Lecture Notes: Condensed Matter Theory I (TKM1)

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I. INTRODUCTION

Condensed matter physics is concerned with the behavior of large aggregates of atoms or molecules in liquid or solid form. It is one of the largest branches of physics, with a wide variety of different systems, approaches, challenges and concepts. Often, it is subdivided in soft condensed matter physics and hard condensed matter physics. While the transition between the two branches is gradual, one way to distinguish them is by the role of quantum mechanics for the elementary excitations of the systems. Soft condensed matter physics (the physics of polymers, liquid crystals, the statistical mechanics of bio-molecules etc.) is frequently termed "$\hbar = 0$"-physics, stressing that classical dynamics suffices for an understanding of the motion and aggregation of these systems. In distinction, for hard condensed matter physics, i.e. "$\hbar = 1$"-physics, the motion of electrons, lattice vibrations etc. is determined by Schrödinger's equation.

Physics is a basic science and its ultimate purpose is the accumulation of new knowledge. In addition, condensed matter physics is closely connected to materials science as well as mechanical, chemical, and electric engineering that focus on the design of novel materials and devices, ranging from better batteries, thermoelectric devices for waste heat conversion to superconductors, magnets, all the way to better agents in drug delivery. This applied aspect of condensed matter physics is exciting and important. Still, we should not forget that the field also contributes to the accumulation of fundamental knowledge and to major philosophical issues of our times. The value of Planck's quantum, $\hbar$, or of the electron charge, e, are defined via solid state effects in semiconductors and metals (the quantum Hall effect and the Josephson effect). It is quite amazing that these fundamental constants of nature are not determined in an experiment at a particle accelerator but rather in a solid state laboratory. Other frequently cited examples about the fundamental importance of condensed matter physics are that the famous Higgs particle was first proposed in the context of superconducting phase transitions, that asymptotic freedom (important for our current understanding of hadronization of quarks) occurs in case of the Kondo effect of a magnetic impurity in a metal, that fractional charges emerge naturally in the context of the fractional Quantum Hall effect etc. etc. The beauty of condensed matter physics is that it combines hands-on applications with the development of fundamentally new concepts, often even in the same material!

Lets discuss one epistemological issue that is heavily debated these days: Particle and string theorists search to find a better way to formulate the fundamental laws of physics. This is very exciting research. But suppose for a moment, we knew the fundamental "theory of everything" (TOE). Does this mean that the physics would stop existing as a basic science? Well, in condensed matter physics we have a TOE since 1927, yet major discoveries continue to take place. The TOE of condensed matter physics is the many particle Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi \tag{1}$$

with Hamiltonian

$$H = T_e + T_i + V_{ee} + V_{ii} + V_{ei} \tag{2}$$

with individual terms:

$$\begin{aligned} T_e &= -\sum_{j=1}^{N_e}\frac{\hbar^2}{2m}\nabla_j^2 \quad \text{and} \quad T_i = -\sum_{l=1}^{N_i}\frac{\hbar^2}{2M_l}\nabla_l^2 \\ V_{ee} &= \sum_{j,j'=1}^{N_e}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} \text{ and } V_{ii} = \sum_{l,l'=1}^{N_i}\frac{e^2 Z_l Z_{l'}}{|\mathbf{R}_l - \mathbf{R}_{l'}|} \\ V_{ei} &= -\sum_{j,l=1}^{N_e,N_i}\frac{e^2 Z_l}{|\mathbf{r}_j - \mathbf{R}_l|}. \end{aligned} \tag{3}$$

Here $\mathbf{r}_j$ ($\mathbf{R}_l$) refers to the coordinates of the N_e (N_i) electrons (nuclei) with mass m (M_l). Z_l is the corresponding nuclear charge. The wave function depends in first quantization on all coordinates

$$\Psi\left(\mathbf{r}_1, \cdots, \mathbf{r}_{N_e}, \mathbf{R}_1, \cdots, \mathbf{R}_{N_i}\right) = \Psi\left(\{\mathbf{r}_j\}, \{\mathbf{R}_l\}\right). \tag{4}$$

With the exception of radiation effects and spin-orbit interaction (both can easily be included into the formalism) can all phenomena of condensed matter physics be described by this Hamiltonian and the corresponding equation of motion. At least there is no experiment (or Gedankenexperiment) that is in conflict with this assertion. Thus, the "theory of everything" of condensed matter physics is well known and established. It would however be foolish to believe that phenomena like superconductivity, the fractional quantum Hall effect, electron localization etc. could be derived from Eqs.1,2. Instead a combination of experimental ingenuity, symmetry based reasoning, and a clever analysis of the relevant time and length scales of a given problem (formalized in terms of the renormalization group theory) ultimately allows for such conclusions and lead to conceptually new insights. The message

is that the knowledge of a fundamental "theory of everything" has very little bearing on the fascinating possibilities that emerge when many particles interact with each other and organize into new states of matter. There is no reason, other than habit and accepted custom, to believe that the situation is much different in other areas of physics, such as particle physics or quantum gravity. These issues have been lucidly discussed by by Phillip W. Anderson, Science **177**, 393–396 (1972) and, more recently, by Robert B. Laughlin and David Pines (Proceedings of the National Academy of Sciences **97**, 28-31 (2000).

II. QUANTUM THEORY OF SOLIDS

A. The Born-Oppenheimer approximation

We start our analysis of Eqs.1,2. Great progress in our understanding can be made if one recognizes that the two kinetic energy parts of the Hamiltonian are very different. The ratio of the masses of the electrons and nuclei is small.

$$m/M_l \simeq 10^{-3}/Z_l \ll 1. \tag{5}$$

Thus, the motion of the nuclei is much slower compared to that of the electron and we can decouple their dynamics. This decoupling goes back to Max Born and Robert Oppenheimner (1927). One assumes that on the time scale of the electrons the nuclei are frozen. To this end we assume that the positions of the nuclei are fixed and play for the electronic wave function,

$$\psi\left(\mathbf{r}_1, \cdots, \mathbf{r}_{N_e}; \mathbf{R}_1, \cdots, \mathbf{R}_{N_i}\right) = \psi\left(\{\mathbf{r}_j\}; \{\mathbf{R}_l\}\right) \tag{6}$$

solely the role of given parameters. This leads to the simplified Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi = H_{\rm el}\psi \tag{7}$$

with electronic Hamiltonian

$$H_{\rm el} = T_e + V_{ee} + V_{ei}. \tag{8}$$

From the perspective of the electrons the electron-ion Coulomb interaction plays a role of an "external" potential:

$$V_{ei} = \sum_{j=1}^{N_e} U\left(\mathbf{r}_j\right) \tag{9}$$

where $U(\mathbf{r}_j)$ is the single particle potential that originates from the nuclei:

$$U(\mathbf{r}_j) = -\sum_{l=1}^{N_i} \frac{e^2 Z_l}{|\mathbf{r}_j - \mathbf{R}_l|}. \tag{10}$$

The time independent Schrödinger equation

$$H_{\rm el}\psi_n = E_{{\rm el},n}\psi_n \tag{11}$$

determines the eigenvalues of the electronic system that depend parametrically on the ion positions

$$E_{{\rm el},n} = E_{{\rm el},n}(\mathbf{R}_1, \cdots, \mathbf{R}_{N_i}). \tag{12}$$

Next we check whether this approximate treatment is indeed appropriate for $m/M_l \ll 1$. We use the fact that, no matter whether our decoupling is correct or not, the ψ_n form a complete set of states for the electronic variables. This allows to expand the full wave function

$$\Psi(\{\mathbf{r}_j\}, \{\mathbf{R}_l\}) = \sum_n \psi_n(\{\mathbf{r}_j\}; \{\mathbf{R}_l\})\, \Phi_n(\{\mathbf{R}_l\}) \tag{13}$$

Formally, the $\Phi_n(\{\mathbf{R}_l\})$ are the coefficients of this expansion into a complete set of states. Physically, they correspond to the amplitude of the ions to be found at positions $\{\mathbf{R}_l\}$ if the electrons are in the state ψ_n. We insert this ansatz into the full Schrödinger equation

$$\begin{aligned} H\Psi &= (T_e + T_i + V_{ee} + V_{ii} + V_{ei}) \sum_n \psi_n \Phi_n \\ &= \sum_n (T_e + T_i + V_{ee} + V_{ii} + V_{ei})\, \psi_n \Phi_n \\ &= \sum_n (E_{{\rm el},n} + T_i + V_{ii})\, \psi_n \Phi_n \end{aligned} \tag{14}$$

It holds immediately:

$$V_{ii}\psi_n\Phi_n = \psi_n V_{ii}\Phi_n. \tag{15}$$

In addition we have

$$\begin{aligned} T_i\psi_n\Phi_n &= -\sum_{l=1}^{N_i} \frac{\hbar^2}{2M_l}\nabla_l^2\psi_n\Phi_n \\ &= -\sum_{l=1}^{N_i} \frac{\hbar^2}{2M_l}\, \nabla_l\left((\nabla_l\psi_n)\,\Phi_n + \psi_n\nabla_l\Phi_n\right) \\ &= -\sum_{l=1}^{N_i} \frac{\hbar^2}{2M_l}\, \left(\left(\nabla_l^2\psi_n\right)\Phi_n + 2\,(\nabla_l\psi_n)\,\nabla_l\Phi_n + \psi_n\nabla_l^2\Phi_n\right) \end{aligned} \tag{16}$$

Suppose we are allowed to ignore the first two terms. Then follows:

$$\left(E_{\mathrm{el},n} + T_i + V_{ii}\right) \psi_n \Phi_n \simeq \psi_n \left(E_{\mathrm{el},n} + T_i + V_{ii}\right) \Phi_n. \tag{17}$$

Thus, after the solution of the electronic problem is accomplished, we have to solve the purely ionic Schrödinger equation

$$\left(T_i + V_{ii}^{eff}\right) \Phi_n = \mathcal{E} \Phi_n \tag{18}$$

with effective ion-ion interaction $V_{ii}^{eff} = V_{ii} + E_{\mathrm{el},n}$. This determines the ionic wave function and finally the total energy eigenvalue $\mathcal{E}$. A coupled problem of ions and electrons is therefore simplified into two separate problems of the two subsystems.

To justify this approach it must obviously hold that the two terms

$$-\frac{\hbar^2}{2M_l} \left(\left(\nabla_l^2 \psi_n\right) \Phi_n + 2 \left(\nabla_l \psi_n\right) \nabla_l \Phi_n\right) \tag{19}$$

are negligible compared to $\frac{\hbar^2}{2M_l}\, \psi_n \nabla_l^2 \Phi_n$. This must be checked a posteriori, after the wave functions ψ_n and Φ_n are determined. At this point it is a little bit to early to do this analysis. As the course proceeds, we will be able to perform this calculation and we will find:

$$\begin{aligned}
\frac{\hbar^2}{2M}\, \psi_n \nabla_l^2 \Phi_n &\simeq \left(\frac{m}{M}\right)^{1/2} \varepsilon_F \psi_n \Phi_n, \\
\frac{\hbar^2}{M}\, \left(\nabla_l \psi_n\right) \nabla_l \Phi_n &\simeq \left(\frac{m}{M}\right)^{3/4} \varepsilon_F \psi_n \Phi_n, \\
\frac{\hbar^2}{2M_l}\, \left(\nabla_l^2 \psi_n\right) \Phi_n &\simeq \frac{m}{M} \varepsilon_F \psi_n \Phi_n,
\end{aligned} \tag{20}$$

For $m/M \ll 1$ follows that terms that contain a derivative $\nabla_l \psi_n$ can be neglected relative to the leading term $\frac{\hbar^2}{2M}\, \psi_n \nabla_l^2 \Phi_n$.

We conclude, that the Born-Oppenheimer approximation, valid in the limit $m/M \ll 1$, justifies the investigation of a purely electronic Hamiltonian

$$H_{\mathrm{el}} = -\sum_{j=1}^{N_e} \frac{\hbar^2}{2m} \nabla_j^2 + \sum_{j=1}^{N_e} U\left(\mathbf{r}_j\right) + \sum_{j,j'=1}^{N_e} \frac{e^2}{\left|\mathbf{r}_j - \mathbf{r}_{j'}\right|}. \tag{21}$$

Still, the problem is only defined if we know the positions of the nuclei. In case of crystalline solids, where the nuclei are arranged on a periodic lattice, the potential $U\left(\mathbf{r}\right)$ is periodic with respect to the discrete translations of the crystal, which simplifies this aspect of the problem significantly.

After we established $H_{\rm el}$ as effective theory of the electronic system only, we study the impact of the potential $U(\mathbf{r})$ in case of periodic lattices. To this end we first ignore the electron-electron interaction $e^2 |\mathbf{r}_j - \mathbf{r}_{j'}|^{-1}$. This seems at first glance a foolish thing to do, as the Coulomb interaction between electrons is neither small nor irrelevant. At this point we make this assumption without further justification and come back to it later. We will see that there are numerous situation where the behavior of the electrons is effectively described by non-interacting fermions, while in other cases (quasi-one dimensional systems, systems where plasma excitations of the electrons matter, systems that order magnetically etc.) the neglect of the Coulomb interaction cannot be justified.

Once electrons are noninteracting the Hamiltonian is a sum over single particle Hamiltonians

$$H_{\rm el} = \sum_{j=1}^{N_e} \mathcal{H}(\mathbf{p}_j, \mathbf{r}_j)$$

with

$$\mathcal{H}(\mathbf{p}, \mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 \ + U(\mathbf{r}).$$

Since we assumed that the electrons are non-interacting, their thermodynamic behavior is that of an ideal Fermi gas. The remaining task, needed to analyze this Fermi gas, is to determine the single particle eigenfunctions $\varphi_n(\mathbf{r})$ and the corresponding eigenvalues ε_n of $\mathcal{H}$. Before we discuss these issues we repeat the statistical mechanics of quantum gases and the formalism of second quantization.

III. QUANTUM STATISTIC OF IDEA GASES

We consider consequences of indistinguishability in quantum statistics. The quantity of interest in statistical mechanics is the partition function

$$Z = \mathrm{tr} e^{\beta H} = \sum_{\alpha} \exp(-\beta E_\alpha) \tag{22}$$

where the sum is over all many body states $|\alpha\rangle$ with energy E_α and $\beta = \frac{1}{k_B T}$. Once we know Z we can determine all thermodynamic quantities of a given equilibrium system. For example, the Boltzmann probability

$$p_\alpha = \frac{1}{Z}\exp(-\beta E_\alpha)$$

is normalized ($\sum_\alpha p_\alpha = 1$) because of the denominator Z. The mean energy is

$$\begin{aligned} U &= \langle H \rangle = \sum_\alpha E_\alpha p_\alpha = \frac{1}{Z} \sum_\alpha E_\alpha e^{-\beta E_\alpha} \\ &= -\frac{\partial}{\partial \beta} \log Z \end{aligned} \tag{23}$$

For the entropy holds

$$\begin{aligned} S &= -k_B \sum_\alpha p_\alpha \log p_\alpha = -\frac{k_B}{Z} \sum_\alpha e^{-\beta E_\alpha} \left(-\beta E_\alpha - \log Z\right) \\ &= \frac{1}{T} U + k_B \log Z \end{aligned} \tag{24}$$

From thermodynamics we know that $F = U - TS$ is the free energy. Thus, it follows:

$$F\left(T, V, N\right) = -k_B T \log Z. \tag{25}$$

In some situations one can also include variable particle numbers and one has to obtain the grand canonical partition function

$$Z_g = \mathrm{tr} e^{\beta H} = \sum_\alpha \exp\left(-\beta \left(E_\alpha - \mu N_\alpha\right)\right) \tag{26}$$

where N_α is the number of particles in the state $|\alpha\rangle$. In this gas holds for the grand potential (or Gibbs free energy)

$$\Omega\left(T, V, \mu\right) = -k_{\mathrm{B}} T \log Z_g. \tag{27}$$

and the mean particle number is

$$\langle N \rangle = \frac{1}{Z_g} \sum_\alpha N_\alpha \exp\left(-\beta \left(E_\alpha - \mu N_\alpha\right)\right) = -\frac{\partial \Omega}{\partial \mu}. \tag{28}$$

For indistinguishable particles it would be necessary to introduce the symmetrized or antisymmetrized states in order to perform the above sum, which is technically very complicated. A way out of this situation is the so called second quantization, which simply respects the fact that labeling particles was a stupid thing to begin with and that one should characterize a quantum many particle system differently. If the label of a particle has no meaning, a quantum state is completely determined if one knows which states of the system are occupied by particles and which not. The states of an ideal quantum gas are obviously the momenta since the momentum operator

$$\widehat{\mathbf{p}}_l = \frac{\hbar}{i} \nabla_l \tag{29}$$

commutes with the Hamiltonian of an ideal quantum system

$$H = \sum_{l=1}^{N} \frac{\widehat{\mathbf{p}}_l^2}{2m}. \tag{30}$$

In case of interacting systems the set of allowed momenta do not form the eigenstates of the system, but at least a complete basis the eigenstates can be expressed in. Thus, we characterize a quantum state by the set of numbers

$$n_1, n_2, ...n_M \tag{31}$$

which determine how many particles occupy a given quantum state with momentum p_1, p_2, $...p_M$. In a one dimensional system of size L those momentum states are

$$p_l = \frac{\hbar 2\pi l}{L} \tag{32}$$

which guarantee a periodic wave function. For a three dimensional system we have

$$\mathbf{p}_{l_x,l_y,l_z} = \frac{\hbar 2\pi \left(l_x \mathbf{e}_x + l_y \mathbf{e}_y + l_z \mathbf{e}_z\right)}{L}. \tag{33}$$

A convenient way to label the occupation numbers is therefore $n_{\mathbf{p}}$ which determined the occupation of particles with momentum eigenvalue $\mathbf{p}$. Obviously, the total number of particles is:

$$N = \sum_{\mathbf{p}} n_{\mathbf{p}} \tag{34}$$

whereas the energy of the system is

$$E = \sum_{\mathbf{p}} n_{\mathbf{p}} \varepsilon\left(\mathbf{p}\right) \tag{35}$$

If we now perform the summation over all states we can just write

$$Z = \sum_{\{n_{\mathbf{p}}\}} \exp\left(-\beta \sum_{\mathbf{p}} n_{\mathbf{p}} \varepsilon\left(\mathbf{p}\right)\right) \delta_{N,\sum_{\mathbf{p}} n_{\mathbf{p}}} \tag{36}$$

where the Kronecker symbol $\delta_{N,\sum_{\mathbf{p}} n_{\mathbf{p}}}$ensures that only configurations with correct particle number are taken into account.

Returning to our earlier problem of noninteracting quantum gases we therefore find

$$Z_g = \sum_{\{n_{\mathbf{p}}\}} \exp\left(-\beta \sum_{\mathbf{p}} n_{\mathbf{p}} \left(\varepsilon\left(\mathbf{p}\right) - \mu\right)\right) \tag{37}$$

for the grand partition function. This can be rewritten as

$$Z_g = \sum_{n_{\mathbf{p}1}} \sum_{n_{\mathbf{p}2}} ... \prod_{\mathbf{p}} e^{-\beta n_{\mathbf{p}}(\varepsilon(\mathbf{p})-\mu)} = \prod_{\mathbf{p}} \sum_{n_{\mathbf{p}}} e^{-\beta n_{\mathbf{p}}(\varepsilon(\mathbf{p})-\mu)} \tag{38}$$

Fermions: In case of fermions $n_{\mathbf{p}} = 0, 1$ such that

$$Z_{g\mathrm{FD}} = \prod_{\mathbf{p}} \left(1 + e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right) \tag{39}$$

which gives (FD stands for Fermi-Dirac)

$$\Omega_{\mathrm{FD}} = -k_{\mathrm{B}}T \sum_{\mathbf{p}} \log\left(1 + e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right) \tag{40}$$

Bosons: In case of bosons $n_{\mathbf{p}}$ can take any value from zero to infinity and we obtain

$$\sum_{n_{\mathbf{p}}} e^{-\beta n_{\mathbf{p}}(\varepsilon(\mathbf{p})-\mu)} = \sum_{n_{\mathbf{p}}} \left(e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right)^{n_{\mathbf{p}}} = \frac{1}{1 - e^{-\beta(\varepsilon(\mathbf{p})-\mu)}} \tag{41}$$

which gives (BE stands for Bose-Einstein)

$$Z_{g\mathrm{BE}} = \prod_{\mathbf{p}} \left(1 - e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right)^{-1} \tag{42}$$

as well as

$$\Omega_{\mathrm{BE}} = k_{\mathrm{B}}T \sum_{\mathbf{p}} \log\left(1 - e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right). \tag{43}$$

A. Analysis of the ideal fermi gas

We start from

$$\Omega = -k_{\mathrm{B}}T \sum_{\mathbf{p}} \log\left(1 + e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right) \tag{44}$$

which gives

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_{\mathbf{p}} \frac{e^{-\beta(\varepsilon(\mathbf{p})-\mu)}}{1 + e^{-\beta(\varepsilon(\mathbf{p})-\mu)}} = \sum_{\mathbf{p}} \frac{1}{e^{\beta(\varepsilon(\mathbf{p})-\mu)} + 1} = \sum_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle \tag{45}$$

i.e. we obtain the averaged occupation number of a given quantum state

$$\langle n_{\mathbf{p}} \rangle = \frac{1}{e^{\beta(\varepsilon(\mathbf{p})-\mu)} + 1} \tag{46}$$

Often one uses the symbol $f\left(\varepsilon\left(\mathbf{p}\right) - \mu\right) = \langle n_{\mathbf{p}} \rangle$. The function

$$f\left(\omega\right) = \frac{1}{e^{\beta\omega} + 1} \tag{47}$$

is called Fermi distribution function. For $T = 0$ this simplifies to

$$\langle n_{\mathbf{p}} \rangle = \begin{cases} 1 & \varepsilon(\mathbf{p}) < \mu \\ 0 & \varepsilon(\mathbf{p}) > \mu \end{cases} \tag{48}$$

States below the energy μ are singly occupied (due to Pauli principle) and states above μ are empty. $\mu(T = 0) = E_{\mathrm{F}}$ is also called the Fermi energy.

In many cases will we have to do sums of the type

$$I = \sum_{\mathbf{p}} f(\varepsilon(\mathbf{p})) = \frac{V}{h^3} \int d^3 p f(\varepsilon(\mathbf{p})) \tag{49}$$

these three dimensional integrals can be simplified by introducing the density of states

$$\rho(\omega) = V \int \frac{d^3 p}{h^3} \delta(\omega - \varepsilon(\mathbf{p})) \tag{50}$$

such that

$$I = \int d\omega \rho(\omega) f(\omega) \tag{51}$$

We can determine $\rho(\omega)$ by simply performing a substitution of variables $\omega = \varepsilon(p)$ if $\varepsilon(\mathbf{p}) = \varepsilon(p)$ only depends on the magnitude $|\mathbf{p}| = p$ of the momentum

$$I = \frac{V 4\pi}{h^3} \int p^2 dp f(\varepsilon(p)) = \frac{V 4\pi}{h^3} \int d\omega \frac{dp}{d\omega} p^2(\omega) f(\omega) \tag{52}$$

such that

$$\rho(\omega) = V \frac{4\pi m}{h^3} \sqrt{2m\omega} = V A_0 \sqrt{\omega} \tag{53}$$

with $A_0 = \frac{4\pi}{h^3} \sqrt{2} m^{3/2}$. Often it is more useful to work with the density of states per particle

$$\rho_0(\omega) = \frac{\rho(\omega)}{\langle N \rangle} = \frac{V}{\langle N \rangle} A_0 \sqrt{\omega}. \tag{54}$$

We use this approach to determine the chemical potential as function of $\langle N \rangle$ for $T = 0$.

$$\langle N \rangle = \langle N \rangle \int \rho_0(\omega) n(\omega) d\omega = \langle N \rangle \int_0^{E_{\mathrm{F}}} \rho_0(\omega) d\omega = V A_0 \int_0^{E_{\mathrm{F}}} \omega^{1/2} d\omega = V \frac{2}{3} A_0 E_{\mathrm{F}}^{3/2} \tag{55}$$

which gives

$$E_{\mathrm{F}} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 \langle N \rangle}{V} \right)^{2/3} \tag{56}$$

If $V = d^3 N$ it holds that $E_{\mathrm{F}} \sim \frac{\hbar^2}{2m} d^{-2}$. Furthermore it holds that

$$\rho_0(E_F) = \frac{V}{\langle N \rangle} \frac{2m}{4\pi^2 \hbar^2} \left(\frac{6\pi^2 \langle N \rangle}{V} \right)^{1/3} = \frac{3}{2} \frac{1}{E_{\mathrm{F}}} \tag{57}$$

Equally we can analyze the internal energy

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\log Z_g = -\frac{\partial}{\partial\beta}\sum_{\mathbf{p}}\log\left(1+e^{-\beta(\varepsilon(\mathbf{p})-\mu)}\right) \\ &= \sum_{\mathbf{p}}\frac{\varepsilon\left(\mathbf{p}\right)}{e^{\beta(\varepsilon(\mathbf{p})-\mu)}+1} \end{aligned} \tag{58}$$

such that

$$U=\sum_{\mathbf{p}}\varepsilon\left(\mathbf{p}\right)\left\langle n_{\mathbf{p}}\right\rangle=\int\rho\left(\omega\right)\omega n\left(\omega-\mu\right)d\omega=\frac{3}{5}\left\langle N\right\rangle E_{\mathrm{F}} \tag{59}$$

At finite temperatures, the evaluation of the integrals is a bit more subtle. The details, which are only technical, will be discussed in a separate handout. Here we will concentrate on qualitative results. At finite but small temperatures the Fermi function only changes in a regime $\pm k_{\mathrm{B}}T$ around the Fermi energy. In case of metals for example the Fermi energy with $d\simeq 1-10\mathring{A}$ leads to $E_{\mathrm{F}}\simeq 1...10\mathrm{eV}$ i.e. $E_F/k_{\mathrm{B}}\simeq 10^4...10^5\mathrm{K}$ which is huge compared to room temperature. Thus, metals are essentially always in the quantum regime whereas low density systems like doped semiconductors behave more classically.

If we want to estimate the change in internal energy at a small but finite temperature one can argue that there will only be changes of electrons close to the Fermi level. Their excitation energy is $\sim k_{\mathrm{B}}T$ whereas the relative number of excited states is only $\rho_0\left(E_F\right)k_{\mathrm{B}}T$. Due to $\rho_0\left(E_F\right)\sim\frac{1}{E_{\mathrm{F}}}$ it follows in metals $\rho_0\left(E_F\right)k_{\mathrm{B}}T\ll 1$. We therefore estimate

$$U\simeq\frac{3}{5}\left\langle N\right\rangle E_{\mathrm{F}}+\left\langle N\right\rangle\rho_0\left(E_F\right)\left(k_{\mathrm{B}}T\right)^2+... \tag{60}$$

at lowest temperature. This leads then to a specific heat at constant volume

$$c_V=\frac{C_V}{\left\langle N\right\rangle}=\frac{1}{\left\langle N\right\rangle}\frac{\partial U}{\partial T}\sim 2k_{\mathrm{B}}^2\rho_0\left(E_F\right)T=\gamma T \tag{61}$$

which is linear, with a coefficient determined by the density of states at the Fermi level. The correct result (see handout3 and homework 5) is

$$\gamma=\frac{\pi^2}{3}k_{\mathrm{B}}^2\rho_0\left(E_F\right) \tag{62}$$

which is almost identical to the one we found here. Note, this result does not depend on the specific form of the density of states and is much more general than the free electron case with a square root density of states.

Similarly one can analyze the magnetic susceptibility of a metal. Here the energy of the up ad down spins is different once a magnetic field is applied, such that a magnetization

$$\begin{aligned} M &= \mu_B \left(\langle N_\uparrow \rangle - \langle N_\downarrow \rangle \right) \\ &= \mu_B \langle N \rangle \left(\int_0^{E_\mathrm{F}} \rho_0 \left(\omega + \mu_B B \right) - \rho_0 \left(\omega - \mu_B B \right) \right) d\omega \end{aligned} \tag{63}$$

For small field we can expand $\rho_0 \left(\omega + \mu_B B \right) \simeq \rho_0 \left(\omega \right) + \frac{\partial \rho_0(\omega)}{\partial \omega} \mu_B B$ which gives

$$\begin{aligned} M &= 2\mu_B^2 \langle N \rangle B \int_0^{E_\mathrm{F}} \frac{\partial \rho_0 \left(\omega \right)}{\partial \omega} d\omega \\ &= 2\mu_B^2 \langle N \rangle B \rho_0 \left(E_F \right) \end{aligned} \tag{64}$$

This gives for the susceptibility

$$\chi = \frac{\partial M}{\partial B} = 2\mu_B^2 \langle N \rangle \rho_0 \left(E_F \right). \tag{65}$$

Thus, one can test the assumption to describe electrons in metals by considering the ratio of χ and C_V which are both proportional to the density of states at the Fermi level.

B. The ideal Bose gas

Even without calculation is it obvious that ideal Bose gases behave very differently at low temperatures. In case of Fermions, the Pauli principle enforced the occupation of all states up to the Fermi energy. Thus, even at $T = 0$ are states with rather high energy involved. The ground state of a Bose gas is clearly different. At $T = 0$ all bosons occupy the state with lowest energy, which is in our case $\mathbf{p} = \mathbf{0}$. An interesting question is then whether this macroscopic occupation of one single state remains at small but finite temperatures. Here, a macroscopic occupation of a single state implies

$$\lim_{\langle N \rangle \to \infty} \frac{\langle n_\mathbf{p} \rangle}{\langle N \rangle} > 0. \tag{66}$$

We start from the partition function

$$\Omega_\mathrm{BE} = k_\mathrm{B} T \sum_\mathbf{p} \log \left(1 - e^{-\beta(\varepsilon(\mathbf{p}) - \mu)} \right) \tag{67}$$

which gives for the particle number

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_\mathbf{p} \frac{1}{e^{\beta(\varepsilon(\mathbf{p}) - \mu)} - 1}. \tag{68}$$

Thus, we obtain the averaged occupation of a given state

$$\langle n_{\mathbf{p}} \rangle = \frac{1}{e^{\beta(\varepsilon(\mathbf{p})-\mu)}-1}. \tag{69}$$

Remember that Eq.68 is an implicit equation to determine $\mu(\langle N \rangle)$. We rewrite this as

$$\langle N \rangle = \int d\omega \rho(\omega) \frac{1}{e^{\beta(\omega-\mu)}-1}. \tag{70}$$

The integral diverges if $\mu > 0$ since then for $\omega \simeq \mu$

$$\langle N \rangle \int d\omega \frac{\rho(\omega)}{\beta(\omega-\mu)} \to \infty \tag{71}$$

if $\rho(\mu) \neq 0$. Since $\rho(\omega) = 0$ if $\omega < 0$ it follows

$$\mu \leq 0. \tag{72}$$

The case $\mu = 0$ need special consideration. At least for $\rho(\omega) \sim \omega^{1/2}$, the above integral is convergent and we should not exclude $\mu = 0$.

Lets proceed by using

$$\rho(\omega) = V A_0 \sqrt{\omega} \tag{73}$$

with $A_0 = \frac{4\pi}{h^3}\sqrt{2}m^{3/2}$. Then follows

$$\begin{aligned} \frac{\langle N \rangle}{V} &= A_0 \int_0^\infty d\omega \frac{\sqrt{\omega}}{e^{\beta(\omega-\mu)}-1} \\ &< A_0 \int_0^\infty d\omega \frac{\sqrt{\omega}}{e^{\beta\omega}-1} \\ &= A_0 (k_B T)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{e^x - 1} \end{aligned} \tag{74}$$

It holds

$$\int_0^\infty dx \frac{x^{1/2}}{e^x-1} = \frac{\sqrt{\pi}}{2} \varsigma\left(\frac{3}{2}\right) \simeq 2.32 \tag{75}$$

We introduce

$$k_B T_0 = a_0 \frac{\hbar^2}{m} \left(\frac{\langle N \rangle}{V}\right)^{2/3} \tag{76}$$

with

$$a_0 = \frac{2\pi}{\varsigma\left(\frac{3}{2}\right)^{2/3}} \simeq 3.31. \tag{77}$$

The above inequality is then simply:

$$T_0 < T. \tag{78}$$

Our approach clearly is inconsistent for temperatures below T_0 (Note, except for prefactors, $k_B T_0$ is a similar energy scale than the Fermi energy in ideal fermi systems). Another way to write this is that

$$\langle N \rangle < \langle N \rangle \left(\frac{T}{T_0} \right)^{3/2}. \tag{79}$$

Note, the right hand side of this equation does not depend on $\langle N \rangle$. It reflects that we could not obtain all particle states below T_0.

The origin of this failure is just the macroscopic occupation of the state with $\mathbf{p} = \mathbf{0}$. It has zero energy but has been ignored in the density of states since $\rho(\omega = 0) = 0$. By introducing the density of states we assumed that no single state is relevant (continuum limit). This is obviously incorrect for $\mathbf{p} = \mathbf{0}$. We can easily repair this if we take the state $\mathbf{p} = \mathbf{0}$ explicitly into account.

$$\langle N \rangle = \sum_{\mathbf{p} > \mathbf{0}} \frac{1}{e^{\beta(\varepsilon(\mathbf{p}) - \mu)} - 1} + \frac{1}{e^{-\beta\mu} - 1} \tag{80}$$

for all finite momenta we can again introduce the density of states and it follows

$$\langle N \rangle = \int d\omega \rho(\omega) \frac{1}{e^{\beta(\omega - \mu)} - 1} + \frac{1}{e^{-\beta\mu} - 1} \tag{81}$$

The contribution of the last term

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} \tag{82}$$

is only relevant if

$$\lim_{\langle N \rangle \to \infty} \frac{N_0}{\langle N \rangle} > 0. \tag{83}$$

If $\mu < 0$, N_0 is finite and $\lim_{\langle N \rangle \to \infty} \frac{N_0}{\langle N \rangle} = 0$. Thus, below the temperature $T = T_0$ the chemical potential must vanish in order to avoid the above inconsistency. For $T < T_0$ follows therefore

$$\langle N \rangle = \langle N \rangle \left(\frac{T}{T_0} \right)^{3/2} + N_0 \tag{84}$$

which gives us the temperature dependence of the occupation of the $\mathbf{p} = \mathbf{0}$ state: If $T < T_0$

$$N_0 = \langle N \rangle \left(1 - \left(\frac{T}{T_0} \right)^{3/2} \right). \tag{85}$$

and $N_0 = 0$ for $T > T_0$. Then $\mu < 0$.

For the internal energy follows

$$U = \int d\omega \rho(\omega) \omega \frac{1}{e^{-\beta(\omega - \mu)} - 1} \tag{86}$$

which has no contribution from the "condensate" which has $\omega = 0$. The way the existence of the condensate is visible in the energy is via $\mu\left(T < T_0\right) = 0$ such that for $T < T_0$

$$U = VA_0 \int d\omega \frac{\omega^{3/2}}{e^{-\beta\omega} - 1} = VA_0 \left(k_B T\right)^{5/2} \int_0^\infty dx \frac{x^{3/2}}{e^{-x} - 1} \tag{87}$$

It holds again $\int_0^\infty dx \frac{x^{3/2}}{e^{-x}-1} = \frac{3}{4}\sqrt{\pi}\varsigma\left(5/2\right) \simeq 1.78$. This gives

$$U = 0.77 \left\langle N \right\rangle k_B T \left(\frac{T}{T_0}\right)^{3/2} \tag{88}$$

leading to a specific heat (use $U = \alpha T^{5/2}$)

$$C = \frac{\partial U}{\partial T} = \frac{5}{2}\alpha T^{3/2} = \frac{5}{2}\frac{U}{T} \sim T^{3/2}. \tag{89}$$

This gives

$$S = \int_0^T \frac{c\left(T'\right)}{T'} dT' = \frac{5}{2}\alpha \int_0^T T'^{1/2} dT' = \frac{5}{3}\alpha\ T^{3/2} = \frac{5}{3}\frac{U}{T} \tag{90}$$

which leads to

$$\Omega = U - TS - \mu N = -\frac{2}{3}U \tag{91}$$

The pressure below T_0 is

$$p = -\frac{\partial \Omega}{\partial V} = \frac{5}{3}\frac{\partial U}{\partial V} = 0.08 \frac{m^{3/2}}{\hbar^3} \left(k_B T\right)^{5/2} \tag{92}$$

which is independent of V. This determines the phase boundary

$$p_c = p_c\left(v_c\right) \tag{93}$$

with specific volume $v = \frac{V}{\langle N \rangle}$ at the transition:

$$p_c = 1.59 \frac{\hbar^2}{m} v^{-5/3}. \tag{94}$$

IV. SECOND QUANTIZATION

A. The harmonic oscillator: raising and lowering operators

Lets first reanalyze the harmonic oscillator with potential

$$V\left(x\right) = \frac{m\omega^2}{2} x^2 \tag{95}$$

where ω is the frequency of the oscillator. One of the numerous approaches we use to solve this problem is based on the following representation of the momentum and position operators:

$$\begin{aligned} \widehat{x} &= \sqrt{\frac{\hbar}{2m\omega}}\left(\widehat{a}^\dagger + \widehat{a}\right) \\ \widehat{p} &= i\sqrt{\frac{m\hbar\omega}{2}}\left(\widehat{a}^\dagger - \widehat{a}\right). \end{aligned} \tag{96}$$

From the canonical commutation relation

$$[\widehat{x}, \widehat{p}] = i\hbar \tag{97}$$

follows

$$\begin{aligned} \left[\widehat{a}, \widehat{a}^\dagger\right] &= 1 \\ [\widehat{a}, \widehat{a}] &= \left[\widehat{a}^\dagger, \widehat{a}^\dagger\right] = 0. \end{aligned} \tag{98}$$

Inverting the above expression yields

$$\begin{aligned} \widehat{a} &= \sqrt{\frac{m\omega}{2\hbar}}\left(\widehat{x} + \frac{i}{m\omega}\widehat{p}\right) \\ \widehat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\left(\widehat{x} - \frac{i}{m\omega}\widehat{p}\right) \end{aligned} \tag{99}$$

demonstrating that $\widehat{a}^\dagger$ is indeed the operator adjoined to $\widehat{a}$. We also defined the operator

$$\widehat{N} = \widehat{a}^\dagger\widehat{a} \tag{100}$$

which is Hermitian and thus represents a physical observable. It holds

$$\begin{aligned} \widehat{N} &= \frac{m\omega}{2\hbar}\left(\widehat{x} - \frac{i}{m\omega}\widehat{p}\right)\left(\widehat{x} + \frac{i}{m\omega}\widehat{p}\right) \\ &= \frac{m\omega}{2\hbar}\widehat{x}^2 + \frac{1}{2m\hbar\omega}\widehat{p}^2 - \frac{i}{2\hbar}\left[\widehat{p}, \widehat{x}\right] \\ &= \frac{1}{\hbar\omega}\left(\frac{\widehat{p}^2}{2m} + \frac{m\omega^2}{2}\widehat{x}^2\right) - \frac{1}{2}. \end{aligned} \tag{101}$$

We therefore obtain

$$\widehat{H} = \hbar\omega\left(\widehat{N} + \frac{1}{2}\right). \tag{102}$$

Since the eigenvalues of $\widehat{H}$ are given as $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ we conclude that the eigenvalues of the operator $\widehat{N}$ are the integers n that determine the eigenstates of the harmonic oscillator.

$$\widehat{N}\left|n\right\rangle = n\left|n\right\rangle. \tag{103}$$

Using the above commutation relation $\left[\widehat{a},\widehat{a}^{\dagger}\right]=1$ we were able to show that

$$\begin{aligned}\widehat{a}\,|n\rangle &= \sqrt{n}\,|n-1\rangle \\ \widehat{a}^{\dagger}\,|n\rangle &= \sqrt{n+1}\,|n+1\rangle\end{aligned} \tag{104}$$

The operator $\widehat{a}^{\dagger}$ and $\widehat{a}$ raise and lower the quantum number (i.e. the number of quanta). For these reasons, these operators are called creation and annihilation operators.

B. second quantization of noninteracting bosons

While the above results were derived for the special case of the harmonic oscillator there is a similarity between the result

$$E_n=\hbar\omega\left(n+\frac{1}{2}\right) \tag{105}$$

for the oscillator and our expression

$$E_{\{n_{\mathbf{p}}\}}=\sum_{\mathbf{p}}\varepsilon_{\mathbf{p}}n_{\mathbf{p}} \tag{106}$$

for the energy of a many body system, consisting of non-interacting indistinguishable particles. While n in case of the oscillator is the quantum number label, we may alternatively argue that it is the *number of oscillator quanta in the oscillator.* Similarly we can consider the many body system as a collection of a set of harmonic oscillators labelled by the single particle quantum number $\mathbf{p}$ (more generally by $\mathbf{p}$ and the spin). The state of the many body system was characterized by the set $\{n_{\mathbf{p}}\}$ of occupation numbers of the states (the number of particles in this single particle state). We the generalize the wave function $|n\rangle$ to the many body case

$$|\{n_{\mathbf{p}}\}\rangle=|n_1,n_2,...,n_{\mathbf{p}},...\rangle \tag{107}$$

and introduce operators

$$\begin{aligned}\widehat{a}_{\mathbf{p}}\,|n_1,n_2,...,n_{\mathbf{p}},...\rangle &= \sqrt{n_{\mathbf{p}}}\,|n_1,n_2,...,n_{\mathbf{p}}-1,...\rangle \\ \widehat{a}^{\dagger}_{\mathbf{p}}\,|n_1,n_2,...,n_{\mathbf{p}},...\rangle &= \sqrt{n_{\mathbf{p}}+1}\,|n_1,n_2,...,n_{\mathbf{p}}+1,...\rangle\end{aligned} \tag{108}$$

That obey

$$\left[\widehat{a}_{\mathbf{p}},\widehat{a}^{\dagger}_{\mathbf{p}'}\right]=\delta_{\mathbf{p},\mathbf{p}'}. \tag{109}$$

It is obvious that these operators commute if $\mathbf{p} \neq \mathbf{p}'$. For $\mathbf{p} = \mathbf{p}'$ follows

$$\begin{aligned} \widehat{a}_{\mathbf{p}}\widehat{a}_{\mathbf{p}}^{\dagger} \left|n_1, n_2, ..., n_{\mathbf{p}}, ...\right\rangle &= \sqrt{n_{\mathbf{p}}+1}\widehat{a}_{\mathbf{p}} \left|n_1, n_2, ..., n_{\mathbf{p}}+1, ...\right\rangle \\ &= (n_{\mathbf{p}}+1) \left|n_1, n_2, ..., n_{\mathbf{p}}, ...\right\rangle \end{aligned} \tag{110}$$

and

$$\begin{aligned} \widehat{a}_{\mathbf{p}}^{\dagger}\widehat{a}_{\mathbf{p}} \left|n_1, n_2, ..., n_{\mathbf{p}}, ...\right\rangle &= \sqrt{n_{\mathbf{p}}}\widehat{a}_{\mathbf{p}}^{\dagger} \left|n_1, n_2, ..., n_{\mathbf{p}}-1, ...\right\rangle \\ &= n_{\mathbf{p}} \left|n_1, n_2, ..., n_{\mathbf{p}}, ...\right\rangle \end{aligned} \tag{111}$$

which gives $\widehat{a}_{\mathbf{p}}\widehat{a}_{\mathbf{p}}^{\dagger} - \widehat{a}_{\mathbf{p}}^{\dagger}\widehat{a}_{\mathbf{p}} = 1$. Thus the commutation relation follow even if the operators are not linear combinations of position and momentum. It also follows

$$\widehat{n}_{\mathbf{p}} = \widehat{a}_{\mathbf{p}}^{\dagger}\widehat{a}_{\mathbf{p}} \tag{112}$$

for the operator of the number of particles with single particle quantum number $\mathbf{p}$. The total number operator is $\widehat{N} = \sum_{\mathbf{p}} \widehat{a}_{\mathbf{p}}^{\dagger}\widehat{a}_{\mathbf{p}}$. Similarly, the Hamiltonian in this representation is given as

$$\widehat{H} = \sum_{\mathbf{p}} \varepsilon_{\mathbf{p}}\widehat{a}_{\mathbf{p}}^{\dagger}\widehat{a}_{\mathbf{p}} \tag{113}$$

which gives the correct matrix elements.

We generalize the problem and analyze a many body system of particles with single particle Hamiltonian

$$\widehat{h} = \frac{\widehat{\mathbf{p}}^2}{2m} + U\left(\widehat{\mathbf{r}}\right) \tag{114}$$

which is characterized by the single particle eigenstates

$$\widehat{h} \left|\phi_{\alpha}\right\rangle = \varepsilon_{\alpha} \left|\phi_{\alpha}\right\rangle . \tag{115}$$

α is the label of the single particle quantum number. We can then introduce the occupation number representation with

$$\left|n_1, n_2, ..., n_{\alpha}, ...\right\rangle \tag{116}$$

and corresponding creation and destruction operators $\left[\widehat{a}_{\alpha}, \widehat{a}_{\alpha'}^{\dagger}\right] = \delta_{\alpha,\alpha'}$. We can then perform a unitary transformation among the states

$$\left|\beta\right\rangle = \sum_{\alpha} U_{\beta\alpha} \left|\alpha\right\rangle = \sum_{\alpha} \left|\alpha\right\rangle \left\langle\alpha|\beta\right\rangle \tag{117}$$

The states $|\beta\rangle$ are in general not the eigenstates of the single particle Hamiltonian (they only are if $U_{\beta\alpha} = \langle\alpha|\beta\rangle = \delta_{\alpha\beta}$). We can nevertheless introduce creation and destruction operators of these states, that are most naturally defined as:

$$\widehat{a}_\beta = \sum_\alpha \langle\beta|\alpha\rangle \, \widehat{a}_\alpha \tag{118}$$

and the corresponding adjoined equation

$$\widehat{a}_\beta^\dagger = \sum_\alpha \langle\beta|\alpha\rangle^* \, \widehat{a}_\alpha^\dagger. \tag{119}$$

This transformation preserves the commutation relation (see below for an example).

We can for example chose the basis β as the eigenbasis of the potential. Then holds in second quantization

$$\widehat{U} = \sum_\beta \langle\beta \left|U\left(\mathbf{r}\right)\right| \beta\rangle \, a_\beta^\dagger a_\beta \tag{120}$$

and we can transform the result as

$$\begin{aligned} \widehat{U} &= \sum_{\beta,\alpha,\alpha'} \langle\alpha|\beta\rangle \, \langle\beta \left|U\left(\mathbf{r}\right)\right| \beta\rangle \, \langle\beta|\alpha'\rangle \, \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'} \\ &= \sum_{\alpha,\alpha'} \langle\alpha \left|U\left(\mathbf{r}\right)\right| \alpha'\rangle \, \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'} \end{aligned} \tag{121}$$

It holds of course $\langle\alpha \left|U\left(\mathbf{r}\right)\right| \alpha'\rangle = \int d^3r \phi_\alpha\left(\mathbf{r}\right) U\left(\mathbf{r}\right) \phi_{\alpha'}\left(\mathbf{r}\right)$.

In particular, we can chose $|\beta\rangle = |\mathbf{r}\rangle$ such that $\langle\beta|\alpha\rangle = \langle\mathbf{r}|\alpha\rangle = \phi_\alpha\left(\mathbf{r}\right)$. In this case we use the notation $\widehat{a}_{\mathbf{r}} = \widehat{\psi}\left(\mathbf{r}\right)$ and our unitary transformations are

$$\begin{aligned} \widehat{\psi}\left(\mathbf{r}\right) &= \sum_\alpha \phi_\alpha\left(\mathbf{r}\right) \widehat{a}_\alpha \\ \widehat{\psi}^\dagger\left(\mathbf{r}\right) &= \sum_\alpha \phi_\alpha^*\left(\mathbf{r}\right) \widehat{a}_\alpha^\dagger \end{aligned} \tag{122}$$

The commutation relation is then $\delta_{\alpha,\alpha'}$

$$\begin{aligned} \left[\widehat{\psi}\left(\mathbf{r}\right), \widehat{\psi}\left(\mathbf{r}'\right)\right] &= \sum_{\alpha,\alpha'} \phi_\alpha\left(\mathbf{r}\right) \phi_{\alpha'}^*\left(\mathbf{r}'\right) \left[\widehat{a}_\alpha, \widehat{a}_{\alpha'}^\dagger\right] \\ &= \sum_\alpha \phi_\alpha\left(\mathbf{r}\right) \phi_\alpha^*\left(\mathbf{r}'\right) = \sum_\alpha \langle\mathbf{r}|\alpha\rangle \, \langle\alpha|\mathbf{r}'\rangle \\ &= \langle\mathbf{r}|\mathbf{r}'\rangle = \delta\left(\mathbf{r} - \mathbf{r}'\right) \end{aligned} \tag{123}$$

and it follows

$$\widehat{U} = \int d^3r U\left(\mathbf{r}\right) \widehat{\psi}^\dagger\left(\mathbf{r}\right) \widehat{\psi}\left(\mathbf{r}\right) \tag{124}$$

Similarly holds for the kinetic energy

$$\begin{aligned}\widehat{T} &= -\frac{\hbar^2}{2m}\int d^3r d^3r' \left\langle \mathbf{r}\left|\nabla^2\right|\mathbf{r}'\right\rangle \widehat{\psi}^\dagger(\mathbf{r})\,\widehat{\psi}(\mathbf{r}') \\ &= -\frac{\hbar^2}{2m}\int d^3r d^3r' \widehat{\psi}^\dagger(\mathbf{r})\,\nabla^2\delta(\mathbf{r}-\mathbf{r}')\,\widehat{\psi}(\mathbf{r}') \\ &= -\frac{\hbar^2}{2m}\int d^3r \widehat{\psi}^\dagger(\mathbf{r})\,\nabla^2\widehat{\psi}(\mathbf{r}) \end{aligned} \tag{125}$$

Thus we find

$$\begin{aligned} H &= \sum_\alpha \varepsilon_\alpha \widehat{a}_\alpha^\dagger \widehat{a}_\alpha \\ &= \int d^3r \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla^2}{2m}+U(\mathbf{r})\right)\widehat{\psi}(\mathbf{r}) \end{aligned} \tag{126}$$

With the help of the field operators $\widehat{\psi}(\mathbf{r})$ and $\widehat{\psi}^\dagger(\mathbf{r})$ is it possible to bring the many body Hamiltonian in occupation number representation into the same form as the Hamiltonian of a single particle.

C. Example 1: a single particle

We consider the most general wave function of a single spinless boson:

$$|\psi_\alpha\rangle = \int d^3r \phi_\alpha(\mathbf{r})\,\widehat{\psi}^\dagger(\mathbf{r})\,|0\rangle \tag{127}$$

where $|0\rangle$ is the completely empty system. Let the Hamiltonian be

$$H = \int d^3r \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\widehat{\psi}(\mathbf{r}) \tag{128}$$

It follows

$$\begin{aligned} H|\psi_\alpha\rangle &= \int d^3r \int d^3r' \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\phi_\alpha(\mathbf{r}')\,\widehat{\psi}(\mathbf{r})\,\widehat{\psi}^\dagger(\mathbf{r}')\,|0\rangle \\ &= \int d^3r \int d^3r' \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\phi_\alpha(\mathbf{r}')\,\widehat{\psi}^\dagger(\mathbf{r}')\,\widehat{\psi}(\mathbf{r})\,|0\rangle \\ &\quad + \int d^3r \int d^3r' \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\phi_\alpha(\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}')\,|0\rangle \end{aligned} \tag{129}$$

The first term disappears since $\widehat{\psi}(\mathbf{r})\,|0\rangle = 0$ for the empty state. Performing the integration over $\mathbf{r}'$ gives

$$\begin{aligned} H|\psi_\alpha\rangle &= \int d^3r \widehat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\phi_\alpha(\mathbf{r})\,|0\rangle \\ &= \int d^3r \left[\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m}+U(\mathbf{r})\right)\phi_\alpha(\mathbf{r})\right]\widehat{\psi}^\dagger(\mathbf{r})\,|0\rangle \end{aligned} \tag{130}$$

Thus, we need to find the eigenvalue of and eigenfunction of

$$\left(-\frac{\hbar^2\nabla^2}{2m}+U\left(\mathbf{r}\right)\right)\phi_\alpha\left(\mathbf{r}\right)=\varepsilon_\alpha\phi_\alpha\left(\mathbf{r}\right) \tag{131}$$

to obtain

$$H\left|\psi_\alpha\right\rangle=\varepsilon_\alpha\int d^3r\ \phi_\alpha\left(\mathbf{r}\right)\widehat{\psi}^\dagger\left(\mathbf{r}\right)\left|0\right\rangle=\varepsilon_\alpha\left|\psi_\alpha\right\rangle. \tag{132}$$

Thus, for a single particle problem we recover the original formulation of the "first quantization". The function $\phi\left(\mathbf{r}\right)$ in Eq.127 is therefore the wave function of the single particle problem.

Using $\widehat{\psi}^\dagger\left(\mathbf{r}\right)=\sum_\alpha\phi_\alpha^*\left(\mathbf{r}\right)\widehat{a}_\alpha^\dagger$ follows $\widehat{a}_\alpha^\dagger=\int d^3r\phi_\alpha\left(\mathbf{r}\right)\widehat{\psi}^\dagger\left(\mathbf{r}\right)$ and our above wave function is nothing but

$$\left|\psi_\alpha\right\rangle=\widehat{a}_\alpha^\dagger\left|0\right\rangle \tag{133}$$

Applying the Hamiltonian to the wave function in this basis is obviously giving the same answer.

$$H\left|\psi_\alpha\right\rangle=\sum_{\alpha'}\varepsilon_{\alpha'}\widehat{a}_{\alpha'}^\dagger\widehat{a}_{\alpha'}\widehat{a}_\alpha^\dagger\left|0\right\rangle=\varepsilon_a\left|\psi_\alpha\right\rangle \tag{134}$$

D. Second quantization of interacting bosons

Next we analyze the formulation of particle-particle interactions within the second quantization. We consider a two body interaction $\widehat{V}$ that has, by definition, matrix elements that depend on the states of two particles. Thus the expression for a single particle where

$$\widehat{U}=\sum_{\alpha,\alpha'}\left\langle\alpha\left|U\right|\alpha'\right\rangle\widehat{a}_\alpha^\dagger\widehat{a}_{\alpha'} \tag{135}$$

will be determined by a matrix elements of the kind:

$$\left\langle\alpha\gamma\left|V\right|\alpha'\gamma'\right\rangle=\int d^3rd^3r'\phi_\alpha^*\left(\mathbf{r}\right)\phi_\gamma^*\left(\mathbf{r}'\right)V\left(\mathbf{r},\mathbf{r}'\right)\phi_{\alpha'}\left(\mathbf{r}'\right)\phi_{\gamma'}\left(\mathbf{r}\right). \tag{136}$$

In general there will be a two particle basis $\left|\alpha\gamma\right\rangle$ where the interaction is diagonal

$$\widehat{V}\left|\alpha\gamma\right\rangle=V_{\alpha\gamma}\left|\alpha\gamma\right\rangle \tag{137}$$

where $V_{\alpha\gamma}=\left\langle\alpha\gamma\left|V\right|\alpha\gamma\right\rangle$. In this basis we can proceed just like for the interaction $\widehat{U}$, where the operator was given by $\sum_\alpha\left\langle\alpha\left|U\right|\alpha\right\rangle\widehat{a}_\alpha^\dagger\widehat{a}_\alpha$. In case of a two particle interaction we

have contributions if there are two particles, one in state α the other in state γ. This the interaction must be

$$\widehat{V} = \frac{1}{2}\sum_{\alpha\gamma} V_{\alpha\gamma}\widehat{P}_{\alpha\gamma} \tag{138}$$

where $\widehat{P}_{\alpha\beta}$ is the operator which counts the number of pairs of particles in the states $|\alpha\rangle$ and $|\gamma\rangle$. The prefactor $\frac{1}{2}$ takes into account that each pair is considered only once.

If $|\alpha\rangle = |\gamma\rangle$, the number of pairs is $n_\alpha\left(n_\alpha - 1\right)$, while for $|\alpha\rangle \neq |\gamma\rangle$ it is $n_\alpha n_\gamma$, where the n_α are the occupation numbers of those states. It follows

$$\begin{aligned}\widehat{P}_{\alpha\gamma} &= \widehat{n}_\alpha\widehat{n}_\gamma - \delta_{\alpha\gamma}\widehat{n}_\alpha \\ &= a_\alpha^\dagger a_\gamma^\dagger a_\alpha a_\gamma = a_\alpha^\dagger a_\gamma^\dagger a_\gamma a_\alpha\end{aligned} \tag{139}$$

and we find

$$\widehat{V} = \frac{1}{2}\sum_{\alpha\gamma} V_{\alpha\gamma}a_\alpha^\dagger a_\gamma^\dagger a_\gamma a_\alpha = \frac{1}{2}\sum_{\alpha\gamma}\left\langle\alpha\gamma\left|V\right|\alpha\gamma\right\rangle a_\alpha^\dagger a_\gamma^\dagger a_\gamma a_\alpha \tag{140}$$

Transforming this expression into an arbitrary basis $|\mu\rangle = \sum_\alpha |\alpha\rangle\langle\alpha|\mu\rangle$, we insert the operators in the new basis

$$\begin{aligned}\widehat{a}_\alpha^\dagger &= \sum_\lambda \langle\lambda|\alpha\rangle\,\widehat{a}_\lambda^\dagger. \\ \widehat{a}_\alpha &= \sum_\lambda \langle\alpha|\lambda\rangle\,\widehat{a}_\lambda\end{aligned} \tag{141}$$

and it follows

$$\widehat{V} = \frac{1}{2}\sum_{\alpha\gamma,\lambda\mu\rho\nu}\langle\lambda|\alpha\rangle\langle\mu|\gamma\rangle\left\langle\alpha\gamma\left|V\right|\alpha\gamma\right\rangle\langle\alpha|\rho\rangle\langle\gamma|\nu\rangle\, a_\lambda^\dagger a_\mu^\dagger a_\rho a_\nu \tag{142}$$

which simplifies to:

$$\widehat{V} = \frac{1}{2}\sum_{\lambda\mu\rho\nu}\left\langle\lambda\mu\left|V\right|\rho\nu\right\rangle a_\lambda^\dagger a_\mu^\dagger a_\rho a_\nu \tag{143}$$

If for example

$$\left\langle\mathbf{r},\mathbf{r}'\left|V\right|\mathbf{r}''\mathbf{r}'''\right\rangle = v\left(\mathbf{r}-\mathbf{r}'\right)\delta\left(\mathbf{r}''-\mathbf{r}'\right)\delta\left(\mathbf{r}'''-\mathbf{r}\right) \tag{144}$$

for an interaction that only depends on the distance between the two particles, it follows

$$\widehat{V} = \frac{1}{2}\int d^3r d^3r' v\left(\mathbf{r}-\mathbf{r}'\right)\widehat{\psi}^\dagger\left(\mathbf{r}\right)\widehat{\psi}^\dagger\left(\mathbf{r}'\right)\widehat{\psi}\left(\mathbf{r}'\right)\widehat{\psi}\left(\mathbf{r}\right). \tag{145}$$

E. Second quantization of noninteracting fermions

1. *The fermionic "harmonic oscillator"*

When we introduced the second quantized representation for bosons we took advantage of the fact that the eigenstates of a free bose system

$$E = \sum_{\boldsymbol{\alpha}} \varepsilon_\alpha n_\alpha \tag{146}$$

could be expressed in terms of the set $\{n_\alpha\}$ of occupation numbers. In case of bosons these occupation numbers were allowed to take all integer values $n_a = 0, 1, \cdots, \infty$, reminiscent of the quantum number of the harmonic oscillator. The latter then led to the introduction of creation and annihilation operators of the bosons, where the occupation number operator of a given state was $\widehat{n}_\alpha = \widehat{a}^\dagger_\alpha \widehat{a}_a$. The Hamiltonian was then written as

$$\widehat{H} = \sum_{\boldsymbol{\alpha}} \varepsilon_\alpha \widehat{n}_\alpha \tag{147}$$

Obviously, this approach cannot be used to describe fermions where $n_\alpha = 0$ or 1. In case of fermions, the single particle quantum state always includes the spin, for example $\alpha = (\mathbf{k}, \sigma)$.

We need to find the fermion analog to the harmonic oscillator, i.e. a state that only allows for the two occupations $n_\alpha = 0$ or 1. We want to express the Hamiltonian for a single quantum state as

$$\widehat{h} = \varepsilon \widehat{n} \tag{148}$$

This is easily done with the help of a (2×2) matrix representation (note, these matrices have nothing to do with the spin of the system). If we introduce

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{149}$$

for the empty and occupied state, it holds

$$\widehat{n} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{150}$$

We can equally introduce lowering and raising operators

$$\widehat{a}\,|0\rangle = 0 \quad \text{and } \widehat{a}\,|1\rangle = |0\rangle \tag{151}$$

as well as

$$\widehat{a}^\dagger |1\rangle = 0 \quad \text{and } \widehat{a}^\dagger |0\rangle = |1\rangle \,. \tag{152}$$

It follows easily that this is accomplished by

$$\widehat{a} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \widehat{a}^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \,. \tag{153}$$

As in case of bosons, $\widehat{a}^\dagger$ is the adjoined operator of $\widehat{a}$.

The action of these operators of a state with arbitrary occupation is then

$$\begin{aligned} \widehat{a} |n\rangle &= n |n-1\rangle = n |1-n\rangle \\ \widehat{a}^\dagger |n\rangle &= (1-n) |n+1\rangle = (1-n) |1-n\rangle \end{aligned} \tag{154}$$

If we now determine $a^\dagger a$ it follows

$$\widehat{a}^\dagger \widehat{a} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{155}$$

and we have, just as for bosons,

$$\widehat{n} = \widehat{a}^\dagger \widehat{a}. \tag{156}$$

However, an important difference is of course that now holds

$$\widehat{a}\widehat{a}^\dagger + \widehat{a}^\dagger \widehat{a} = 1 \tag{157}$$

in addition we immediately see

$$\widehat{a}^\dagger \widehat{a}^\dagger = \widehat{a}\widehat{a} = 0 \tag{158}$$

Fermionic creation and annihilation operators do not commute, they anticommute:

$$\begin{aligned} \left[\widehat{a}, \widehat{a}^\dagger\right]_+ &= 1 \\ \left[\widehat{a}^\dagger, \widehat{a}^\dagger\right]_+ &= \left[\widehat{a}, \widehat{a}\right]_+ = 0. \end{aligned} \tag{159}$$

Note, we could have introduced equally

$$\widehat{a} = -\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \widehat{a}^\dagger = -\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \,. \tag{160}$$

with the only change that now $\widehat{a} |1\rangle = -|0\rangle$ and $\widehat{a}^\dagger |0\rangle = -|1\rangle$ and all other results remain unchanged.

2. Many fermi states

To generalize the single fermi result to many fermions we the any body wave function in occupation number representation

$$|n_1, n_2, \ldots, n_\alpha, \ldots\rangle \tag{161}$$

We then need to analyze the creation and annihilation operators $\widehat{a}^\dagger_\alpha$ and $\widehat{a}_a$for the individual states, respectively.

At first glance it is natural to introduce$(1-n)\,|n+1\rangle$

$$\begin{aligned}
\widehat{a}_a\,|n_1, n_2, \ldots, n_\alpha, \ldots\rangle &= n_\alpha\,|n_1, n_2, \ldots, n_\alpha - 1, \ldots\rangle \\
\widehat{a}^\dagger_a\,|n_1, n_2, \ldots, n_\alpha, \ldots\rangle &= (1-n_\alpha)\,|n_1, n_2, \ldots, n_\alpha + 1, \ldots\rangle
\end{aligned} \tag{162}$$

(**Note, these equations will turn out to be incorrect!**)

This implies however that

$$\left[\widehat{a}_\alpha, \widehat{a}^\dagger_\alpha\right]_+ = 1 \tag{163}$$

while for different states $\alpha \neq \alpha'$ follows

$$\left[\widehat{a}_\alpha, \widehat{a}^\dagger_{\alpha'}\right]_+ = 2\widehat{a}_\alpha \widehat{a}^\dagger_{\alpha'} \tag{164}$$

a result that follows from $\left[\widehat{a}_\alpha, \widehat{a}^\dagger_{\alpha'}\right] = 0$ for $\alpha \neq \alpha'$. If we now want to transform from one basis to another, with

$$|l\rangle = \sum_\alpha |\alpha\rangle\,\langle\alpha|l\rangle \tag{165}$$

Just like in case of bosons the new operators should be linear combinations of the old ones, which yields

$$\widehat{a}_l = \sum_\alpha \langle l|\alpha\rangle\,\widehat{a}_\alpha \tag{166}$$

and the corresponding adjoined equation

$$\widehat{a}^\dagger_l = \sum_\alpha \langle l|\alpha\rangle^*\,\widehat{a}^\dagger_\alpha. \tag{167}$$

We now require

$$\left[\widehat{a}_l, \widehat{a}^\dagger_l\right]_+ = 1 \tag{168}$$

which leads to

$$1 = \sum_{\alpha,\alpha'} \langle l|\alpha\rangle\,\langle\alpha'|l\rangle\,\left[\widehat{a}_\alpha, \widehat{a}^\dagger_{\alpha'}\right]_+ \tag{169}$$

For a complete set of states $\langle l|\alpha\rangle$ this is only possible if

$$\left[\widehat{a}_\alpha, \widehat{a}^\dagger_{\alpha'}\right]_+ = \delta_{\alpha,\alpha'} \tag{170}$$

i.e. for $\alpha \neq \alpha'$ the anticommutator and not the commutator must vanish. We conclude that Eq.162 cannot be correct.

Jordan and Wigner realized that a small change in the definition of these operators can fix the problem. To proceed we need to order the quantum numbers in some arbitrary but fixed way. We then introduce

$$\nu_\alpha = \sum_{\alpha'=1}^{\alpha-1} n_\alpha \tag{171}$$

as the number of occupied states that precede the α-th state. We can then introduce

$$\widehat{a}_\alpha = (-1)^{\nu_\alpha} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \widehat{a}^\dagger = (-1)^{\nu_\alpha} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{172}$$

The matrix acts on the occupation of the α-th state. As shown above, a prefactor -1 in the definition of these operators causes no problem. It then follows

$$\begin{aligned}
\widehat{a}_a \,|n_1, n_2, \ldots, n_\alpha, \ldots\rangle &= (-1)^{\nu_\alpha}\, n_\alpha \,|n_1, n_2, \ldots, n_\alpha - 1, \ldots\rangle \\
&= (-1)^{\nu_\alpha}\, n_\alpha \,|n_1, n_2, \ldots, 1 - n_\alpha, \ldots\rangle \\
\widehat{a}^\dagger_a \,|n_1, n_2, \ldots, n_\alpha, \ldots\rangle &= (-1)^{\nu_\alpha}\, (1 - n_\alpha) \,|n_1, n_2, \ldots, n_\alpha + 1, \ldots\rangle \\
&= (-1)^{\nu_\alpha}\, (1 - n_\alpha) \,|n_1, n_2, \ldots, 1 - n_\alpha, \ldots\rangle
\end{aligned} \tag{173}$$

It obviously holds that

$$\left[\widehat{a}_\alpha, \widehat{a}^\dagger_\alpha\right]_+ = 1 \tag{174}$$

We next analyze (assume α' prior to α)

$$\begin{aligned}
\widehat{a}_{a'}\widehat{a}^\dagger_a \,|n_1, \ldots, n_{\alpha'}, \ldots, n_\alpha, \ldots\rangle &= (-1)^{\nu_\alpha}\, (1 - n_\alpha)\, \widehat{a}_{a'} \,|n_1, \ldots, n_{\alpha'}, \ldots, 1 - n_\alpha, \ldots\rangle \\
&= (-1)^{\nu_\alpha + \nu_{\alpha'}}\, n_{\alpha'}\, (1 - n_\alpha) \,|n_1, \ldots, 1 - n_{\alpha'}, \ldots, 1 - n_\alpha, \ldots\rangle
\end{aligned}$$

On the other hand:

$$\begin{aligned}
\widehat{a}^\dagger_a\widehat{a}_{a'} \,|n_1, \ldots, n_{\alpha'}, \ldots, n_\alpha, \ldots\rangle &= (-1)^{\nu_{\alpha'}}\, n_{\alpha'}\widehat{a}^\dagger_a \,|n_1, \ldots, 1 - n_{\alpha'}, \ldots, n_\alpha, \ldots\rangle \\
&= (-1)^{\nu_\alpha + \nu_{\alpha'} - 1}\, n_{\alpha'}\, (1 - n_\alpha) \,|n_1, \ldots, 1 - n_{\alpha'}, \ldots, 1 - n_\alpha, \ldots\rangle
\end{aligned}$$

It then follows

$$\widehat{a}_{a'}\widehat{a}_a^\dagger + \widehat{a}_a^\dagger \widehat{a}_{a'} = (-1)^{\nu_\alpha + \nu_{\alpha'}} \left(n_{\alpha'} \left(1 - n_\alpha \right) - n_{\alpha'} \left(1 - n_\alpha \right) \right) = 0 \tag{175}$$

The same holds of course if we assume α' to occur after α.

Thus, we find

$$\left[\widehat{a}_\alpha, \widehat{a}_{\alpha'}^\dagger \right]_+ = \delta_{\alpha,\alpha'} \tag{176}$$

as desired, yielding after a unitary transformation

$$\left[\widehat{a}_l, \widehat{a}_{l'}^\dagger \right]_+ = \sum_{\alpha,\alpha'} \langle l|\alpha\rangle \langle \alpha'|l'\rangle \left[\widehat{a}_\alpha, \widehat{a}_{\alpha'}^\dagger \right]_+ = \delta_{l,l'} \tag{177}$$

i.e. the anticommutation relation of fermionic operators is independent on the specific representation.

The Hamiltonian of noninteracting fermions is then

$$H = \sum_\alpha \varepsilon_\alpha \widehat{a}_\alpha^\dagger \widehat{a}_\alpha \tag{178}$$

which in case of free particles reads

$$H = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} \widehat{a}_{\mathbf{k},\sigma}^\dagger \widehat{a}_{\mathbf{k},\sigma} \tag{179}$$

where $\mathbf{k}$ goes over all momentum values and $\sigma = \pm\frac{1}{2}$.

To incorporate interaction effects is now rather similar to the case of bosons. We start from the two particle basis $|\alpha\gamma\rangle$ where the interaction is diagonal

$$\widehat{V} \left| \alpha\gamma \right\rangle = V_{\alpha\gamma} \left| \alpha\gamma \right\rangle . \tag{180}$$

Here $V_{\alpha\gamma} = \langle \alpha\gamma \left| V \right| \alpha\gamma \rangle$. In this basis we can proceed just like for bosons. In case of a two particle interaction we have contributions if there are two particles, one in state α the other in state γ. This the interaction must be

$$\widehat{V} = \frac{1}{2} \sum_{\alpha\gamma} V_{\alpha\gamma} \widehat{P}_{\alpha\gamma} \tag{181}$$

where $\widehat{P}_{\alpha\beta}$ is the operator which counts the number of pairs of particles in the states $|\alpha\rangle$ and $|\gamma\rangle$. The prefactor $\frac{1}{2}$ takes into account that each pair is considered only once. It follows again

$$\begin{aligned}\widehat{P}_{\alpha\gamma} &= \widehat{n}_\alpha \widehat{n}_\gamma - \delta_{\alpha\gamma}\widehat{n}_\alpha \\ &= a_\alpha^\dagger a_\alpha a_\gamma^\dagger a_\gamma - \delta_{\alpha\gamma} a_\alpha^\dagger a_\alpha \\ &= -a_\alpha^\dagger a_\gamma^\dagger a_\alpha a_\gamma + a_\alpha^\dagger \delta_{\alpha\gamma} a_\gamma - \delta_{\alpha\gamma} a_\alpha^\dagger a_\alpha \\ &= a_\alpha^\dagger a_\gamma^\dagger a_\alpha a_\gamma \end{aligned} \tag{182}$$

and we find

$$\widehat{V} = \frac{1}{2}\sum_{\alpha\gamma} V_{\alpha\gamma} a_\alpha^\dagger a_\gamma^\dagger a_\gamma a_\alpha \tag{183}$$

just as in case of bosons. Transforming this expression into an arbitrary basis $|\mu\rangle = \sum_\alpha |\alpha\rangle \langle\alpha|\mu\rangle$ where $\widehat{a}_\mu = \sum_\alpha \langle\mu|\alpha\rangle \widehat{a}_\alpha$ it holds

$$\widehat{V} = \frac{1}{2}\sum_{\lambda\mu\rho\nu} \langle \lambda\mu \left| V \right| \rho\nu\rangle \, a_\lambda^\dagger a_\mu^\dagger a_\rho a_\nu \tag{184}$$

If for example

$$\langle \mathbf{r}, \mathbf{r}' \left| V \right| \mathbf{r}''\mathbf{r}'''\rangle = v\left(\mathbf{r}-\mathbf{r}'\right)\delta\left(\mathbf{r}''-\mathbf{r}'\right)\delta\left(\mathbf{r}'''-\mathbf{r}\right) \tag{185}$$

for an interaction that only depends on the distance between the two particles, it follows

$$\widehat{V} = \frac{1}{2}\int d^3r d^3r' v\left(\mathbf{r}-\mathbf{r}'\right)\widehat{\psi}^\dagger\left(\mathbf{r}\right)\widehat{\psi}^\dagger\left(\mathbf{r}'\right)\widehat{\psi}\left(\mathbf{r}'\right)\widehat{\psi}\left(\mathbf{r}\right). \tag{186}$$

3. Example 1: free electron gas

We want to derive the ground state wave function of the free electron gas. The Hamiltonian of an individual electron is

$$h = -\frac{\hbar^2\nabla^2}{2m} \tag{187}$$

which leads to the single particle eigenvalues

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}. \tag{188}$$

The Hamiltonian of the many fermion system is then

$$H = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} \widehat{a}_{\mathbf{k},\sigma}^\dagger \widehat{a}_{\mathbf{k},\sigma}. \tag{189}$$

The ground state wave function is the state where all single particle states with energy

$$\varepsilon_{\mathbf{k}} < E_F \tag{190}$$

are occupied and all states above the Fermi energy are empty. ,

$$E_F = \frac{\hbar^2}{2m} \quad \left(\frac{3\pi^2 \langle N \rangle}{V}\right)^{2/3} \tag{191}$$

was determined earlier. The ground state wave function is then

$$|\Psi_0\rangle = \prod_{\mathbf{k},\sigma(\varepsilon_{\mathbf{k}}<E_F)} \widehat{a}^\dagger_{\mathbf{k},\sigma} |0\rangle \tag{192}$$

This state is normalized:

$$\begin{aligned} \langle \Psi_0 | \Psi_0 \rangle &= \left\langle 0 \left| \prod_{\mathbf{k},\sigma(\varepsilon_{\mathbf{k}}<E_F)} \widehat{a}_{\mathbf{k},\sigma} \widehat{a}^\dagger_{\mathbf{k},\sigma} \right| 0 \right\rangle \\ &= \left\langle 0 \left| \prod_{\mathbf{k},\sigma(\varepsilon_{\mathbf{k}}<E_F)} \left(1 - \widehat{a}^\dagger_{\mathbf{k},\sigma} \widehat{a}_{\mathbf{k},\sigma}\right) \right| 0 \right\rangle \\ &= \prod_{\mathbf{k},\sigma(\varepsilon_{\mathbf{k}}<E_F)} \langle 0|0\rangle = 1 \end{aligned} \tag{193}$$

and it is indeed the eigenstate of the problem

$$H |\Psi_0\rangle = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} \widehat{a}^\dagger_{\mathbf{k},\sigma} \widehat{a}_{\mathbf{k},\sigma} |\Psi_0\rangle \tag{194}$$

It follows immediately that

$$\widehat{a}^\dagger_{\mathbf{k},\sigma} \widehat{a}_{\mathbf{k},\sigma} \prod_{\mathbf{q},\sigma(\varepsilon_{\mathbf{q}}<E_F)} \widehat{a}^\dagger_{\mathbf{q},\sigma} |0\rangle = \theta\left(E_F - \varepsilon_{\mathbf{k}}\right) |\Psi_0\rangle . \tag{195}$$

Either $\mathbf{k}$ is among the states below the Fermi surface or it isn't. This yields

$$H |\Psi_0\rangle = E_0 |\Psi_0\rangle \tag{196}$$

with

$$E_0 = \sum_{\mathbf{k},\sigma} \theta\left(E_F - \varepsilon_{\mathbf{k}}\right) \varepsilon_{\mathbf{k}} \tag{197}$$

The states that contribute to the ground state energy are all those with an energy below E_F. Since $\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$ is implies that the magnitude of the momentum must be smaller than a given value

$$\frac{\hbar^2 k^2}{2m} < \frac{\hbar^2 k_F^2}{2m} = E_F \tag{198}$$

Here k_F is the so called Fermi momentum. All momentum states inside the sphere of radius k_F are occupied. Those outside are empty. Our above result for the Fermi energy yields

$$k_F = \left(3\pi^2\rho\right)^{1/3} \tag{199}$$

where $\rho = \langle N \rangle / V$ is the electron density.

F. Example 2: two particles

The natural state of two noninteracting particles is

$$\left|\psi_{\alpha,\alpha'}\right\rangle = \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'}^\dagger \left|0\right\rangle \tag{200}$$

Applying the Hamiltonian

$$H = \sum_\alpha \varepsilon_\alpha \widehat{a}_\alpha^\dagger \widehat{a}_\alpha \tag{201}$$

to this wave function gives

$$\begin{aligned} H\left|\psi_{\alpha,\alpha'}\right\rangle &= \sum_\gamma \varepsilon_\gamma \widehat{a}_\gamma^\dagger \widehat{a}_\gamma \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'}^\dagger \left|0\right\rangle \\ &= -\sum_\gamma \varepsilon_\gamma \widehat{a}_\gamma^\dagger \widehat{a}_\alpha^\dagger \widehat{a}_\gamma \widehat{a}_{\alpha'}^\dagger \left|0\right\rangle + \varepsilon_\alpha \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'}^\dagger \left|0\right\rangle \\ &= -\varepsilon_{\alpha'} \widehat{a}_{\alpha'}^\dagger \widehat{a}_\alpha^\dagger \left|0\right\rangle + \varepsilon_\alpha \widehat{a}_\alpha^\dagger \widehat{a}_{\alpha'}^\dagger \left|0\right\rangle \\ &= \left(\varepsilon_\alpha + \varepsilon_{\alpha'}\right)\left|\psi_{\alpha,\alpha'}\right\rangle \end{aligned} \tag{202}$$

The eigenvalue is $E_{\alpha,\alpha'} = \varepsilon_\alpha + \varepsilon_{\alpha'}$. The wave function can also be written as

$$\left|\psi_{\alpha,\alpha'}\right\rangle = \frac{1}{\sqrt{2}} \int d^3r d^3r' \phi_\alpha\left(\mathbf{r}\right) \phi_{\alpha'}\left(\mathbf{r}'\right) \widehat{\psi}^\dagger\left(\mathbf{r}\right) \widehat{\psi}^\dagger\left(\mathbf{r}'\right) \left|0\right\rangle \tag{203}$$

Since a labelling of the particles is not necessary within the second quantization, there is no need to symmetrize $\phi_\alpha\left(\mathbf{r}\right) \phi_{\alpha'}\left(\mathbf{r}'\right)$ in this formulation.

To determine the wave function in real space we analyze

$$\Psi_{\alpha\alpha'}\left(\mathbf{r},\mathbf{r}'\right) = \left\langle \mathbf{r},\mathbf{r}' | \psi_{\alpha,\alpha'}\right\rangle \tag{204}$$

It holds

$$\left|\mathbf{r},\mathbf{r}'\right\rangle = \widehat{\psi}^\dagger\left(\mathbf{r}\right) \widehat{\psi}^\dagger\left(\mathbf{r}'\right) \left|0\right\rangle \tag{205}$$

such that

$$\langle \mathbf{r}, \mathbf{r}' | = \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}(\mathbf{r}) \tag{206}$$

and we can analyze

$$\begin{aligned} \left\langle \mathbf{r}, \mathbf{r}' | \psi_{\alpha,\alpha'} \right\rangle &= \frac{1}{\sqrt{2}} \int d^3r'' d^3r''' \phi_\alpha(\mathbf{r}'') \phi_{\alpha'}(\mathbf{r}''') & (207) \\ &\times \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}(\mathbf{r}) \widehat{\psi}^\dagger(\mathbf{r}'') \widehat{\psi}^\dagger(\mathbf{r}''') | 0 \rangle & (208) \end{aligned}$$

It holds

$$\begin{aligned} \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}(\mathbf{r}) \widehat{\psi}^\dagger(\mathbf{r}'') \widehat{\psi}^\dagger(\mathbf{r}''') | 0 \rangle &= -\langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}^\dagger(\mathbf{r}'') \widehat{\psi}(\mathbf{r}) \widehat{\psi}^\dagger(\mathbf{r}''') | 0 \rangle \\ &\quad + \delta(\mathbf{r} - \mathbf{r}'') \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}^\dagger(\mathbf{r}''') | 0 \rangle \\ &= -\delta(\mathbf{r} - \mathbf{r}''') \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}^\dagger(\mathbf{r}'') | 0 \rangle \\ &\quad + \delta(\mathbf{r} - \mathbf{r}'') \langle 0 | \widehat{\psi}(\mathbf{r}') \widehat{\psi}^\dagger(\mathbf{r}''') | 0 \rangle \\ &= -\delta(\mathbf{r} - \mathbf{r}''') \delta(\mathbf{r}' - \mathbf{r}'') + \delta(\mathbf{r} - \mathbf{r}'') \delta(\mathbf{r}' - \mathbf{r}''') \end{aligned}$$

Inserting this yields

$$\Psi_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') = \frac{1}{\sqrt{2}} \left(\phi_\alpha(\mathbf{r}) \phi_{\alpha'}(\mathbf{r}') - \phi_\alpha(\mathbf{r}') \phi_{\alpha'}(\mathbf{r}) \right) \tag{209}$$

This is of course the correct result for the wave function of two indistinguishable fermions.

V. PERIODIC STRUCTURES AND BLOCH THEOREM

Following our Born-Oppenheimer decoupling we consider the ionic problem of the coupled electron-ion system, governed by the Schrödinger equation:

$$\left(T_i + V_{ii}^{eff} \right) \Phi_n = \mathcal{E} \Phi_n \tag{210}$$

with effective ion-ion interaction $V_{ii}^{eff} = V_{ii} + E_{\mathrm{el},n}$. Here, the $E_{\mathrm{el},n}$ are determined by the electronic Schrödinger equation

$$H_{\mathrm{el}} = -\sum_{j=1}^{N_e} \frac{\hbar^2}{2m} \nabla_j^2 + \sum_{j=1}^{N_e} U(\mathbf{r}_j) + \sum_{j,j'=1}^{N_e} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|}.$$

The atoms in a solid tend to order in a crystalline form, i.e. most systems arrange their atomic constituents at sufficiently low temperatures in a periodic lattice. here are a

number of exceptions, such as glasses (systems believed to be kinetically unable to reach the crystalline ground state), quasicrystals (possibly metastable structures that arrange in highly ordered, yet non-crystalline form), or He (forming in equilibrium a quantum fluid without periodic order, related to its large zero-point fluctuations of the crystalline state). The reason for the periodic arrangement is ultimately the dominance of the potential energy term V_{ii}^{eff} over the kinetic energy T_i.

Thus, it holds

$$\Phi_n(\mathbf{R}_i) = e^{i\phi}\Phi_n(\mathbf{R}_i + \mathbf{t})$$

where $\mathbf{t}$ is a vector that characterizes the periodic structure.

We can write

$$\mathbf{t} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$$

where the $\mathbf{a}_i$ are the primitive translation vectors and the l_i are integers. The three primitive translation vectors span a parallelepiped with volume

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3).$$

This parallelepiped is also called the primitive unit cell of the crystalline solid. Inside this unit cell one might find a number of distinct atoms, at locations $\mathbf{r}_l$ relative to the origin of the primitive cell. The set of the atoms within the unit cell and their corresponding locations are refereed to as the basis of the unit cell. The choice of the primitive translation vectors and thus, of the primitive unit cell is not unique. A very convenient choice is the Wigner-Seitz cell. The Wigner–Seitz cell around a lattice point is defined as the locus of points in space that are closer to that lattice point than to any of the other lattice points. A Wigner–Seitz cell is a primitive cell spanning the entire Bravais lattice without leaving any gaps or holes. Its volume is given by Ω defined above. The cell may be chosen by first picking a lattice point. Then, lines are drawn to all nearby (closest) lattice points. At the midpoint of each line, another line is drawn normal to each of the first set of lines. In the case of a three-dimensional lattice, a perpendicular plane is drawn at the midpoint of the lines between the lattice points. By using this method, the smallest area (or volume) is enclosed in this way and is called the Wigner–Seitz primitive cell. All area (or space) within the lattice will be filled by this type of primitive cell and will leave no gaps.

Consider now a set of points $\mathbf{t}$ constituting a Bravais lattice, and a plane wave defined

by:

$$e^{i\mathbf{r}\cdot\mathbf{K}}$$

If this plane wave has the same periodicity as the Bravais lattice, then it satisfies the equation:

$$e^{i(\mathbf{t}+\mathbf{r})\cdot\mathbf{K}} = e^{i\mathbf{r}\cdot\mathbf{K}}$$

such that

$$e^{i\mathbf{t}\cdot\mathbf{K}}$$

the reciprocal lattice as the set of all vectors $\mathbf{K}$ that satisfy the above identity for all lattice point position vectors $\mathbf{t}$. Thus

$$\mathbf{t}\cdot\mathbf{K} = 2\pi m$$

with integer m. This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original lattice. The reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{\Omega}\mathbf{a}_2 \times \mathbf{a}_3, \\
\mathbf{b}_2 &= \frac{2\pi}{\Omega}\mathbf{a}_3 \times \mathbf{a}_1, \\
\mathbf{b}_3 &= \frac{2\pi}{\Omega}\mathbf{a}_1 \times \mathbf{a}_2.
\end{aligned}$$

where

$$\mathbf{K} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

with integers m_i. The Brillouin zone is a primitive unit cell of the reciprocal lattice. In other words, the Wigner–Seitz cell in the reciprocal lattice is the first Brillouin zone.

The simple cubic Bravais lattice, with cubic primitive cell of side a, has for its reciprocal a simple cubic lattice with a cubic primitive cell of side $2\pi/a$. The cubic lattice is therefore said to be self-dual, having the same symmetry in reciprocal space as in real space. The reciprocal lattice to an face-centered cubic (FCC) lattice is the body-centered cubic (BCC) lattice and vice versa. The reciprocal to a simple hexagonal Bravais lattice with lattice constants c and a is another simple hexagonal lattice with lattice constants $2\pi/c$ and $4\pi/\left(\sqrt{3}a\right)$ rotated through 30° about the c axis with respect to the direct lattice. The reciprocal lattice of the reciprocal lattice is the original, or direct lattice.

Consider a lattice periodic function, such as the electron density $\rho(\mathbf{r})$. Due to its periodicity, we can expand it in a Fourier series

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}},$$

where the periodicity implies that $\mathbf{K}$ is a vector of the reciprocal lattice. In order to determine the Fourier coefficients, we write multiply $\rho(\mathbf{r})$ with $e^{-i\mathbf{K}\cdot\mathbf{r}}$ and integrate over the volume

$$\begin{aligned}\int_V d^3r\rho(\mathbf{r})\, e^{-i\mathbf{K}\cdot\mathbf{r}} &= \sum_{\mathbf{K}'} \rho_{\mathbf{K}'} \int_V d^3r e^{i\mathbf{K}'\cdot\mathbf{r}} e^{-i\mathbf{K}\cdot\mathbf{r}} \\ &= \sum_{\mathbf{K}'} \rho_{\mathbf{K}'} V \delta_{\mathbf{K}',\mathbf{K}} = V\rho_{\mathbf{K}}\end{aligned}$$

which yields

$$\rho_{\mathbf{K}} = \frac{1}{V}\int_V d^3r\rho(\mathbf{r})\, e^{-i\mathbf{K}\cdot\mathbf{r}}.$$

When we evaluate this integral it is, given the periodicity, sufficient to integrate only over the unit cell with volume V_0

$$\rho_{\mathbf{K}} = \frac{1}{V_0}\int_{V_0} d^3r\rho(\mathbf{r})\, e^{-i\mathbf{K}\cdot\mathbf{r}}.$$

Suppose the masses are distributed in point form

$$\rho(\mathbf{r}) = M\sum_{\mathbf{t}} \delta(\mathbf{r}-\mathbf{t})$$

it follows

$$\begin{aligned}\rho_{\mathbf{K}} &= \frac{M}{V_0}\sum_{\mathbf{t}}\int_{V_0} d^3r\delta(\mathbf{r}-\mathbf{t})\, e^{-i\mathbf{K}\cdot\mathbf{r}} \\ &= \frac{M}{V_0}e^{-i\mathbf{K}\cdot\mathbf{t}_0} = \frac{M}{V_0}\end{aligned}$$

where $\mathbf{t}_0$ is the one Bravais lattice point inside the unit cell. We obtain

$$\rho(\mathbf{r}) = \frac{M}{V_0}\sum_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}.$$

In particular, we find the identity

$$\sum_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} = V_0\sum_{\mathbf{t}}\delta(\mathbf{r}-\mathbf{t}).$$

Scattering measurements can determine the Fourier coefficients $\rho_{\mathbf{K}}$. Our above results implies that all Fourier coefficients are exactly the same. This is indeed only true in case of a system with only one point-like atom per unit cell. Lets consider two pointlike atoms per unit cell, one at the origin and one at $\mathbf{a}_1/2$. It follows

$$\rho(\mathbf{r}) = M_1 \sum_{\mathbf{t}} \delta(\mathbf{r}-\mathbf{t}) + M_2 \sum_{\mathbf{t}} \delta(\mathbf{r}-\mathbf{t}-\mathbf{a}_1/2).$$

If we determine the Fourier coefficients of this expression we find

$$\begin{aligned}\rho_{\mathbf{K}} &= \frac{M_1}{V_0} + \frac{M_2}{V_0} e^{-i\mathbf{K}\cdot\mathbf{a}_1/2}. \\ &= \frac{M_1}{V_0} + \frac{M_2}{V_0} e^{-im_1\mathbf{b}_1\cdot\mathbf{a}_1/2} \\ &= \frac{M_1}{V_0} + \frac{M_2}{V_0} e^{-i\pi m_1} = \frac{M_1}{V_0} + (-1)^{m_1}\frac{M_2}{V_0}\end{aligned}$$

The structure inside the unit cell is therefore reflected in a modulation of the density components in the reciprocal lattice. This is a general property that is being used to determine the structure of complex unit cells.

A. Bloch Theorem

Potential of ions are periodic with periods being the vectors of the Bravais lattice. We are looking for the eigenfunctions of the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})$$

where $U(\mathbf{r}) = U(\mathbf{r}+\mathbf{t})$. According to the **Bloch Theorem**, the eigenstates have the following form:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is periodic, i.e., $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}+\mathbf{t})$ and $\mathbf{k}$ is Element of the first Brillouin zone.

To prove the theorem we define translation operator $T_{\mathbf{t}}$ such that $T_{\mathbf{t}} f(\mathbf{r}) = f(\mathbf{r}+\mathbf{t})$. $T_{\mathbf{t}}$ is unitary (unitary operators satisfy $U^{-1} = U^{\dagger}$). We have obviously

$$T_{\mathbf{t}}^{-1} = T_{-\mathbf{t}} \tag{211}$$

To obtain $T_{\mathbf{t}}^{\dagger}$ we note the following

$$\begin{aligned}\langle\phi_1|\, T_{\mathbf{t}}\,|\phi_2\rangle &= \int d^3r\phi_1^*(\mathbf{r})T_{\mathbf{t}}\phi_2(\mathbf{r}) \\ &= \int d^3r\phi_1^*(\mathbf{r})\phi_2(\mathbf{r}+\mathbf{t}) \\ &= \int d^3r\phi_1^*(\mathbf{r}-\mathbf{t})\phi_2(\mathbf{r}) \\ &= \int d^3r(T_{-\mathbf{t}}\phi_1(\mathbf{r}))^*\phi_2(\mathbf{r}) \end{aligned} \tag{212}$$

Thus $T_{\mathbf{t}}^{\dagger} = T_{-\mathbf{t}} = T_{\mathbf{t}}^{-1}$.

Furthermore, $T_{\mathbf{t}}$ commutes with H, $[T_{\mathbf{t}}, H] = 0$.

$$T_{\mathbf{t}}H\psi = H(\mathbf{r}+\mathbf{t})\psi(\mathbf{r}+\mathbf{t}) = H(\mathbf{r})\psi(\mathbf{r}+\mathbf{t}) = HT_{\mathbf{t}}\psi \tag{213}$$

All operators $T_{\mathbf{t}}$ commute with each other.

$$T_{\mathbf{t}_1}T_{\mathbf{t}_2}\psi = T_{\mathbf{t}_2}T_{\mathbf{t}_1}\psi = \psi(\mathbf{r}+\mathbf{t}_1+t_{\mathbf{r}}) \tag{214}$$

which implies

$$T_{\mathbf{t}_1}T_{\mathbf{t}_2} = T_{\mathbf{t}_2}T_{\mathbf{t}_1} = T_{\mathbf{t}_1+\mathbf{t}_2}. \tag{215}$$

This means that the set of operators H, $T_{\mathbf{t}}$ (all of them) have common eigenstates (a full set of them).

$$H\psi = E\psi \tag{216}$$

$$T_{\mathbf{t}}\psi = c_{\mathbf{t}}\psi \tag{217}$$

From unitarity follows $|c_{\mathbf{t}}| = 1$. From commutativity of $T_{\mathbf{t}}$: $c_{\mathbf{t}_1}c_{\mathbf{t}_2} = c_{\mathbf{t}_1+\mathbf{t}_2}$.

$\mathbf{t}$ are the vectors of Bravais lattice. Thus $\mathbf{t} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$. This gives

$$c_{\mathbf{t}} = (c_{\mathbf{a}_1})^{n_1}(c_{\mathbf{a}_2})^{n_2}(c_{\mathbf{a}_3})^{n_3} \tag{218}$$

We define $c_{\mathbf{a}_j} = e^{2\pi i x_j}$. Then

$$c_{\mathbf{t}} = e^{2\pi i(n_1x_1+n_2x_2+n_3x_3)} \tag{219}$$

Now we start using the reciprocal lattice. We define $\mathbf{k} = \sum x_j \mathbf{b}_j$ where $\mathbf{b}_j$ are the elementary vectors of the reciprocal lattice. Then we can rewrite as follows

$$c_{\mathbf{t}} = e^{i\mathbf{k}\cdot\mathbf{t}} \tag{220}$$

Indeed, $\mathbf{k}\cdot\mathbf{t} = \sum_{jl} x_j n_l \mathbf{b}_j \cdot \mathbf{a}_l = 2\pi \sum_j x_j n_j$ (for reciprocal lattice we have $\mathbf{b}_j \cdot \mathbf{a}_l = 2\pi\delta_{jl}$).

Thus we obtain

$$T_{\mathbf{t}}\psi = e^{i\mathbf{k}\cdot\mathbf{t}}\psi \ , \tag{221}$$

i.e., each eigenvector is characterized by a vector $\mathbf{k}$. Thus we have

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}) \ , \tag{222}$$

where $u(\mathbf{r}+\mathbf{t}) = u(\mathbf{r})$. (We can define u as $e^{-i\mathbf{k}\cdot\mathbf{r}}\psi$).

Thus all eigenstates are split into families, characterized by different vectors $\mathbf{k}$. Only $\mathbf{k}$ belonging to the first Brillouin zone (the Wigner-Seitz unit of the reciprocal lattice) or any other primitive unite of the reciprocal lattice give different families. This follows from $e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{t}} = e^{i\mathbf{k}\cdot\mathbf{t}}$. Indeed, if $\mathbf{k}$ is outside the first Brillouin zone, then we can find $\mathbf{K}$ in the reciprocal lattice so that $\mathbf{q} = \mathbf{k} - \mathbf{K}$ is in the first Brillouin zone. Then we use

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} u = e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{K}\cdot\mathbf{r}} u = e^{i\mathbf{q}\cdot\mathbf{r}} \tilde{u} \ , \tag{223}$$

where $\tilde{u} \equiv e^{-i\mathbf{K}\cdot\mathbf{r}} u$ and $\tilde{u}(\mathbf{r}+\mathbf{R}) = \tilde{u}(\mathbf{r})$.

In each family we introduce the index n counting the states of the family. The functions u depend on $\mathbf{k} \in$ first B.Z. and on n. Thus, finally we obtain:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \, . \tag{224}$$

B. Born-von Karmann boundary conditions

The B-v-K conditions read:

$$\psi(\mathbf{r} + N_j \mathbf{a}_j) = \psi(\mathbf{r}) \ , \tag{225}$$

for $j = 1, 2, 3$ and $N_1, N_2, N_3 \gg 1$. The total number of primitive cells is then $N_1 N_2 N_3$.

This limits the possible values of $\mathbf{k}$. Namely we must have $e^{iN_j \mathbf{k}\cdot\mathbf{a}_j} = 1$. With $\mathbf{k} = \sum x_j \mathbf{b}_j$ where $\mathbf{b}_j$ are the elementary vectors of the reciprocal lattice we obtain $x_j = m_j/N_j$.

Although it would be better to chose all allowed values of $\mathbf{k}$ within the first Brillouin zone it is simpler here to use a different primitive cell in the reciprocal lattice. Namely we can chose $m_j = 0, 1, ..., N_j - 1$. This gives

$$\mathbf{k} = \sum_j \frac{m_j}{N_j} \mathbf{b}_j \ , \tag{226}$$

for $m_j = 0, 1, ..., N_j - 1$. There are $N = N_1 N_2 N_3$ allowed vectors $\mathbf{k}$.

The volume in the reciprocal lattice per one vector $\mathbf{k}$:

$$\Delta k_1 \Delta k_2 \Delta k_3 = \Delta \mathbf{k}_1 \cdot (\Delta \mathbf{k}_2 \times \Delta \mathbf{k}_3) = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right)$$
$$= \frac{1}{N} \frac{(2\pi)^3}{\Omega} \ , \tag{227}$$

where $\Omega \equiv \frac{V}{N} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$.

To calculate a sum over the whole primitive cell (1-st B.Z.) we use in the limit of large N:

$$\sum_{\mathbf{k}} = \int \frac{d^3k}{\Delta k_1 \Delta k_2 \Delta k_3} \to \frac{N\Omega}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int d^3k \tag{228}$$

1. Schrödinger equation with B-K boundary conditions

We expand both the wave function and the potential in the basis of momentum states, i.e., plane waves. Thus:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} \, e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{229}$$

The boundary conditions, e.g., those of Born-von Karmann, make the set of $\mathbf{k}$-vectors discrete:

$$\mathbf{k} = \sum_j \frac{m_j}{N_j} \mathbf{b}_j \ , \tag{230}$$

where $m_j \in \mathbf{Z}$. The sum is not limited to the first Brillouin zone.

The potential energy is a periodic function (Bravais-lattice). Thus it can be expanded as

$$U(\mathbf{r}) = \sum_{\mathbf{Q}} U_{\mathbf{Q}} e^{i\mathbf{Q}\cdot\mathbf{r}} \ , \tag{231}$$

where $\mathbf{Q}$ runs over the reciprocal lattice. We have

$$U_{\mathbf{Q}} = \frac{1}{\Omega} \int_{P.U.} d^3r \, U(\mathbf{r}) e^{-i\mathbf{Q}\cdot\mathbf{r}} \ , \tag{232}$$

where the integration is over a primitive unit of the Bravais lattice and Ω is the volume of the primitive unit. Since U is real (Hermitian) we have $U_{-\mathbf{Q}} = U^*_{\mathbf{Q}}$.

The Schrödinger equation now reads

$$\begin{aligned} E\psi &= E\sum_{\mathbf{q}} c_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}} = \left(-\frac{\hbar^2}{2m}\nabla^2 + U\right)\psi \\ &= \sum_{\mathbf{q}} \frac{\hbar^2 q^2}{2m} c_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}} + \sum_{\mathbf{Q},\mathbf{q}} U_{\mathbf{Q}} c_{\mathbf{q}}\, e^{i(\mathbf{Q}+\mathbf{q})\cdot\mathbf{r}} \\ &= \sum_{\mathbf{q}} \frac{\hbar^2 q^2}{2m} c_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}} + \sum_{\mathbf{Q},\mathbf{q}} U_{\mathbf{Q}} c_{\mathbf{q}-\mathbf{Q}}\, e^{i\mathbf{q}\cdot\mathbf{r}} \ , \end{aligned} \tag{233}$$

where in the last line we substituted $\mathbf{q} \to \mathbf{q} - \mathbf{Q}$. The coefficients in front of each harmonics must satisfy this equation. Thus

$$\left(E - \frac{\hbar^2 q^2}{2m}\right) c_{\mathbf{q}} = \sum_{\mathbf{Q}} U_{\mathbf{Q}} c_{\mathbf{q}-\mathbf{Q}} \ . \tag{234}$$

We see that only $\mathbf{q}$'s related by a vector of the reciprocal lattice influence each other. Each such family can be characterized by a vector in the 1-st Brillouin zone. Thus, in each family we introduce $\mathbf{k}$ and all the $\mathbf{q}$'s in the family are given by $\mathbf{k} + \mathbf{K}$, where $\mathbf{K}$ runs over the reciprocal lattice. This gives

$$\left(E - \frac{\hbar^2 (\mathbf{k}+\mathbf{K})^2}{2m}\right) c_{\mathbf{k}+\mathbf{K}} = \sum_{\mathbf{Q}} U_{\mathbf{Q}} c_{\mathbf{k}+\mathbf{K}-\mathbf{Q}} \ . \tag{235}$$

The number of equations for each $\mathbf{k} \in$ 1-st B.Z. is infinite as $\mathbf{K}$ runs over the whole reciprocal lattice.

We will use the index n to count the solutions of Eq. (235). The solution number n is a set $c_{n,\mathbf{k}+\mathbf{K}}$ for all vectors $\mathbf{K} \in$ reciprocal lattice. Since Eq. (235) is a Schrödinger equation and the sets $c_{n,\mathbf{k}+\mathbf{K}}$ are the wave functions, they are orthonormal, i.e.,

$$\sum_{\mathbf{K}} c^*_{n_1,\mathbf{k}+\mathbf{K}} c_{n_2,\mathbf{k}+\mathbf{K}} = \delta_{n_1,n_2} \ , \tag{236}$$

and complete

$$\sum_{n} c^*_{n,\mathbf{k}+\mathbf{K}_1} c_{n,\mathbf{k}+\mathbf{K}_2} = \delta_{\mathbf{K}_1,\mathbf{K}_2} \ . \tag{237}$$

(Note that $\mathbf{K}$ serves here as coordinate of the wave function.)

The eigenstates in the coordinate representation then read

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{n,\mathbf{k}+\mathbf{K}}\, e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}} c_{n,\mathbf{k}+\mathbf{K}}\, e^{i\mathbf{K}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \ , \tag{238}$$

where

$$u_{n,\mathbf{k}}(\vec{r}) \equiv \sum_{\mathbf{K}} c_{n,\mathbf{k}+\mathbf{K}}\, e^{i\mathbf{K}\cdot\mathbf{r}} \ . \tag{239}$$

Now, if we slightly change $\mathbf{k}$, only the LHS of the equation (235) changes slightly. One can expect that in each family n the states and the eigen-energies change smoothly. We obtain bands.

2. Properties of the Bloch states

Bloch states are orthonormal.

- We obtain

$$\begin{aligned}\int d^3r\, \psi^*_{n_1,\mathbf{k}_1}(\mathbf{r})\psi_{n_2,\mathbf{k}_2}(\mathbf{r}) &= \sum_{\mathbf{K}_1,\mathbf{K}_2} c^*_{n_1,\mathbf{k}_1+\mathbf{K}_1} c_{n_2,\mathbf{k}_2+\mathbf{K}_2} \int d^3r\, e^{i(\mathbf{k}_2+\mathbf{K}_2-\mathbf{k}_1-\mathbf{K}_1)} \\ &= V \sum_{\mathbf{K}_1,\mathbf{K}_2} c^*_{n_1,\mathbf{k}_1+\mathbf{K}_1} c_{n_2,\mathbf{k}_2+\mathbf{K}_2} \delta_{\mathbf{k}_2+\mathbf{K}_2,\mathbf{k}_1+\mathbf{K}_1} \ , \end{aligned} \tag{240}$$

Since $\mathbf{k}_1$ and $\mathbf{k}_2$ both are in the 1-st B.Z. we have $\delta_{\mathbf{k}_2+\mathbf{K}_2,\mathbf{k}_1+\mathbf{K}_1} = \delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{K}_1,\mathbf{K}_2}$. Thus

$$\begin{aligned}\int d^3r\, \psi^*_{n_1,\mathbf{k}_1}(\mathbf{r})\psi_{n_2,\mathbf{k}_2}(\mathbf{r}) &= \delta_{\mathbf{k}_1,\mathbf{k}_2} V \sum_{\mathbf{K}_1} c^*_{n_1,\mathbf{k}_1+\mathbf{K}_1} c_{n_2,\mathbf{k}_1+\mathbf{K}_1} \\ &= V\delta_{\mathbf{k}_1,\mathbf{k}_2}\, \delta_{n_1,n_2} \ . \end{aligned} \tag{241}$$

In the thermodynamic limit $V \to \infty$ we have $V\delta_{\mathbf{k}_1,\mathbf{k}_2} \to (2\pi)^3\delta(\mathbf{k}_1 - \mathbf{k}_2)$.

Basis of Bloch states is complete.

-

$$\begin{aligned}&\sum_n \sum_{\mathbf{k}\in 1.\mathrm{B.Z}} \psi^*_{n,\mathbf{k}}(\mathbf{r}_1)\psi_{n,\mathbf{k}}(\mathbf{r}_2) \\ &= \sum_n \sum_{\mathbf{k}\in 1.\mathrm{B.Z}} \sum_{\mathbf{K}_1,\mathbf{K}_2} c^*_{n,\mathbf{k}+\mathbf{K}_1} c_{n,\mathbf{k}+\mathbf{K}_2}\, e^{-i\mathbf{K}_1\cdot\mathbf{r}_1} e^{i\mathbf{K}_2\cdot\mathbf{r}_2} e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)} \\ &= \sum_{\mathbf{k}\in 1.\mathrm{B.Z}} \sum_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot(\mathbf{r}_2-\mathbf{r}_1)} = V\delta(\mathbf{r}_2-\mathbf{r}_1) \ . \end{aligned} \tag{242}$$

Momentum and crystal momentum

- The vector $\hbar\mathbf{k}$ is not the momentum and the Bloch states are not eigenstates of the momentum operator. Indeed

$$\widehat{\mathbf{p}}\psi_{n,\mathbf{k}} = -i\hbar\boldsymbol{\nabla}\psi_{n,\mathbf{k}} = \hbar\mathbf{k}\psi_{n,\mathbf{k}} + e^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\nabla}u_{n,\mathbf{k}} \; . \tag{243}$$

  The vector $\hbar\mathbf{k}$ is called "crystal momentum".

In order to determine the expectation value of the momentum operator

$$\begin{aligned}
\langle n\mathbf{k}\left|\widehat{\mathbf{p}}\right|n\mathbf{k}\rangle &= -i\hbar\int_V d^3r e^{-i\mathbf{k}\cdot\mathbf{r}}u^*_{n\mathbf{k}}(\mathbf{r})\,\boldsymbol{\nabla}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \\
&= \hbar\mathbf{k}\int_V d^3r\left|u^*_{n\mathbf{k}}(\mathbf{r})\right|^2 - i\hbar\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\,\boldsymbol{\nabla}u_{n\mathbf{k}}(\mathbf{r}) \\
&= \hbar\mathbf{k} - i\hbar\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\,\boldsymbol{\nabla}u_{n\mathbf{k}}(\mathbf{r})\,.
\end{aligned}$$

We insert $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ into the Schrödinger equation

$$\left(-\frac{\hbar^2\nabla^2}{2m} + U - i\frac{\hbar^2}{m}\mathbf{k}\cdot\boldsymbol{\nabla} - E_{n\mathbf{k}} + \frac{\hbar^2k^2}{2m}\right)u_{n\mathbf{k}}(\mathbf{r}) = 0$$

We change $\mathbf{k}\to\mathbf{k}+\delta\mathbf{k}$ which yields $E_{n\mathbf{k}}\to E_{n\mathbf{k}}+\delta E_{n\mathbf{k}} = E_{n\mathbf{k}} + (\partial E_{n\mathbf{k}}/\partial\mathbf{k})\cdot\delta\mathbf{k}$ as well as $u_{n\mathbf{k}}\to u_{n\mathbf{k}}+\delta u_{n\mathbf{k}}$ and it follows

$$\left(-\frac{\hbar^2\nabla^2}{2m} + U - i\frac{\hbar^2}{m}\mathbf{k}\cdot\boldsymbol{\nabla} - E_{n\mathbf{k}} + \frac{\hbar^2k^2}{2m}\right)\delta u_{n\mathbf{k}} = i\frac{\hbar^2}{m}\delta\mathbf{k}\cdot\boldsymbol{\nabla}u_{n\mathbf{k}} + \delta E_{n\mathbf{k}}u_{n\mathbf{k}} - \frac{\hbar^2\mathbf{k}\cdot\delta\mathbf{k}}{m}u_{n\mathbf{k}}$$

This is an inhomogeneous differential equation for $\delta u_{n\mathbf{k}}$ with inhomogeneity on the right hand side. In order for a unique solution to exist, the solution of the homogeneous equation, i.e. $u_{n\mathbf{k}}$, must be orthogonal to the inhomogeneity:

$$\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\left(i\frac{\hbar^2}{m}\delta\mathbf{k}\cdot\boldsymbol{\nabla}u_{n\mathbf{k}} + \delta E_{n\mathbf{k}}u_{n\mathbf{k}} - \frac{\hbar^2\mathbf{k}\cdot\delta\mathbf{k}}{m}u_{n\mathbf{k}}\right) = 0.$$

Inserting $\delta E_{n\mathbf{k}}$ yields

$$\delta\mathbf{k}\cdot\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\left(i\frac{\hbar^2}{m}\boldsymbol{\nabla}u_{n\mathbf{k}} + (\partial E_{n\mathbf{k}}/\partial\mathbf{k})\,u_{n\mathbf{k}} - \frac{\hbar^2\mathbf{k}}{m}u_{n\mathbf{k}}\right) = 0$$

Since this should be true for an arbitrary $\delta\mathbf{k}$ we obtain

$$\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\left(i\frac{\hbar^2}{m}\boldsymbol{\nabla}u_{n\mathbf{k}} + (\partial E_{n\mathbf{k}}/\partial\mathbf{k})\,u_{n\mathbf{k}} - \frac{\hbar^2\mathbf{k}}{m}u_{n\mathbf{k}}\right) = 0$$

which yields

$$-i\hbar\int_V d^3r u^*_{n\mathbf{k}}(\mathbf{r})\,\boldsymbol{\nabla}u_{n\mathbf{k}} = m\hbar^{-1}(\partial E_{n\mathbf{k}}/\partial\mathbf{k}) - \hbar\mathbf{k}$$

such that

$$\langle n\mathbf{k}\,|\widehat{\mathbf{p}}|\,n\mathbf{k}\rangle \;= m\hbar^{-1}\left(\partial E_{n\mathbf{k}}/\partial\mathbf{k}\right) = m\mathbf{v}_{n\mathbf{k}}.$$

This, essential for the determination of the momentum is the energy dispersion $E_{n\mathbf{k}}$. Here we also introduced the velocity $\mathbf{v}_{n\mathbf{k}} = \hbar^{-1}\left(\partial E_{n\mathbf{k}}/\partial\mathbf{k}\right)$.

Discreetness of states indexed by n.

- The Schrödinger equation for a given $\mathbf{k}$

$$\left(E - \frac{\hbar^2(\mathbf{k}+\mathbf{K})^2}{2m}\right) c_{\mathbf{k}+\mathbf{K}} = \sum_{\mathbf{Q}} U_{\mathbf{Q}} c_{\mathbf{k}+\mathbf{K}-\mathbf{Q}} \tag{244}$$

can be rewritten for the function

$$u_{\mathbf{k}}(\mathbf{r}) \equiv \sum_{\mathbf{K}} c_{\mathbf{k}+\mathbf{K}}\, e^{i\mathbf{K}\cdot\mathbf{r}}\ . \tag{245}$$

as

$$\left(E - \frac{\hbar^2(\mathbf{k}-i\boldsymbol{\nabla})^2}{2m}\right) u_{\mathbf{k}}(\mathbf{r}) = U(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})\ , \tag{246}$$

accompanied by the periodic boundary conditions $u_{\mathbf{k}}(\mathbf{r}+\mathbf{t}) = u_{\mathbf{k}}(\mathbf{r})$. The problem thus must be solved in one primitive unit of the Bravais lattice and can give only discreet spectrum.

VI. ALMOST FREE ELECTRONS.

We start from the Schrödinger equation

$$\left(E_{n,\mathbf{k}} - \frac{\hbar^2(\mathbf{k}+\mathbf{K})^2}{2m}\right) c_{n,\mathbf{k}+\mathbf{K}} = \sum_{\mathbf{Q}} U_{\mathbf{Q}} c_{n,\mathbf{k}+\mathbf{K}-\mathbf{Q}} \tag{247}$$

for the coefficients of the function

$$u_{n,\mathbf{k}}(\vec{r}) \equiv \sum_{\mathbf{K}} c_{n,\mathbf{k}+\mathbf{K}}\, e^{i\mathbf{K}\cdot\mathbf{r}}\ . \tag{248}$$

Renaming $\mathbf{K}_1 \equiv \mathbf{K}$ and $\mathbf{K}_2 \equiv \mathbf{K} - \mathbf{Q}$ we obtain

$$\left(E_{n,\mathbf{k}} - \frac{\hbar^2(\mathbf{k}+\mathbf{K}_1)^2}{2m}\right) c_{n,\mathbf{k}+\mathbf{K}_1} = \sum_{\mathbf{K}_2} U_{\mathbf{K}_1-\mathbf{K}_2} c_{n,\mathbf{k}+\mathbf{K}_2} \tag{249}$$

We start from the limit of free electrons $U = 0$. The solutions of (249) are trivial: for each n there is $\mathbf{K}_n$ such that

$$E_{n,\mathbf{k}} = \epsilon^{(0)}_{n,\mathbf{k}} \equiv \frac{\hbar^2(\mathbf{k}+\mathbf{K}_n)^2}{2m} \tag{250}$$

n and $c_{n,\mathbf{k}+\mathbf{K}_l} = \delta_{n,l}$.

Now consider $U \neq 0$. First, $U_{\mathbf{Q}=0}$ gives a total shift of energy. Thus, we take it into account and put $U_{\mathbf{Q}=0} = 0$. There are two possibilities:

1) For a given $\mathbf{k}$ there are no other vectors of the reciprocal lattice $\mathbf{K}_l$ such that $\epsilon^{(0)}_{l,\mathbf{k}} \approx \epsilon^{(0)}_{n,\mathbf{k}}$ (more precisely the difference of the two energies of order or smaller than U). Then we are in the situation of the non-degenerate perturbation theory. This gives for $l \neq n$

$$c_{n,\mathbf{k}+\mathbf{K}_l} = \frac{U_{\mathbf{K}_l-\mathbf{K}_n}}{\epsilon^{(0)}_{n,\mathbf{k}} - \epsilon^{(0)}_{l,\mathbf{k}}} + O(U^2) \tag{251}$$

and for the band energy we obtain

$$E_{n,\mathbf{k}} = \epsilon^{(0)}_{n,\mathbf{k}} + \sum_{l\neq n} \frac{U_{\mathbf{K}_n-\mathbf{K}_l} U_{\mathbf{K}_l-\mathbf{K}_n}}{\epsilon^{(0)}_{n,\mathbf{k}} - \epsilon^{(0)}_{l,\mathbf{k}}} + O(U^3) \tag{252}$$

The bands repel each other.

2) There are some (at least one in addition to $\mathbf{K}_n$) vectors $\mathbf{K}_l \neq \mathbf{K}_n$ such that $\epsilon^{(0)}_{l,\mathbf{k}} \approx \epsilon^{(0)}_{n,\mathbf{k}}$. We denote all m such vectors (including $\mathbf{K}_n$) by $\mathbf{K}_l$ with $l = 1, \ldots, m$. The degenerate perturbation theory tells us to solve the following system of m equations ($j = 1, \ldots, m$):

$$\left(E_{\mathbf{k}} - \frac{\hbar^2(\mathbf{k}+\mathbf{K}_j)^2}{2m} \right) c_{\mathbf{k}+\mathbf{K}_j} = \sum_{i=1}^{m} U_{\mathbf{K}_j-\mathbf{K}_i} c_{\mathbf{k}+\mathbf{K}_i} \tag{253}$$

Consider a special, but most important case when the degeneracy is between two energies corresponding to vectors $\mathbf{K}_1$ and $\mathbf{K}_2$. First we note that the condition on $\mathbf{k}$ for this to happen coincides with the one for the Bragg scattering of the X-rays. Namely, the condition of degeneracy reads $|\mathbf{k}+\mathbf{K}_1| = |\mathbf{k}+\mathbf{K}_2| = |\mathbf{k}+\mathbf{K}_1-(\mathbf{K}_1-\mathbf{K}_2)|$. Introducing $\mathbf{q} \equiv \mathbf{k}+\mathbf{K}_1$ and $\mathbf{K} \equiv \mathbf{K}_1 - \mathbf{K}_2$ ($\mathbf{K} \in$ reciprocal lattice) we see that the relation between the wave vectors in the expanded band picture $\mathbf{q} = \mathbf{k}+\mathbf{K}_1$ and $\mathbf{q}-\mathbf{K} = \mathbf{k}+\mathbf{K}_2$ is like between the wave vectors of the incident and the reflected waves in the Bragg scattering. Both have to end at the so called "Bragg plane" as depicted in Fig. 1. In particular the condition on $\mathbf{q}$ reads $|\mathbf{q}\cdot\mathbf{K}| = \frac{1}{2}|\mathbf{K}|$.

The eigenvalues are determined as zeros of the determinant of the following matrix

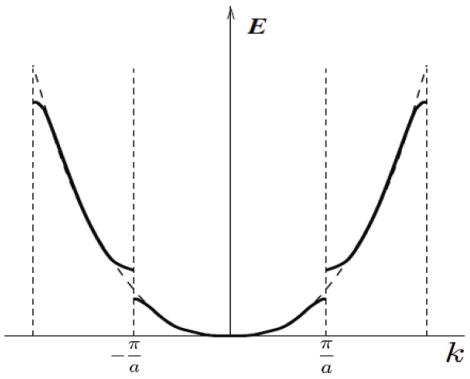
$$\begin{pmatrix} E_{\mathbf{k}} - \epsilon^{(0)}_{1,\mathbf{k}} & -U_{\mathbf{K}} \\ -U_{-\mathbf{K}} & E_{\mathbf{k}} - \epsilon^{(0)}_{2,\mathbf{k}} \end{pmatrix} \tag{254}$$

The solutions read

$$E_{\vec{k}} = \frac{\epsilon^{(0)}_{1,\mathbf{k}} + \epsilon^{(0)}_{2,\mathbf{k}}}{2} \pm \sqrt{\left(\frac{\epsilon^{(0)}_{1,\mathbf{k}} - \epsilon^{(0)}_{2,\mathbf{k}}}{2} \right)^2 + |U_{\mathbf{K}}|^2} \tag{255}$$

In particular, the splitting exactly at the Bragg plain, where $\epsilon^{(0)}_{1,\mathbf{k}} = \epsilon^{(0)}_{2,\mathbf{k}}$ is given by $E_{2,\mathbf{k}} - E_{1,\mathbf{k}} = 2|U_{\mathbf{K}}|$.

Example in 1D:



Extended zone and Bragg scattering at
the BZ boundary in one dimension.

VII. TIGHT BINDING APPROXIMATION

A. Wannier functions

One can show that the Bloch states can be presented in a different form:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \ , \tag{256}$$

where $\mathbf{R}$ is a vector of the Bravais lattice and

$$\begin{aligned} w_n(\mathbf{k}) &= \frac{1}{N} \sum_{\mathbf{k}\in 1.\ \text{B.Z.}} \psi_{n,\mathbf{k}}(\mathbf{r}) \\ &= \frac{V}{N} \int_{1.\ \text{B.Z.}} \frac{d^3k}{(2\pi)^3} \psi_{n,\mathbf{k}}(\mathbf{r}) \, . \end{aligned} \tag{257}$$

By operation of translation we obtain

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}\in 1.\ \text{B.Z.}} \psi_{n,\mathbf{k}}(\mathbf{r}-\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}\in 1.\ \text{B.Z.}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) \ . \tag{258}$$

Indeed, substituting Eq.(258) into Eq.(256) we obtain

$$\begin{aligned}\psi_{n,\mathbf{k}}(\mathbf{r}) &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \frac{1}{N} \sum_{\mathbf{q}\in 1.\ \text{B.Z.}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) \\ &= \sum_{\mathbf{q}\in 1.\ \text{B.Z.}} \delta_{\mathbf{k},\mathbf{q}}\, \psi_{n,\mathbf{q}}(\vec{r}) = \psi_{n,\mathbf{k}}(\vec{r}) \ . \end{aligned} \tag{259}$$

Wannier functions of different bands n are orthogonal. Also orthogonal are the Wannier functions of the same band but shifted to different $\mathbf{R}$'s.

B. Schrödinger equation for Wannier functions

Assume the total potential is a sum of atomic ones (for a simple Bravais lattice with one atom per unit):

$$U(\mathbf{r}) = \sum_{\mathbf{R}} U_a(\mathbf{r}-\mathbf{R}) \ . \tag{260}$$

Then from

$$H\psi_{n,\mathbf{k}} = \left(-\frac{\hbar^2\Delta}{2m} + \sum_{\mathbf{R}} U_a(\mathbf{r}-\mathbf{R}) \right) \psi_{n,\mathbf{k}} = E_{n,\mathbf{k}}\psi_{n,\mathbf{k}} \tag{261}$$

we obtain

$$E_{n,\mathbf{k}} \sum_{\vec{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) = \left(-\frac{\hbar^2\Delta}{2m} + \sum_{\mathbf{R}_1} U_a\left(\mathbf{r}-\mathbf{R}_1\right) \right) e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \ . \tag{262}$$

In the r.h.s. we separate the terms with $\mathbf{R}_1 = \mathbf{R}$ from those where $\mathbf{R}_1 \neq \mathbf{R}$:

$$\begin{aligned} E_{n,\mathbf{k}} \sum_{\vec{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) &= \sum_{\mathbf{R}} \left(-\frac{\hbar^2\Delta}{2m} + U_a\left(\mathbf{r}-\mathbf{R}\right) \right) e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \\ &+ \sum_{\mathbf{R}} \sum_{\mathbf{R}_1\neq\mathbf{R}} U_a\left(\mathbf{r}-\mathbf{R}_1\right)\ e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \\ &= \sum_{\mathbf{R}} \left(-\frac{\hbar^2\Delta}{2m} + U_a\left(\mathbf{r}-\mathbf{R}\right) \right) e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \\ &+ \sum_{\vec{R}} \Delta U(\mathbf{r},\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \ , \end{aligned} \tag{263}$$

where $\Delta U(\mathbf{r},\mathbf{R}) \equiv \sum_{\mathbf{R}_1\neq\mathbf{R}} U_a(\mathbf{r}-\mathbf{R}_1) = U(\mathbf{r}) - U_a(\mathbf{r}-\mathbf{R})$.

C. Linear Combination of Atomic Orbitals (LCAO)

Simplest approximation for the Wannier function $w = \sum_m b_m\phi_m$ where ϕ_m are the atomic orbitals, such that $H_a\phi_m = E_{a,m}\phi_m$. This can be, e.g., a multiplet of the orbital momentum

L with $2L+1$ degenerate states (we omit the band index n). This gives

$$\sum_m b_m (E_{\mathbf{k}} - E_{a,m}) \sum_{\vec{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_m(\mathbf{r}-\mathbf{R}) = \sum_m b_m \sum_{\vec{R}} \Delta U(\mathbf{r},\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} \phi_m(\mathbf{r}-\mathbf{R}) \ ,$$

We have restricted our Hilbert space to linear combinations of atomic orbitals $\phi_m(\mathbf{r}-\mathbf{R})$ shifted to all vectors of the Bravais lattice. While we cannot guarantee that Eq. (**??**) holds exactly (in the whole Hilbert space) we can choose the coefficients b_m and the energy $E_{\vec{k}}$ so that Eq. (**??**) holds in our restricted space. That is we demand that Eq. (**??**) projected on all $\phi_m(\mathbf{r}-\mathbf{R})$ holds. Due to the periodicity of the l.h.s. and the r.h.s. of Eq. (**??**) it is sufficient to project only on $\phi_m(\mathbf{r})$.

Projecting on $\phi_l(\mathbf{r})$ we obtain

$$\begin{aligned} &(E_{\mathbf{k}} - E_{a,l}) b_l + \sum_m b_m (E_{\mathbf{k}} - E_{a,m}) \sum_{\mathbf{R}\neq\mathbf{0}} e^{i\mathbf{k}\cdot\mathbf{R}} \int d^3r \phi_l^*(\mathbf{r}) \phi_m(\mathbf{r}-\mathbf{R}) \\ &= \sum_m b_m \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int d^3r \phi_l^*(\mathbf{r}) \Delta U(\mathbf{r},\mathbf{R}) \phi_m(\mathbf{r}-\mathbf{R}) \ , \end{aligned} \tag{264}$$

Introducing

$$S_{l,m}(\mathbf{R}) \equiv \int d^3r \phi_l^*(\mathbf{r}) \phi_m(\mathbf{r}-\mathbf{R}) \tag{265}$$

and

$$t_{l,m}(\mathbf{R}) \equiv \int d^3r \phi_l^*(\mathbf{r}) \Delta U(\mathbf{r},\mathbf{R}) \phi_m(\mathbf{r}-\mathbf{R}) \tag{266}$$

we obtain

$$\begin{aligned} &(E_{\vec{k}} - E_{a,l}) b_l + \sum_m b_m (E_{\mathbf{k}} - E_{a,m}) \sum_{\mathbf{R}\neq\mathbf{0}} e^{i\mathbf{k}\cdot\mathbf{R}} S_{l,m}(\mathbf{R}) \\ &= \sum_m b_m \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} t_{l,m}(\mathbf{R}) \ , \end{aligned} \tag{267}$$

This is a homogeneous matrix equation on coefficients b_m. To have solutions one has to demand that the determinant of the matrix vanishes, This determines the band energies $E_{n,\mathbf{k}}$. The number of bands is equal to the number of states in the multiplet.

D. Single orbital (s states), one band

We obtain

$$E_{\mathbf{k}} = E_a + \frac{\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} t\,(\mathbf{R})}{1 + \sum_{\mathbf{R}\neq\mathbf{0}} e^{i\mathbf{k}\cdot\mathbf{R}} S(\mathbf{R})} \ , \tag{268}$$

Assume that only nearest neighbors matrix elements, do not vanish (and also $t(\mathbf{0})$). It is important to note that $S(\mathbf{R}) \ll 1$. Thus

$$E_{\mathbf{k}} \approx E_a + t(\mathbf{0}) + \sum_{\mathbf{R},nn} e^{i\mathbf{k}\cdot\mathbf{R}} t\left(\mathbf{R}\right) \ , \tag{269}$$

Then, for different Bravais lattices with one ion per primitive cell we obtain:

1) 1-D lattice with step a.

$$E_k = E_a + t(0) + 2W\cos(ak) \ , \tag{270}$$

where $W = t(a)$.

2) sc-lattice, $\mathbf{a}_1 = a\mathbf{x}, \mathbf{a}_2 = a\mathbf{y}, \mathbf{a}_3 = a\mathbf{z}$, $\phi(\mathbf{r})$ is rotational symmetric:

$$E_{\mathbf{k}} = E_a + h(0) + 2t\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right) \ , \tag{271}$$

where $W = t\left(a\right)$.

3) bcc-lattice. One of the possible choices of the primitive basis is: $\mathbf{a}_1 = a\mathbf{x}, \mathbf{a}_2 = a\mathbf{y}, \mathbf{a}_3 = \frac{1}{2}a(\mathbf{x}+\mathbf{y}+\mathbf{z})$, however the nearest neighbors are at $\mathbf{R} = \frac{a}{2}(\pm\mathbf{x}\pm\mathbf{y}\pm\mathbf{z})$. Altogether 8 neighbors each at distance $\sqrt{3}a/2$. We obtain

$$E_{\vec{k}} = E_a + t(0) + 8W\cos(ak_x/2)\cos(ak_y/2)\cos(ak_z/2) \ , \tag{272}$$

where $W = t(\sqrt{3}a/2)$. (Interesting exercise: show that the reciprocal lattice in fcc).

E. Alternative formulation of tight-binding method

Each primitive cell is characterized by states $|\mathbf{R}, m\rangle$. Index m can count either states of the same atom or states of different atoms in the cell. For example in graphen we would have $m = A, B$, where A and B denote sub-lattices. The overlaps of different states vanish: $\langle \mathbf{R}_1, m_1| \, |\mathbf{R}_2, m_2\rangle = \delta_{\mathbf{R}_1,\mathbf{R}_2}\delta_{m_1,m_2}$. One postulates a tunneling Hamiltonian

$$H = \sum_{\mathbf{R}_1,m_1} \sum_{\mathbf{R}_2,m_2} t_{m_1,m_2}(\mathbf{R}_1 - \mathbf{R}_2) a^\dagger_{\mathbf{R}_2,m_2} a_{\mathbf{R}_1,m_1} \tag{273}$$

The Hamiltonian is Hermitian, i.e., $t_{m_1,m_2}(\mathbf{R}) = t^*_{m_2,m_1}(-\mathbf{R})$.

The Bloch states:

$$|\psi_{\mathbf{R}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_m b_m a^\dagger_{\mathbf{R},m} \, |0\rangle \ . \tag{274}$$

The Wannier w.f.: $|w\rangle = \sum_m b_m a^\dagger_{\mathbf{R}_2,m_2}|0\rangle$.

The energies and the coefficients b_m are determined by substituting the Bloch wave function into the Schrödinger equation: $H|\psi_{\mathbf{R}}\rangle = E_{\mathbf{k}}|\psi_{\mathbf{R}}\rangle$.

We obtain

$$\begin{aligned} H|\psi_{\mathbf{R}}\rangle &= \sum_{\mathbf{R}_1,m_1}\sum_{\mathbf{R}_2,m_2} t_{m_1,m_2}(\mathbf{R}_1-\mathbf{R}_2)a^\dagger_{\mathbf{R}_2,m_2}a_{\mathbf{R}_1,m_1}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\sum_m b_m a^\dagger_{\mathbf{R},m}|0\rangle \\ &= -\sum_{\mathbf{R}_1,m_1}\sum_{\mathbf{R}_2,m_2} t_{m_1,m_2}(\mathbf{R}_1-\mathbf{R}_2)a^\dagger_{\mathbf{R}_2,m_2}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\sum_m b_m a^\dagger_{\mathbf{R},m}a_{\mathbf{R}_1,m_1}|0\rangle \\ &\quad + \sum_{\mathbf{R}_1,m_1}\sum_{\mathbf{R}_2,m_2} t_{m_1,m_2}(\mathbf{R}_1-\mathbf{R}_2)e^{i\mathbf{k}\cdot\mathbf{R}_1}b_{m_1}a^\dagger_{\mathbf{R}_2,m_2}|0\rangle \\ &= E_{\mathbf{k}}\sum_{\mathbf{R}_2} e^{i\mathbf{k}\cdot\mathbf{R}_2}\sum_{m_2} b_{m_2}a^\dagger_{\mathbf{R}_2,m_2}|0\rangle \end{aligned} \tag{275}$$

Comparing coefficients in front of $a^\dagger_{\mathbf{R}_2,m_2}|0\rangle$ we obtain

$$\sum_{\mathbf{R}_1,m_1} t_{m_1,m_2}(\mathbf{R}_1-\mathbf{R}_2)e^{i\mathbf{k}\cdot\mathbf{R}_1}b_{m_1} = E_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_2}b_{m_2}\ . \tag{276}$$

With $\mathbf{R}\equiv\mathbf{R}_1-\mathbf{R}_2$

$$\sum_{\mathbf{R},m_1} e^{i\mathbf{k}\cdot\mathbf{R}}b_{m_1}\,t_{m_1,m_2}(\mathbf{R}) = E_{\mathbf{k}}b_{m_2}\ . \tag{277}$$

We again have reduced the problem to a matrix equation.

1. *Example: Copper-Oxide High temperature superconductors*

The copper oxide high T_c superconductors are attracted the attention of the condensed matter physics community for a number of decades now. Here we want to develop a simple model to describe the electronic states in the vicinity of the Fermi level. Consider for example the system $La_{2-x}Sr_xCuO_4$. Electronically interesting states are usually those that are not associated with closed electronic shells. It is known that elements like La or Sr tend to donate electrons to obtain a closed shell configuration. From the periodic table follows that La^{3+} and Sr^{2+} are the corresponding valence states. Generally, oxygen tends to attract two electrons to achieve its closed shell configuration, i.e. one can assume (for a more detailed discussion, see below) an O^{2-} valence state. Charge neutrality then determines the valence v_{Cu} of copper. Consider first $x=0$ and we obtain:

$$2\times 3 + v_{\mathrm{Cu}} - 4\times 2 = 0 \tag{278}$$

yielding $v_{\rm Cu} = 2$. The electronic configuration of Copper is $\mathrm{Ar}3d^{10}4s^1$, where Ar stands for the closed shell configuration of argon. Thus, we expect for a Cu^{2+} state an electronic configuration $\mathrm{Ar}3d^9$, i.e. with one hole per $3d$-shell. In a spherical environment all $3d$ orbitals are degenerate Already a cubic environment leads to a so called crystal field splitting of the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ orbitals from the $3d_{x^2-y^2}$ and $3d_{z^2-3r^2}$ orbitals. These two subsets of orbitals are still degenerate among each other. However, the crystal structure of the cuprates is tetragonal which leads to a further splitting of the $3d_{x^2-y^2}$ and $3d_{z^2-3r^2}$ orbitals. The energetically highest orbital is the $3d_{x^2-y^2}$ orbital. Thus, to achieve the $3d^9$ configuration, the electron will be transferred from the $3d_{x^2-y^2}$ to the oxygen states. This leaves us with a model of a single hole in the $3d_{x^2-y^2}$ orbital of copper. For $x > 0$, i.e. substituting Sr for La, charge neutrality implies

$$(2-x)\times 3 + x\times 2 + v_{\rm Cu} - 4\times 2 = 0 \tag{279}$$

which leads to

$$v_{\rm Cu} = 2 + x. \tag{280}$$

Substitution of La by Sr yields therefore additional hole doping.

Now, the Cu-sites are arranged on a square lattice, with weak hybridization perpendicular to those planes. In between two copper sites is an oxygen site. The key orbital of those oxygen states are the $2p_x$ and the $2p_y$ orbitals, depending of whether they connect two copper sites along the x- or y-axis. Consider the overlap integral

$$t_{x^2-y^2,x}(a\mathbf{x}) = \int d^3r \phi^*_{x^2-y^2}(\mathbf{r})\Delta U(\mathbf{r}, a\mathbf{x})\phi_x(\mathbf{r}-a\mathbf{x}) \tag{281}$$

and

$$t_{x^2-y^2,x}(-a\mathbf{x}) = \int d^3r \phi^*_{x^2-y^2}(\mathbf{r})\Delta U(\mathbf{r}, -a\mathbf{x})\phi_x(\mathbf{r}+a\mathbf{x}) \tag{282}$$

The potential $\Delta U(\mathbf{r}, \mathbf{R})$ is given by:

$$\Delta U(\mathbf{r}, \mathbf{R}) = \sum_{\mathbf{R}_1 \neq \mathbf{R}} U_a(\mathbf{r}-\mathbf{R}_1) = U(\mathbf{r}) - U_a(\mathbf{r}-\mathbf{R}) \tag{283}$$

Thus, in case of inversion symmetry (which exists in case of the copper-oxides) we have:

$$\Delta U(\mathbf{r}, \mathbf{R}) = \Delta U(-\mathbf{r}, -\mathbf{R}) \tag{284}$$

Since $\phi_{x^2-y^2}(\mathbf{r}) = \phi_{x^2-y^2}(-\mathbf{r})$ and $\phi_x(\mathbf{r}) = -\phi_x(-\mathbf{r})$, follows

$$t_{pd} \equiv t_{x^2-y^2,x}(a\mathbf{x}) = -t_{x^2-y^2,x}(-a\mathbf{x}) \tag{285}$$

The same is true for the y-direction.

Thus, if we confine ourselves to the overlap between those nearest neighbor copper and oxygen states it follows:

$$E_{\mathbf{k}} b_{m_2} = \sum_{\mathbf{R}, m_1} t_{m_1, m_2}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} b_{m_1} \tag{286}$$

performing the sum explicitly yields:

$$\begin{aligned} E_{\mathbf{k}} b_d &= \varepsilon_d b_d + t_{pd}\left(1 - e^{-ik_x a}\right) b_{p_x} + t_{pd}\left(1 - e^{-ik_y a}\right) b_{p_y} \\ E_{\mathbf{k}} b_{p_x} &= \varepsilon_p b_{p_x} + t_{pd}\left(1 - e^{ik_x a}\right) b_d \\ E_{\mathbf{k}} b_{p_y} &= \varepsilon_p b_{p_y} + t_{pd}\left(1 - e^{ik_y a}\right) b_d \end{aligned} \tag{287}$$

which implies that we determine E from the eigenvalues of

$$\widehat{a} = \begin{pmatrix} \varepsilon_d - E & t_{pd}\left(1 - e^{-ik_x a}\right) & t_{pd}\left(1 - e^{-ik_y a}\right) \\ t_{pd}\left(1 - e^{ik_x a}\right) & \varepsilon_p - E & 0 \\ t_{pd}\left(1 - e^{ik_y a}\right) & 0 & \varepsilon_p - H \end{pmatrix} \tag{288}$$

It holds

$$\det \widehat{a} = (\varepsilon_p - E)\left(\varepsilon_p \varepsilon_d - 4t_{pd}^2 - (\varepsilon_p + \varepsilon_d) E + E^2 + 2t_{pd}^2 (\cos k_x a + \cos k_y a)\right) \tag{289}$$

and we obtain

$$E_{\pm} = \frac{1}{2}\left(\varepsilon_p + \varepsilon_d \pm \sqrt{(\varepsilon_p - \varepsilon_d)^2 + 16 t_{pd}^2 \gamma(\mathbf{k})}\right) \tag{290}$$

and

$$E_0 = \varepsilon_p \tag{291}$$

where

$$\gamma(\mathbf{k}) = 1 - \frac{1}{2}(\cos(k_x a) + \cos(k_y a)) \tag{292}$$

Thus, we obtain a bonding a non-bonding and an antibonding band. The bonding and antibonding bands are mixtures of copper and oxygen states that hybridize. Charge neuality demands that the number of holes in the lowest (bonding) band is $1 + x$.

This model is not yet sufficient to describe the physics of the copperoxides. A prediction of this model would be that the material for $x = 0$ would be a metal, as the Fermi level is

in the middle of the band. A widely accepted model that includes electron correlations is the Hubbard model with

$$H = H_{tight-binding} + U \sum_{\mathbf{R}} n_{d\mathbf{R}\uparrow} n_{d\mathbf{R}\downarrow} \tag{293}$$

where $n_{d\mathbf{R}\sigma} = d^{\dagger}_{\mathbf{R}\sigma} d_{\mathbf{R}\sigma}$ is the occupation number on the copper site. The strong local Coulomb repulsion strongly suppresses charge fluctuations and for $x = 0$ and for sufficiently large values of U does indeed lead to an insulating state. This state is called a Mott insulator.

VIII. ELECTRON-ELECTRON INTERACTIONS

A. The role of long range Coulomb interactions

Until now we have ignored the electron-electron Coulomb interaction. To get a first qualitative sense for the role of this important interaction, we consider a simplified model where the electronic band structure is given by a parabolic band with $E_{\mathbf{k}} = \hbar k^2/(2m)$. Here m could also stand for the effective mass that results from the inclusion of the periodic lattice. Thus we analyze the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_i \boldsymbol{\nabla}^2_{\mathbf{r}_i} + \frac{1}{2} \frac{e^2}{4\pi\varepsilon} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{294}$$

In order to get a qualitative understanding of the role of the interaction term it is always useful to introduce a dimensionless measure. To this end we consider a system with electron density n. The resulting characteristic length scale of the problem is the mean electron distance

$$d = n^{1/d} \tag{295}$$

where d is the dimension of space. This is useful in particular due to the fact that a realization of the above Hamiltonian is achieved in semiconductor heterostructures, where in a narrow inversion layer an effective two dimensional system has been realized, i.e. $d = 2$. If we now introduce dimensionless positions

$$\mathbf{x}_i = \mathbf{r}_i / d \tag{296}$$

we can rewrite the above Hamiltonian as

$$H = \frac{\hbar^2}{2md^2}\left(-\sum_i \boldsymbol{\nabla}^2_{\mathbf{x}_i} + \frac{\alpha}{4\pi}\sum_{i\neq j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}\right) \tag{297}$$

where we introduced a dimensionless strength of the interaction

$$\alpha = \frac{e^2 md}{\hbar^2 \varepsilon} = \frac{d}{a_B} \tag{298}$$

where $a_B = \frac{\hbar^2\varepsilon}{me^2}$ is the Bohr radius known from the Hydrogen atom problem. Here the dielectric constant ε of the solid (or in $d = 2$, the dielectric constant of the substrate) can lead to larger values compared to the canonical value in vacuum $a_{B,0} = \frac{\hbar^2}{me^2} = 0.529177249 \times 10^{-10}\,\mathrm{m}$.

These considerations imply that systems with high electron density (which for the above energy dispersion would be metallic) have small values of d, i.e. small values of the electron-electron interaction. This somewhat surprising result is a consequence of the fact that the kinetic energy only dominates once the crystal momenta are large, which is the case in dense systems. In this high-density limit we will find that the electron-electron interaction can frequently be ignores or treated in a simplifies perturbative way as small corrections to the kinetic energy. The main effect will be shown to be the emergence of plasma-oscillations (collective density oscillations). On the other hand, in dilute systems, where the electron-electron interaction becomes large compared to a_B, interactions are expected to be dominant. Here the kinetic energy can often be considered a small perturbation compared to the electron-electron interaction. The ground state is then a result of the optimal Coulomb interaction, At fixed density this leads to the formation of an electron crystal, referred to as the Wigner crystal. The kinetic energy leads solely to vibrations of the electrons in the crystal, similar to lattice vibrations of atoms in solids.

The above conclusions are a direct consequence of the assumed parabolic spectrum. Another, system of current interest in graphene, where electrons near isolated point in the BZ have a linear spectrum. In this case we would start from the Hamiltonian

$$H = -i\hbar v \sum_i \boldsymbol{\sigma}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i} + \frac{1}{2}\frac{e^2}{4\pi\varepsilon}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{299}$$

where $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ is the two dimensional vector of Pauli matrices, acting in the space of the two atoms per unit cell. In terms of dimensionless length scales, follows

$$H = -i\frac{\hbar v}{d}\left(\sum_i \boldsymbol{\sigma}\cdot\boldsymbol{\nabla}_{\mathbf{x}_i} + \frac{\alpha}{4\pi}\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}\right), \tag{300}$$

where

$$\alpha = \frac{e^2}{\hbar v \varepsilon} \tag{301}$$

is a density-independent coupling strength. This is a result of the fact that both, the kinetic and the potential energy, are proportional to inverse length-scales. Inserting the value of the electron velocity of graphene yields $\alpha \simeq 2.2/\varepsilon$ and can be tuned by varying the dielectric constant of the substrate. The key aspect of these considerations is that even the same interaction leads to quite different behavior, depending on the nature of the band-structure of a system. For example, the value of the velocity of graphene which implies $\alpha < 2.2$, excludes the option of a Wigner crystal in this system.

B. Hartree-Fock approximation

The Hartree-Fock approximation is among the simplest methods to treat interactions in many body systems. Here the dynamic problem of interacting electrons is replaced by an effective one-electron problem, where electrons are moving in a static field caused by the other electrons.

We consider in second quantization the Hamiltonian of the many electron problem

$$\begin{aligned} H \; = \; & \sum_{\sigma} \int d^3 r \psi_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m} + U(\mathbf{r}) \right) \psi_{\sigma}(\mathbf{r}) \\ & + \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3 r d^3 r' v(\mathbf{r}-\mathbf{r}') \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma'}^{\dagger}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) . \end{aligned} \tag{302}$$

The main spirit of the Hartree-Fock approximation is based on the identity

$$AB = (A - \langle A \rangle)(B - \langle B \rangle) + A \langle B \rangle + B \langle A \rangle - \langle A \rangle \langle B \rangle . \tag{303}$$

The first term is the joint deviation of the operators A and B from their expectation values. This first term is called the correlation of the two operators AB and is being ignored in the Hartree-Fock approach:

$$AB \simeq A \langle B \rangle + B \langle A \rangle - \langle A \rangle \langle B \rangle . \tag{304}$$

On the level of operators in the Hamiltonian, constants (like the last term $\langle A \rangle \langle B \rangle$) are frequently being ignored. In case of the electron-electron interaction the corresponding

approximation is

$$\psi_\sigma^\dagger(\mathbf{r})\,\psi_{\sigma'}^\dagger(\mathbf{r}')\,\psi_{\sigma'}(\mathbf{r}')\,\psi_\sigma(\mathbf{r}) \simeq \left\langle\psi_\sigma^\dagger(\mathbf{r})\,\psi_\sigma(\mathbf{r})\right\rangle\psi_{\sigma'}^\dagger(\mathbf{r}')\,\psi_{\sigma'}(\mathbf{r}') + \left\langle\psi_{\sigma'}^\dagger(\mathbf{r}')\,\psi_{\sigma'}(\mathbf{r}')\right\rangle\psi_\sigma^\dagger(\mathbf{r})\,\psi_\sigma(\mathbf{r})$$
$$-\left\langle\psi_\sigma^\dagger(\mathbf{r})\,\psi_{\sigma'}(\mathbf{r}')\right\rangle\psi_{\sigma'}^\dagger(\mathbf{r}')\,\psi_\sigma(\mathbf{r}) - \left\langle\psi_{\sigma'}^\dagger(\mathbf{r}')\,\psi_\sigma(\mathbf{r})\right\rangle\psi_\sigma^\dagger(\mathbf{r})\,\psi_{\sigma'}(\mathbf{r}').$$

Thus, if we introduce

$$\rho_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = \left\langle\psi_\sigma^\dagger(\mathbf{r})\,\psi_{\sigma'}(\mathbf{r}')\right\rangle$$

it follows for the Hamiltonian

$$H_{\mathrm{HF}} = \sum_\sigma\int d^3r\psi_\sigma^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m} + U(\mathbf{r}) + U_H(\mathbf{r})\right)\psi_\sigma(\mathbf{r})$$
$$-\sum_{\sigma,\sigma'}\int d^3rd^3r'\psi_\sigma^\dagger(\mathbf{r})\,v(\mathbf{r}-\mathbf{r}')\,\rho_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})\,\psi_{\sigma'}(\mathbf{r}') \tag{305}$$

where

$$U_H(\mathbf{r}) = \sum_{\sigma'}\int d^3r'v(\mathbf{r}-\mathbf{r}')\,\rho_{\sigma'\sigma'}(\mathbf{r}',\mathbf{r}')$$
$$= \frac{e^2}{4\pi\varepsilon}\int d^3r'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{306}$$

with electron density

$$\rho(\mathbf{r}) = \sum_{\sigma'}\rho_{\sigma'\sigma'}(\mathbf{r}',\mathbf{r}'). \tag{307}$$

The last term in H_{HF} is the Fock term It cannot be expressed in terms of the electron density alone. Still H_{HF} is a one particle Hamiltonian albeit with a non-local effective potential.

We expand

$$\psi_\sigma(\mathbf{r}) = \sum_\alpha\varphi_\alpha(\mathbf{r})\,c_{\alpha\sigma} \tag{308}$$

is $\varphi_\alpha(\mathbf{r}) = \langle\mathbf{r}|\alpha\rangle$ is some complete set of states (for example $a = \mathbf{k}$,n in case of Bloch electrons). Then we obtain

$$H_{\mathrm{HF}} = \sum_{\sigma,\sigma'}\sum_{\alpha\beta}H_{\alpha\beta}^{\sigma\sigma'}c_{\alpha\sigma}^\dagger c_{\beta\sigma'} \tag{309}$$

with matrix elements

$$H_{\alpha\beta}^{\sigma\sigma'} = H_{\alpha\beta}^0\delta_{\sigma\sigma'} + \sum_{\gamma\delta}\sum_{\sigma''}V_{\alpha\gamma\delta\beta}\left\langle c_{\gamma\sigma''}^\dagger c_{\delta\sigma''}\right\rangle\delta_{\sigma\sigma'} - \sum_{\gamma\delta}V_{\alpha\gamma\beta\delta}\left\langle c_{\gamma\sigma'}^\dagger c_{\delta\sigma}\right\rangle \tag{310}$$

determined by the non-interacting matrix elements

$$H_{\alpha\beta}^0 = \int d^3r\varphi_\alpha^*(\mathbf{r})\left(-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m} + U(\mathbf{r})\right)\varphi_\beta(\mathbf{r}) \tag{311}$$

as well as the two-particle matrix elements:

$$V_{\alpha\beta\gamma\delta} = \int d^3r d^3r' \varphi^*_\alpha(\mathbf{r}) \varphi^*_\beta(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') \varphi_\gamma(\mathbf{r}') \varphi_\delta(\mathbf{r}). \tag{312}$$

To solve the Hartree-Fock equations one starts from a trial ansatz for the matrix elements $\left\langle c^\dagger_{\gamma\sigma'} c_{\delta\sigma} \right\rangle$. Given a basis set, the $V_{\alpha\beta\gamma\delta}$ are given and only need be determined once. The next step is to evaluate all matrix elements of $H^{\sigma\sigma'}_{\alpha\beta}$. Diagonalization of $H^{\sigma\sigma'}_{\alpha\beta}$ leads to the eigenvalues of a problem that is formally noninteracting, i.e. the occupations of this one-particle problem can be analyzed explicitly. This leads to $\left\langle c^\dagger_{\gamma\sigma'} c_{\delta\sigma} \right\rangle$ and we can compare it with our initial guess. If it agrees, the Hartree Fock equations are solved. Otherwise, we may take those recalculated expectation values $\left\langle c^\dagger_{\gamma\sigma'} c_{\delta\sigma} \right\rangle$ as starting point for the subsequent evaluation of the $H^{\sigma\sigma'}_{\alpha\beta}$ until the procedure converges.

C. Stoner Theory of Ferromagnetism

The Stoner theory of ferromagnetism is a famous application of the Hartree-Fock approach. We first make a simplifying assumption for the relevant matrix elements $V_{\alpha\beta\gamma\delta}$. We consider only one band and take a single particle basis $\varphi_\alpha(\mathbf{r}) = \langle \mathbf{r}|\alpha\rangle$ as Wannier functions, i.e. $\alpha = i$ corresponds to a lattice site. Then we only include the matrix element with same sites (i.e. $\alpha = \beta = \gamma = \delta = i$)

$$U \equiv V_{iiii} = \int d^3r d^3r' \varphi^*_i(\mathbf{r}) \varphi^*_i(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') \varphi_i(\mathbf{r}') \varphi_i(\mathbf{r}) \tag{313}$$

Then follows with the additional assumption that there is a well defined spin-quantization axis $\left\langle c^\dagger_{i\sigma'} c_{i\sigma} \right\rangle = \delta_{\sigma\sigma'} \langle n_{i\sigma} \rangle$

$$\begin{aligned} H^{\sigma\sigma'}_{ij} &= \left(H^0_{ij} + \sum_{\sigma''} U \langle n_{i\sigma''} \rangle - U \langle n_{i\sigma} \rangle \right) \delta_{\sigma\sigma'} \\ &= \left(H^0_{ij} + U \langle n_{i\overline{\sigma}} \rangle \delta_{ij} \right) \delta_{\sigma\sigma'} \end{aligned} \tag{314}$$

Here we introduced the notation that $\overline{\sigma}$ is the spin opposite to σ. The resulting single-particle Hamiltonian is therefore

$$H_{\mathrm{HF}} = \sum_{ij,\sigma} \left(H^0_{ij} + U \langle n_{i\overline{\sigma}} \rangle \delta_{ij} \right) c^\dagger_{i\sigma} c_{j\sigma}. \tag{315}$$

This result could have been obtained from the above approximation for AB with $A = n_{i\uparrow}$ and $B = n_{i\downarrow}$ if we start from the Hubbard Hamiltonian

$$H_{\rm HF} = \sum_{ij,\sigma} H^0_{ij} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \tag{316}$$

Thus, we perform the decoupling

$$n_{i\uparrow} n_{i\downarrow} \simeq \langle n_{i\uparrow} \rangle \, n_{i\downarrow} + \langle n_{i\downarrow} \rangle \, n_{i\uparrow} - \langle n_{i\downarrow} \rangle \, \langle n_{i\uparrow} \rangle \, . \tag{317}$$

Ignoring the constant shift in the overall energy, this leads to exactly the same single-particle Hamiltonian $H_{\rm HF}$. To solve this problem we assume that lattice translation invariance in unbroken, i.e. $\langle n_{i\uparrow} \rangle = \langle n_\uparrow \rangle$ which allows Fourier transformation to Block states

$$H_{\rm HF} = \sum_{\mathbf{k},\sigma} \left(\varepsilon_{\mathbf{k}} - \mu + U \langle n_{\bar\sigma} \rangle \right) c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \tag{318}$$

which allows immediately to determine the occupations of momentum states

$$\begin{aligned} \langle n_{\mathbf{k}\sigma} \rangle &= \left\langle c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \right\rangle \\ &= \frac{1}{\exp\left(\beta \left(\varepsilon_{\mathbf{k}} - \mu + U \langle n_{\bar\sigma} \rangle \right) \right) + 1} \end{aligned} \tag{319}$$

The occupation in real space follows as

$$\langle n_{i\sigma} \rangle = \frac{1}{N} \sum_{\mathbf{k} \in BZ} \langle n_{\mathbf{k}\sigma} \rangle \, e^{i \mathbf{k} \cdot \mathbf{R}_i}. \tag{320}$$

Given the assumed translation invariance we can evaluate this sum at any lattice site i and take for convenience $\mathbf{R}_i = 0$:

$$\langle n_\sigma \rangle = \frac{1}{N} \sum_{\mathbf{k} \in BZ} \frac{1}{\exp\left(\beta \left(\varepsilon_{\mathbf{k}} - \mu + U \langle n_{\bar\sigma} \rangle \right) \right) + 1} \tag{321}$$

This is a coupled equation for the occupations of the two spin states. Introducing

$$n = \langle n_\uparrow \rangle + \langle n_\downarrow \rangle \tag{322}$$

for the total charge density and

$$m = \langle n_\uparrow \rangle - \langle n_\downarrow \rangle \tag{323}$$

for the spin polarization (which will determine the macroscopic magnetization

$$M = N \mu_B m \tag{324}$$

with Bohr magneton μ_B. It follows

$$\langle n_\sigma \rangle = \frac{1}{2}\left(n + \sigma m\right) \tag{325}$$

and we find

$$n = \frac{1}{N}\sum_{\mathbf{k}\in BZ}\sum_{\sigma}\frac{1}{e^{\beta\left(\varepsilon_{\mathbf{k}}-\mu+\frac{U}{2}(n-\sigma m)\right)}+1}, \tag{326}$$

and

$$m = \frac{1}{N}\sum_{\mathbf{k}\in BZ}\sum_{\sigma}\frac{\sigma}{e^{\beta\left(\varepsilon_{\mathbf{k}}-\mu+\frac{U}{2}(n-\sigma m)\right)}+1}. \tag{327}$$

The first equation can be used to determine the chemical potential μ of the system. It is convenient to absorb the spin independent shift $\frac{U}{2}n$ into a redefinition of $\mu \to \mu_r = \mu - Un/2$. Here we concentrate on the second term. that becomes

$$\begin{aligned} m &= \frac{1}{N}\sum_{\mathbf{k}\in BZ}\left(\frac{1}{e^{\beta\left(\varepsilon_{\mathbf{k}}-\mu_r-\frac{U}{2}m\right)}+1}-\frac{1}{e^{\beta\left(\varepsilon_{\mathbf{k}}-\mu_r+\frac{U}{2}m\right)}+1}\right) \\ &= \frac{1}{N}\sum_{\mathbf{k}\in BZ}\frac{\sinh\left(\beta U m/2\right)}{\cosh\left(\beta U m/2\right)+\cosh\left(\beta\left(\varepsilon_{\mathbf{k}}-\mu_r\right)\right)} \end{aligned} \tag{328}$$

Obviously, one solution of this nonlinear equation is always $m = 0$. To check whether there are other solutions we write the sum over momenta in terms of an integral over the density of states

$$m = \int d\omega \rho\left(\omega\right)\frac{\sinh\left(\beta U m/2\right)}{\cosh\left(\beta U m/2\right)+\cosh\left(\beta\left(\omega-\mu_r\right)\right)} \tag{329}$$

which is normalized to one $\int d\omega \rho\left(\omega\right) = 1$. This follows from the definition

$$\rho\left(\omega\right) = \frac{1}{N}\sum_{\mathbf{k}\in BZ}\delta\left(\omega-\varepsilon_{\mathbf{k}}\right) \tag{330}$$

along with the fact that there are exactly N crystal momenta in the BZ:

$$\begin{aligned} \int d\omega \rho\left(\omega\right) &= \frac{1}{N}\sum_{\mathbf{k}\in BZ}\int d\omega \delta\left(\omega-\varepsilon_{\mathbf{k}}\right) \\ &= \frac{1}{N}\sum_{\mathbf{k}\in BZ} 1 = 1. \end{aligned} \tag{331}$$

At high temperatures follows with $\sinh\left(x \ll 1\right) \simeq x$ and $\cosh\left(x \ll 1\right) \simeq 1$

$$m = m\frac{U}{4k_BT}\int d\omega \rho\left(\omega\right) = m\frac{U}{4k_BT}. \tag{332}$$

Since by assumption $k_B T \gg U$ it follows that only $m = 0$ is an allowed solution. Suppose we are looking for very small, but finite m as solutions, which justifies a Taylor expansion on the right hand side:

$$m = am - bm^3 + \cdots \tag{333}$$

with coefficients:

$$\begin{aligned} a &= \frac{U\beta}{2} \int d\omega \rho(\omega) \frac{1}{1 + \cosh(\beta(\omega - \mu_r))} \\ b &= -\frac{U^3\beta^3}{48} \int d\omega \rho(\omega) \frac{\cosh(\beta(\omega - \mu_r)) - 2}{(1 + \cosh(\beta(\omega - \mu_r)))^2} \end{aligned} \tag{334}$$

Nontrivial solutions with small m can only exist if $a > 1$ and $b > 0$. Thus, at the transition from ordered state to disordered state yields

$$\frac{U\beta_c}{2} \int d\omega \rho(\omega) \frac{1}{1 + \cosh(\beta_c(\omega - \mu_r))} = 1 \tag{335}$$

An interesting limit is $T_c \to 0$ which addresses the issue of when does the ferromagnetic ground state is allowed to exist. Here we use that

$$\delta(x) = \lim_{\alpha \to \infty} \frac{\alpha}{\cosh(\alpha x)} \tag{336}$$

such that $T_c \to 0$ corresponds to

$$\frac{U}{2} \rho(\mu_r) = 1. \tag{337}$$

Thus, at $T = 0$ a ferromagnetic ground state is expected for $U\rho(\mu_r)/2 > 1$. This condition is called the Stoner criterion.

In case where $b < 0$ the transition cannot have an infinitesimally small solution. However a detailed analysis yields that a discontinuous jump to a finite value is possible. This behavior corresponds to a first order phase transition.

D. Landau Theory of Fermi-liquids

The key concept underlying Fermi liquid theory is adiabacity, i.e. the assumption that the low energy excitations of an interacting Fermi system are in one-to-one correspondence to the excitations of a non-interacting Fermi gas. The theory was originally developed for ^{3}He, which at low temperatures is a structureless fermion due to the net spin 1/2 in the

nucleus. The proton charge is compensated by the two electrons that forma a singlet state and therefore don't contribute to the total spin of the system. One simplifying aspect of ^{3}He is the absence of an underlying crystalline lattice. The bare dispersion is then given in form of the free particle dispersion

$$\varepsilon_{\mathbf{k}}^{\text{free}} = \frac{\hbar k^2}{2m}. \tag{338}$$

The quantum numbers of the excited states of a free fermi gas are the occupations $n_{\mathbf{k}\sigma}$ of single particle states, the corresponding single particle states are characterized by momentum and spin: $|\mathbf{k}\sigma\rangle$.

Momentum and spin of excitations can only serve as quantum numbers if an excitation with $|\mathbf{k}\sigma\rangle$ doesn't immediately decay into other states. To demonstrate that the decay rate of fermions with excitation energies $\ll k_B T$ is indeed small, we use Fermi's golden rule for the decay of one particle with energy ε above the Fermi surface. Assume further that all other states below the Fermi surface are filled and those outside the Fermi surface are empty. Then we would consider a collision of the particle with energy ε with an occupied state of energy ε_2 leading to final states with energy ε_3 and ε_4 outside the Fermi sea. Measuring all energies relative to the Fermi surface we obtain for the decay rate

$$\begin{aligned}\Gamma \;=\; & V^2 \int d\varepsilon_2 \rho\left(\varepsilon_2\right) \int d\varepsilon_3 \rho\left(\varepsilon_3\right) \int d\varepsilon_4 \rho\left(\varepsilon_4\right) \\ & \times f\left(\varepsilon_2\right)\left(1-f\left(\varepsilon_3\right)\right)\left(1-f\left(\varepsilon_4\right)\right) \delta\left(\varepsilon+\varepsilon_2-\varepsilon_3-\varepsilon_4\right)\end{aligned} \tag{339}$$

Here, the integration should go over all energies with finite density of states. Since the integral is convergent and dominated by small energies, we can without problem extend the integration limit to $\pm\infty$. First we integrate over ε_2:

$$\Gamma = V^2 \rho_F^3 \int d\varepsilon_3 \int d\varepsilon_4 \; f\left(\varepsilon_3+\varepsilon_4-\varepsilon\right)\left(1-f\left(\varepsilon_3\right)\right)\left(1-f\left(\varepsilon_4\right)\right). \tag{340}$$

where we also approximated all densities of states by their value at the Fermi level. Next we take into account that for $T=0$, $\varepsilon_3, \varepsilon_4 > 0$ and $\varepsilon_3+\varepsilon_4 < \varepsilon$, which determines the integration limits

$$\Gamma\left(\varepsilon\right) = V^2 \rho_F^3 \int_0^{\varepsilon} d\varepsilon_3 \int_0^{\varepsilon-\varepsilon_3} d\varepsilon_4 = \frac{1}{2} V^2 \rho_F^3 \varepsilon^2 \tag{341}$$

Similarly we can perform the integration at $\varepsilon = 0$ and for finite temperatures. Now

$$\begin{aligned}\Gamma\left(T\right) \;&=\; V^2 \rho_F^3 \int d\varepsilon_3 \int d\varepsilon_4 \; \frac{1}{e^{\beta\left(\varepsilon_3+\varepsilon_4\right)}+1} \frac{1}{e^{-\beta\varepsilon_3}+1} \frac{1}{e^{-\beta\varepsilon_4}+1} \\ &=\; V^2 \rho_F^3 \int d\varepsilon_3 \frac{\varepsilon_3}{e^{\beta\varepsilon_3}-1} \frac{1}{e^{-\beta\varepsilon_3}+1} = V^2 \rho_F^3 \frac{\pi^2}{4} \left(k_B T\right)^2.\end{aligned} \tag{342}$$

Thus we find that for sufficiently small energy is $\Gamma \ll \max(\varepsilon, k_B T)$. In case of a wave function, where damping leads to

$$\psi(t) \propto \exp\left(-i\frac{\varepsilon t}{\hbar} - \frac{1}{\hbar}\Gamma t\right) \tag{343}$$

it implies that the coherent oscillations go on for many periods until the damping leads to a suppression of the oscillating amplitude. Thus, we demonstrated that single particle excitations above the Fermi energy do not immediately radiate and decay.

In the ground state we continue to assume that the system is characterized by a filled Fermi sea with

$$n_{\mathbf{k}\sigma}^{(0)} = \theta(k_F - k) \tag{344}$$

where k_F is the same as for an ideal Fermi gas with same density:

$$\begin{aligned} \frac{N}{V} &= 2\int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}\sigma}^{(0)} \\ &= \frac{1}{\pi^2}\int_0^{k_F} k^2 dk = \frac{k_F^3}{3\pi^2} \end{aligned} \tag{345}$$

which yields $k_F = (3\pi^2 N/V)^{1/3}$. Excitations are now characterized by changes $\delta n_{\mathbf{k}\sigma}$ of the occupations, i.e.

$$n_{\mathbf{k}\sigma} = n_{\mathbf{k}\sigma}^{(0)} + \delta n_{\mathbf{k}\sigma}. \tag{346}$$

The corresponding change in energy is then given by

$$\delta E = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}\sigma} \delta n_{\mathbf{k}\sigma}. \tag{347}$$

Since the labelling of quantum numbers is the same compared to the free fermi system, purely statistical aspects, like the entropy, should also only be determined by the corresponding ideal fermi gas expressions. This implies

$$S = -k_B \sum_{\mathbf{k},\sigma} \left(n_{\mathbf{k}\sigma} \log n_{\mathbf{k}\sigma} + (1 - n_{\mathbf{k}\sigma}) \log(1 - n_{\mathbf{k}\sigma})\right) \tag{348}$$

Maximizing this expression with the condition that $E = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}$ and $N = \sum_{\mathbf{k},\sigma} n_{\mathbf{k}\sigma}$, yields

$$n_{\mathbf{k}\sigma} = \frac{1}{e^{\beta\varepsilon_{\mathbf{k}\sigma}} + 1}. \tag{349}$$

where the excitation energy $\varepsilon_{\mathbf{k}\sigma}$ is measured relative to the Fermi energy. Near E_F we make the assumption

$$\varepsilon_{\mathbf{k}\sigma} \simeq \varepsilon_{\mathbf{k}\sigma}^0 = v(k - k_F) \tag{350}$$

where the parameter $v = k_F/m^*$ is often expressed in terms of the effective mass m^*. This immediately leads to the density of states

$$\rho_F = \frac{m^* k_F}{\pi^2 \hbar^2} \tag{351}$$

that is enhanced by the factor m^*/m compared to the free fermion expression. An immediate consequence of this modified density of states emerges or the heat capacity

$$\begin{aligned} C &= \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}\sigma} \frac{d}{dT} n_{\mathbf{k}\sigma} = \rho_F \int_{-\infty}^{\infty} d\varepsilon \varepsilon \frac{d}{dT} \frac{1}{e^{\varepsilon/(k_B T)} + 1} \\ &= \gamma T \end{aligned} \tag{352}$$

where

$$\gamma = \frac{\pi^2 k_B^2}{3} \rho_F = \frac{m^*}{m} \gamma_{\text{free}} \tag{353}$$

where γ_{free} is the heat capacity of non-interacting fermions.

A key additional aspect of the Landau theory is that changes in the occupations $\delta n_{\mathbf{k}\sigma}$ will lead to changes $\delta\varepsilon_{\mathbf{k}\sigma}$ of the quasi-particle energies. Thus one writes generally

$$\varepsilon_{\mathbf{k}\sigma} = \varepsilon^0_{\mathbf{k}\sigma} + \delta\varepsilon_{\mathbf{k}\sigma} \tag{354}$$

where

$$\delta\varepsilon_{\mathbf{k}\sigma} = \frac{1}{N} \sum_{\mathbf{k}',\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} \delta n_{\mathbf{k}'\sigma'} \tag{355}$$

where $f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}$ is a phenomenological interaction parameter that determines the extend to which the energy of state $|\mathbf{k},\sigma\rangle$ is affected by a change in population $\delta n_{\mathbf{k}'\sigma'}$ of $|\mathbf{k}',\sigma'\rangle$. If we do not want to have a preference of one spin direction over the other (in the absence of an external magnetic field) we write

$$f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} = f^s_{\mathbf{k},\mathbf{k}'} + \sigma\sigma' f^a_{\mathbf{k},\mathbf{k}'}. \tag{356}$$

In addition we assume that all relevant momenta are on the Fermi surface, i.e. $\mathbf{k} = k_F \mathbf{e}_{\mathbf{k}}$ and $\mathbf{k}' = k_F \mathbf{e}_{\mathbf{k}'}$ where $\mathbf{e}^2_{\mathbf{k}} = \mathbf{e}^2_{\mathbf{k}'} = 1$ are unit vectors. In an isotropic system like ^{3}He, with no preferred direction, one expects that $f^{s,a}_{\mathbf{k},\mathbf{k}'}$ only depend on the angle θ between $\mathbf{k}$ and $\mathbf{k}'$, i.e. on $\cos\theta_{\mathbf{k},\mathbf{k}'} = \mathbf{e}_{\mathbf{k}} \cdot \mathbf{e}_{\mathbf{k}'}$:

$$f^{s,a}_{\mathbf{k},\mathbf{k}'} = f^{s,a}\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right). \tag{357}$$

Since $f^{s,a}$ are of dimension energy, dimensionless quantities follow via

$$F^{s,a} = \rho_F f^{s,a}. \tag{358}$$

We expand $F^{s,a}\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right)$ in Legendre polynomials

$$F^{s,a}\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right)=\sum_{l=0}^{\infty}\left(2l+1\right)F_l^{s,a}P_l\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right) \tag{359}$$

and use the usual representation in terms of spherical harmonics

$$F^{s,a}\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right)=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}F_l^{s,a}Y_{lm}\left(\mathbf{e}_{\mathbf{k}}\right)Y_{lm}^{*}\left(\mathbf{e}_{\mathbf{k}'}\right). \tag{360}$$

The orthogonality of the Legendre polynomials

$$\frac{1}{2}\int_{-1}^{1}d\cos\theta P_l\left(\cos\theta\right)P_{l'}\left(\cos\theta\right)=\frac{\delta_{l,l'}}{2l+1} \tag{361}$$

allows for the representation

$$\begin{aligned}
F_l^{s,a} &= \frac{1}{2}\int_{-1}^{1}d\cos\theta F^{s,a}\left(\cos\theta\right)P_{l'}\left(\cos\theta\right)\\
&= \frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta F^{s,a}\left(\cos\theta\right)P_{l'}\left(\cos\theta\right)\\
&= \frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta\int d\varepsilon F^{s,a}\left(\cos\theta\right)P_{l'}\left(\cos\theta\right)\delta\left(\varepsilon\right)\\
&= \frac{2}{\rho_F}\frac{1}{N}\sum_{\mathbf{k}'}F_{\mathbf{k},\mathbf{k}'}^{s,a}P_l\left(\cos\theta_{\mathbf{k},\mathbf{k}'}\right)\delta\left(\varepsilon_{\mathbf{k}}\right).
\end{aligned} \tag{362}$$

Suppose we are at $T=0$ we add an external perturbation of the type

$$\delta\varepsilon_{\mathbf{k}\sigma}^{0}=v_l^{\sigma}Y_{lm}\left(\mathbf{e}_{\mathbf{k}}\right) \tag{363}$$

where the spherical harmonic determines the directional dependence on the momentum and v_l^{σ} is the amplitude of the perturbation. In case of an external magnetic field holds $\delta\varepsilon_{\mathbf{k}\sigma}^{0}=-\sigma\mu_B B$, i.e. we have $m=l=0$ and, due to $Y_{00}=4\pi$, $v_0^{\sigma}=-\sigma\mu_B B/4\pi$. A change in the chemical potential $\delta\mu$ amounts to $\delta\varepsilon_{\mathbf{k}\sigma}^{0}=-\delta\mu$, i.e. $m=l=0$ and $v_0^{\sigma}=-\delta\mu/4\pi$. This allows us to determine physical observables like the magnetic susceptibility

$$\chi_s=\frac{1}{V}\left.\frac{\partial M}{\partial B}\right|_{B=0} \tag{364}$$

with magnetization $M=\mu_B\sum_{\mathbf{k},\sigma}\sigma n_{\mathbf{k}\sigma}$. Another option is the charge susceptibility

$$\chi_c=\frac{1}{V}\left.\frac{\partial N}{\partial\left(\delta\mu\right)}\right|_{\delta\mu=0} \tag{365}$$

with particle number $N = \sum_{\mathbf{k},\sigma} n_{\mathbf{k}\sigma}$. χ_c is closely related to the compressibility

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p}$$

In case where the free energy of a system can be written as

$$F(V,N) = Nf(n) \tag{366}$$

where $n = N/V$ is the particle density, it follows

$$p = -\left.\frac{\partial F}{\partial V}\right|_N = n^2 \frac{\partial f(n)}{\partial n} \tag{367}$$

which allows us to write

$$\frac{1}{\kappa} = -V\left.\frac{\partial P}{\partial V}\right|_N = n\frac{\partial p}{\partial n} \tag{368}$$

On the other hand it holds for the chemical potential

$$\mu = \left.\frac{\partial F}{\partial N}\right|_N = f(n) + n\frac{\partial f(n)}{\partial n} \tag{369}$$

The change of the pressure and chemical with density are then:

$$\begin{aligned} \frac{\partial p}{\partial n} &= 2n\frac{\partial f(n)}{\partial n} + n^2\frac{\partial^2 f(n)}{\partial n^2} \\ \frac{\partial \mu}{\partial n} &= 2\frac{\partial f(n)}{\partial n} + n\frac{\partial^2 f(n)}{\partial n^2} \end{aligned} \tag{370}$$

which implies

$$\frac{\partial p}{\partial n} = n\frac{\partial \mu}{\partial n} \tag{371}$$

and we obtain

$$\kappa = n^{-2}\frac{\partial n}{\partial \mu}. \tag{372}$$

In case of a free Fermi gas follows

$$\begin{aligned} \chi_s^0 &= \mu_B^2 \rho_F^0 \\ \chi_s &= \rho_F^0. \end{aligned} \tag{373}$$

where the mass is m.

Since fermions of a Fermi liquid are interacting it there is no reason that an external field or chemical potential change will change the quasiparticle energies $\varepsilon_{\mathbf{k}\sigma}$ in the exact same fashion. Thus, we assume

$$\begin{aligned} \delta\varepsilon_{\mathbf{k}\sigma} &= \delta\varepsilon_{\mathbf{k}\sigma}^0 + \frac{1}{N}\sum_{\mathbf{k}',\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}\delta n_{\mathbf{k}'\sigma'} \\ &= t_l^\sigma Y_{lm}(\mathbf{e}_\mathbf{k}) \end{aligned} \tag{374}$$

where in general $t_l^\sigma \neq v_l^\sigma$. Suppose there is such an energy shift, then we can determine the associated particle density shift from Eq.349

$$\begin{aligned} n_{\mathbf{k}\sigma} &= \frac{1}{e^{\beta\left(\varepsilon^0_{\mathbf{k}\sigma}+\delta\varepsilon_{\mathbf{k}\sigma}\right)}+1} \\ &= \theta\left(k_F-k\right)-\delta\left(\varepsilon^0_{\mathbf{k}\sigma}\right)\delta\varepsilon_{\mathbf{k}\sigma} \end{aligned} \tag{375}$$

which yields

$$\delta n_{\mathbf{k}\sigma} = -\delta\left(\varepsilon^0_{\mathbf{k}\sigma}\right)\delta\varepsilon_{\mathbf{k}\sigma}. \tag{376}$$

This result can now be inserted into Eq.374 which yields

$$\delta\varepsilon_{\mathbf{k}\sigma} = \delta\varepsilon^0_{\mathbf{k}\sigma} - \frac{1}{N}\sum_{\mathbf{k}',\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}\delta\left(\varepsilon^0_{\mathbf{k}'\sigma'}\right)\delta\varepsilon_{\mathbf{k}'\sigma'} \tag{377}$$

or equivalently

$$t_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) = v_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) - \frac{1}{N}\sum_{\mathbf{k}',\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}\delta\left(\varepsilon^0_{\mathbf{k}'\sigma'}\right) t_l^{\sigma'} Y_{lm}\left(\mathbf{e}_{\mathbf{k}'}\right) \tag{378}$$

Now we can use the above expansion of $f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}$ in spherical harmonics

$$\begin{aligned} t_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) &= v_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) - \frac{\rho_F}{2}\int d\Omega_{\mathbf{k}'}\sum_{\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} t_l^{\sigma'} Y_{lm}\left(\mathbf{e}_{\mathbf{k}'}\right) \\ &= v_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) - \frac{\rho_F}{2}\int \frac{d\Omega_{\mathbf{k}'}}{4\pi}\sum_{\sigma'} f_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} t_l^{\sigma'} Y_{lm}\left(\mathbf{e}_{\mathbf{k}'}\right) \\ &= v_l^\sigma Y_{lm}\left(\mathbf{e}_\mathbf{k}\right) - \frac{1}{2}\int d\Omega_{\mathbf{k}'}\sum_{\sigma'}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}\left(F^s_{l'}+\sigma\sigma' F^a_{l'}\right) \\ &\quad \times Y_{l'm'}\left(\mathbf{e}_\mathbf{k}\right) Y^*_{l'm'}\left(\mathbf{e}_{\mathbf{k}'}\right) t_l^{\sigma'} Y_{lm}\left(\mathbf{e}_{\mathbf{k}'}\right) \end{aligned} \tag{379}$$

We use the orthogonality of the spherical harmonics

$$\int d\Omega_{\mathbf{k}'} Y^*_{l'm'}\left(\mathbf{e}_{\mathbf{k}'}\right) Y_{lm}\left(\mathbf{e}_{\mathbf{k}'}\right) = \delta_{ll'}\delta_{mm'} \tag{380}$$

and obtain

$$t_l^\sigma = v_l^\sigma - \frac{1}{2}\sum_{\sigma'} t_l^{\sigma'}\left(F^s_l + \sigma\sigma' F^a_l\right) \tag{381}$$

If we consider for example a change in the chemical potential with, $v_0^\sigma = -\delta\mu/4\pi$, it follows for $t_0^\sigma = t_0$ spin independent, that

$$t_0 = v_0 - t_0 F^s_0 \tag{382}$$

which leads to

$$t_0 = \frac{v_0}{1+F_0^s}. \tag{383}$$

It is now straightforward to determine the charge susceptibility via

$$\begin{aligned}\chi_c &= \frac{1}{V}\frac{\partial N}{\partial(\delta\mu)} = -\frac{1}{4\pi}\frac{1}{V}\frac{\partial N}{\partial v_0} \\ &= -\frac{1}{4\pi}\frac{1}{V}\frac{\partial N}{\partial t_0}\frac{\partial t_0}{\partial v_0} \\ &= -\frac{1}{1+F_0^s}\frac{1}{4\pi}\frac{1}{V}\frac{\partial N}{\partial t_0}.\end{aligned} \tag{384}$$

To determine $\frac{-1}{4\pi}\frac{1}{V}\frac{\partial N}{\partial t_0}$ we use

$$n_{\mathbf{k}\sigma} = \frac{1}{e^{\beta\left(\frac{k_F}{m^*}(k-k_F)+4\pi t_0\right)}+1}$$

The derivative of $N = \sum_{\mathbf{k},\sigma} n_{\mathbf{k}\sigma}$ with respect to t_0 can be performed, e.g. by resorting to our above result for the charge susceptibility of a free electron gas (with the difference that we need to consider the effective mass, not the bare mass). It follows $\frac{-1}{4\pi}\frac{1}{V}\frac{\partial N}{\partial t_0} = \rho_F$ and we obtain

$$\chi_c = \frac{\rho_F}{1+F_0^s}$$

Thus, the charge susceptibility is different from the free fermi gas value in two ways. First, in the density of states the mass m is replaced by the effective mass m^*. In addition the interactions lead to an overall coefficient $(1+F_0^s)^{-1}$. The theory is therefore stable as long as $F_0^s < -1$. If $F_0^s \to -1$ the system will undergo a transition to a regime where different densities phase segregate. An analogous analysis can be performed for the spin susceptibility (homework).

IX. DYNAMICS OF BLOCH ELECTRONS

A. Semi-classical equation of motion of Bloch electrons

We want to describe the evolution of electron's wave function when a weak and slowly changing external field is added. That is the Hamiltonian now reads

$$H = \frac{\left(-i\hbar\boldsymbol{\nabla} + \frac{e}{c}\mathbf{A}(\mathbf{r})\right)^2}{2m} + U(\mathbf{r}) - e\phi(\mathbf{r}) \ , \tag{385}$$

where (the signs are consistent with negative charge, that is $e = |e| > 0$, but the charge of the electron is $-e < 0$.) The potential $U(\mathbf{r})$ is periodic while $\mathbf{A}$ and ϕ change little on the scale of primitive cell of the Bravais lattice (slow fields).

Our aim to prove that the electrons in the band n with energy $E_n(\mathbf{k})$ are governed by the following effective Hamiltonian

$$H_{\text{eff},n} = E_n\left(-i\boldsymbol{\nabla} + \frac{e}{\hbar c}\mathbf{A}\right) - e\phi \ . \tag{386}$$

B. Wave packet argument

We localize the electron of a certain band n into a wave packet:

$$\Phi(\mathbf{r}) = \int d^3k\, g(\mathbf{k})\psi_{n,\mathbf{k}}(\mathbf{k}) = \int d^3k\, g(\mathbf{k})u_{n,\mathbf{k}}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{387}$$

The function $g(\mathbf{k})$ is centered around a certain crystal momentum $\mathbf{k}_0$ and has a width Δk such that the width of the wave packet in the real space Δr is small enough. The two are related as $\Delta k \Delta r \sim 1$.

The time evolution of the wave packet is given by

$$\Phi(\mathbf{r}, t) = \int d^3k\, g(\mathbf{k})u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r} - i\epsilon_{n,\mathbf{k}}t/\hbar}. \tag{388}$$

We expand around $\mathbf{k}_0$ and $\epsilon_{n,\mathbf{k}_0}$. We assume one can approximate $u_{n,\mathbf{k}}(\mathbf{r}) \approx u_{n,\mathbf{k}_0}$ in the whole interval of Δk. Then

$$\Phi(\mathbf{r}, t) \approx u_{n,\mathbf{k}_0}(\vec{r})e^{i\mathbf{k}_0\cdot\mathbf{r} - i\epsilon_{n,\mathbf{k}_0}t/\hbar}\int d^3\delta k\, g(\mathbf{k})e^{i\delta\mathbf{k}\cdot\left(\mathbf{r} - \frac{\partial\epsilon_{n,\mathbf{k}}}{\partial\mathbf{k}}t/\hbar\right)}. \tag{389}$$

Thus we conclude that the wave packet propagates with the velocity

$$\mathbf{v} = \frac{\partial\mathbf{r}}{\partial t} = \frac{1}{\hbar}\frac{\partial\epsilon_{n,\mathbf{k}}}{\partial\mathbf{k}} \ . \tag{390}$$

Assume now the electron is influenced by an electric field $\mathbf{E}$. The work done by the field pro unit of time is $-e\mathbf{E}\cdot\mathbf{v}$. This work is "used" to change the energy of the electron. Thus we obtain

$$\frac{\partial\epsilon}{\partial t} = \frac{\partial\epsilon_{n,\mathbf{k}}}{\partial\mathbf{k}}\frac{d\mathbf{k}}{dt} = \hbar\mathbf{v}\cdot\frac{d\mathbf{k}}{dt} = -e\mathbf{E}\cdot\mathbf{v} \ . \tag{391}$$

Thus we obtain

$$\hbar\frac{d\mathbf{k}}{dt} = -e\mathbf{E} \ . \tag{392}$$

The quasi-momentum $\hbar\mathbf{k}$ satisfies the same equation as the usual momentum for free electrons!

C. Proof for potential perturbation (not for vector potential)

We consider the following problem

$$H = \frac{(-i\hbar\boldsymbol{\nabla})^2}{2m} + U(\mathbf{r}) + U_{\text{ext}}(\mathbf{r}) = H_0 + U_{\text{ext}}(\mathbf{r}) \ , \tag{393}$$

Here U is the periodic lattice potential and $U_{\text{ext}} = -e\phi$ is the external and weak potential. More precisely what has to be weak is the external electric field, i.e., $\sim \boldsymbol{\nabla} U_{\text{ext}}$.

We want to solve the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{394}$$

We expand $\psi(t)$ in basis of Wannier functions

$$\psi(t) = \sum_{n,\mathbf{R}} a_{n,\mathbf{R}}(t) w_n(\mathbf{r}-\mathbf{R}) \tag{395}$$

Recall the representation of a Bloch wave function

$$\psi_{n,\mathbf{k}}(\vec{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R}) \ . \tag{396}$$

In this case $a_{n,\mathbf{R}} = e^{i\mathbf{k}\cdot\mathbf{R}}$. Wannier functions are given by

$$w_n(\mathbf{r}) = \frac{1}{N}\sum_{\mathbf{k}\in 1.\ \text{B.Z.}} \psi_{n,\mathbf{k}}(\mathbf{r}) \ . \tag{397}$$

and

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}\in 1.\ \text{B.Z.}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) \ . \tag{398}$$

First we investigate how H_0 acts on the (shifted) Wannier functions using the fact $H_0\psi_{n,\vec{k}} = \epsilon_{n,k}\psi_{n,k}$.

$$\begin{aligned} H_0 w_n(\mathbf{r}-\mathbf{R}) &= \frac{1}{N}\sum_{\mathbf{k}\in 1.\ \text{B.Z.}} e^{-i\mathbf{k}\cdot\mathbf{R}} H_0\psi_{n,\mathbf{k}}(\mathbf{r})\backslash \\ &= \frac{1}{N}\sum_{\mathbf{k}\in 1.\ \text{B.Z.}} e^{-i\mathbf{k}\cdot\mathbf{R}} \varepsilon_{n,\mathbf{k}}\psi_{n,\mathbf{k}}(\mathbf{r}) \ . \end{aligned} \tag{399}$$

We use now the Wannier expansion (396) and obtain

$$\begin{aligned} H_0 w_n(\mathbf{r}-\mathbf{R}) &= \sum_{\mathbf{R}_1}\frac{1}{N}\sum_{\mathbf{k}\in 1.\ \text{B.Z.}} \varepsilon_{n,\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_1-\mathbf{R})} w_n(\mathbf{r}-\mathbf{R}_1) \\ &= \sum_{\mathbf{R}_1} \varepsilon_n(\mathbf{R}_1-\mathbf{R}) w_n(\mathbf{r}-\mathbf{R}_1) \ , \end{aligned} \tag{400}$$

where

$$\varepsilon_n(\mathbf{R}) \equiv \frac{1}{N} \sum_{\mathbf{k}\in 1.\ \text{B.Z.}} \varepsilon_{n,\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \ . \tag{401}$$

The Schrödinger equation now reads:

$$\begin{aligned} & i\hbar\frac{\partial\psi}{\partial t} = i\hbar\sum_{n,\mathbf{R}} \dot{a}_{n,\mathbf{R}}(t) w_n(\mathbf{r}-\mathbf{R}) \\ = \ & H\psi = (H_0 + U_{\text{ext}})\psi = \sum_{n_2,\mathbf{R}_2} a_{n_2,\mathbf{R}_2}(t)(H_0 + U_{\text{ext}}) w_{n_2}(\mathbf{r}-\mathbf{R}_2) \\ = \ & \sum_{n_2,\mathbf{R}_2} a_{n_2,\mathbf{R}_2}(t) \sum_{\mathbf{R}_1} \varepsilon_{n_2}(\mathbf{R}_1-\mathbf{R}_2) w_{n_2}(\mathbf{r}-\mathbf{R}_1) \\ & + \sum_{n_2,\mathbf{R}_2} a_{n_2,\mathbf{R}_2}(t) U_{\text{ext}} w_{n_2}(\mathbf{R}-\mathbf{R}_2) \ . \end{aligned} \tag{402}$$

The Wannier functions form a complete orthonormal basis. Thus we just compare the coefficients:

$$\begin{aligned} i\hbar\dot{a}_{n,\mathbf{R}} \ = \ & \sum_{\mathbf{R}_2} a_{n,\mathbf{R}_2}\varepsilon_{n_2}(\mathbf{R}-\mathbf{R}_2)) \\ & + \sum_{n_2,\mathbf{R}_2} a_{n_2,\mathbf{R}_2} \int d^3r \, w_n^*(\mathbf{r}-\mathbf{R}) U_{\text{ext}}(\mathbf{r}) w_{n_2}(\mathbf{r}-\mathbf{R}_2) \ . \end{aligned} \tag{403}$$

The first term in the r.h.s. of (403) is rewritten as follows

$$\begin{aligned} & \sum_{\mathbf{R}_2} a_{n,\mathbf{R}_2}\varepsilon_n(\mathbf{R}-\mathbf{R}_2) = \sum_{\mathbf{R}_1} \varepsilon_n(\mathbf{R}_1) a_{n,\mathbf{R}-\mathbf{R}_1} = \sum_{\vec{R}_1} \varepsilon_n(\mathbf{R}_1) e^{-i\mathbf{R}_1\cdot(-i\boldsymbol{\nabla})} a_{n,\mathbf{R}} \\ = \ & \varepsilon_n(\mathbf{k}\to -i\boldsymbol{\nabla}) a_{n,\mathbf{R}} \ . \end{aligned} \tag{404}$$

Here we have used $a_{n,\mathbf{R}-\mathbf{R}_1} = e^{-i\mathbf{R}_1\cdot(-i\boldsymbol{\nabla})} a_{n,\mathbf{R}}$. That is already here we consider $a_{n,\mathbf{R}}$ as a well behaved function in all the space, i.e., $a_{n,\mathbf{r}}$.

The second term of the r.h.s. of (403) is approximated as

$$\sum_{n_2,\mathbf{R}_2} a_{n_2,\mathbf{R}_2} \int d^3r \, w_n^*(\mathbf{r}-\mathbf{R}) U_{\text{ext}}(\mathbf{r}) w_{n_2}(\mathbf{r}-\mathbf{R}_2) \approx U_{\text{ext}}(\mathbf{R}) a_{n,\mathbf{R}} \ . \tag{405}$$

That is only diagonal matrix elements of U_{ext} are left. Since U_{ext} is slowly changing in space, i.e,. it changes very little on the scale of primitive cell, while the Wannier functions are localized on the scale of a cell this approximation is justified.

Thus, the SE for the "envelope" wave function $a_{n,\vec{R}}$ reads

$$i\hbar\dot{a}_{n,\mathbf{R}} = \left[\epsilon_n(-i\boldsymbol{\nabla}) + U_{\text{ext}}(\mathbf{R})\right] a_{n,\mathbf{R}} \ . \tag{406}$$

If we now "forget" that $a_{n,\vec{R}}$ is defined only in the locations $\vec{R}$ and define it in the whole space, $a_{n,\mathbf{r}}$ we obtain a Schrödinger equation with the effective Hamiltonian $H_{\text{eff},n} = \varepsilon_n(-i\boldsymbol{\nabla}) + U_{\text{ext}}(\mathbf{r})$. In presence of vector potential it becomes (with no proof given here)

$$H_{\text{eff},n} = \varepsilon_n\left(-i\boldsymbol{\nabla} + \frac{e}{\hbar c}\mathbf{A}\right) - e\phi \ . \tag{407}$$