

Integrative lecture on Condensed Matter Physics

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Fall -2019

Part II

Who I am? Why am I here? Why are you here?

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Bio

- Researcher (RTD-a) at University of Rome
- 2 postdocs
- Phd in Physics
- Undergrad and master
- Interests: Design of quantum materials and climbing

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I made these slides from different sources, including books: **Ashcroft, Kittel, Simon (Oxford) and public websites.** Some of the figures were done by myself and others adapted from the internet. You can share, mutilate or remove slides from this pdf **[in case let me know of typos or corrections]**.

Bear in mind: This material is intended as a guide for you to assimilate concepts. In no circumstance, it covers all the content that was given during the main lecture.

Calendar of supporting lectures on CMP 2019 (Part I)

Lectures colored in blue are in
PART_I_integrative-CMP_fall_2019.pdf

2019 October

M	T	W	T	F	S	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

2019 November

M	T	W	T	F	S	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	

1st Midterm exam

Lectures colored in green are in
PART_II_integrative-CMP_fall_2019.pdf

2019 December

M	T	W	T	F	S	S
						1
2	3	4	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22
23	24	25	26	27	28	29
30	31					

2020 January

M	T	W	T	F	S	S
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

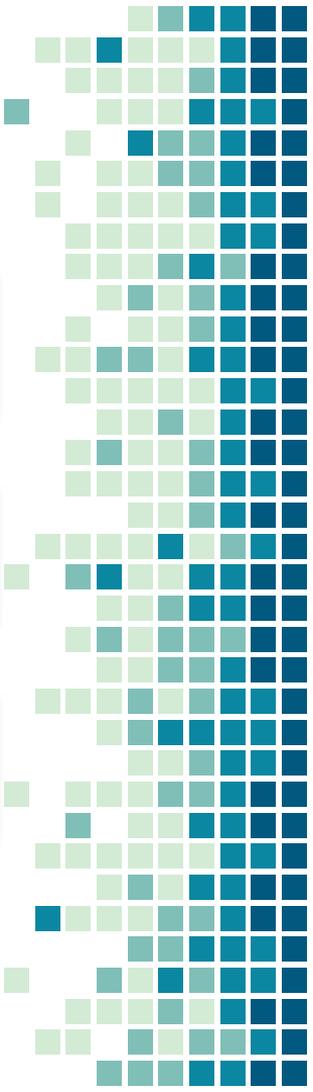
2nd Midterm exam

Outline

Electrons in a Periodic Potential (here)

Transport phenomena in metals (*in hands out notes*)

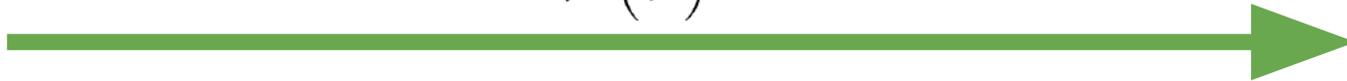
Semiconductor Physics (*in hands out notes*)



Start: “Electrons in a Periodic Potential”

We can rank these models as a function of the strength of the lattice **potential**

$$V(r)$$

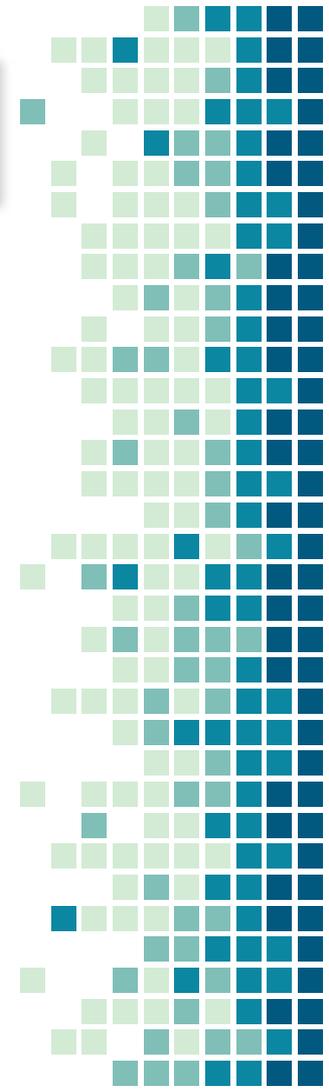


Free electron

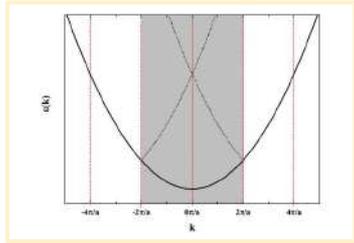
Nearly Free
electrons model

Tight-binding
model or (LCAO)

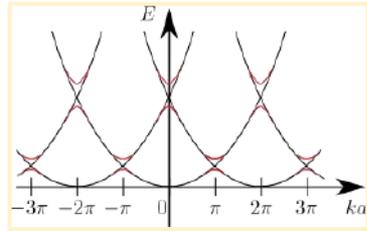
Isolated atoms



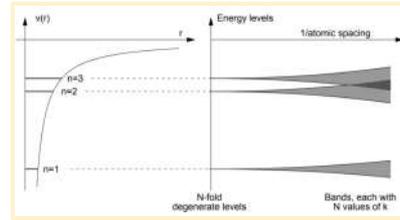
Road map to understand these models



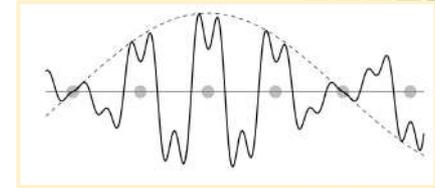
1) Free electron form a Fermi sea



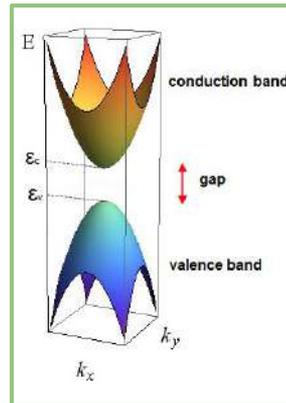
2) Isolated atoms: discrete orbitals



3) Hybridization of orbitals: LCAO



4) Bloch theorem



5) Band structures

Sommerfeld free-electron model

Atoms in a metal provide conduction electrons from their outer shells (often s-shells). These electrons can be described as waves, analogous to phonons. **The Hamiltonian of a free electron is:**

$$\mathcal{H}_0 = \frac{\mathbf{p}^2}{2m}$$

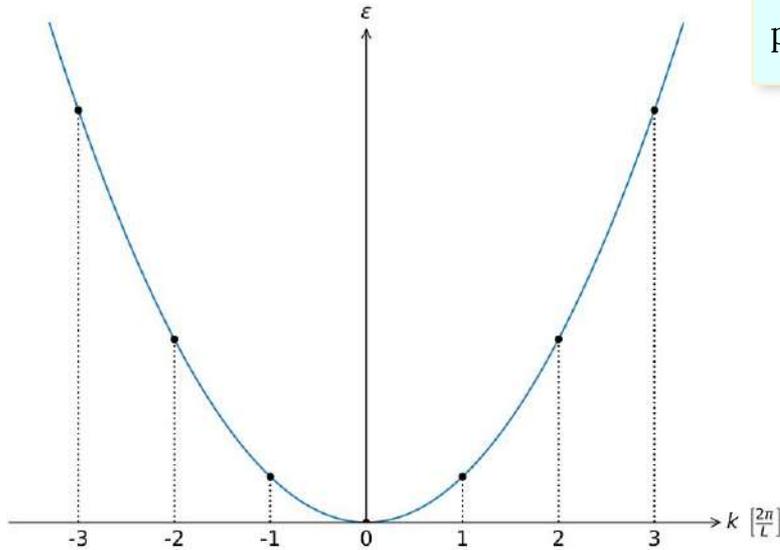
$$\mathcal{H}_0 = \frac{\mathbf{p}^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Rightarrow \varepsilon = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

If we impose periodic boundary conditions, $\psi(x, y, z) = \psi(x + L, y + L, z + L)$

it follows that the allowed wavenumbers are given by

$$k_x = \frac{2\pi p}{L}, \quad k_y = \frac{2\pi q}{L}, \quad k_z = \frac{2\pi r}{L} \Rightarrow \varepsilon = \frac{2\pi^2 \hbar^2}{mL^2} (p^2 + q^2 + r^2).$$

The quantization of k-space is exactly analogous to that for phonons



The difference with phonons is that electrons are *fermions*, implying that there are only 2 electron states (due to spin) per k-value.

In order to compute the density of states. We start by expressing the **total number of states N** as an integral over k-space. Assuming three dimensions and spherical symmetry (the dispersion in the free electron model is isotropic), we find

$$N = 2 \left(\frac{L}{2\pi} \right)^3 \int d\mathbf{k} = 2 \left(\frac{L}{2\pi} \right)^3 4\pi \int k^2 dk = \frac{V}{\pi^2} \int k^2 dk,$$

where the factor 2 represents spin degeneracy, and $(L/2\pi)^3$ is the density of points in k-space.

By using $k = \frac{\sqrt{2m\varepsilon}}{\hbar}$ and $dk = \frac{1}{\hbar} \sqrt{\frac{m}{2\varepsilon}} d\varepsilon$

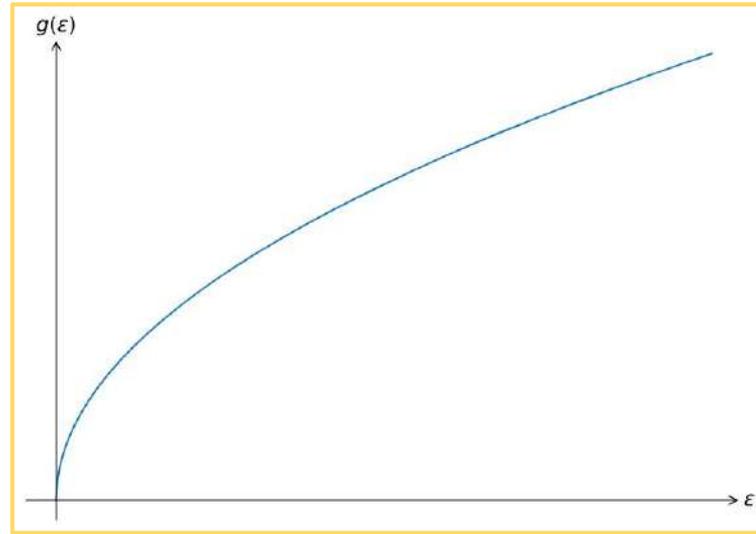
we can rewrite the expression as:

$$N = \frac{V}{\pi^2} \int \frac{2m\varepsilon}{\hbar^3} \sqrt{\frac{m}{2\varepsilon}} d\varepsilon = \frac{Vm^{3/2}}{\pi^2\hbar^3} \int \sqrt{2\varepsilon} d\varepsilon$$

So we find for the density of states:

$$g(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{Vm^{3/2}\sqrt{2\varepsilon}}{\pi^2\hbar^3} \propto \sqrt{\varepsilon}$$

- For 1D: $g(\varepsilon) = \frac{2L}{\pi} \frac{dk}{d\varepsilon} \propto 1/\sqrt{\varepsilon}$
- For 2D: $g(\varepsilon) = \frac{kL^2}{\pi} \frac{dk}{d\varepsilon} \propto \text{constant}$



Given the number of electrons in a system, we can now fill up these states starting from the lowest energy until we run out of electrons, at which point we reach the Fermi energy.

Fermi energy, Fermi wavevector, Fermi wavelength

At $T=0$, the total number of electrons is given by the integral over the density of states up to the *Fermi energy* ε_F :

$$N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon \stackrel{3D}{=} \frac{V}{3\pi^2 \hbar^3} (2m\varepsilon_F)^{3/2}.$$

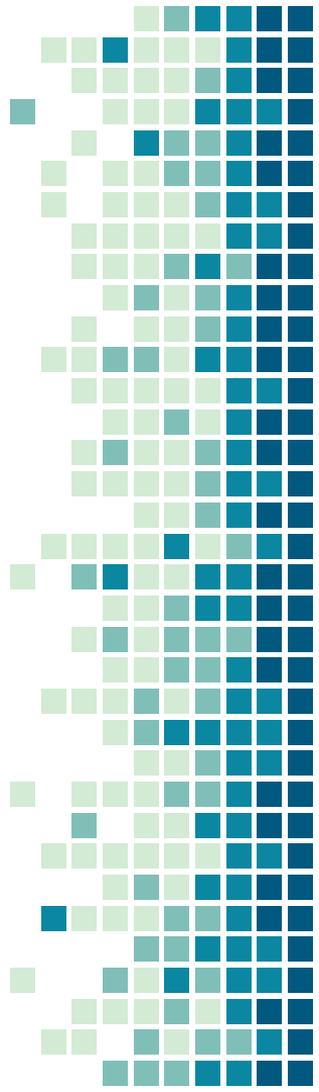
N denotes the total number of electrons in the system

Alternatively, we can express N as an integral over k -space up to the *Fermi wavenumber*, which is the wavenumber associated with the Fermi energy: $k_F = \sqrt{2m\varepsilon_F}/\hbar$

$$N \stackrel{3D}{=} 2 \frac{L^3}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 dk = 2 \frac{V}{(2\pi)^3} \frac{4}{3} \pi k_F^3$$

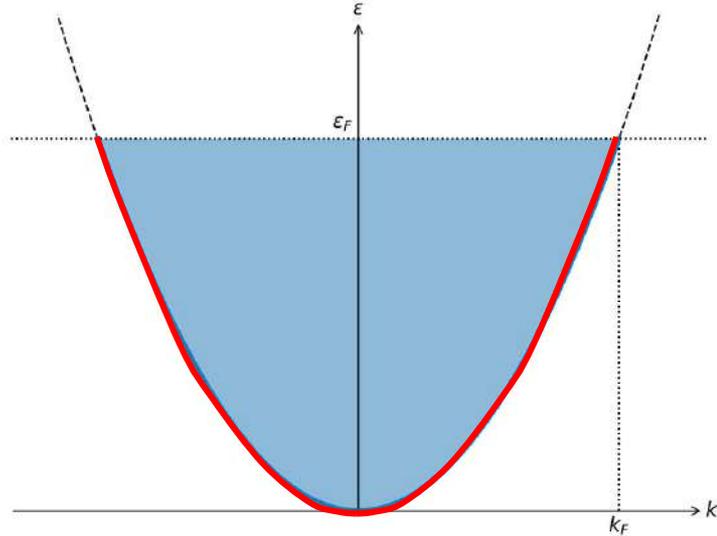
These equations allow us to relate ε_F and k_F to the electron density N/V :

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}, \text{ and } k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}.$$



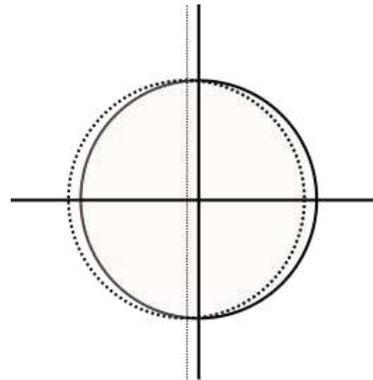
From the last equation it follows that the *Fermi wavelength* $\lambda_F \equiv 2\pi/k_F$ is on the order of the atomic spacing for typical free electron densities in metals.

For copper, the Fermi energy is ~ 7 eV. It would take a temperature of $\sim 70,000$ K for electrons to gain such energy through a thermal excitation! The *Fermi velocity* $v_F = \hbar k_F/m \approx 1,750$ km/s



Red line represents all filled states at $T=0$. This is called the Fermi sea.

Fermi surface = all points in k -space with $\epsilon = \epsilon_F$. For free electrons in 3D, the Fermi surface is the surface of a sphere.



All transport takes place near the Fermi surface.

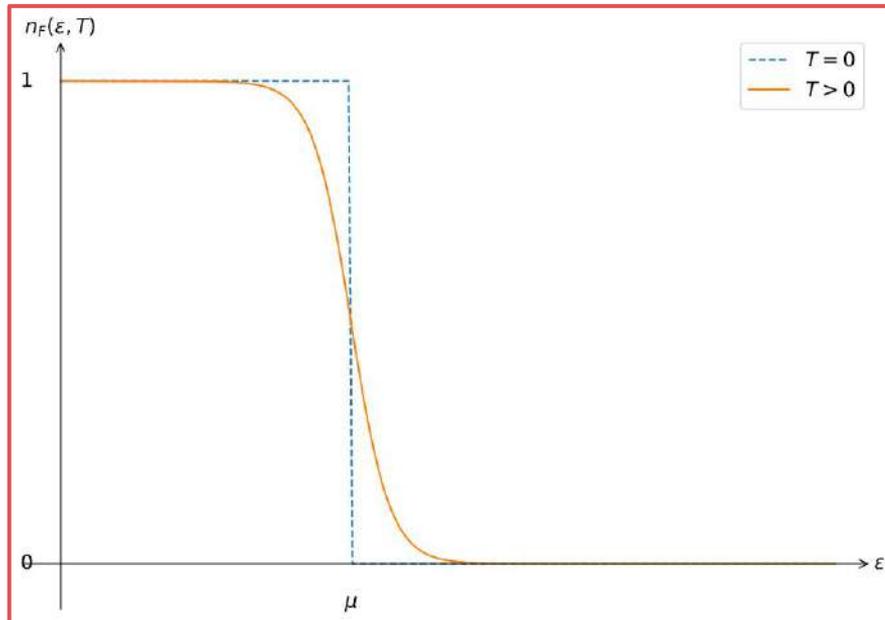
Finite temperature, heat capacity

We now extend it to $T > 0$ by including a temperature dependent occupation function $n_F(\epsilon, T)$ into our expression for the total number of electrons:

$$N = \int_0^{\infty} n_F(\epsilon, T) g(\epsilon) d\epsilon,$$

where the probability for a certain electron state to be occupied is given by the Fermi-Dirac distribution

$$n_F(\epsilon, T) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$



The chemical potential is $\mu = \epsilon_F$ if $T=0$.

Typically $\epsilon_F/k_B \sim 70,000 \text{ K}$ ($\sim 7 \text{ eV}$), whereas room temperature is only 300 K ($\sim 25 \text{ meV}$). Therefore, thermal smearing occurs only very close to the Fermi energy.

Including the temperature dependence, one can calculate the electronic contribution to the heat capacity $C_{V,e}$

A finite temperature causes electrons in the top triangle to be excited to the bottom triangle. Because the base of this triangle scales with $k_B T$ and its height with $g(\epsilon_F)$, it follows that the number of excited electrons:

$$N_{\text{exc}} \approx g(\epsilon_F) k_B T$$

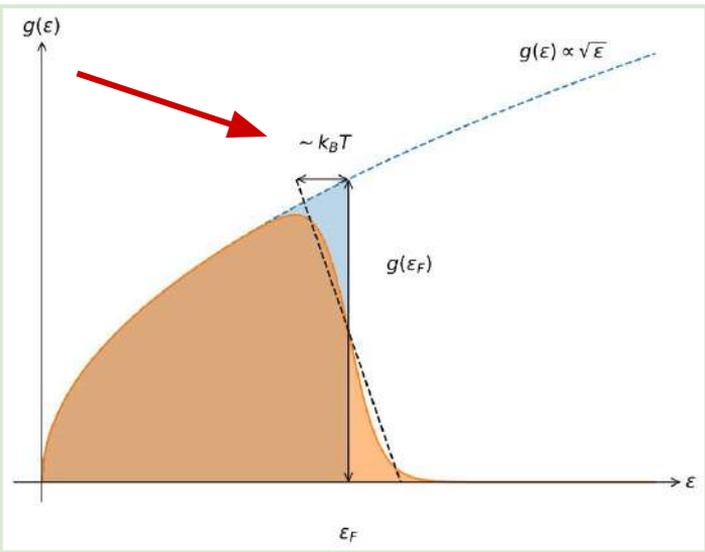
$$E(T) - E(0) = N_{\text{exc}} k_B T \approx g(\epsilon_F) k_B^2 T^2.$$

$$C_{V,e} = \frac{dE}{dT} \approx 2g(\epsilon_F) k_B^2 T = \dots = 3N k_B \frac{T}{T_F} \propto T,$$

$$N = \frac{2}{3} \epsilon_F g(\epsilon_F) \quad T_F = \frac{\epsilon_F}{k_B}$$

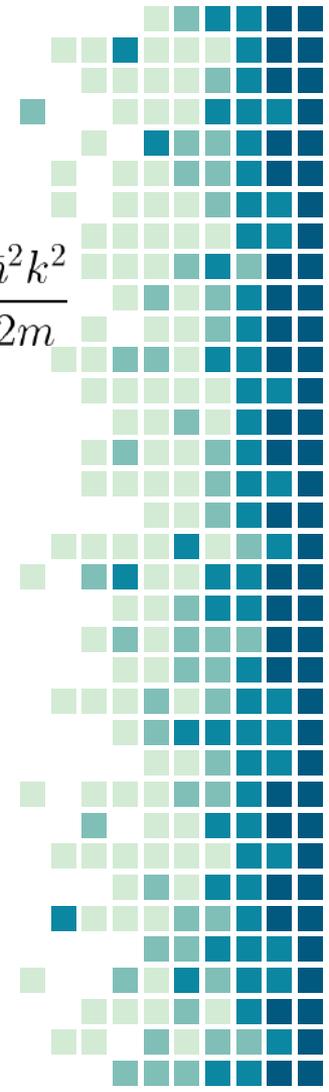
Q: How does $C_{V,e}$ relate to the phonon contribution $C_{V,p}$?

- At room temperature, $C_{V,p} = 3N k_B \gg C_{V,e}$
- Near $T = 0$, $C_{V,p} \propto T^3$ and $C_{V,e} \propto T \rightarrow$ competition.

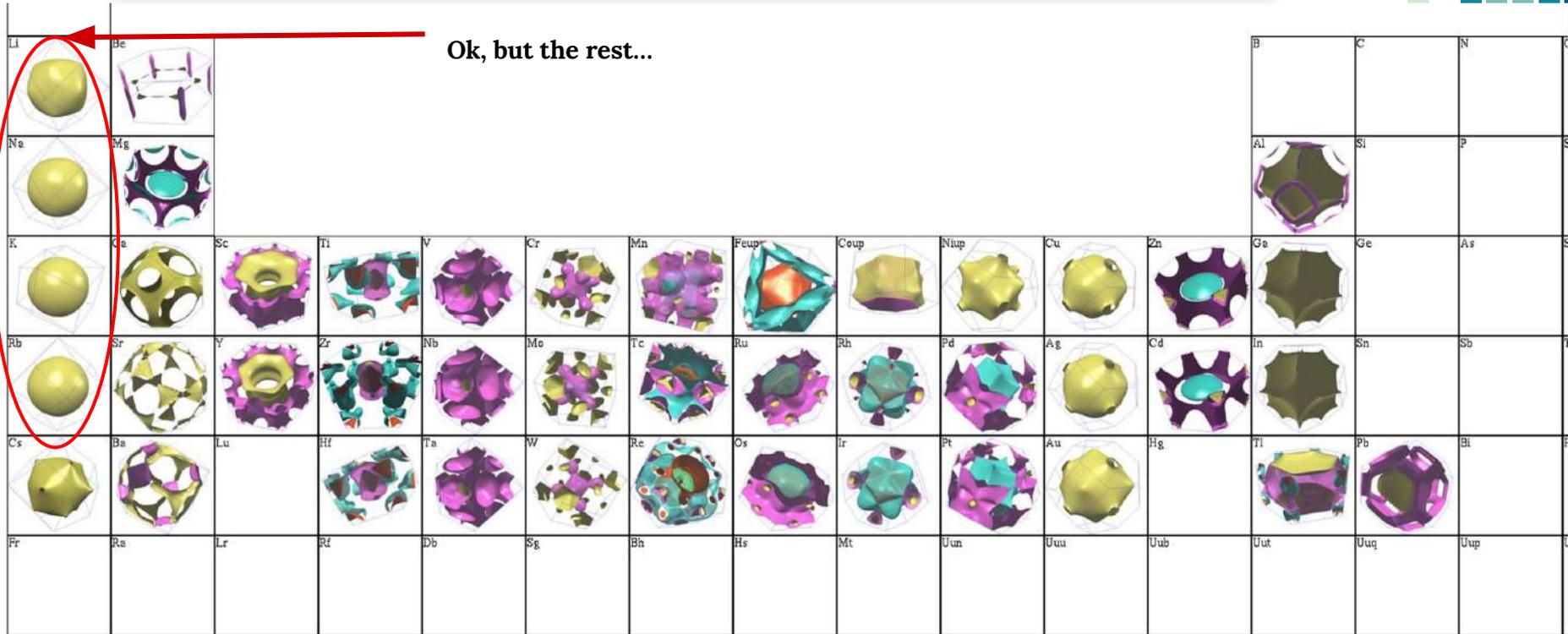


Wrapping up of Sommerfeld free-electron model

1. The Sommerfeld free electron model treats electrons as waves with dispersion $\varepsilon = \frac{\hbar^2 k^2}{2m}$
2. The density of states (DOS) can be derived from the dispersion relation. This procedure is general, and analogous to e.g. that for phonons.
3. The Fermi-Dirac distribution describes the probability an electron state is occupied.
4. The free-electron heat capacity is linear with T.
5. The scaling of heat capacity with T can be derived quickly by estimating the nr of particles in an energy range $\mathbf{k}_B T$, using the DOS.



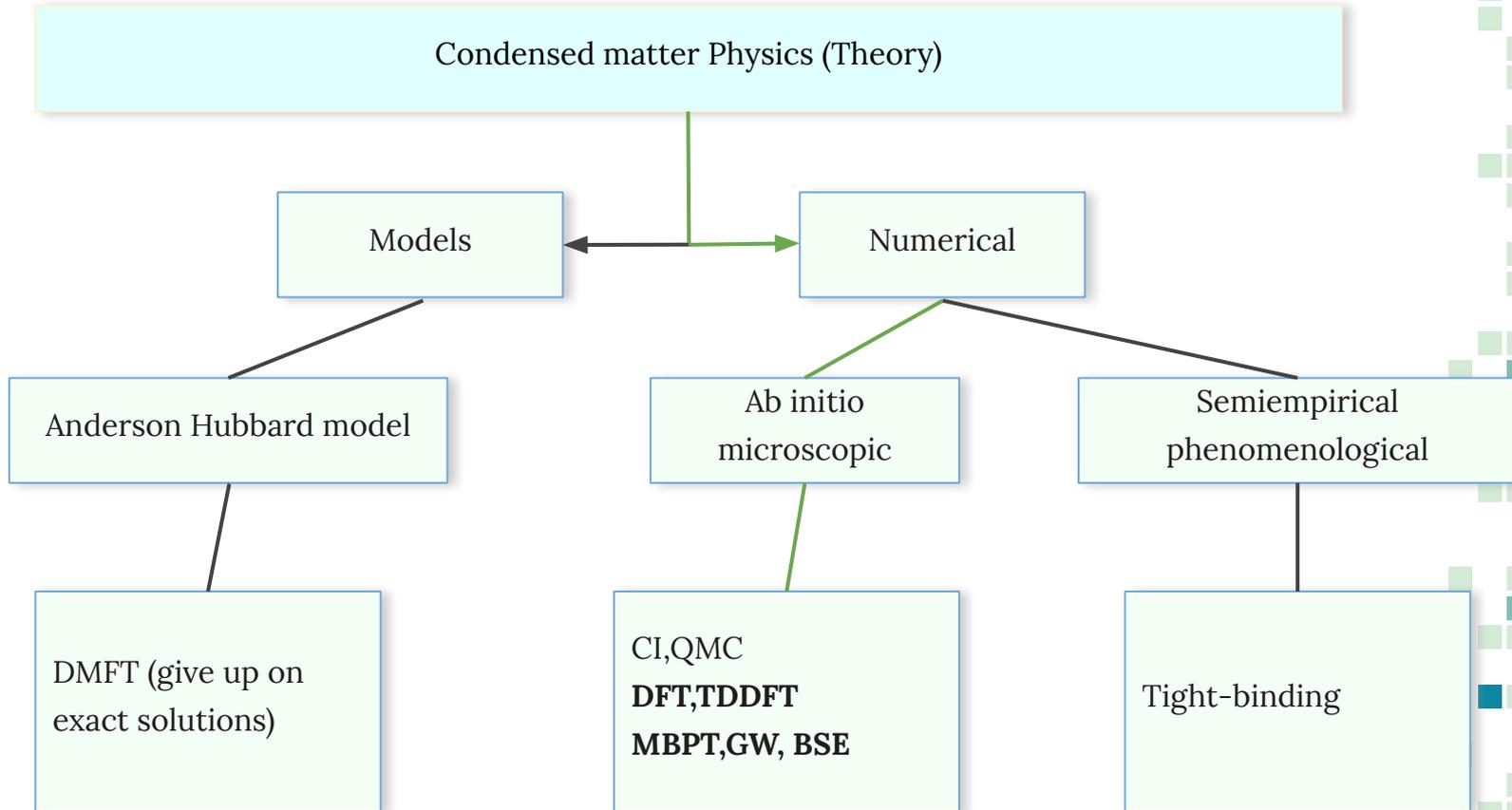
Periodic table of Fermi surface of elemental metals (Kohn-Sham DFT)



1. T.-S. Choy, J. Naset, J. Chen, S. Hershfield, and C. Stanton. A database of fermi surface in virtual reality modeling language (vrml). *Bulletin of The American Physical Society*, 45(1):L36-42, 2000.

Interlude of transitory topics. I want to spice it up a bit.

CMP is essential, and we need more **bright students** coming to contribute to this field.



Everything is described by the Schrödinger equation:

$$H\psi = E\psi,$$

with H the sum of kinetic energy and Coulomb interaction, so for hydrogen we have:

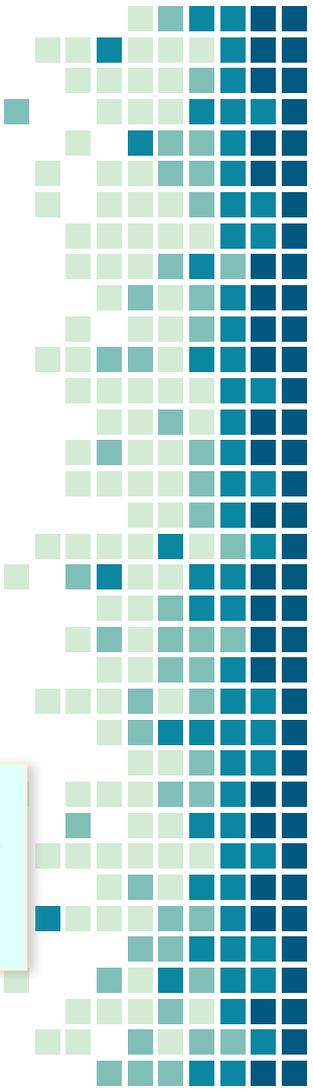
$$\psi(\mathbf{r}) \quad H = -\hbar^2 \frac{\partial^2}{2m\partial\mathbf{r}^2} - \frac{e^2}{4\pi\epsilon_0|r|}$$

So for helium we have: $\psi(\mathbf{r}_1, \mathbf{r}_2)$

$$H = -\hbar^2 \frac{\partial^2}{2m\partial\mathbf{r}_1^2} - \hbar^2 \frac{\partial^2}{2m\partial\mathbf{r}_2^2} - \frac{2e^2}{4\pi\epsilon_0|r_1|} - \frac{2e^2}{4\pi\epsilon_0|r_2|} + \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|},$$

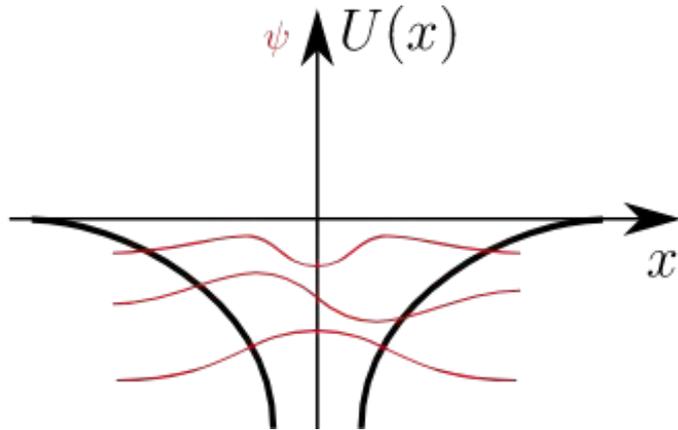
which means we need to find eigenvalues and eigenvectors of a 6-dimensional differential equation!

Cu has 29 electrons, so to find the electronic spectrum of Copper we would need to solve an **87-dimensional** Schrödinger equation, and there is no way in the world we can do so!



This exponential growth in complexity with the number of interacting quantum particles is why many-body quantum physics is very much an open area in solid state physics.

However we need to focus on what is possible to do, and apply heuristic rules based on the accumulated knowledge of how atoms work (hence we will need a bit of chemistry). We need to accept empirical observations as chemical laws even though they work with limited precision, and are "merely" consequences of the Schrödinger equation.



Single electron states have 4 quantum numbers: $|n, l, l_z, s\rangle$

Quantum numbers:

- $n = 1, 2, \dots$ is the azimuthal (principal) quantum number
- $l = 0, 1, \dots, n - 1$ is the angular momentum (also known as s, p, d, f orbitals)
- $l_z = -l, -l + 1, \dots, l$ is the z -component of angular momentum
- s is the spin

It turns out that electrons in all atoms approximately occupy very similar orbitals, only the energies are very different due to the Coulomb interaction. The order of orbital filling is set by several rules:

- **Aufbau principle:** *first fill a complete shell (all electrons with the same n,l) before going to the next one*
- **Madelung's rule:** *first occupy the shells with the lowest $l+n$, and of those with equal $l+n$ those with smaller n*

Therefore shell-filling order is **1s, 2s, 2p, 3s, 3p, 4s, 3d, ...** The electrons in the outermost shell are the only ones participating in chemical reactions and electric conduction. The rest provides a negatively charged cloud that reduces the attraction to the atomic nucleus.

Covalent bonds and linear combination of atomic orbitals

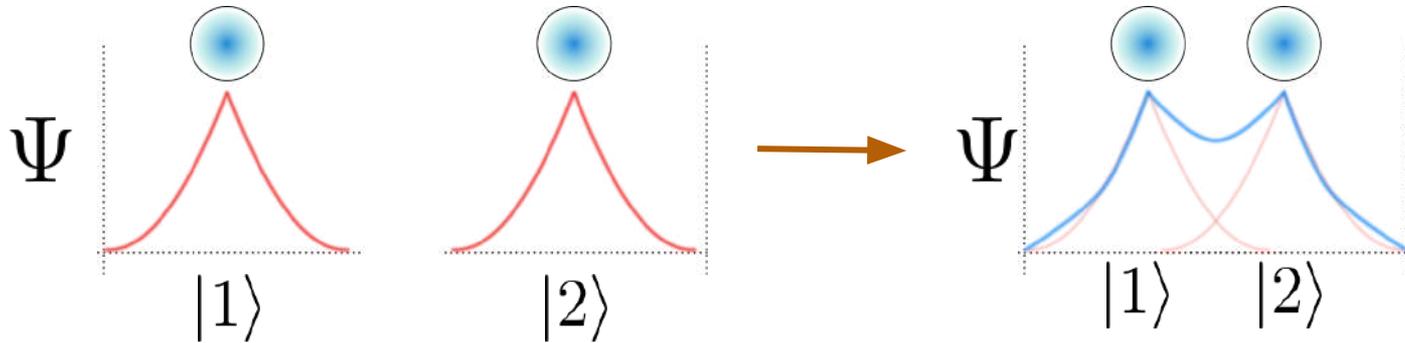
Consider two atoms next to each other.

Since different orbitals of an atom are separated in energy, we consider one orbital per atom (even though this is often a bad starting point and it should only work for **s-orbitals**).

Let's imagine that the atoms are sufficiently far apart, so that the shape of the orbitals or the energy of the orbitals doesn't change much.

Covalent bonds and linear combination of atomic orbitals

If $|1\rangle$ is the wave function of an electron bound to the first atom, and $|2\rangle$ is the wave function of the electron near the second atom, we will search for a solution in form: $|\psi\rangle = \phi_1|1\rangle + \phi_2|2\rangle$ or in other words LCAO.



$$E \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} = \begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix}$$

For simplicity let's assume now that $\langle \mathbf{1} | \mathbf{2} \rangle = 0$, so that ψ is normalized whenever $|\phi_1|^2 + |\phi_2|^2 = 1$

Acting with the Hamiltonian on the LCAO wave function we get an eigenvalue problem:

$$E \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} = \begin{pmatrix} \langle 1 | H | 1 \rangle & \langle 1 | H | 2 \rangle \\ \langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix}$$

It only depends on two parameters remaining of the original problem:

$\langle \mathbf{1} | \mathbf{H} | \mathbf{1} \rangle = \langle \mathbf{2} | \mathbf{H} | \mathbf{2} \rangle \equiv E_0$ is the **onsite energy**, $\langle \mathbf{1} | \mathbf{H} | \mathbf{2} \rangle \equiv -t$ is the **hopping integral** (or just **hopping**).

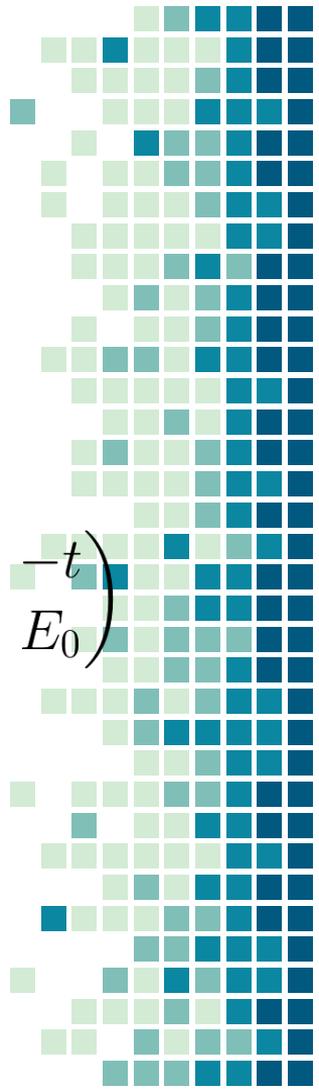
Since we are considering bound states, all orbitals $|\mathbf{n}\rangle$ are purely real $\Rightarrow t$ is real as well. $H = \begin{pmatrix} E_0 & -t \\ -t & E_0 \end{pmatrix}$

Eigenstates & eigenvalues:

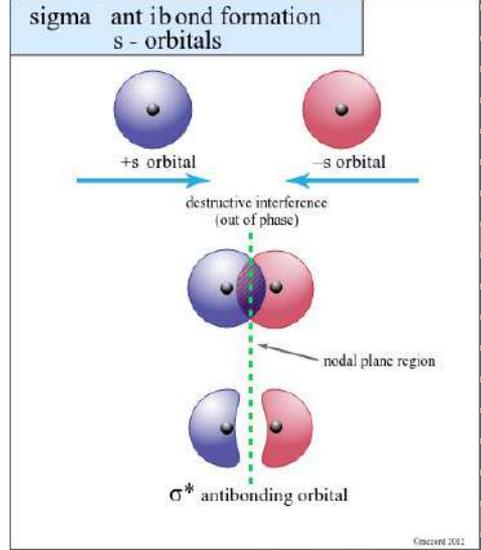
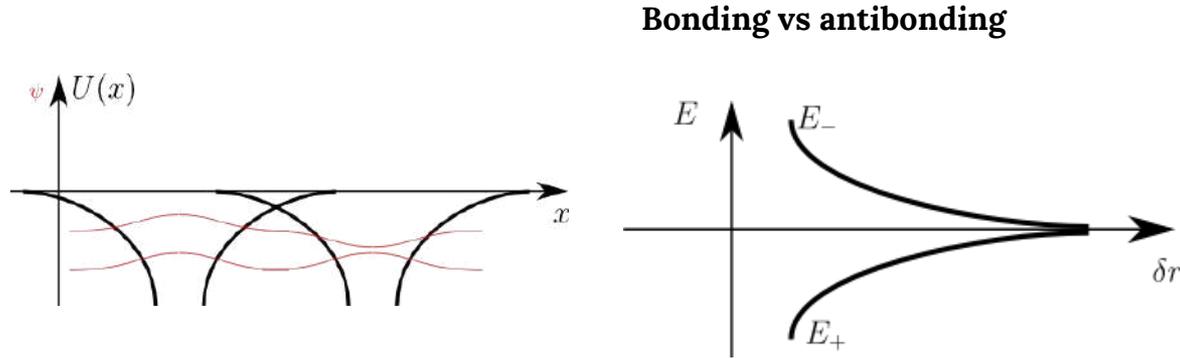
$$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \quad [\text{even/symmetric superposition with } E_+ = E_0 - t]$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) \quad [\text{odd/antisymmetric superposition with } E_- = E_0 + t]$$

Two atoms form a molecule, and ψ_+ and ψ_- are **molecular orbitals**.



An even superposition has a lower kinetic energy (derivative is smaller) \Rightarrow t is positive.



When $|+\rangle$ is occupied by an electron (or two, because there are two states with opposite spin), it makes the atoms attract (or *bond*) because the total energy is lowered. It is therefore called a **bonding orbital**.

An occupied $|-\rangle$ state increases the molecule energy as the atoms move closer \Rightarrow it makes atoms repel, and it is an **antibonding orbital**.

Therefore if each atom has a single electron in the outermost shell, these atoms attract, if there are 0 or 2 electrons, the net electron force cancels (but electrostatic repulsion remains).

Wrapping up LCAO method

1. Electrons in atoms occupy shells, with only the outermost shell contributing to interatomic interaction.
2. The LCAO method reduces the full Hamiltonian to a finite size problem written in the basis of individual orbitals.
3. If two atoms have one orbital and one atom each, electron movement makes the atoms attract.

→ Definition: The tight binding or linear combination of atomic orbitals (LCAO) method is a semi-empirical method that is primarily used to calculate the band structure and **single-particle Bloch states of a material**. The semi-empirical tight binding method is simple and computationally very fast. It therefore tends to be used in calculations of very large systems, with more than around a few thousand atoms in the unit cell.

Nearly free electron model

In free electron model

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

- There is only **one band**
- The band structure **is not periodic in k-space**
- In other words the **BZ** is infinite in **momentum space**

Within the **nearly free electron model** we want to start from the dispersion relation of the free electrons and consider the effect of introducing a weak lattice potential. **Think of it as: *very similar to getting optical and acoustic phonon branches by changing atom masses (and therefore reducing the size of the Brillouin zone).***