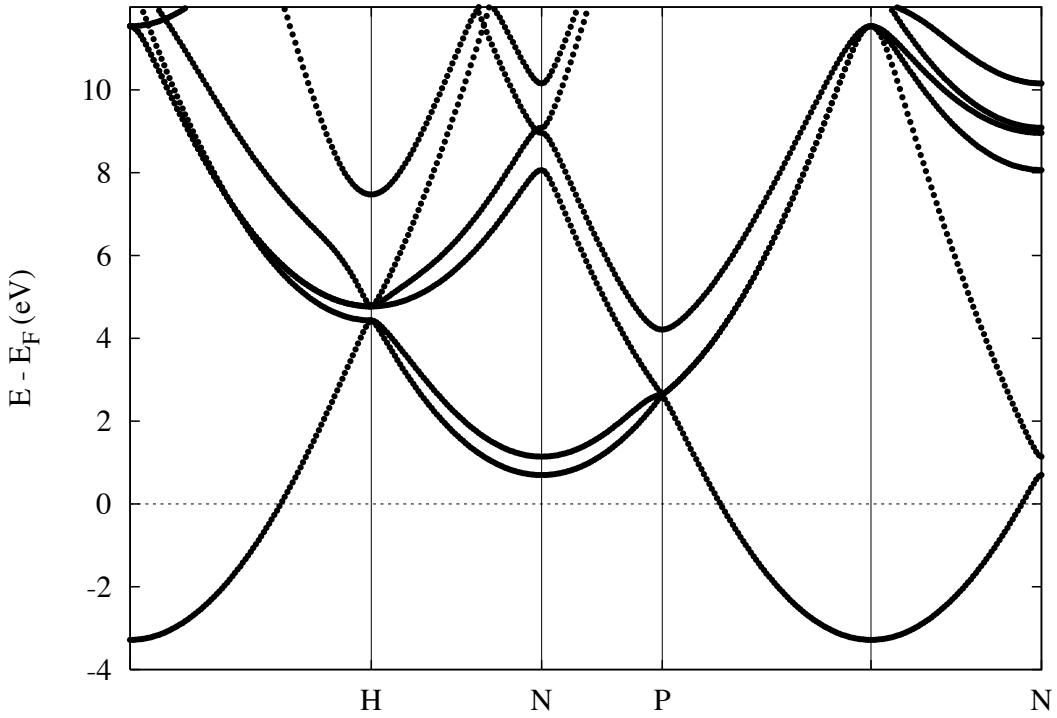


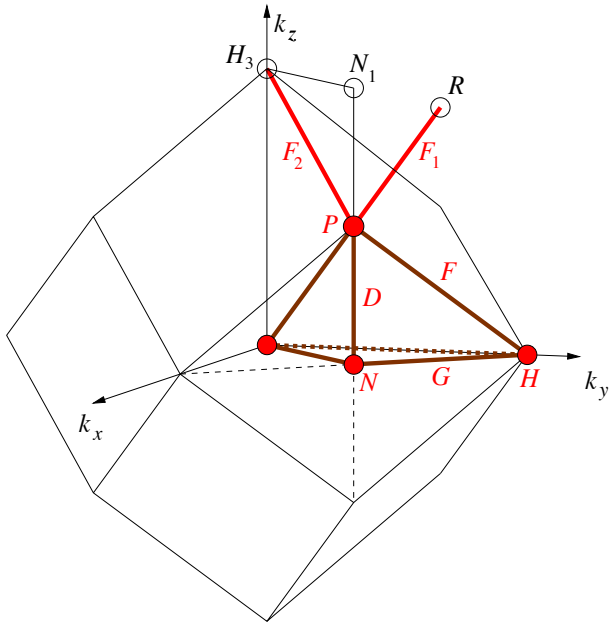
- ground state structure, equilibrium volume, bulk modulus
- derived: phonon spectra, expansion coefficients, etc.

Accuracy vs. Computational Cost



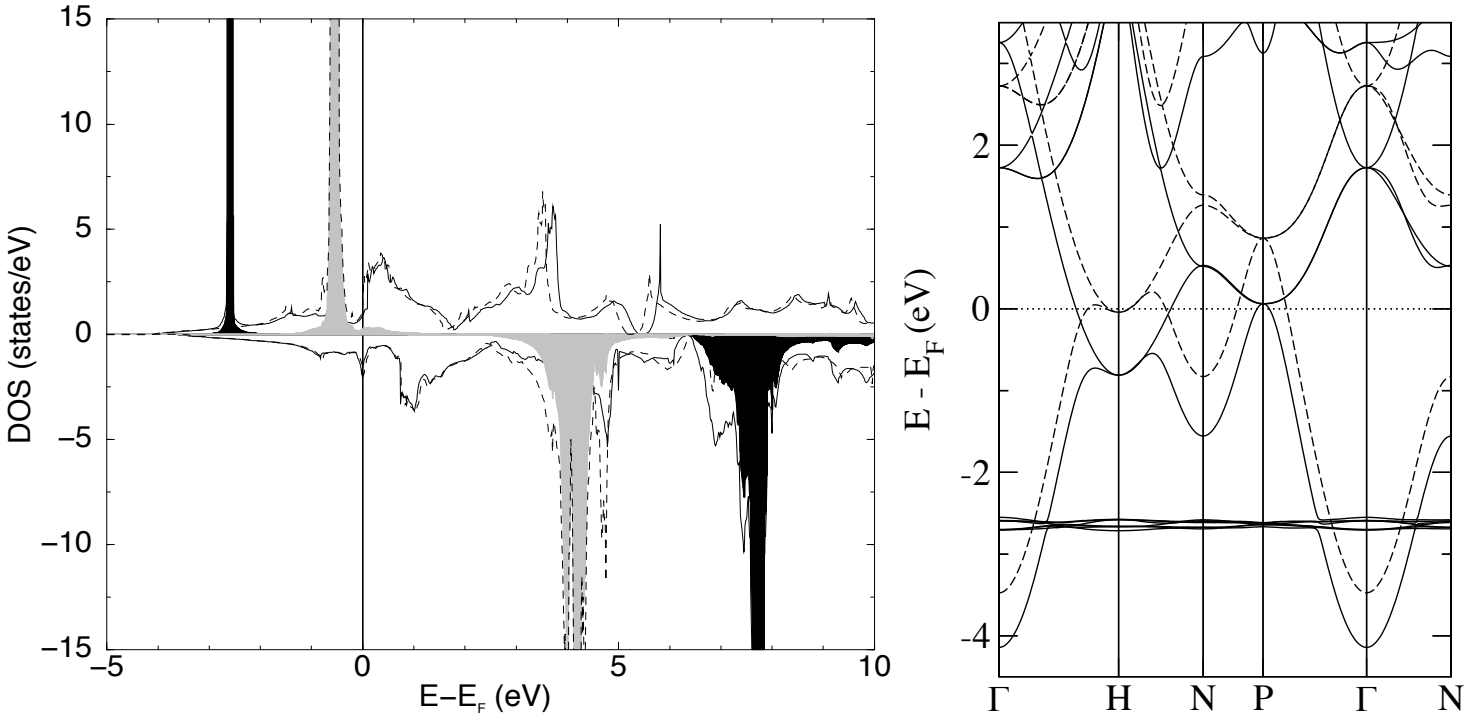
Metals: bcc Na





- s-band: almost a free electron gas
- stronger deviations observed for p-states
- band bottom about 1eV lower than in experiment
- Fermi surface well reproduced!

Europium bandstructure



- s-bands + strongly localized f-electrons
- grey: wrong energetic position from LDA
- black: f-state energies corrected by LDA+U
- beyond DFT: GW approximation, DMFT, etc.

DFT summary

- complexity low (similar to SCF-Hartree)
- ”Good” quantities (energy, density, magnetization) allow determination of e.g.
  - ground state structure, vibrational properties
  - magnetic properties, and interactions
  - energy differences: adsorption energies etc.

  and (with some care) also other quantities like
  - band structures (near the Fermi level)
  - densities of states, e.g. for STM images
  - transport properties

- Limitations are caused by:
  - exchange correlation potentials (strong correlations)
  - some properties are not directly available (e.g. band gaps)
  - wave-functions describe just “auxiliary particles”

DFT summary

- complexity low (similar to SCF-Hartree)
- "Good" quantities (energy, density, magnetization) allow determination of e.g.
  - ground state structure, vibrational properties
  - magnetic properties, and interactions
  - energy differences: adsorption energies etc.

  and (with some care) also other quantities like
  - band structures (near the Fermi level)
  - densities of states, e.g. for STM images
  - transport properties

- Important extensions for magnetic materials
  - Vector-spin-density functional theory

See lecture MM-3

DFT summary

- complexity low (similar to SCF-Hartree)
- ”Good” quantities (energy, density, magnetization) allow determination of e.g.
  - ground state structure, vibrational properties
  - magnetic properties, and interactions
  - energy differences: adsorption energies etc.

  and (with some care) also other quantities like
  - band structures (near the Fermi level)
  - densities of states, e.g. for STM images
  - transport properties

- Important extensions (for bandgaps, excitations, spinwaves, excitons etc.)
  - Time dependent density functional theory
  - Many-Body Perturbation theory (Hedin’s GW-Approximation)

Outline

- Independent electrons
  - lattice periodicity: real and reciprocal lattice
  - Bloch functions and band structure
  - symmetry in periodic crystals
- Interacting electrons
  - Hartree- and Hartree-Fock approximation
  - density functional theory
- Relativistic effects
  - spin-orbit coupling
  - Rashba & Dresselhaus effect
  - topological insulators
  - magnetism and spin-orbit coupling

Relativisitic effects
Spin-Orbit Coupling

- spin-orbit coupling has fascinating realizations and ramifications in solids

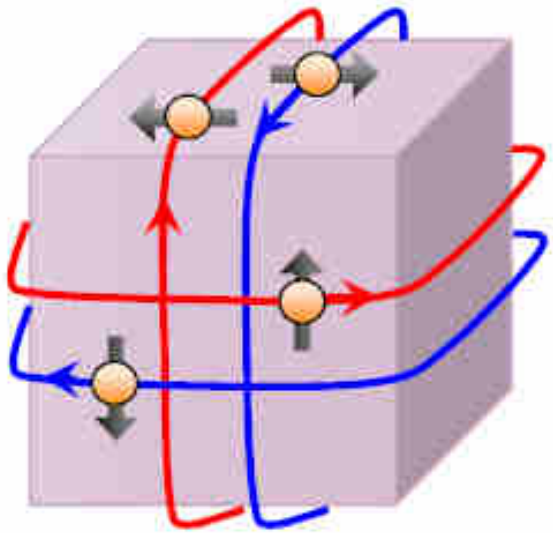
Examples:
- Orbital moments
- Rashba Effect & Dresselhaus Effect
- Topological Insulator and Weyl semimetals
- Anomalous Hall Effect, Spin Hall Effect
- Quantum Spin & Quantum Anomalous Hall Effect
- Spin-Relaxation (Elliot-Yafet, Dyakonov-Perel)
- Spin-orbit torque
- Magnetic Anisotropy
- Dzyaloshinskii-Moriya Interaction
- Magneto-optics

Examples of relativistic effects in solids

magnetite compass (200BC-200AD)

different color of gold and silver

www. bullionweb.de



3D topological insulator

Spin-Orbit Coupling: Space Inversion Symmetry

Elemental solids (Cu, Si, Al….)

For a given band ν the following two states have the same energy $\epsilon_{\mathbf{k}\nu}$

$$\Psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) = [a_{\mathbf{k}\nu}(\mathbf{r})|\uparrow\rangle + b_{\mathbf{k}\nu}(\mathbf{r})|\downarrow\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Psi_{\mathbf{k}\nu\downarrow}(\mathbf{r}) = [a^*_{-\mathbf{k}\nu}(\mathbf{r})|\downarrow\rangle - b^*_{-\mathbf{k}\nu}(\mathbf{r})|\uparrow\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}$$

Proof: $\Psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) = [a_{\mathbf{k}\nu}(\mathbf{r})|\uparrow\rangle + b_{\mathbf{k}\nu}(\mathbf{r})|\downarrow\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}$

time reversal ↓ $-i\sigma_y\hat{C}$ $\quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

$$[a^*_{\mathbf{k}\nu}(\mathbf{r})|\downarrow\rangle - b^*_{\mathbf{k}\nu}(\mathbf{r})|\uparrow\rangle]e^{-i\mathbf{k}\cdot\mathbf{r}}$$

space inversion ↓ $\mathbf{k} \rightarrow -\mathbf{k}$

$$[a^*_{-\mathbf{k}\nu}(\mathbf{r})|\downarrow\rangle - b^*_{-\mathbf{k}\nu}(\mathbf{r})|\uparrow\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}$$

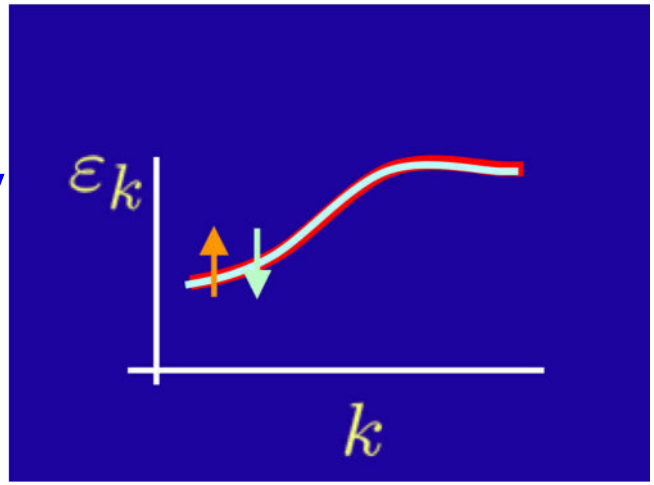
q.e.d.

What happens when space inversion symmetry broken

(GaAs, InSb, interfaces, surfaces, ...)

Time reversal + space inversion symmetry

$$\epsilon_{\mathbf{k}\uparrow} = \epsilon_{\mathbf{k}\downarrow}$$



I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. 76, 323 (2004).

Schrödinger and Dirac

classical Hamiltonian

$$E^2 = m^2c^4 + p^2c^2$$

$$E \to i\hbar\frac{\partial}{\partial t} \qquad \vec{p} \to -i\hbar\vec{\nabla}$$

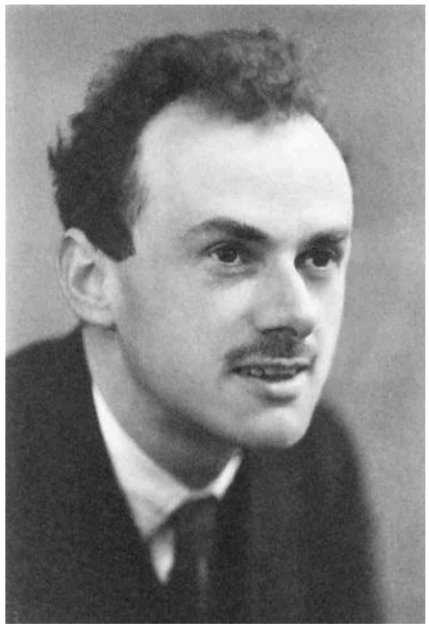


image: Wikipedia

Dirac Equation: $H_{\mathrm{D}} = \boldsymbol{\alpha}\cdot c\mathbf{p} + \beta mc^2 - eV(\mathbf{r})$

4 × 4 Matrices: $\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$

Eq for large & small com'nt:

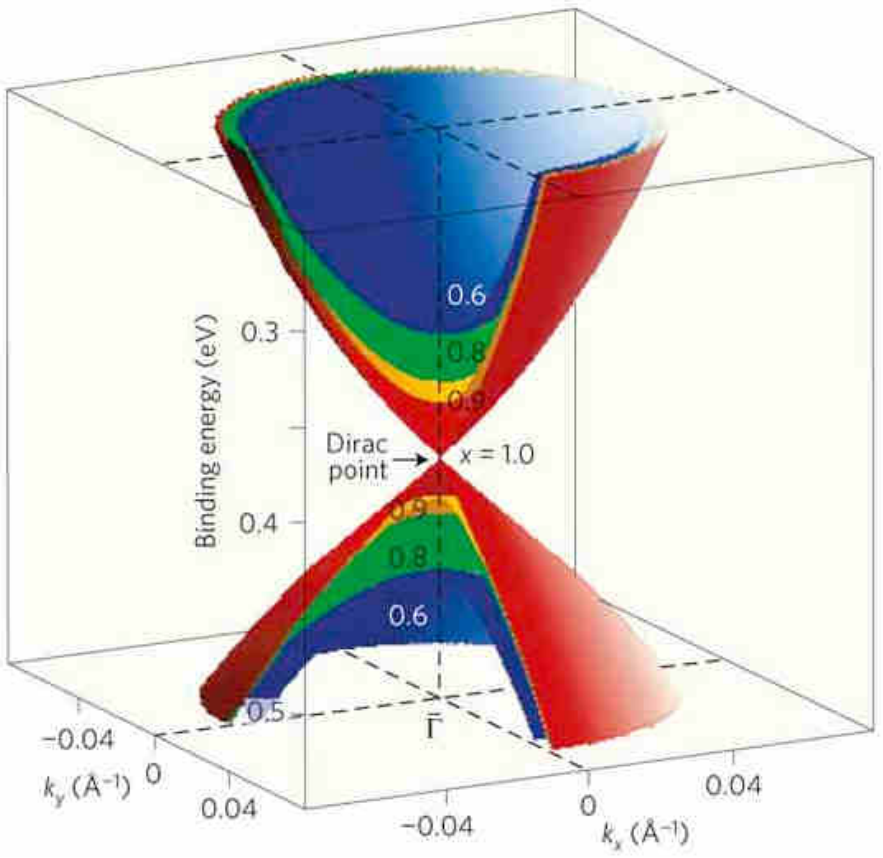
$$(E - 2mc^2 + eV(\mathbf{r}))\psi = \boldsymbol{\sigma}\cdot(c\mathbf{p} + e\mathbf{A}(\mathbf{r}))\chi$$
$$(E + 2mc^2 + eV(\mathbf{r}))\chi = \boldsymbol{\sigma}\cdot(c\mathbf{p} + e\mathbf{A}(\mathbf{r}))\psi$$

2D- Dirac equation

2D solution with Pauli spin matrices: $\alpha_1 = \sigma_x \quad \alpha_2 = \sigma_y \quad \beta = \sigma_z$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{H} = c\vec{\sigma} \cdot \vec{p} + mc^2\sigma_z$$



Sato et al. Nature Phys. 7, 840 (2011)

3D- Dirac equation

Dirac equation with scalar (V) and vector potential (A):

$$\hat{H}\Psi = i\hbar\frac{\partial}{\partial t}\Psi = E'\Psi; \quad \hat{H} = -eV(\vec{r}) + \beta mc^2 + \vec{\alpha}\cdot\left(c\vec{p} + e\vec{A}(\vec{r})\right)$$

bi-spinor wavefunction: $\Psi = \begin{pmatrix}\psi\\ \chi\end{pmatrix}$

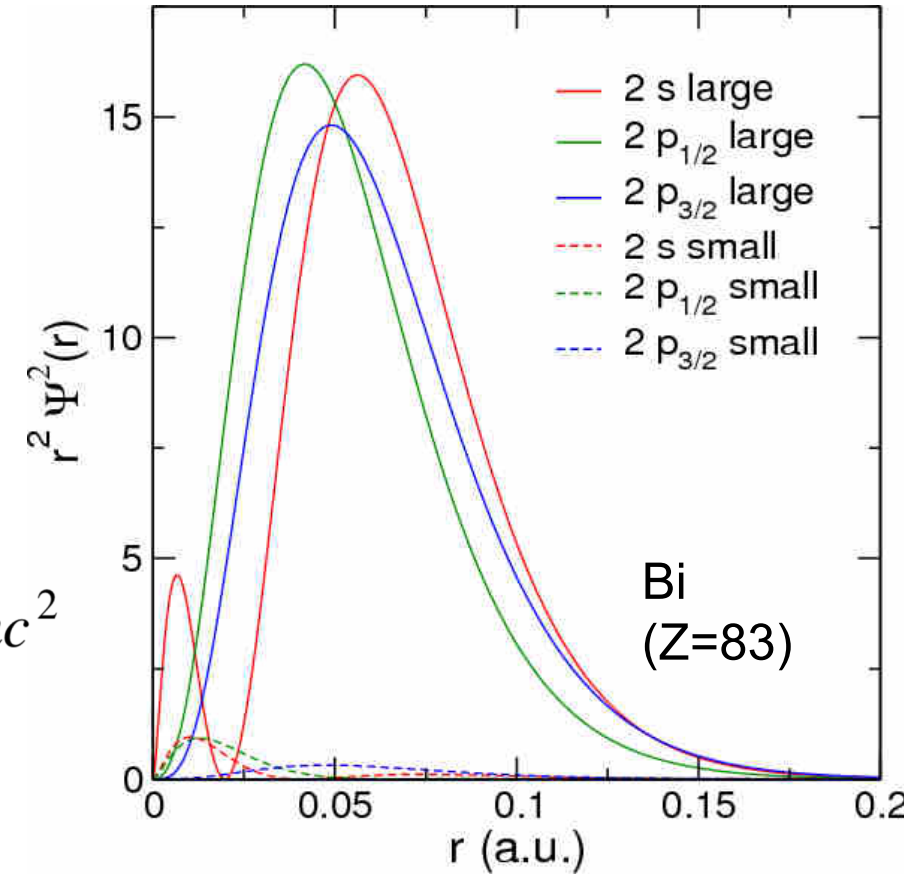
$$\left(E' - mc^2 + eV(\vec{r})\right)\psi = \vec{\sigma}\cdot\left(c\vec{p} + e\vec{A}(\vec{r})\right)\chi$$

$$\left(E' + mc^2 + eV(\vec{r})\right)\chi = \vec{\sigma}\cdot\left(c\vec{p} + e\vec{A}(\vec{r})\right)\psi$$

non-relativistic limit:

$$E' + mc^2 \approx 2mc^2 >> eV(\vec{r}) \qquad E = E' - mc^2$$

$$\left(E + eV(\vec{r}) - \frac{1}{2m}\cdot\left(\vec{p} + \frac{e}{c}\vec{A}(\vec{r})\right)^2\right)\psi = 0$$



Pauli equation

no spin-dependent term appears in the Schrödinger equation:

$$\left(E + eV(\vec{r}) - \frac{1}{2m}\cdot\left(\vec{p} + \frac{e}{c}\vec{A}(\vec{r})\right)^2\right)\psi = 0 \qquad \text{but:} \qquad \psi = \begin{pmatrix}\psi^{\uparrow}\\ \psi^{\downarrow}\end{pmatrix}$$

approximation to Dirac equation keeping terms up to $1/c^2$:

$$\left(E + eV(\vec{r}) - \frac{1}{2m}\cdot\left(\vec{p} + \frac{e}{c}\vec{A}(\vec{r})\right)^2 + \frac{1}{2mc^2}\left(E + eV(\vec{r})\right)^2 + \right.$$

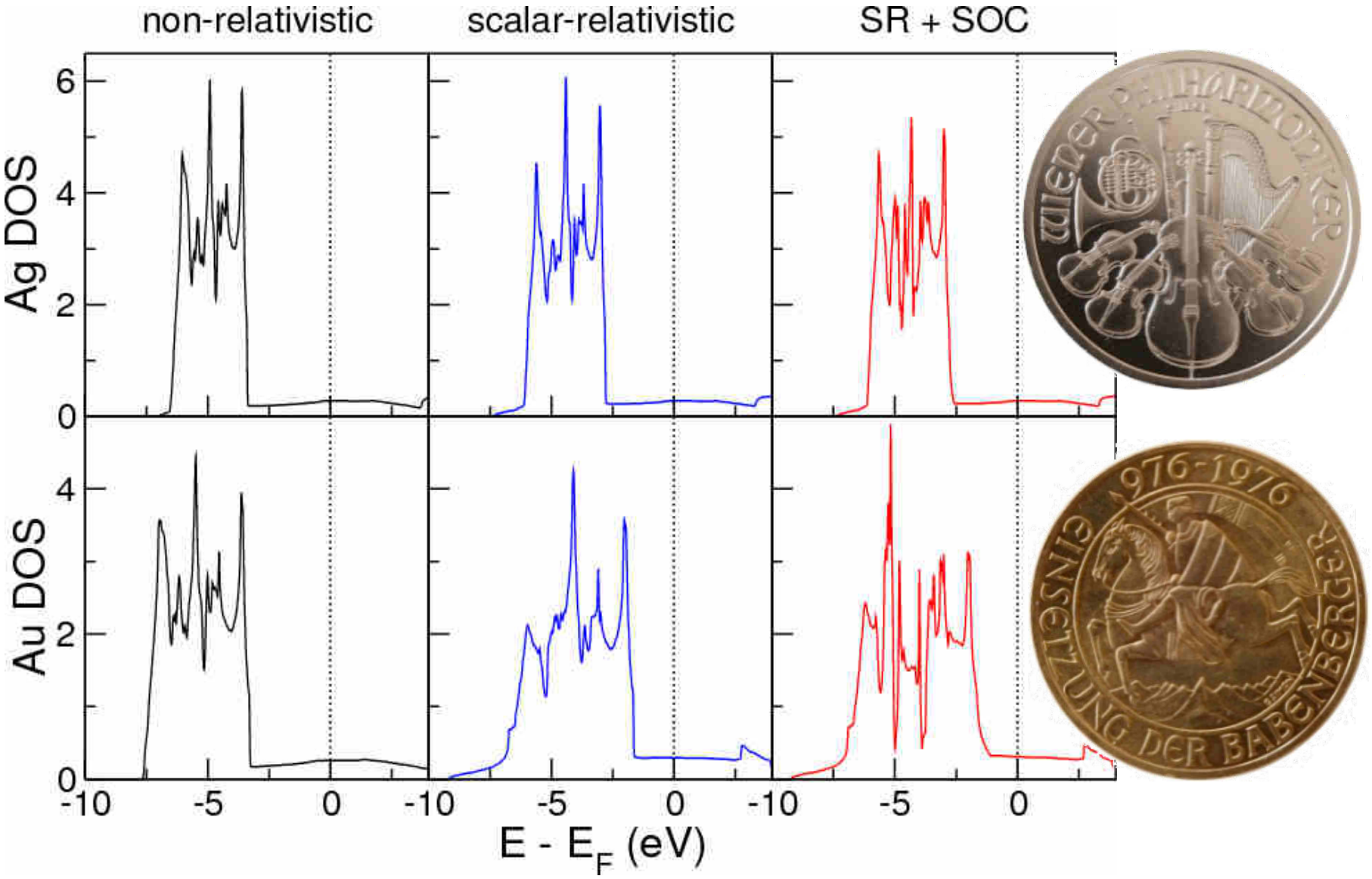
mass-velocity term

$$\left. i\frac{e\hbar}{(2mc)^2}\vec{E}(\vec{r})\cdot\vec{p} - \frac{e\hbar}{(2mc)^2}\vec{\sigma}\cdot\left(\vec{E}(\vec{r})\times\vec{p}\right) - \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{B}(\vec{r})\right)\psi = 0$$

direct implementation in DFT Hamiltonian possible,
SOC & magnetic field term couple the two spin channels

Relativistic effects in Ag and Au

density of states (DOS):



Spin-orbit coupling

interaction with an (internal) magnetic field:

$$\frac{e\hbar}{(2mc)^2}\vec{\sigma}\cdot\left(\vec{E}(\vec{r})\times\vec{p}\right)=\frac{\mu_B}{2mc}\vec{\sigma}\cdot\left(\vec{E}(\vec{r})\times\vec{p}\right)=\frac{\mu_B}{2}\vec{\sigma}\cdot\underbrace{\left(\frac{1}{c}\vec{E}(\vec{r})\times\vec{v}\right)}_{\vec{B}_0(\vec{r})}$$

similar to: $\frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{B}(\vec{r})=\mu_B\vec{\sigma}\cdot\vec{B}(\vec{r})$ with Thomas factor

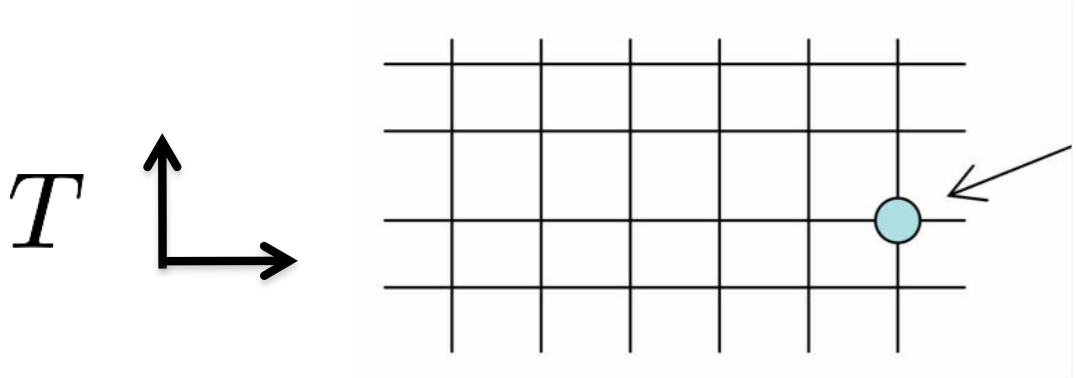
in a central (spherically symmetric) potential (atom):

$$\frac{\mu_B}{2mc}\vec{\sigma}\cdot\left(\vec{E}(\vec{r})\times\vec{p}\right)=\frac{\mu_B}{2mc}\vec{\sigma}\cdot\left(\vec{\nabla}V(\vec{r})\times\vec{p}\right)=\underbrace{\frac{\mu_B}{2mcr}\frac{dV(r)}{dr}}_{\xi}\vec{\sigma}\cdot\left(\vec{r}\times\vec{p}\right)=\xi\vec{\sigma}\cdot\vec{L}$$

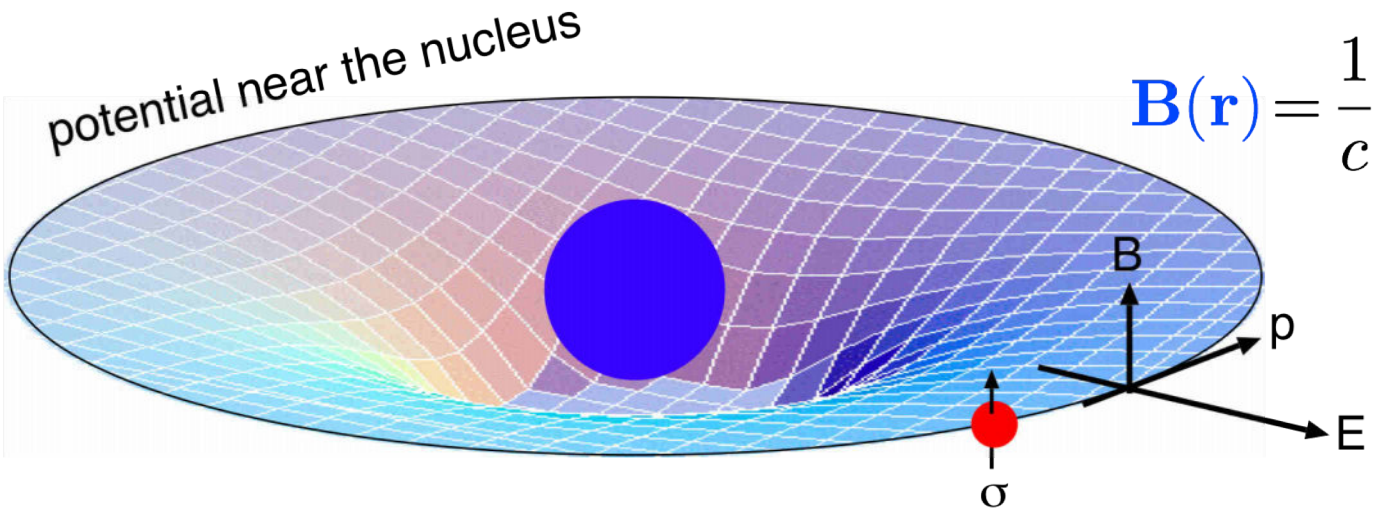
Periodic !! $\xi(\mathbf{r}+\mathbf{T})=\xi(\mathbf{r})$

note that the spin and the orbital momentum (L) couple antiparallel!

Spin-Orbit Coupling

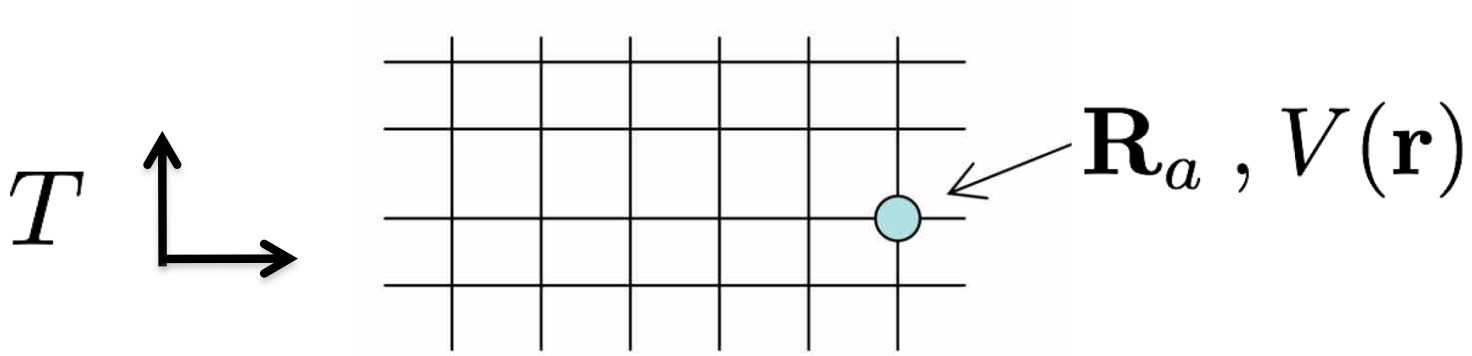


Spin-Orbit Hamiltonian: $H_{\mathrm{SO}} = \frac{\hbar}{(2mc)^2} \underbrace{\nabla V}_{\mathbf{E}(\mathbf{r})} \times \mathbf{p} \cdot \sigma$



$$\mathbf{B}(\mathbf{r}) = \frac{1}{c} \frac{1}{\sqrt{1 - v^2/c^2}} \mathbf{v} \times \mathbf{E}(\mathbf{r})$$

Spin-Orbit Coupling



Spin-Orbit Hamiltonian: $H_{\mathrm{SO}} = \frac{\hbar}{(2mc)^2} \nabla V \times \mathbf{p} \cdot \sigma$

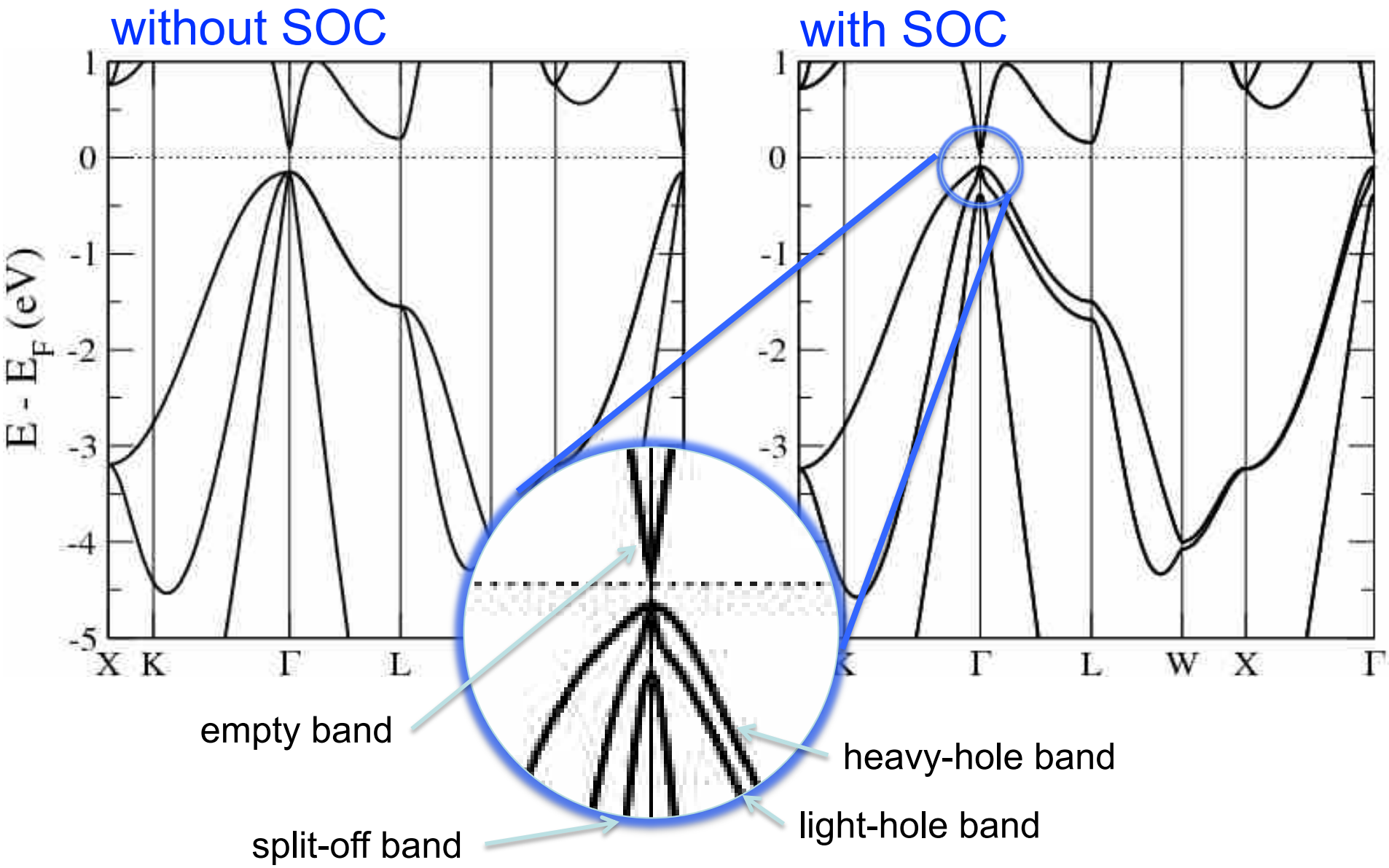
Spherically symmetric potentials: $= \frac{1}{r}\frac{dV(r)}{dr}(\boldsymbol{\sigma} \cdot \mathbf{L}) = \xi \boldsymbol{\sigma} \cdot \mathbf{L}$

Estimate of Spin-Orbit Strength:

$$\xi_{n\ell} \propto \langle n\ell \,|\, \tfrac{1}{r}\tfrac{Z}{r^2} \,|\, n\ell \rangle \propto Z \cdot (\tfrac{Z^3}{a_B^3}) \tfrac{1}{n^3 \ell^2} \propto Z^2$$

- Functional form of WF: $R_{n\ell}(r) \propto r^{\ell}$
- Examples: $\xi_{5d}^{\mathrm{Pt}} = 0.571 \text{ eV}$ $\xi_{6p}^{\mathrm{Pt}} = 2.217 \text{ eV}$

A typical semiconductor: Ge



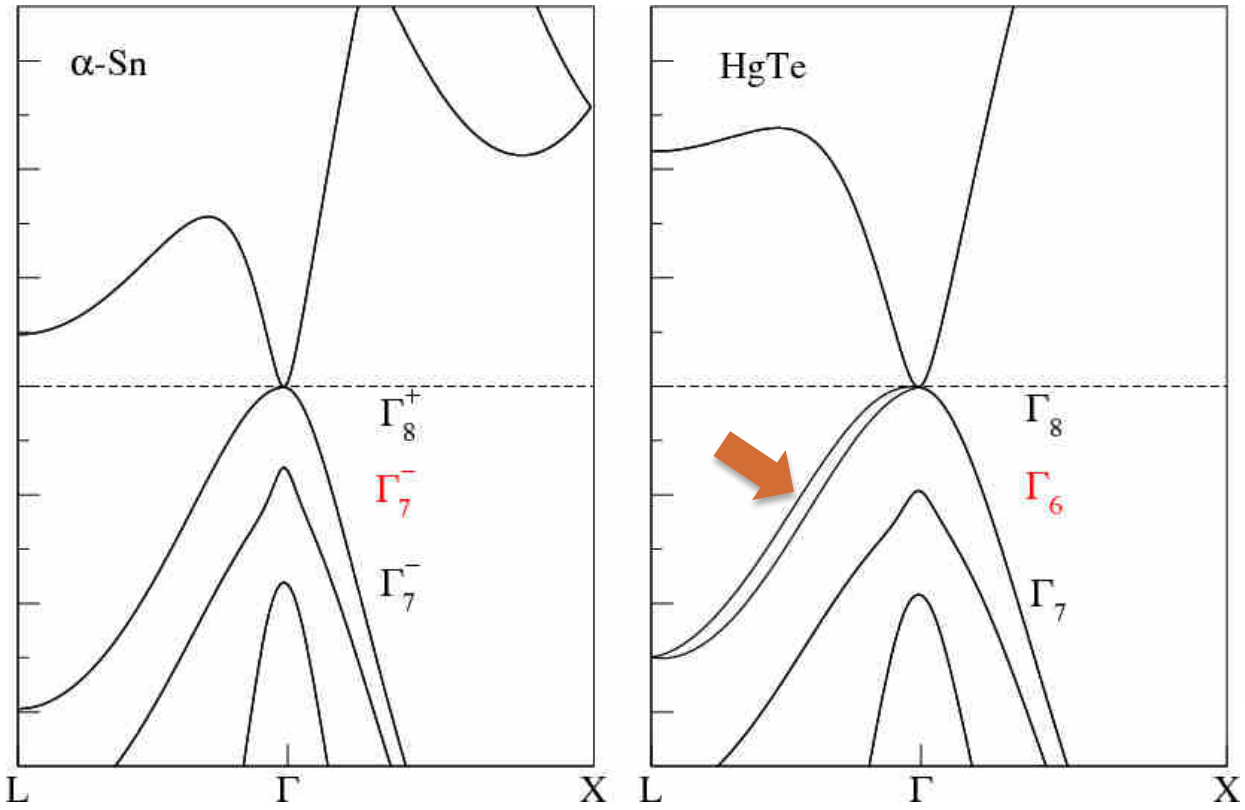
Breaking inversion symmetry: Dresselhaus & Rashba effect

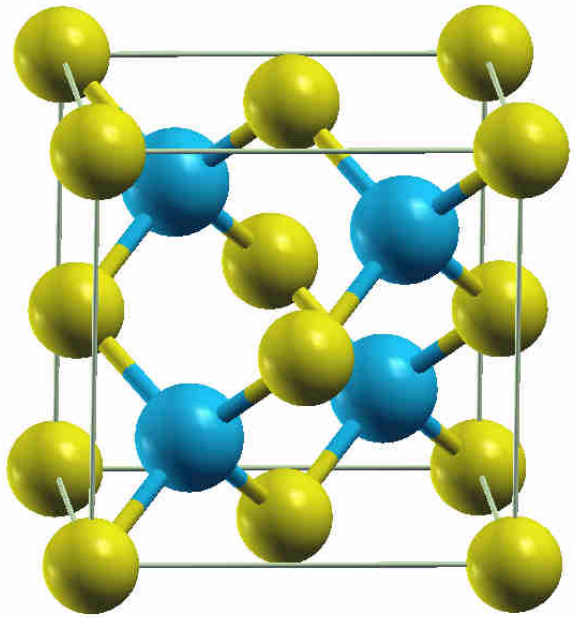
Broken I symmetry: Dresselhaus effect

in presence of SOC: $\epsilon(\vec{k},\uparrow) \neq \epsilon(\vec{k},\downarrow)$ i.e. *k*-dependent spin splitting (here: α k^3)

Dresselhaus Hamiltonian (*k*•*p*-theory, e.g. in (111) direction):

$$\hat{H}_D = \alpha_D\left[\sigma_x p_x\left(p_y^2 - p_z^2\right) + \sigma_y p_y\left(p_z^2 - p_x^2\right) + \sigma_z p_z\left(p_x^2 - p_y^2\right)\right]$$

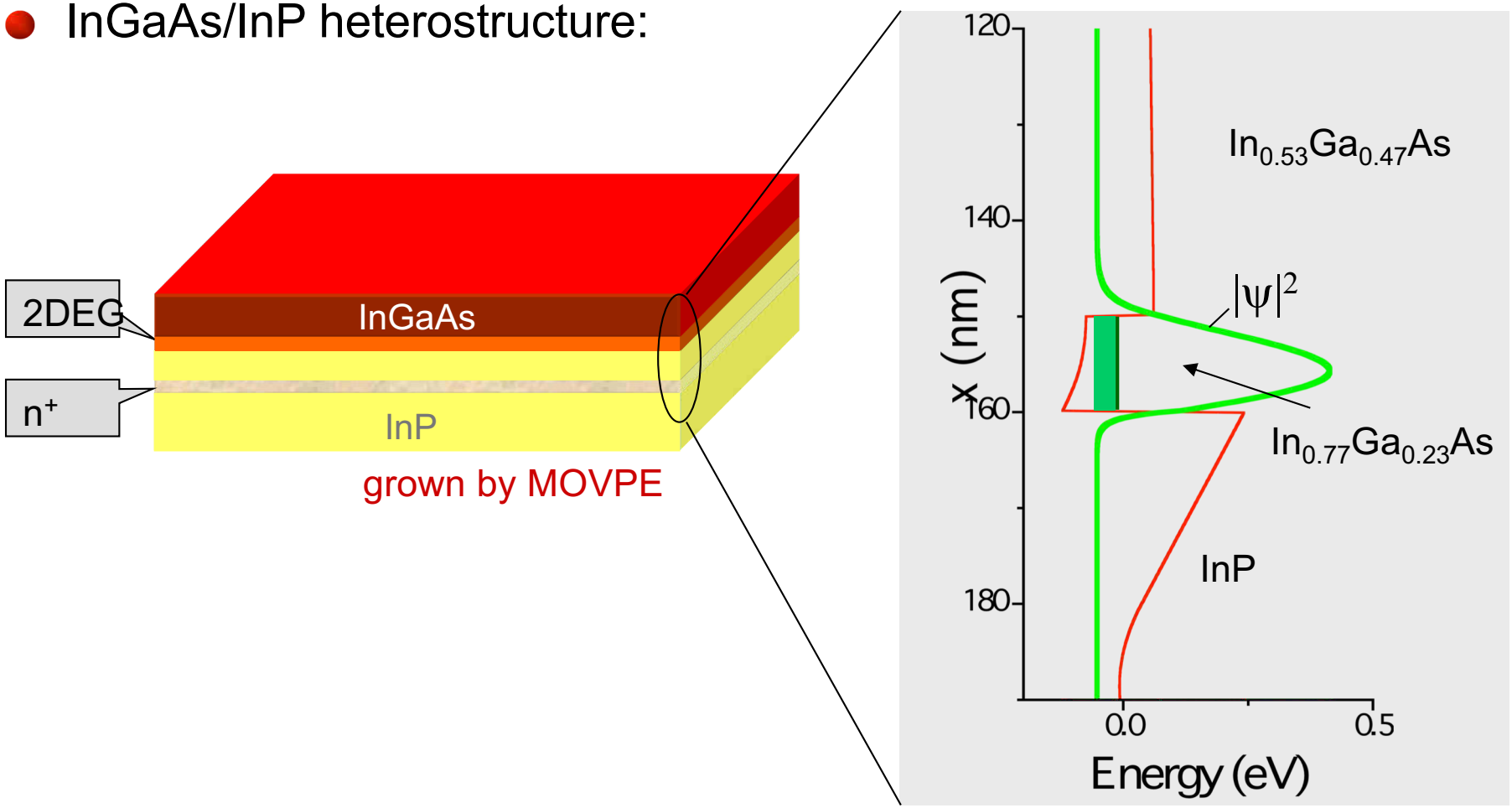




zincblende structure

Two-Dimensional Electron Gas

- InGaAs/InP heterostructure:



- Electrons moving in a $\vec{E}$ field:

Broken I symmetry at a crystal surface

Free electron gas in electric field:

$$\left[-\frac{1}{2}\nabla^2 - \frac{\mu_B}{2mc}\vec{\sigma}\cdot\left(\vec{p}\times\vec{E}(\vec{r})\right)\right]\psi_i = \varepsilon_i\psi_i$$

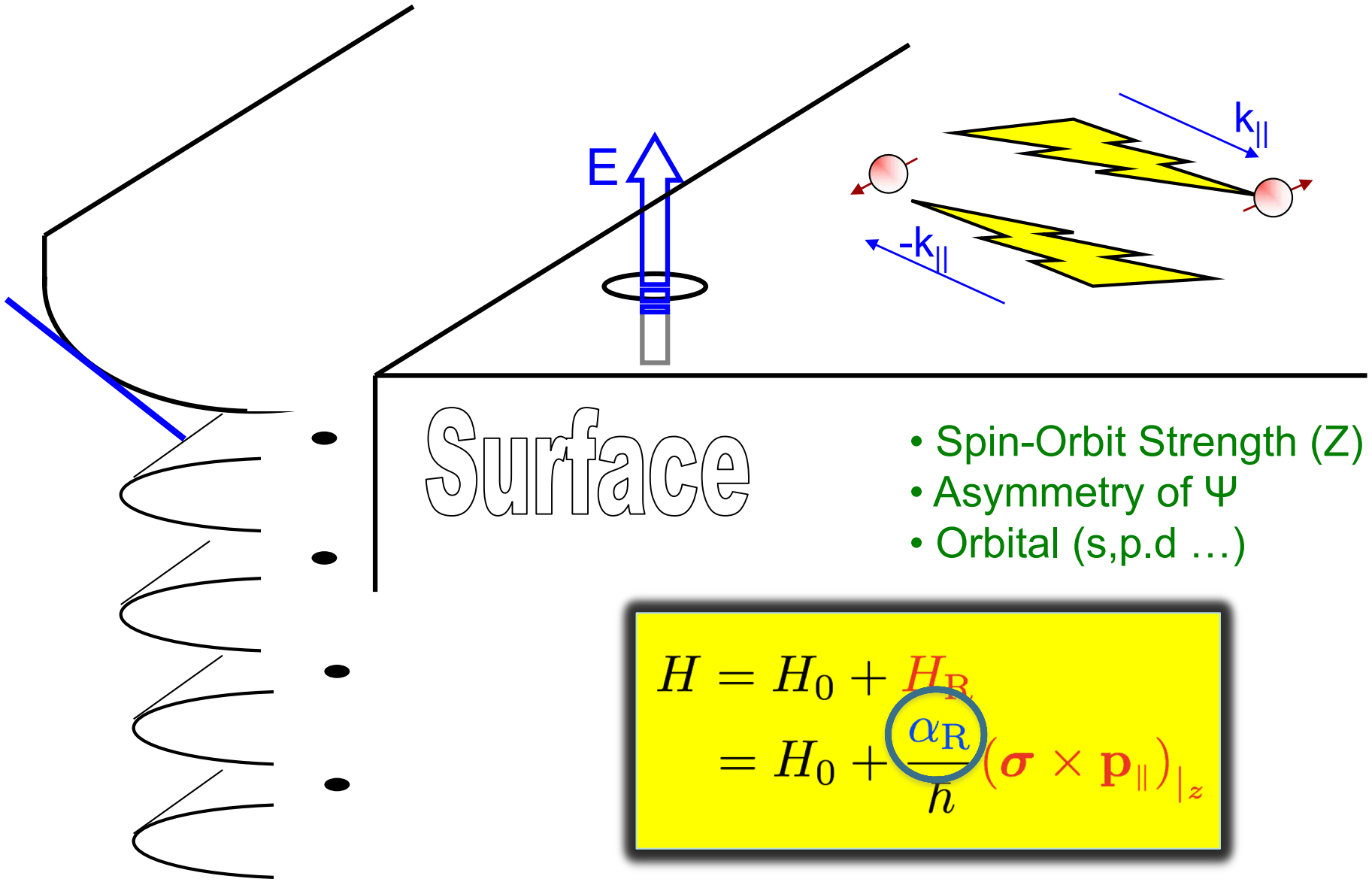
Suppose $\vec{E} = E\vec{e}_z$ and momentum confined in (*x*,*y*) plane:

$$\left[-\frac{1}{2}\nabla^2 + \alpha_R\vec{\sigma}\cdot\left(\vec{k}_{||}\times\vec{e}_z\right)\right]\psi_i = \varepsilon_i\psi_i$$

Rashba Hamiltonian

this describes electrons at a surface or an interface (e.g. doped layer between two semiconductors)

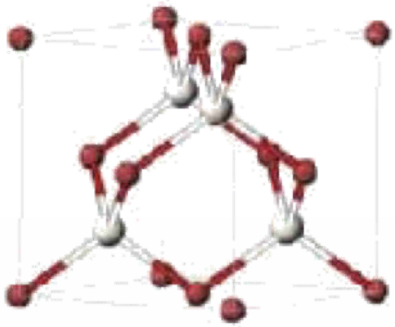
Electrons at Surfaces

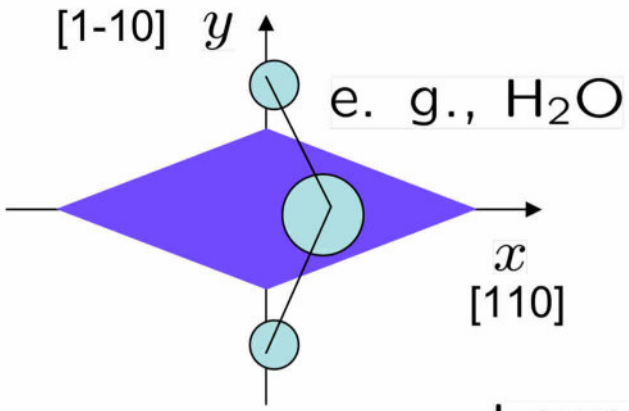


- Spin-Orbit Strength (Z)
- Asymmetry of Ψ
- Orbital (s,p.d …)

$$H = H_0 + H_R$$
$$= H_0 + \frac{\alpha_R}{\hbar}(\boldsymbol{\sigma} \times \mathbf{p}_{\parallel})_{|z}$$

The functional forms of Ω(k): Symmetry Analysis





$$C_{2v}: \; E, C_2, \sigma_v(xz), \sigma_v(yz)$$

Lowest-order symmetry preserving form:

$$H \sim \left(\alpha x^2 + \beta y^2\right) \times z$$

$$k_x \sim x, \quad k_y \sim y, \quad \sigma_x \sim yz, \quad \sigma_y \sim -xz$$

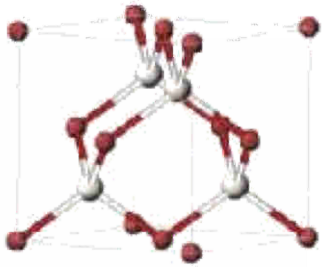
$$H_{so} \sim \alpha \, k_x \sigma_y + \beta \, k_y \sigma_x$$

J. Fabian

The functional forms of Ω(k): Symmetry Analysis

JÜLICH FORSCHUNGSZENTRUM

$$H_{so} \sim \alpha\, k_x\sigma_y + \beta\, k_y\sigma_x$$



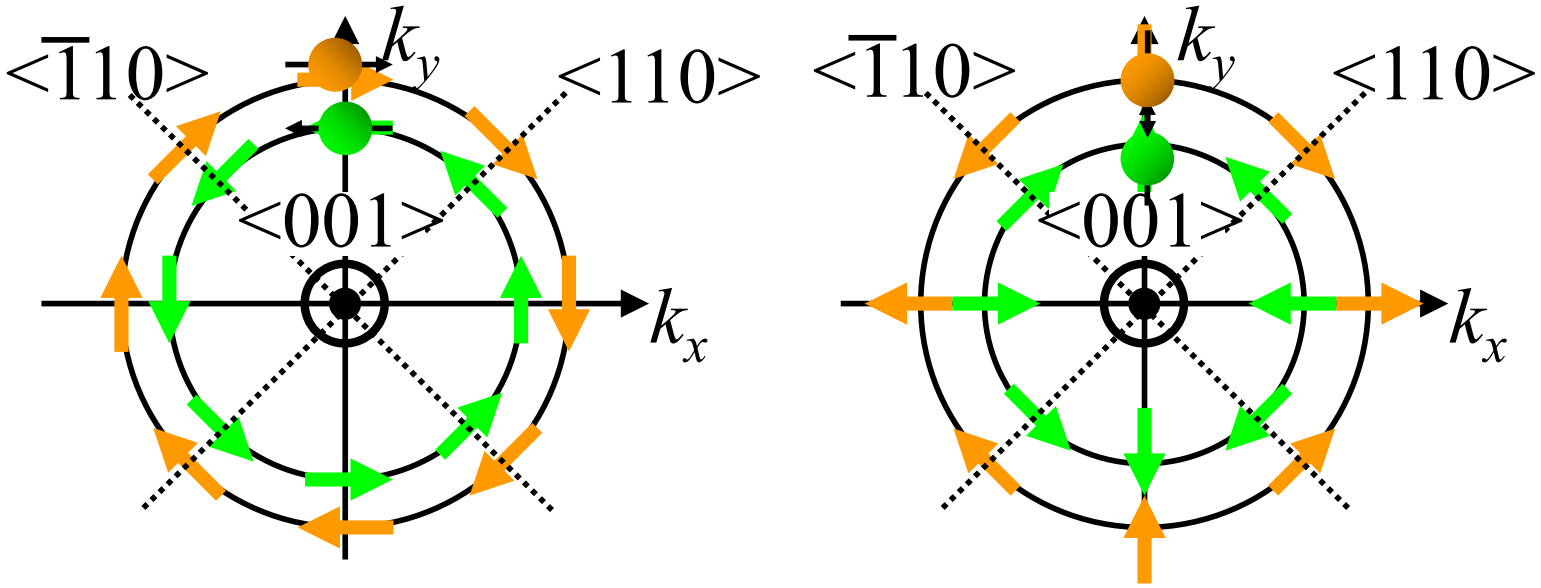
$$H_{so} \sim \frac{1}{2}(\alpha+\beta)(k_x\sigma_y + k_y\sigma_x) + \frac{1}{2}(\alpha-\beta)(k_x\sigma_y - k_y\sigma_x)$$

$$H_{so} = \underbrace{\gamma_D(k_x\sigma_y + k_y\sigma_x)}_{D_{2d}\ \text{Dresselhaus}} + \underbrace{\alpha_{BR}(k_x\sigma_y - k_y\sigma_x)}_{C_{4v}\ \text{Bychkov-Rashba}}$$

J. Fabian

Axis of spin-rotation

Spin Splitting at constant *E* (Energy)



Rashba type
Inversion Asymmetry
by heterostructure

Dresselhaus type
Inversion Asymmetry
in crystal structure

Rashba-Hamiltonian

- Electrons moving in a $\vec{E}$ field: $H = \frac{1}{2m}p_\parallel^2 + \underbrace{\frac{\alpha_\mathrm{R}}{\hbar}(\boldsymbol{\sigma} \times \mathbf{p}_\parallel)_{|z}}_{H_\mathrm{R}}$

- 2D electron gas (in xy-plane)

$$\psi_{\uparrow(\downarrow)}(\mathbf{k}_\parallel, \mathbf{r}_\parallel) = \frac{e^{i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel}}{\sqrt{\Omega}} |\uparrow(\downarrow)\rangle$$

Time reversal: $-i\sigma_y \hat{C}$

$$\psi_{\downarrow(\uparrow)}(-\mathbf{k}_\parallel, \mathbf{r}_\parallel) = \pm i \frac{e^{-i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel}}{\sqrt{\Omega}} \frac{1}{\sqrt{2}} \begin{pmatrix} ie^{-i\varphi/2} \\ \pm e^{i\varphi/2} \end{pmatrix}_z$$

Rashba-Hamiltonian

- Electrons moving in a $\vec{E}$ field: $H = \frac{1}{2m}p_\parallel^2 + \underbrace{\frac{\alpha_\mathrm{R}}{\hbar}(\boldsymbol{\sigma}\times\mathbf{p}_\parallel)_{|z}}_{H_\mathrm{R}}$

- 2D electron gas (in xy-plane)

$$\psi_{\uparrow(\downarrow)}(\mathbf{k}_\parallel,\mathbf{r}_\parallel) = \frac{e^{i\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel}}{\sqrt{\Omega}}|\uparrow(\downarrow)\rangle = \frac{e^{i\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel}}{\sqrt{\Omega}}\frac{1}{\sqrt{2}}\begin{pmatrix} ie^{-i\varphi/2} \\ \pm e^{i\varphi/2}\end{pmatrix}\Big|_z$$

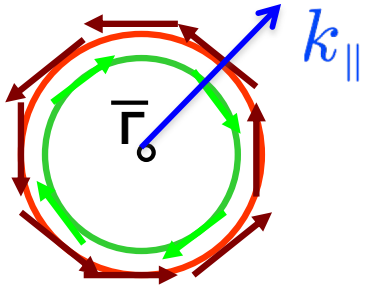
$$\mathbf{k}_\parallel = (k_x,k_y,0) = k_\parallel(\cos\varphi,\sin\varphi,0)$$

- Direction of quantization axis

$$\hat{\mathbf{n}}_\pm(\mathbf{k}_\parallel) = \langle\psi_{\pm\mathbf{k}_\parallel}|\boldsymbol{\sigma}|\psi_{\pm\mathbf{k}_\parallel}|\rangle = \pm\begin{pmatrix}\sin\varphi\\ -\cos\varphi\\ 0\end{pmatrix} \quad \perp \quad \mathbf{k}_\parallel = k_\parallel\begin{pmatrix}\cos\varphi\\ \sin\varphi\\ 0\end{pmatrix}$$

- Time reversal: $-i\sigma_y\hat{C}$, $\varphi\to\varphi+\pi$

$$\hat{\mathbf{n}}_\pm(\mathbf{k}_\parallel) \to \hat{\mathbf{n}}_\mp(-\mathbf{k}_\parallel) \to -\hat{\mathbf{n}}_\pm(-\mathbf{k}_\parallel)$$



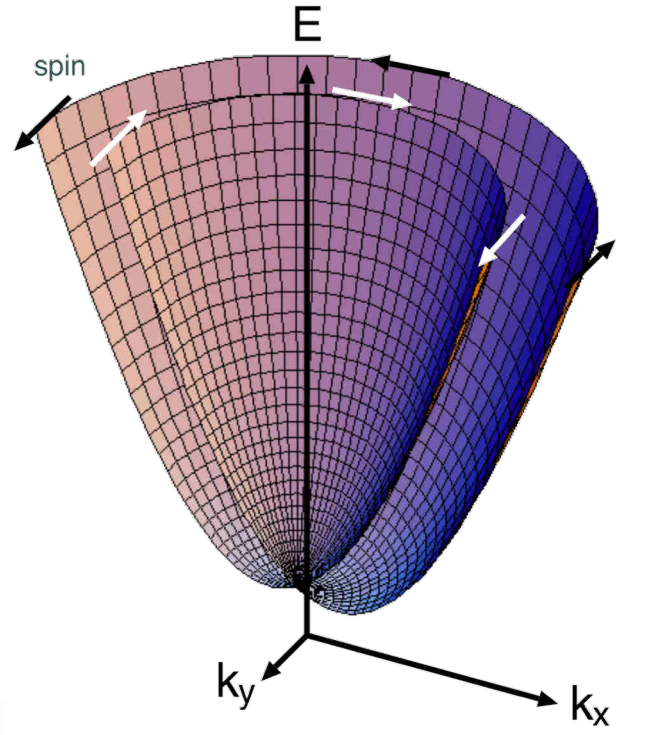
Spin orientation in the Rashba effect

Spin orientation of: $\psi_{\pm\vec{k}_\parallel} = \frac{e^{i\vec{k}_\parallel\cdot\vec{r}_\parallel}}{2\pi}\frac{1}{\sqrt{2}}\begin{pmatrix} ie^{-i\varphi/2} \\ \pm e^{i\varphi/2}\end{pmatrix}$

$$\vec{n}_\pm(\vec{k}_\parallel) = \left\langle \psi_{\pm\vec{k}_\parallel}\left|\vec{\underline{\sigma}}\right|\psi_{\pm\vec{k}_\parallel}\right\rangle = \begin{pmatrix} \sin\varphi \\ -\cos\varphi \\ 0\end{pmatrix}$$

with energies $\varepsilon_\pm = \frac{k_\parallel^2}{2m} \pm \alpha_R k_\parallel$

i.e. the spin is always perpendicular to the propagation direction (spin-momentum locking)!

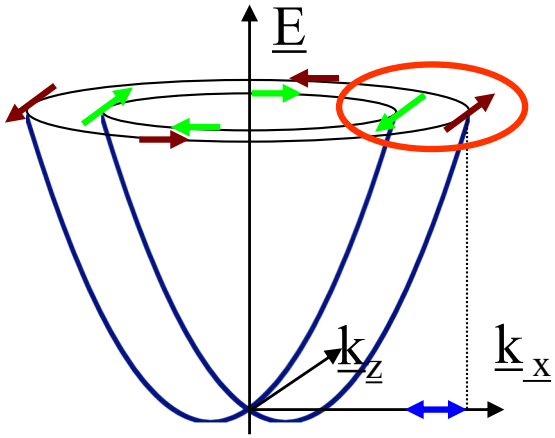


Spin Precession – Datta-Das Spintransistor

- spin precession

$$\begin{bmatrix} 1 \\ 1 \end{bmatrix}_{(+x-pol)} \rightarrow e^{ik_{x1}L}\begin{bmatrix} 1 \\ 0 \end{bmatrix}_{(+z)} + e^{ik_{x2}L}\begin{bmatrix} 0 \\ 1 \end{bmatrix}_{(-z)}$$

$$= e^{ik_{x1}L}\begin{bmatrix} 1 \\ e^{i\Delta k_x L} \end{bmatrix}$$

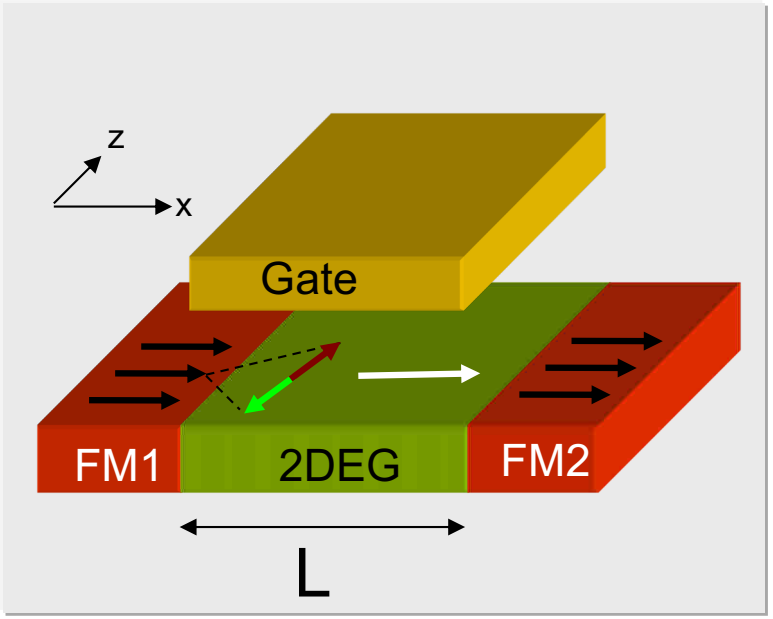


- phase shift

$$\Delta\theta = \Delta k_x L = 2m^*\alpha L/\hbar^2$$

- spin reversal:

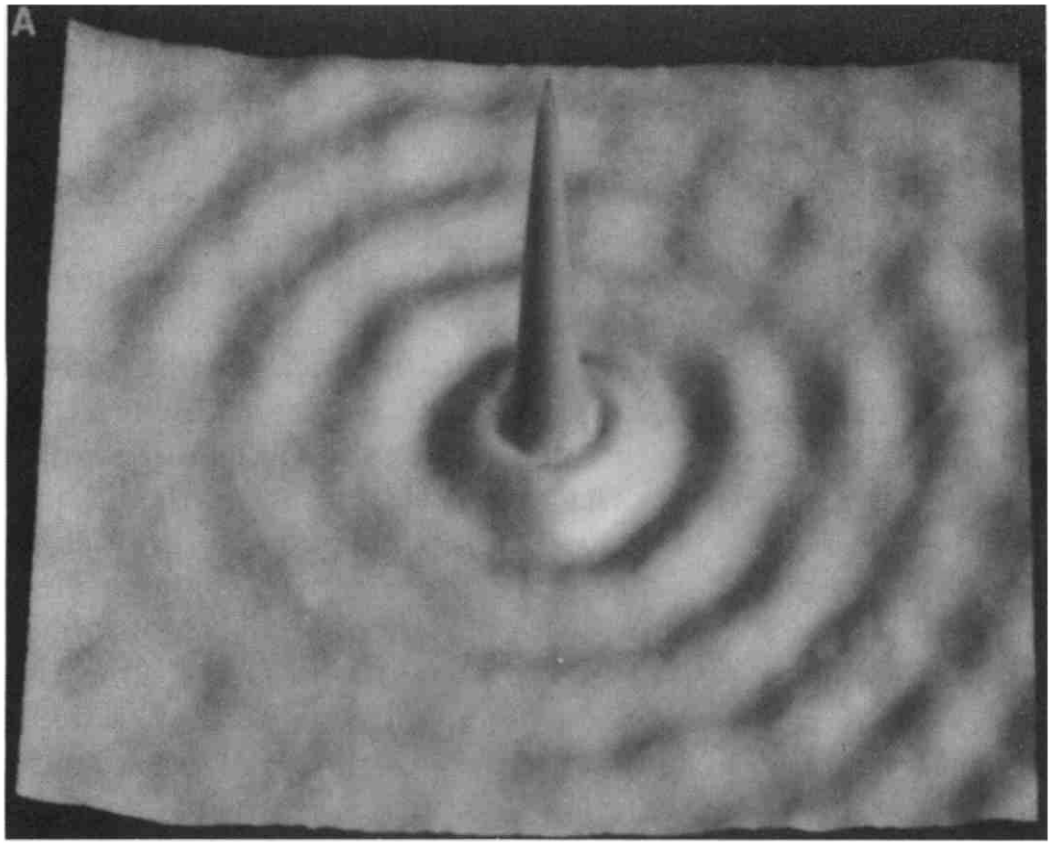
$$\Delta\theta = \pi : \begin{bmatrix} 1 \\ 1 \end{bmatrix}_{(+x-pol)} \longrightarrow \begin{bmatrix} 1 \\ -1 \end{bmatrix}_{(-x-pol)}$$

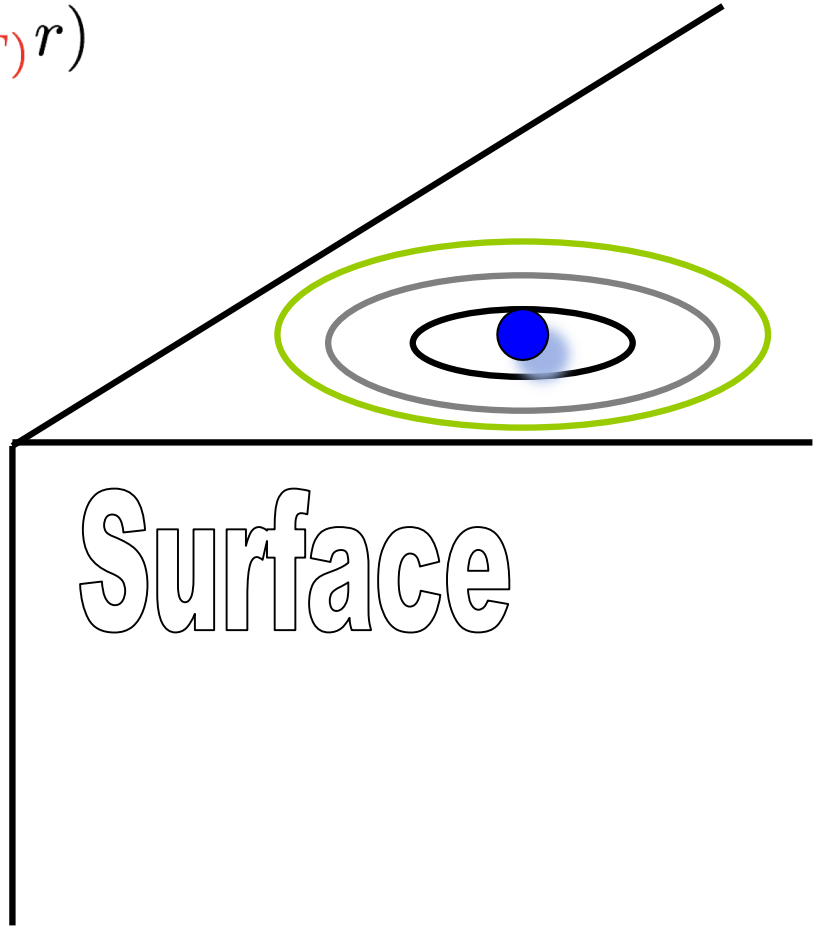


Datta and Das (APL **56**, 1990)

STS : Fe on Cu(111)

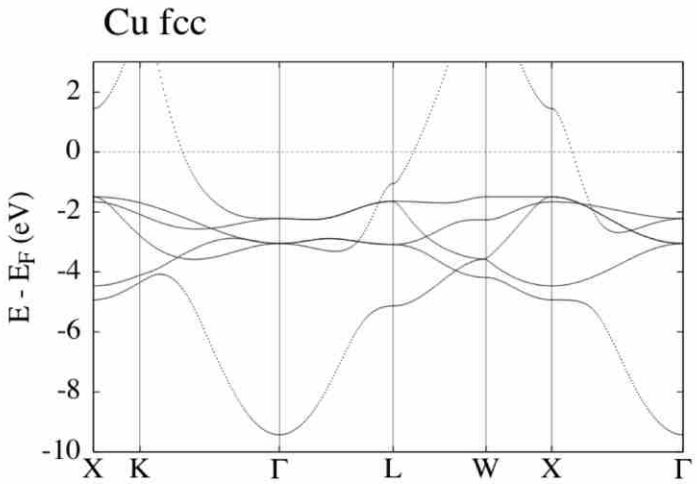
$$\mathrm{STS} \propto \Delta\mathrm{LDOS}(E_{(F)}, r) \propto \frac{1}{kr}\cos(2k_{(F)}r)$$

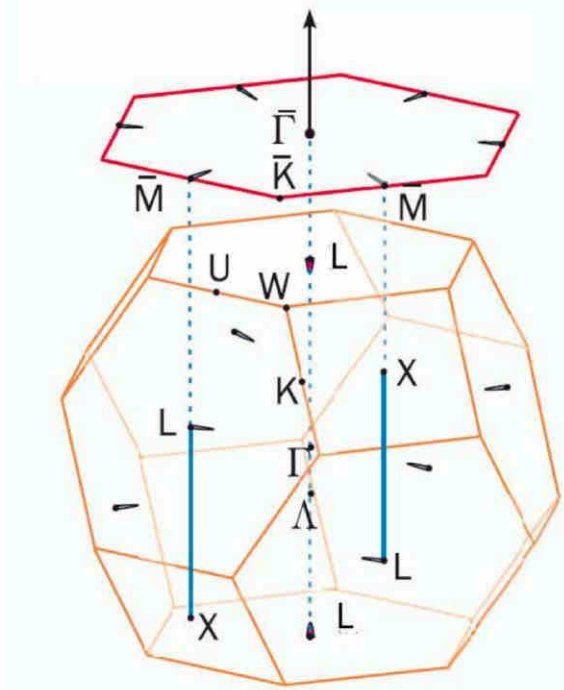


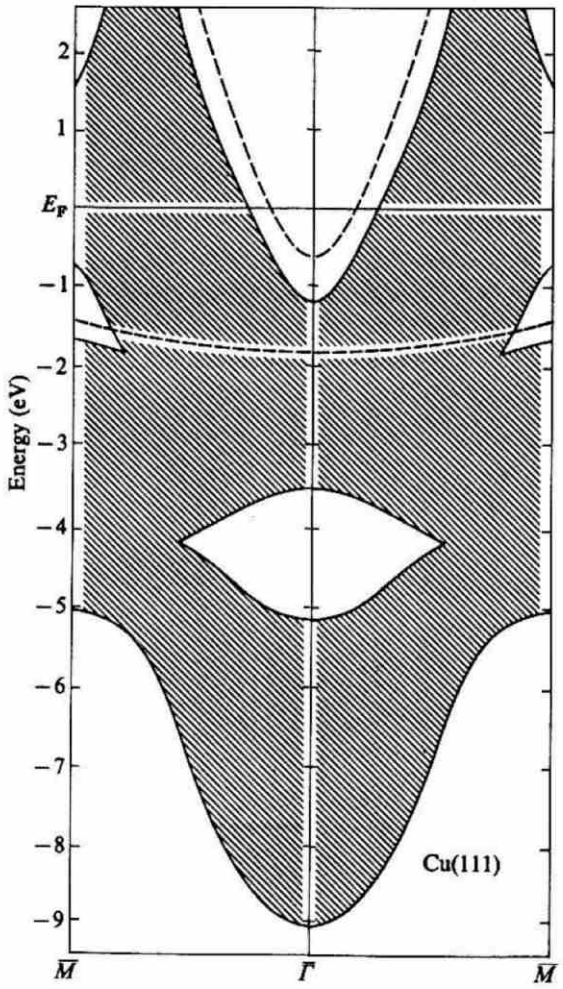


Crommie *etal,* Science 323, 218 (1993)

Two-dimensional Electron Gas







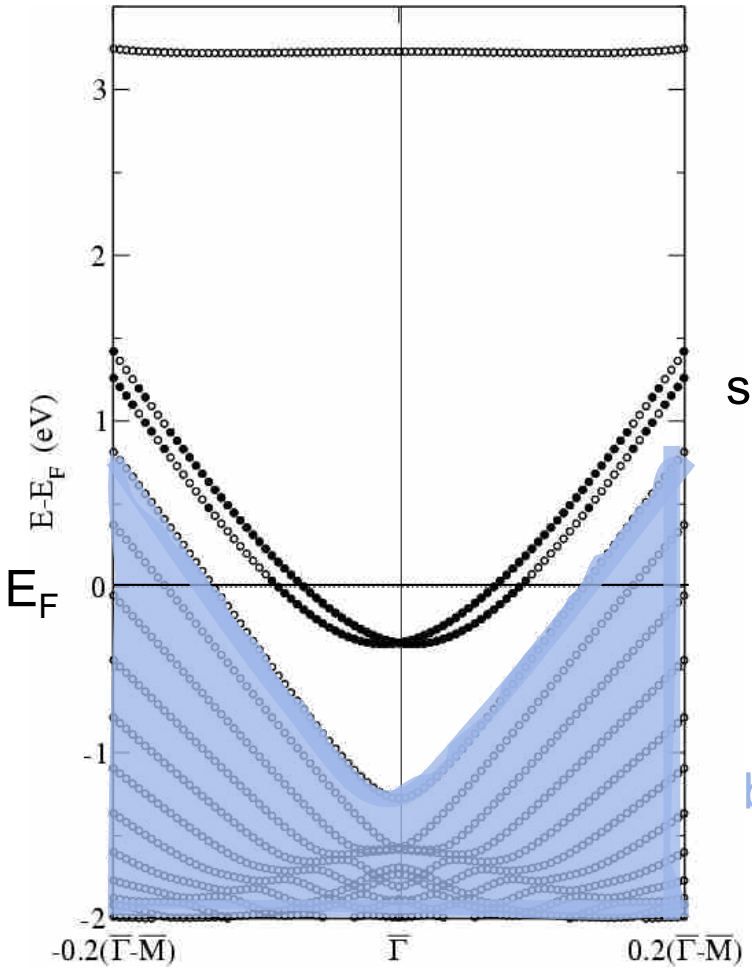
projected bandstructure

Au(111) Surface

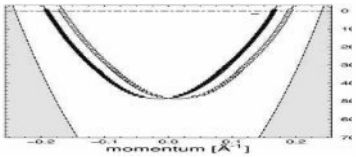
Mitglied der Helmholtz Gemeinschaft

JÜLICH FORSCHUNGSZENTRUM

Theory

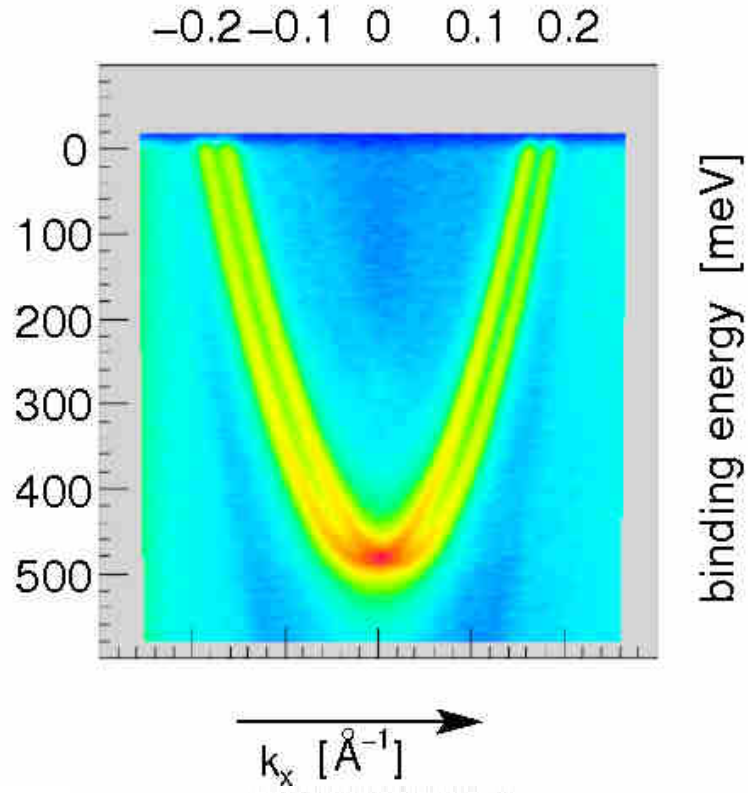


surface states



bulk states

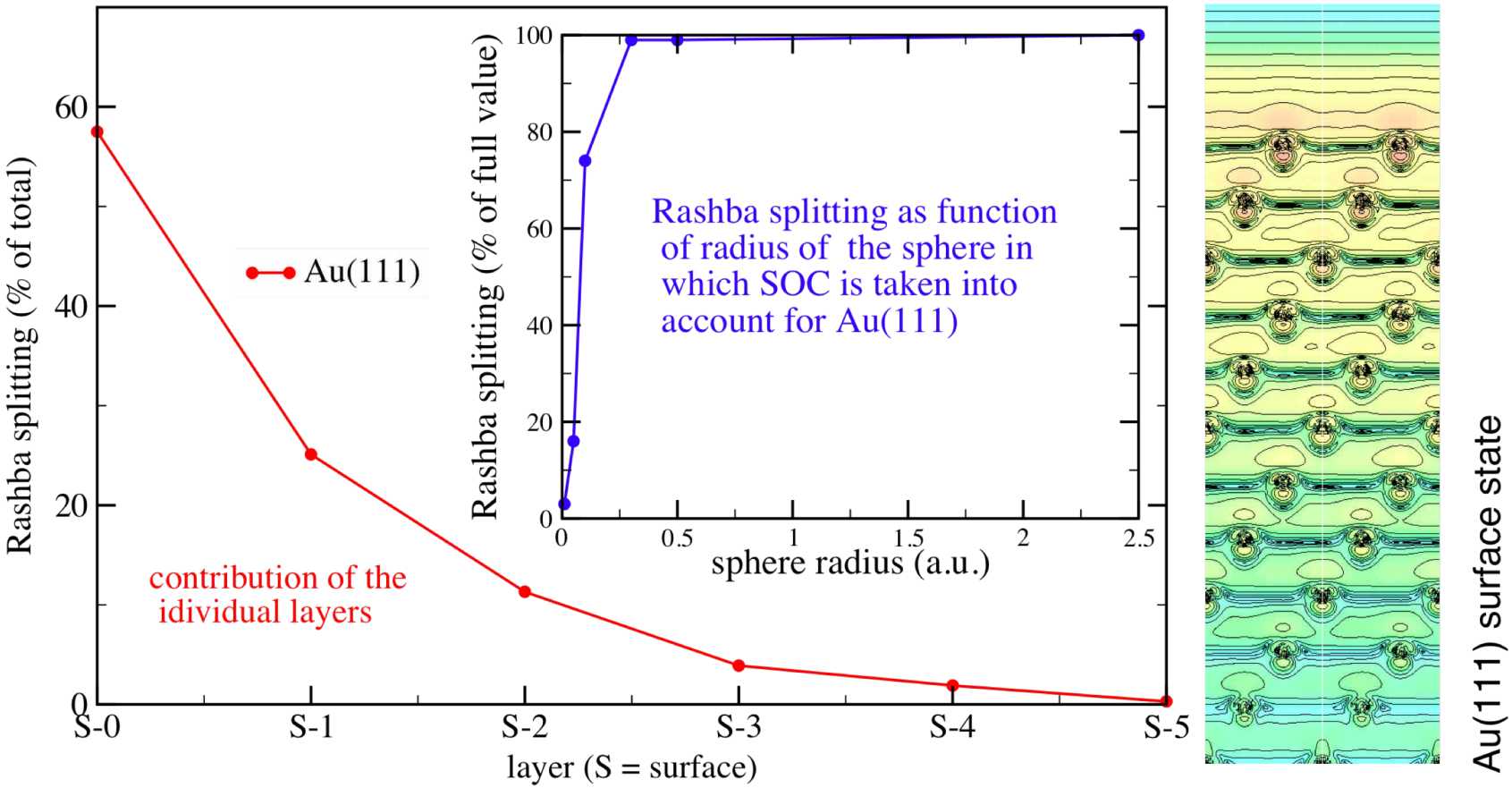
PES Experiment



Lashell et al., PRL 77, 3419 (1996)

Reinert et al., PRB 63, 115415 (2001)

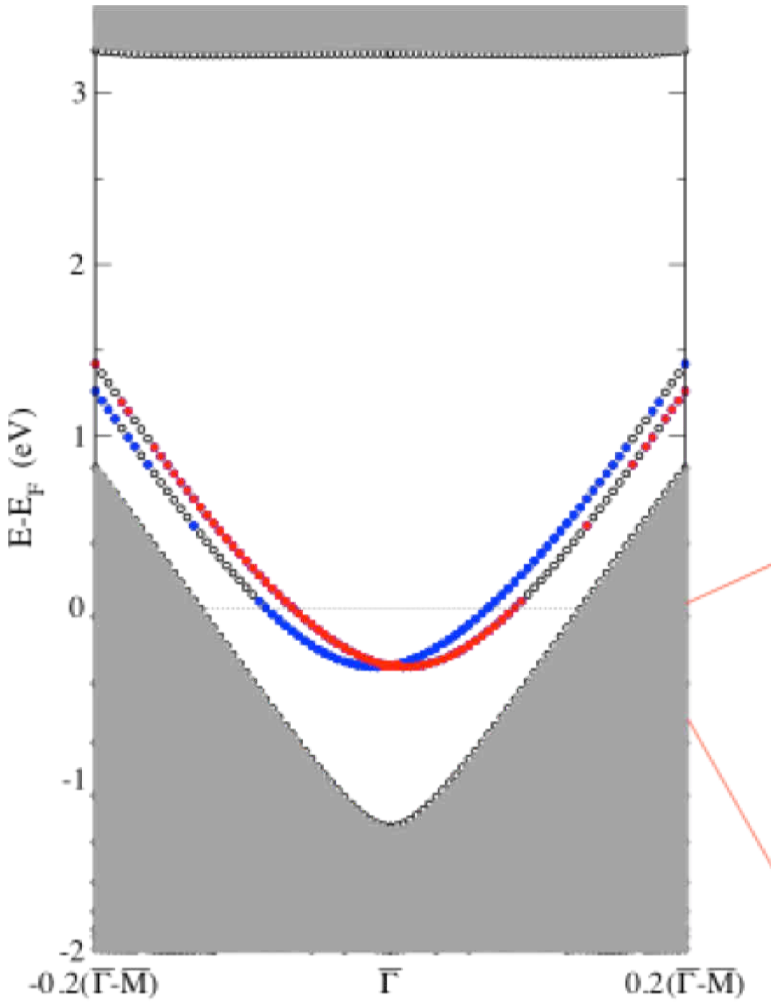
Origin of the Rashba-Splitting



- Layer contribution to Rashba-splitting decays like the surface state into the bulk
- 90% of each layer comes from a region within 0.2 a.u. near the nucleus

Example: coinage metal surfaces

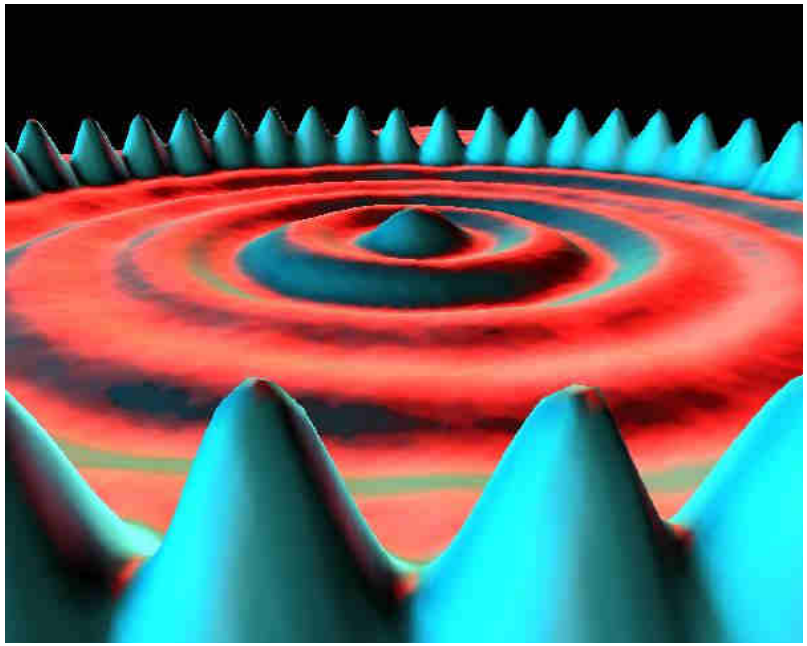
(111) surface states

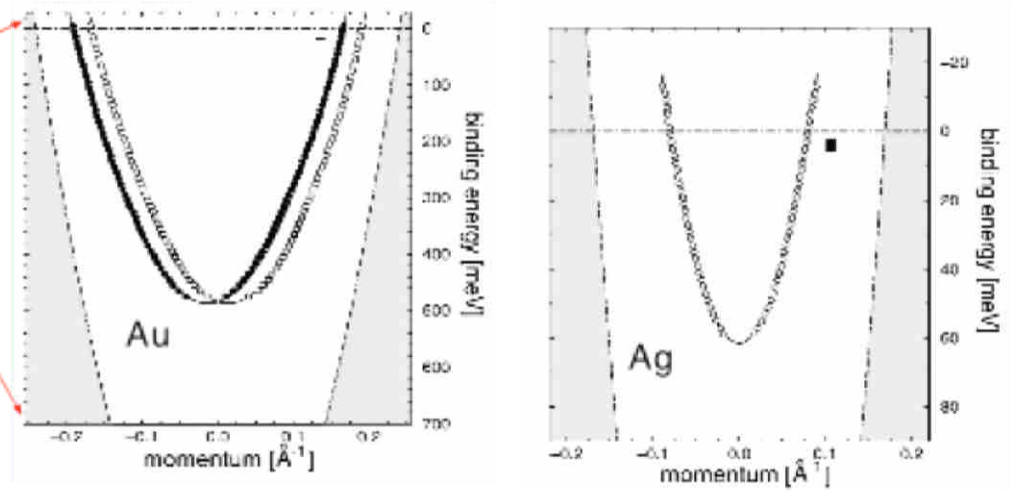


Z(Cu) = 29

Z(Ag) = 47

Z(Au) = 79

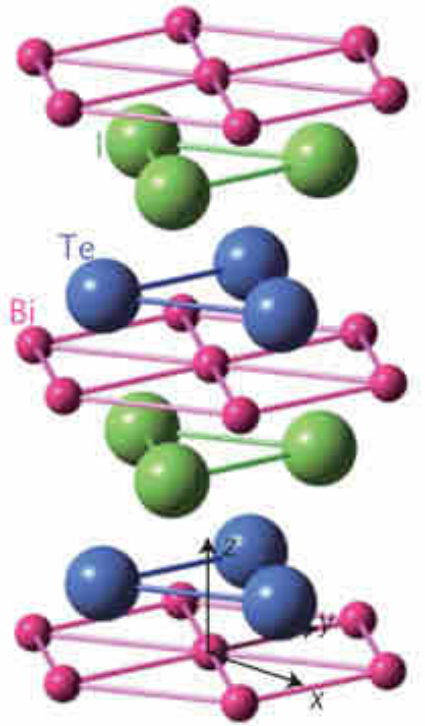


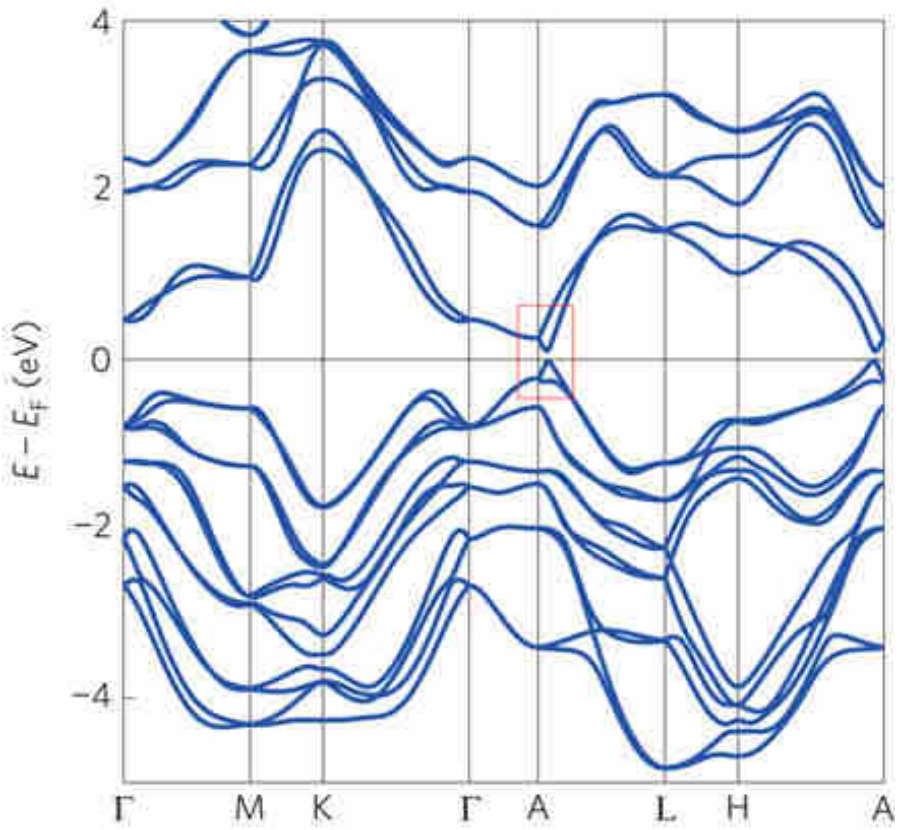


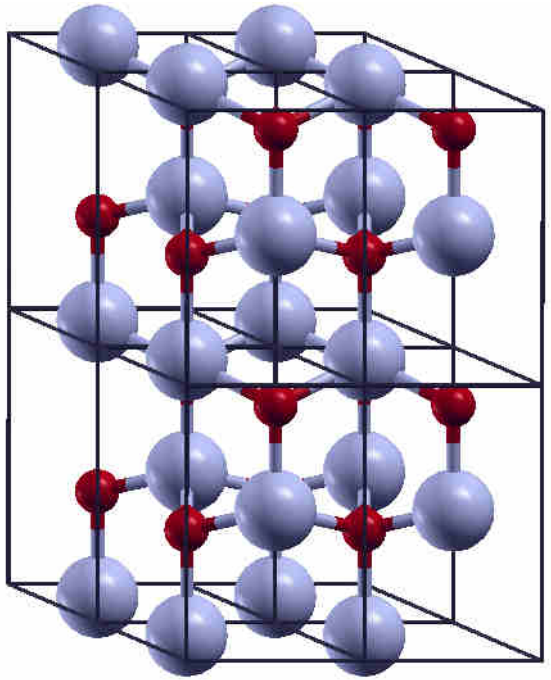
DFT calculations and SP-ARPES agree very well [experiment: Reinert et al., PRB **63**, 115415 (2001)]

Broken I symmetry: Rashba effect

lower symmetry allows terms α *k:* $\hat{H}_R = \alpha_R \left[\sigma_x p_y - \sigma_y p_x \right]$







wurzite structure

Ishizaka et al., Nature Mat. **10**, 521 (2011)

SOC effects in topological insulators

band-inversion in Sb_2Te_3

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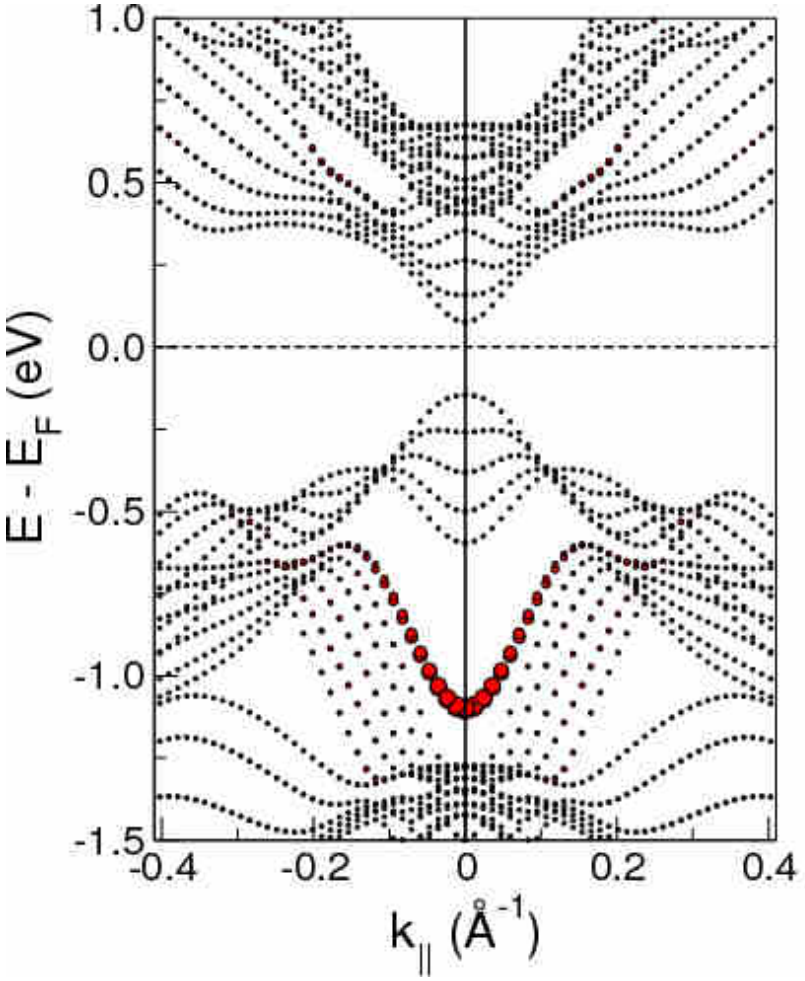
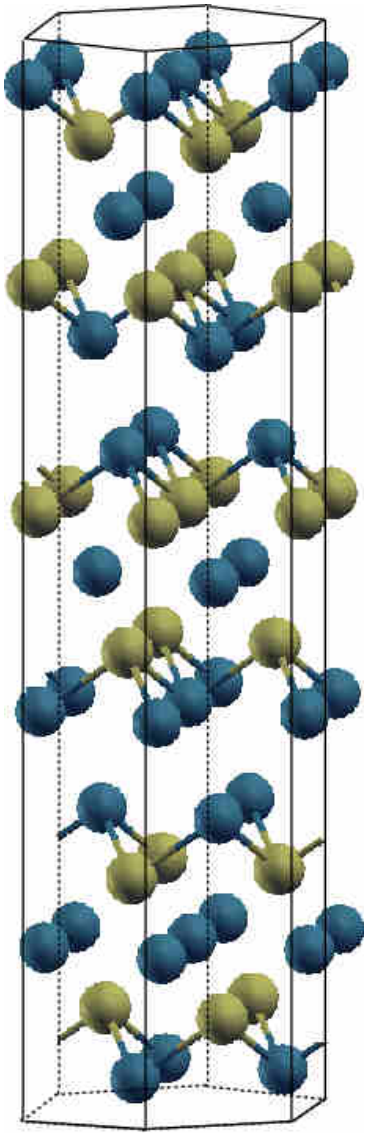
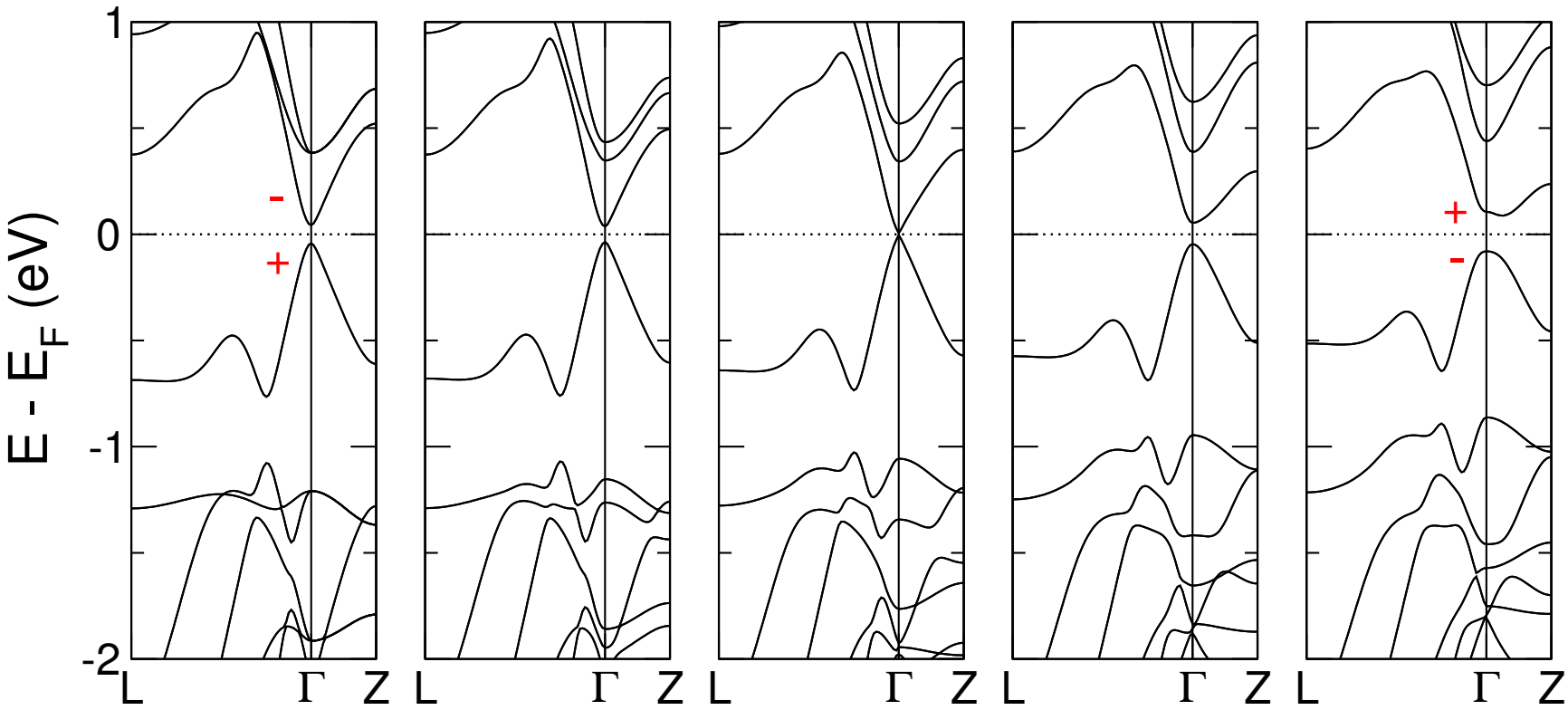
surface without SOC

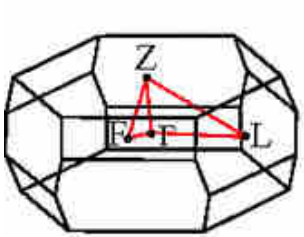




Sb_2Te_3 bulk band structure



increasing SOC strength

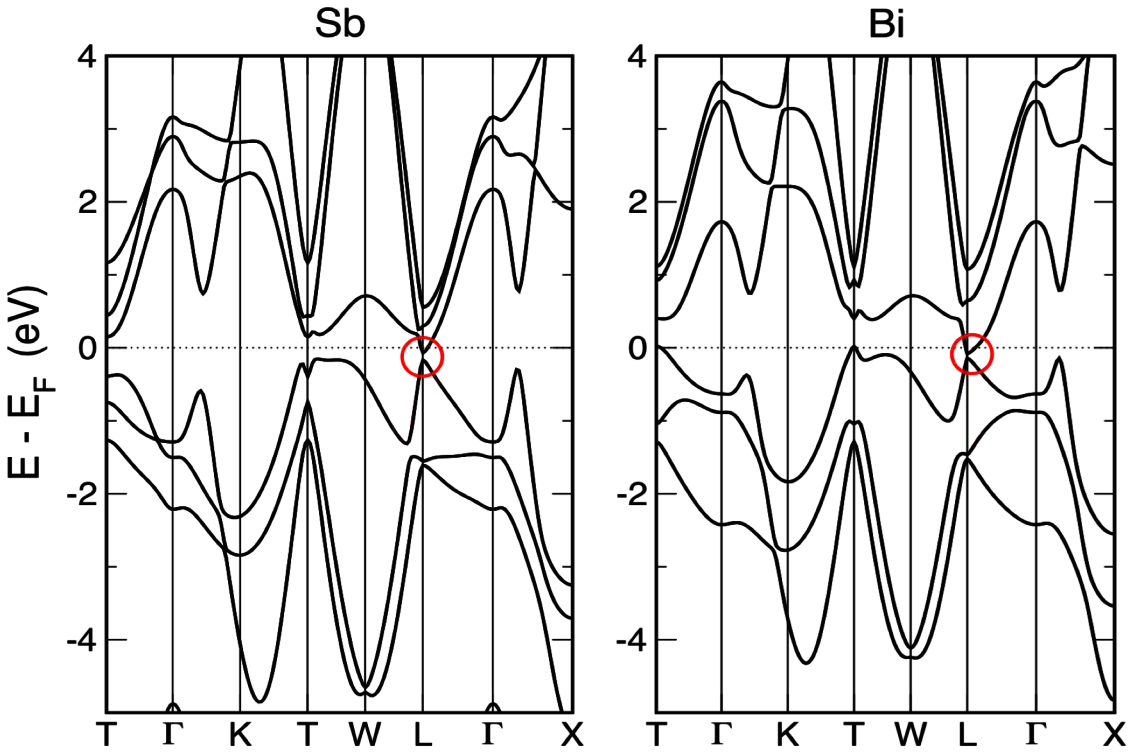


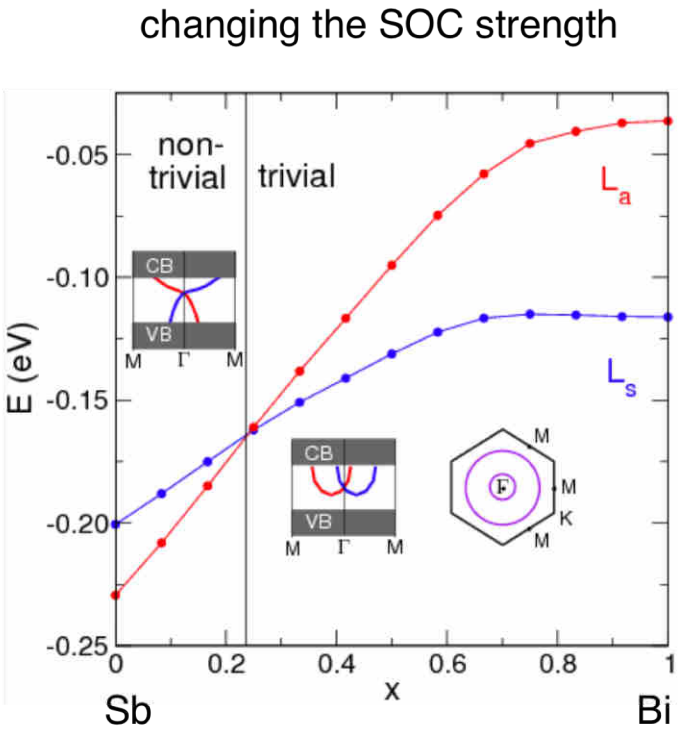
requires symmetry analysis at the Γ point (parity +/-)

band inversion: Bi vs. Sb

bulk Bi: topologically trivial ν=(0;000)

bulk Sb: topological semimetal ν=(1;111)



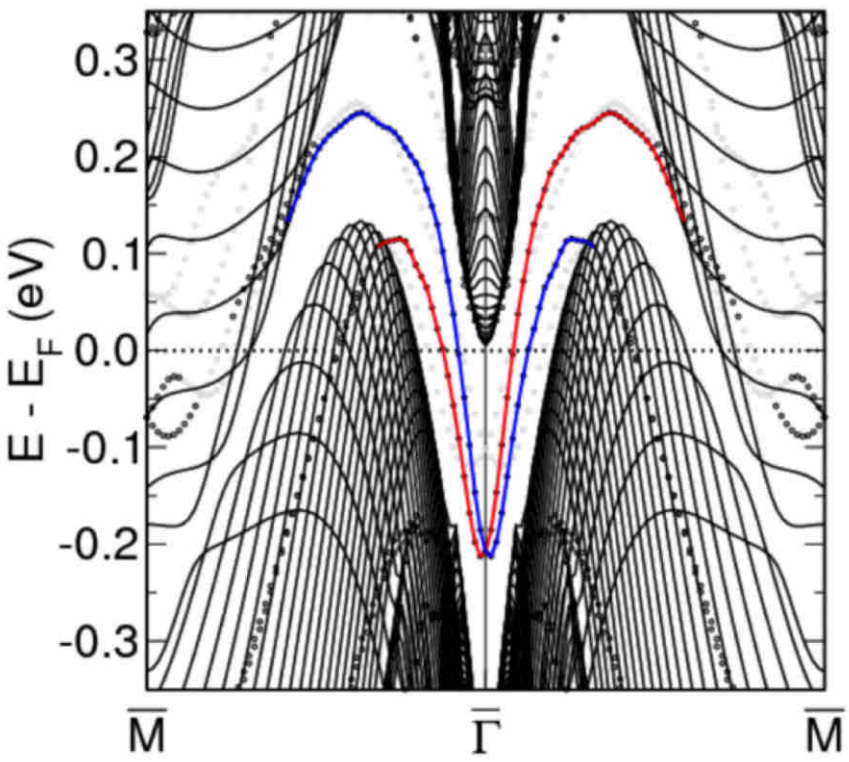


decreasing SOC strength

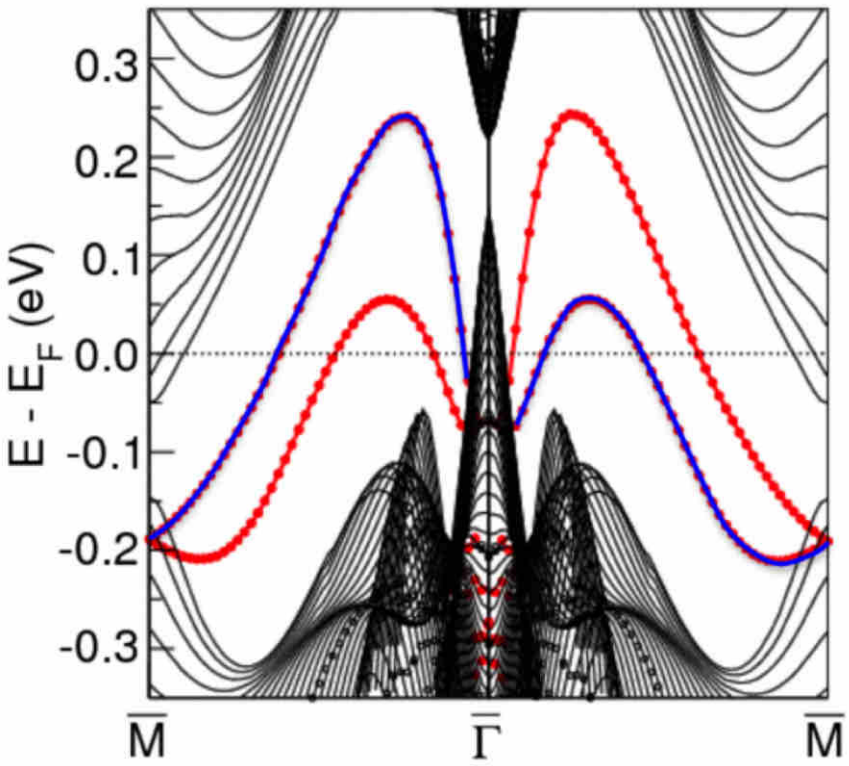
- for vanishing SOC: another band-inversion at T

Sb and Bi surfaces:

Sb(111)



Bi(111)



- Sb: surface state connects valence and conduction band: ν=(1;111)
- Bi: both spin-split branches return to valence band

Summary II:

relativistic effects

- single particle Dirac equation
  - scalar relativistic effects (d-band position Au, Ag)
  - spin-orbit effects
    - *T & S inversion symmetry ($p_{1/2}$-$p_{3/2}$ splitting)*
    - *T inversion symmetry (Rashba & Dresselhaus effect)*
    - *no T inversion symmetry (magneto-crystalline anisotropy)*
  - topological effects
    - *k-space: topological insulators*
    - *real space: magnetic skyrmions*
- two particle effects (Breit correction, dipole-dipole interaction)