Theory of condensed matter

Prof. Dr. Walter Schirmacher, WS 2008/9
Universität Mainz

Contents

3 Electronic structure of crystals and noncrystalline materials

3.1 Mean-field theories for the electronic many-body problem

3.1.1 Preliminary considerations

Let us consider the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{\rm kin} + \mathcal{V}(\mathbf{r}) + \mathcal{V}_{\rm e-e} = \sum_{i=1}^{N} \mathcal{H}_i + \mathcal{V}_{\rm e-e} \tag{3.1a}$$

$$\mathcal{H}_i = \mathcal{H}_{{\rm kin},i} + \mathcal{V}_i = \frac{p_i^2}{2m} + \sum_{\ell=1}^{N_a} v(\mathbf{r}_i - \mathbf{r}_\ell) \tag{3.1b}$$

$$\mathcal{V}_{\rm e-e} = \frac{1}{2}\sum_{i\neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{3.1c}$$

$$\tag{3.1d}$$

Here N_a is the number of atoms, $N = ZN_a$ is the number of electrons and Z is the number of electrons per atoms (usually equal to the atomic number). $\mathbf{r}_i$ denote the electronic positions and $\mathbf{r}_\ell$ the positions of the atoms. We apply the adiabatic principle, i.e. we consider the atomic positions to be fixed and classical. The electronic momentum operator, applied to a *one-electron wave function* $\varphi_i(\mathbf{r})$ is

$$\mathbf{p}_i \varphi_i(\mathbf{r}) = -i\hbar\nabla\varphi_i(\mathbf{r}) \tag{3.2}$$

This is a quantum-mechanical problem with $\sim 10^{23}$ interacting electrons in an external potential. called This *many-body problem* is impossible to solve. With a computer one can deal with several hundred electrons but not more. Therefore one looks for a method of *approximately* reducing the many-body problem to a one-particle problem. Such methods are called *mean-field* methods. We have already come across a mean-field theory, which is the RPA. The RPA is not well-suited for our problem, as it deals with response functions and not with wave functions. For the electronic wavefunctions the *Hartree*, the *Hartree-Fock* and *Density-functional* theories are being used. They are described in the following sections.

3.1.2 Hartree Approximation

If $\mathcal{H}_{\rm ee}$ is absent, the problem is separable and the N-electron wave function takes the form

$$\phi(\mathbf{r}_1, \dots \mathbf{r}_N) = \prod_{i=1}^{N} \varphi_i(\mathbf{r}_i) \tag{3.3}$$

and the wave functions $\varphi_i(\mathbf{r}_i)$ obey the single-electron Schrödinger equation

$$\mathcal{H}_i \varphi(\mathbf{r}_i) = \big[\mathcal{H}_{\rm kin}^{(i)} + \mathcal{V}(i)\big]\varphi(\mathbf{r}_i) = E_i \varphi(\mathbf{r}_i) \tag{3.4}$$

We now use the quantum-mechanical variation principle, which consists in looking for the expectation value $< E >$ of the Hamiltonian *including the interaction* in terms of a *trial wave function*, the parameters of which are chosen such that $E =< \mathcal{H} >$ is minimal. Using the one-particle wavefunction (3.3) as trial function the expectation value E becomes

$$E\big[\varphi_i(\mathbf{r}_i)\big] =< \phi|\mathcal{H}|\phi >= \sum_{i=1}^{N} < \varphi_i|\mathcal{H}_i|\varphi_i > + \frac{e^2}{8\pi\epsilon_0} \sum_{i\neq j} < \varphi_i\varphi_j|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\varphi_i\varphi_j > \tag{3.5}$$

In (3.5) we have assumed that the one-electron wavefunctions are *normalized*:

$$< \varphi_i|\varphi_i >= \int \mathrm{d}^3\mathbf{r}\varphi_i(\mathbf{r}) = 1 \qquad \Leftrightarrow \qquad < \varphi_i|\varphi_i > -1 = 0 \tag{3.6}$$

E is a *number*, which depends on a *function*, which is called a *functional*. For minimizing this functional with respect to all possible functions $\varphi_i(\mathbf{r})$ we require that the *variation* of this functional should vanish, subject to the side condition (3.6). For including the side condition one can add the condition in the second form, times *Lagrange multiplyers* λ_i in the following way to the functional

$$\tilde{E}\big[\varphi_i(\mathbf{r})\big] = E\big[\varphi_i\big] - \sum_i \lambda_i\big[< \varphi_i|\varphi_i > -1)\big] \tag{3.7}$$

In order to mathematically ensure that the *variation* $\delta\tilde{E}$ of $\tilde{E}$ vanishes it is necessary and sufficient that the *variational derivative* of $\tilde{E}$ with respect to the trial functions $\varphi_i(\mathbf{r})$ vanishes:

$$\frac{\delta\tilde{E}\big[\varphi(\mathbf{r})\big]}{\delta\varphi(\mathbf{r})} = 0 \tag{3.8}$$

Mathemathical digression: Variational derivative

Let $F\big[f(\mathbf{r})\big]$ be a functional of the function $f(\mathbf{r})$ defined in $\mathbb{R}^3$. The *variational derivative* is then defined by

$$\frac{\delta F\big[f(\mathbf{r})\big]}{\delta f(\mathbf{r}_0)} = \lim_{\epsilon\to 0} \frac{1}{\epsilon}\Big(F\big[f(\mathbf{r}) + \epsilon\delta(\mathbf{r} - \mathbf{r}_0)\big] - F\big[f(\mathbf{r})\big]\Big). \tag{3.9}$$

Examples:

$$
\begin{aligned}
1) \qquad F\big[f(\mathbf{r})\big] &= \int \mathrm{d}^3\mathbf{r} f(\mathbf{r}) \\
\frac{\delta F\big[f(\mathbf{r})\big]}{\delta f(\mathbf{r}_0)} &= \lim_{\epsilon\to 0}\frac{1}{\epsilon}\bigg(\int \mathrm{d}^3\mathbf{r}\big[f(\mathbf{r})+\epsilon\delta(\mathbf{r}-\mathbf{r}_0)\big]-\int \mathrm{d}^3\mathbf{r} f(\mathbf{r})\bigg)=1 \qquad (3.10a)\\
2) \qquad F\big[f(\mathbf{r})\big] &= \int \mathrm{d}^3\mathbf{r} g(\mathbf{r}) f(\mathbf{r}) \\
\frac{\delta F\big[f(\mathbf{r})\big]}{\delta f(\mathbf{r}_0)} &= \lim_{\epsilon\to 0}\frac{1}{\epsilon}\bigg(\int \mathrm{d}^3\mathbf{r}\big[g(\mathbf{r})f(\mathbf{r})+\epsilon\delta(\mathbf{r}-\mathbf{r}_0)\big]-\int \mathrm{d}^3\mathbf{r} g(\mathbf{r})f(\mathbf{r})\bigg)=g(\mathbf{r}_0) \qquad (3.10b)\\
3) \qquad F\big[f(\mathbf{r})\big] &= \int \mathrm{d}^3\mathbf{r} f(\mathbf{r})^2 \\
\frac{\delta F\big[f(\mathbf{r})\big]}{\delta f(\mathbf{r}_0)} &= \lim_{\epsilon\to 0}\frac{1}{\epsilon}\bigg(\int \mathrm{d}^3\mathbf{r}\big[f(\mathbf{r})+\epsilon\delta(\mathbf{r}-\mathbf{r}_0)\big]^2-\int \mathrm{d}^3\mathbf{r} f(\mathbf{r})^2\bigg) \\
&= \lim_{\epsilon\to 0}\frac{1}{\epsilon}\bigg(\int \mathrm{d}^3\mathbf{r}\big[f(\mathbf{r})^2+2\epsilon f(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_0)\big]-\int \mathrm{d}^3\mathbf{r} f(\mathbf{r})^2\bigg)=2f(\mathbf{r}_0) \qquad (3.10c)
\end{aligned}
$$

I.e. for performing the functional derivative the integral is removed and the integrand is differentiated with respect to $f(\mathbf{r})$.

We now perform the variational derivative of the functional $\tilde{E}$ with respect to the variational single-electron wavefunctions $\varphi_i(\mathbf{r})$ to obtain[1][2]

$$
\bigg(\mathcal{H}_i+\frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\int \mathrm{d}^3\mathbf{r}'\big|\varphi_j(\mathbf{r}'_j)\big|^2\frac{1}{|\mathbf{r}_i-\mathbf{r}'_j|}\bigg)\varphi_i(\mathbf{r}_i)=\lambda_i\varphi_i(\mathbf{r}_i) \qquad (3.11)
$$

We now re-baptize λ_i into E_i and call E_i the *Hartree eigenvalue*. (3.11) is called the *Hartree one-electron Schrödinger equation* or shorter *Hartree equation*.

3.1.3 Hartree-Fock approximation

Within the Hartree description the Pauli Principle has not been taken care of. In order to do so we must *antisymmetrize* the product wave function (3.3). This procedure yields the *Slater determinant*

$$
\phi(\mathbf{r}_1,\dots\,\mathbf{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(\mathbf{r}_1 s_1 & \dots & \varphi_N(\mathbf{r}_1 s_1) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \varphi_1(\mathbf{r}_N s_N) & \dots & \varphi_N(\mathbf{r}_N s_N)\,, \end{vmatrix} \qquad (3.12)
$$

where s_i are the electronic spins.
Applying the same variational procedure as in the Hartee approximation we arrive at the *Hartee-Fock equation*, which are

$$
\begin{aligned}
\bigg(\mathcal{H}_i \;&+\; \frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\int \mathrm{d}^3\mathbf{r}'\big|\varphi_j(\mathbf{r}'_j s_j)\big|^2\frac{1}{|\mathbf{r}_i-\mathbf{r}'_j|}\bigg)\varphi_i(\mathbf{r}_i s_i) \\
&-\; \frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\varphi_j(\mathbf{r}_i s_i)\sum_{j\neq i}\int \mathrm{d}^3\mathbf{r}'\varphi_j(\mathbf{r}'_j s_j)^*\varphi_i(\mathbf{r}_j s_j)\frac{1}{|\mathbf{r}_i-\mathbf{r}'_j|}=E_i\varphi_i(\mathbf{r}_i s_i) \qquad (3.13)
\end{aligned}
$$

These equations were the basis of all molecular-orbital and bandstructure calculations until the end of the 60th.

[1] Note that this result can be obtain in two ways: (*i*) by assuming that the wave functions $\varphi_i(\mathbf{r})$ are real; (*ii*) by assuming that the wave functions are complex functions and taking the derivative with respect to $\varphi_i(\mathbf{r})^*$ and treating $\varphi_i(\mathbf{r})$ and $\varphi_i(\mathbf{r})^*$ as independent functions.

[2] The spin variable s_i has been suppressed, because the Hartree equations do not involve the spin degrees of freedom.

It appeared, however, that the solution of these non-local equations was somewhat cumbersome, and, on the other side in a number of cases the Hartree results appeared more accurate (as compared with spectroscopic measurements) than the Hartree-Fock results. So one was looking for another mean-field scheme, which - in comparison with the Hartree-Fock theory - incorporated the missing "correlations", and involved a local one-electron equation. The result was the *Kohn-Sham equation*, derived within the density-functional theory of *Hohenberg* and *Kohn*.

3.1.4 Density-functional theory

Hohenberg, Kohn and Sham tried to systematically find improved one-electron-type mean-field approximations. First they realized, that the *exact* ground state energy E is a *unique* functional of the total electronic density function $n(\mathbf{r})$.
We just verify this for the *non-interacting* case:

$$\begin{aligned} E_0\big[n(\mathbf{r})\big] &= \sum_{i=1}^{N} < \varphi_i | \big[\mathcal{H}_{\mathrm{kin},i} + \mathcal{V}_i\big] | \varphi_i > = \sum_{i=1}^{N} < \varphi_i | \big[-\mathbf{r}\cdot\nabla\mathcal{V}(\mathbf{r}) + \mathcal{V}(\mathbf{r})\big] | \varphi_i > \\ &= \int \mathrm{d}^3\mathbf{r}\; n(\mathbf{r}) \big[1 - \frac{1}{2}\mathbf{r}\cdot\nabla\big]\mathcal{V}(\mathbf{r}) \\ &\equiv E_{\mathrm{kin}}\big[n(\mathbf{r})\big] + \int \mathrm{d}^3\mathbf{r}\; n(\mathbf{r})\mathcal{V}(\mathbf{r})\,, \end{aligned} \tag{3.14}$$

where the second equality in (3.14) follows from the *virial theorem*.
The *theorems of Hohenberg and Kohn* are

- The ground state of a system of N electrons in an external potential, i.e. all ground-state expectation values are *unique* functionals of the electron density $n(\mathbf{r})$.
- The ground state energy functional $E\big[n(\mathbf{r})\big]$ has a minimum with respect to all other functions $\tilde{n}(\mathbf{r})$ at the correct ground state density $n(\mathbf{r})$.

The functional $E\big[n(\mathbf{r})\big]$ can be written as follows

$$E\big[n(\mathbf{r})\big] = E_0\big[n(\mathbf{r})\big] + \int \mathrm{d}^3\mathbf{r}\; n(\mathbf{r}) \underbrace{\frac{1}{8\pi\epsilon_0}\int \mathrm{d}^3\mathbf{r}'\; n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}}_{v_{\mathrm{eff}}(\mathbf{r})} + E_{\mathrm{xc}}\big[n(\mathbf{r})\big] \tag{3.15}$$

The last term now is the *combined* (unknown) exchange and correlation contribution. The minimal principle now implies

$$0 = \delta E = \int \mathrm{d}^3\mathbf{r}\; n(\mathbf{r}) \left[\frac{\delta E_{\mathrm{kin}}}{\delta n(\mathbf{r})} + \mathcal{V}(\mathbf{r}) + v_{\mathrm{eff}}(\mathbf{r}) + \underbrace{\frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}}_{v_{\mathrm{xc}}(\mathbf{r})} \right] \tag{3.16}$$

For the overall electron density $n(\mathbf{r})$ there is a *side condition*

$$N = \int \mathrm{d}^3\mathbf{r}\; n(\mathbf{r}) \tag{3.17}$$

So we must minimize the functional

$$\tilde{E}\big[n(\mathbf{r})\big] = E\big[n(\mathbf{r})\big] - \mu N\,, \tag{3.18}$$

where the Lagrange multiplier μ can be identified to be the *chemical potential*, which is for electrons in the ground state is just the *Fermi energy* E_F. We obtain the Euler-Lagrange equation

$$0 = \frac{\delta\tilde{E}}{\delta n(\mathbf{r})} = \frac{\delta E_{\mathrm{kin}}}{\delta n(\mathbf{r})} + \mathcal{V}(\mathbf{r}) + v_{\mathrm{eff}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) - \mu \tag{3.19}$$

Now effective single-particle orbitals are introduced with

$$N = \sum_i \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r})\theta(\mu - \epsilon_i) \tag{3.20}$$

where $\theta(x) = 1$ for $x \geq 0$ and otherwise 0 (Heaviside step function) and ϵ_i are one-electron energies, which are the eigen energies of the *Kohn-Sham equations*

$$\left[\frac{-\hbar^2\nabla^2}{2m} + \mathcal{V}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \tag{3.21}$$

and we have for the ground state energy

$$E = \sum_i \epsilon_i\theta(\mu - \epsilon_i) \tag{3.22}$$

Nota bene: As long as we do not know $v_{\text{xc}}(\mathbf{r})$ we cannot do anything!

3.1.5 Local-density aproximation (LDA)

The local-density approximation consists in replacing at any point $\mathbf{r}$, where the self-consistent electron density is $n(\mathbf{r})$ the exchange-correlation energy density E_{xc}/N by that of the free, interacting electron gas, *taken at the homogeneous density* $n \equiv n(\mathbf{r})$.

$$E_{\text{xc}}\big[n(\mathbf{r})\big] = E_{\text{xc}}^{\text{hom}}(n)\Big|_{n=n(\mathbf{r})} \tag{3.23}$$

For example, Gell-Mann and Brückner[3] have calculated the exchange-correlation contribution of the electron gas with the result

$$\frac{E_{xc}(n)}{N} = 0.0622\ln(r_s/a_0) - 0.096\,, \tag{3.24}$$

where a_0 is the Bohr radius and r_s is defined by

$$\frac{1}{n} = \frac{4}{3}\pi r_s^3\,. \tag{3.25}$$

from which would follow

$$v_{xc}(\mathbf{r}) \propto \frac{1}{n(\mathbf{r})} \tag{3.26}$$

Nowadays very accurate calculations of $E_xc(n)$ exist, which are talen for v_{xc} in one-electron calculations based on the LDA.

3.2 Single electrons in a periodic potential

3.2.1 Bloch's theorem

We now exploit our group-theoretical knowledge to electrons obeying the one-electron Schrödinger equation with a potential of the form

$$T_{\mathbf{R}}V(\mathbf{r}) = V(\mathbf{r}) \qquad \Rightarrow T_{\mathbf{R}}\mathcal{H} = \mathcal{H}\,, \tag{3.27}$$

where $T_{\mathbf{R}}$ is a lattice translation from $\mathbf{R} = 0$ to the vector

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\,. \tag{3.28}$$

We know that the wave function must transform as

$$T_{\mathbf{R}}\psi_\alpha(\mathbf{r}) = \sum_{\beta=1}^{d}\Gamma_{\alpha\beta}(T_{\mathbf{R}})\psi_\beta(\mathbf{r})\,, \tag{3.29}$$

[3]Phys. Rev. **106**, 364 (1957)

where d is the dimension of the irreducible representation. However, we know that all irreducible representations of a *commutative group* are one-dimensional. Therefore we have

$$T_{\mathbf{R}}\psi(\mathbf{r}) = \Gamma(\mathbf{R})\psi(\mathbf{r}) \tag{3.30}$$

Since Γ shold be unitary and, on the other hand, is a c-number, we can parametrize Γ as

$$\Gamma(\mathbf{r}) = e^{i\phi(\mathbf{r})} \tag{3.31}$$

Let's parametrize $\Gamma(\mathbf{a}_\ell)$ $\ell = 1, 2, 3$ as

$$\Gamma(\mathbf{a}_\ell) = e^{2\pi i x_\ell} \qquad \text{then}$$

$$\begin{aligned}
\Gamma(\mathbf{R}) &= \Gamma(n_1\mathbf{a}_1)\Gamma(n_2\mathbf{a}_2)\Gamma(n_3\mathbf{a}_3) \\
&= \Gamma(\mathbf{a}_1)^{n_1}\Gamma(\mathbf{a}_2)^{n_2}\Gamma(\mathbf{a}_3)^{n_3} \\
&= e^{2\pi i(n_1x_1 + n_2x_2 + n_3x_3)}
\end{aligned}$$

We now introduce the reciprocal lattice with basis $\mathbf{b}_1, \mathbf{b}_2$ and $\mathbf{b}_3$

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)}\mathbf{a}_2 \times \mathbf{a}_3 \\
\mathbf{b}_2 &= \frac{2\pi}{(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)}\mathbf{a}_3 \times \mathbf{a}_1 \\
\mathbf{b}_3 &= \frac{2\pi}{(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)}\mathbf{a}_1 \times \mathbf{a}_2\,,
\end{aligned} \tag{3.32}$$

and we have

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \tag{3.33}$$

Therefore the exponent in (3.32) can be defined to be a linear combination of the $\mathbf{b}_i$ with the coefficients x_i:

$$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3\,, \tag{3.34}$$

which is called *vector in reciprocal space* (as contrasted to a reciprocal lattice vector, in which the coefficient must be integers).
We can now state Bloch's theorem as follows: A one-electron wave function in a crystalline lattice can be written as

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) \tag{3.35}$$

where $u(\mathbf{r})$ has the translational symmetry of the lattice, i.e.

$$u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r}) \tag{3.36}$$

where $\mathbf{R}$ is a lattice vector. The $\mathbf{k}$ vector characterizes a specific irreducible representation of the system, which acts as a (triple) quantum number and we write

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \tag{3.37}$$

$\psi_{\mathbf{k}}(\mathbf{r})$ is called a *Bloch function.*
We can show that $\psi_{\mathbf{k}}(\mathbf{r})$ has the lattice symmetry of the reciprocal lattice. Let $\mathbf{R}$ be an arbitrary direct lattice vector and $\mathbf{K}$ a reciprocal lattice vector.

$$\begin{aligned}
T_{\mathbf{R}}\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) &= \psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r} + \mathbf{R}) && \text{(3.38a)} \\
&= e^{i(\mathbf{k}+\mathbf{K})\mathbf{R}}\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{R}}\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) && \text{(3.38b)}
\end{aligned}$$

So all $\mathbf{k} + \mathbf{K}$,where $\mathbf{K}$ is any point in the reciprocal lattice are equivalent, i.e. they equivalently represent the translation group. Therefore it is sufficient to use the vectors within the *Wigner-Seitz cell* of the reciprocal lattice as quantum number. This cell is called *First Brillouin zone.*

3.2.2 Born-von-Kármán boundary concitions

We assume that the crystal sample of volume V is a parallel epiped spanned by the primitive translations $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, and continue this epiped periodicalli infinitely into all space directions. The edges of the epiped are assumed to have the lengths $L_i = |\mathbf{a}_i| N_i$, i = 1,2,3, $N = N_1 N_2 N_3$ is the total number of lattice sites within the elemental macroscopic epiped. The Volume is given by $V = L_1 L_2 L_3$. We now impose *periodic boundary conditions* for the Bloch functions

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &= \psi_{\mathbf{k}}(\mathbf{r} + N_\ell \mathbf{a}_\ell) \qquad \ell = 1,2,3 && \text{(3.39a)} \\ \Rightarrow \qquad \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) &= e^{i\mathbf{k}\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) = \psi_(\mathbf{r} + \mathbf{R} + N_\ell \mathbf{a}_\ell) && \text{(3.39b)} \\ &= e^{i\mathbf{k}\mathbf{R}} e^{i\mathbf{k} N_\ell \mathbf{a}_\ell} \psi_{\mathbf{k}}(\mathbf{r})\,, && \text{(3.39c)} \\ & && \text{(3.39d)} \end{aligned}$$

so that we must have

$$e^{i\mathbf{k} N_\ell \mathbf{a}_\ell} = 1 \qquad \ell = 1,2,3\,. \tag{3.40}$$

We have constructed now 3 cyclic groups of orders N_1, N_2, N_3. The $\mathbf{k}$ vector has the form

$$\begin{aligned} \mathbf{k} &= 2\pi\big(x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3\big) && \text{(3.41a)} \\ \Rightarrow \qquad e^{2\pi i N_\ell x_\ell} &= 1 \qquad \ell = 1,2,3 && \text{(3.41b)} \end{aligned}$$

So the x_ℓ must be of the form $x_\ell = \frac{m_\ell}{N_\ell}, m_\ell \in \mathbb{Z}$.
The $\mathbf{k}$ vector is now composed of a set of N rational numbers, which are now the quantum numbers for the crystalline solid. It follows from (3.41a) that the volume of $\mathbf{k}$ space per allowed value of $\mathbf{k}$ is just the small parallel epiped with edges $|\mathbf{b}_\ell|/N_\ell$. so that we can calculate this little volume to be

$$\Delta\mathbf{k} = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_3} \times \frac{\mathbf{b}_3}{N_3} \right) = \frac{1}{N} \mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3 \tag{3.42}$$

Since the spat product of the $\mathbf{b}$'s ist just $(2\pi)^3$, divided the volume of the primitive lattice cell we have

$$\Delta\mathbf{k} = \frac{(2\pi)^3}{V}\,. \tag{3.43}$$

Free electrons

Because the wave functions of free electrons serve as reverence for band structure calculations in metals we want to study the influence of the Born-von-Kármán boundary conditions on the free-electron wave functions. For this aim we assume that the parallel-epiped is a cube of edge length $L_1 = L_2 = L_3 = L$, so that $N = aL^3$ and all three N_i's are equal to $\sqrt[3]{N}$.
The free-electron Schrödinger equation is

$$\frac{\hbar^2 \nabla^2}{2m} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \tag{3.44}$$

and can be solved with e-function ansatz

$$\psi_{\mathbf{k}}(\mathbf{r}) = A e^{i\mathbf{k}\mathbf{r}} \tag{3.45}$$

The eigenvalues then take the form

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \tag{3.46}$$

Using the periodic boundary conditions we can normalize the wave functions as follows

$$\int_V \mathrm{d}^3\mathbf{r} \big|\psi_{\mathbf{k}}(\mathbf{r})\big|^2 = \int_V \mathrm{d}^3\mathbf{r} A^2 = V A^2 = 1 \qquad \Rightarrow \qquad A = \frac{1}{\sqrt{V}} \tag{3.47}$$

The Born-von-Kármán boundary conditions for the free electrons take the form

$$\psi_{\mathbf{k}}(\mathbf{r}+L\mathbf{e}_x)=\psi_{\mathbf{k}}(\mathbf{r}+L\mathbf{e}_y)=\psi_{\mathbf{k}}(\mathbf{r}+L\mathbf{e}_z)=\psi_{\mathbf{k}}(\mathbf{r}) \tag{3.48}$$

from which follows

$$e^{ik_xL}=e^{ik_yL}=e^{ik_zL}=1\,. \tag{3.49}$$

The components of $\mathbf{k}$ must be of the form

$$k_x=\frac{2\pi n_x}{L},\quad k_y\frac{2\pi n_y}{L},\quad k_z=\frac{2\pi n_z}{L},\qquad n_\ell\in(Z)\,. \tag{3.50}$$

and we have for the "coarse-graining volume" again

$$\Delta\mathbf{k}=\frac{(2\pi)^3}{V} \tag{3.51}$$

Calculation of the Fermi wavenumber We now assume that there are N electrons in the box of volume $V=L^3$, which is periodically repeated. Each of the electronic states labelled with k_x,k_y,k_z can be occupied by two elecrons only. In the ground state the electrons want to minimize their energy. This is the reason why the volume in k space occupied by the free electrons is a *sphere*. This sphere is called the *Fermi sphere*, its surface is called *Fermi surface*, and its radius *Fermi wavenumber* k_F. The latter quantity can be calculated as follows: The number of states occupied by the electrons is $N/2$:

$$N=\sum_{\substack{k_x,k_y,k_z\\|\mathbf{k}|<k_f}}2\;=\;2\frac{L^3}{(2\pi)^3}\sum_{n_x}\Delta k_x\sum_{n_y}\Delta k_y\sum_{n_z}\Delta k_z\,1=2\frac{V}{(2\pi)^3}\int_{|\mathbf{k}|<k_f}\mathrm{d}^3\mathbf{k}=\frac{1}{3}\frac{V}{\pi^2}k_F^3 \tag{3.52a}$$

$$\Rightarrow\qquad k_F\;=\;\sqrt[3]{3\pi^2n}\qquad\text{with}\qquad n=\frac{N}{V} \tag{3.52b}$$

The Fermi energy is given by

$$E_F=\lim_{T\to0}\mu(T)=\frac{1}{2m}k_F^2 \tag{3.53}$$

where we have indicated that E_F is the chemical potential in the ground state, which appears in the formula for the average occupation number of a degenerate Fermi gas

$$f(E)=\frac{1}{e^{[E-\mu]/k_BT}+1} \tag{3.54}$$

3.2.3 Quantum mechanics andd the matrix eigenvalue problem

In linear algebra the eigenvalue problem is the solution of a set of homogeneous equations characterized by a $N\times N$ matrix M:

$$\sum_{\alpha'}M_{\alpha\alpha'}u_{\alpha'}=\lambda u_\alpha \tag{3.55}$$

Such homogeneous have always the trivial solution $u_\alpha=0$. Nontrivial solutions exist if and only if

$$\det\{\mathbb{M}-\lambda\mathbb{1}\}=0 \tag{3.56}$$

This *characteristic equation* (or *secular equation*) has n roots $\lambda_1\ldots\lambda_N$ corresponding to N *eigenvectors* $u^{(1)}\ldots u^{(N)}$. These Eigenvectors are calculated from (3.55) with a particular λ_α and from the normalization condition

$$\sum_{\alpha'=1}^{N}|u_{\alpha'}^{(\alpha)}|^2 \tag{3.57}$$

The quantities $u_{\alpha'}^{(\alpha)}$ form an unitary matrix $\mathbb{U}$ and we have

$$\mathbb{U}^\dagger\mathbb{M}\,\mathbb{U}=\mathbb{\Lambda} \tag{3.58}$$

where $\mathbb{\Lambda}$ is a diagonal matrix with all the eigenvalues as entries. One says that $\mathbb{U}$ diagonalizes $\mathbb{M}$.
We now assume that the quantum-mechanical one-electron problem

$$\mathcal{H}_0|\alpha>=E_\alpha|\alpha> \tag{3.59}$$

has been solved, i.e. the Eigenvalues E_α and the basis functions $\phi_\alpha(\mathbf{r}) =< \mathbf{r}|\alpha >$ are known. We now would like to solve the one-electron problem

$$\mathcal{H}|\psi >= E|\psi > \tag{3.60}$$

i.e. we would like to calculate the Eigenvalues E and corresponding eigenfunctions $\psi(\mathbf{r}) =< \mathbf{r}|\psi >$.
We expand $|\psi >$ into linear combinations of $|\alpha >$ (or rather $|\alpha' >$:

$$|\psi >= \sum_{\alpha'} C_{\alpha'}|\alpha' > \tag{3.61}$$

and write the Schrödinger equation (3.60) $\mathcal{H} = \mathcal{H}_0 + \Delta\mathcal{H}$

$$\big(\mathcal{H}_0 + \Delta\mathcal{H}\big)\sum_{\alpha'} C_{\alpha'}|\alpha' >= E\sum_{\alpha'} C_{\alpha'}|\alpha' > \tag{3.62}$$

We multiply from left with $< \alpha|$ and take for granted $< \alpha|\alpha' >= \delta_{\alpha\alpha'}$ to obtain

$$E_\alpha C_\alpha \delta_{\alpha\alpha'} + \sum_{\alpha'} < \alpha|\Delta\mathcal{H}|\alpha' >= EC_\alpha \tag{3.63}$$

If we now define a matrix $\mathbb{H}$ with $\mathbb{H}_{\alpha\alpha} = E_\alpha + < \alpha|\Delta\mathcal{H}|\alpha >$ and $\mathbb{H}_{\alpha\alpha'} = + < \alpha|\Delta\mathcal{H}|\alpha' >$ we have a matrix eigenvalue problem

$$\mathbb{H}C = EC \tag{3.64}$$

which can be solved by the usual methods of linear algebra.

3.2.4 Nearly free electrons

We now assume that the periodic potential in our crystal is somehow *weak*, so that an expansion of the periodic function $u_\mathbf{k}(\mathbf{r})$ into a Fourier series

$$u_\mathbf{k}(\mathbf{r}) = \sum_{\mathbf{K}\in\text{rec.lattice}} \frac{1}{\sqrt{V_{WS}}} C_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\mathbf{r}} \tag{3.65}$$

does not contain too many terms. We can now write the Bloch function as

$$\psi_\mathbf{k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_\mathbf{k}(\mathbf{r}) = \sum_{\mathbf{K}\in\text{rec.lattice}} \frac{1}{\sqrt{V_{WS}}} C_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\mathbf{r}} \equiv \sum_{\mathbf{K}\in\text{rec.lattice}} C_{\mathbf{k}-\mathbf{K}}|\mathbf{k}-\mathbf{K}> \tag{3.66}$$

We now interpret the free-electron states $|\mathbf{k}-\mathbf{K}>$ as solution of the free-electron Schrödinger equation and apply the scheme of the previous section to obtain

$$\underbrace{\frac{\hbar^2}{2m}\big(\mathbf{k}-\mathbf{K}\big)^2}_{E^{(0)}_{\mathbf{k}-\mathbf{K}}} C_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} < \mathbf{k}-\mathbf{K}'|\mathcal{V}|\mathbf{k}-\mathbf{K} > C_{\mathbf{k}-\mathbf{K}'} = E_\mathbf{k} C_{\mathbf{k}-\mathbf{K}} \tag{3.67}$$

which constitutes our diagonalization scheme to calculate the *band structure* $E_\mathbf{k}$
We evaluate $< \mathbf{k}-\mathbf{K}'|\mathcal{V}|\mathbf{k}-\mathbf{K} >\equiv \mathcal{V}_{\mathbf{K}\mathbf{K}'}$

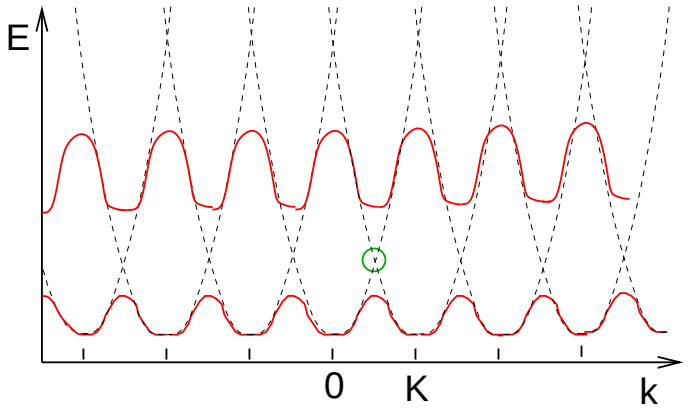
$$\mathcal{V}_{\mathbf{K}\mathbf{K}'} = \int\limits_{V_{WS}} \mathrm{d}^3\mathbf{r} \frac{1}{V_{WS}} < \mathbf{k}-\mathbf{K}'|\mathcal{V}|\mathbf{k}-\mathbf{K} >= e^{-i\mathbf{k}\mathbf{r}} e^{i\mathbf{K}'\mathbf{r}} \mathcal{V}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} e^{-i\mathbf{K}\mathbf{r}} \tag{3.68a}$$

$$= \frac{1}{V_{WS}} \int\limits_{V_{WS}} \mathrm{d}^3\mathbf{r} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} \mathcal{V}(\mathbf{r}) \tag{3.68b}$$

which is just the Fourier component $\mathcal{V}_{\mathbf{Q}=\mathbf{K}-\mathbf{K}'}$ of the Fourier expansion of the periodic potential

$$\mathcal{V}(\mathbf{r}) = \sum_{\mathbf{Q}\in\text{rec.latt.}} e^{i\mathbf{Q}\mathbf{r}} = \mathcal{V}_0 + \sum_{\mathbf{Q}\neq 0} e^{i\mathbf{Q}\mathbf{r}} \tag{3.69}$$

The constant $\mathcal{V}_0$ is usually set 0 by shifting the energy scale.



Let us now simplify the problem and consider only one dimension, so that we have only one k direction. We have sketched the free band structure $E_{k\pm K}$ in the figure. Away from a degeneracy (where the dashed curves cross) one can use stationary perturbation theory to write

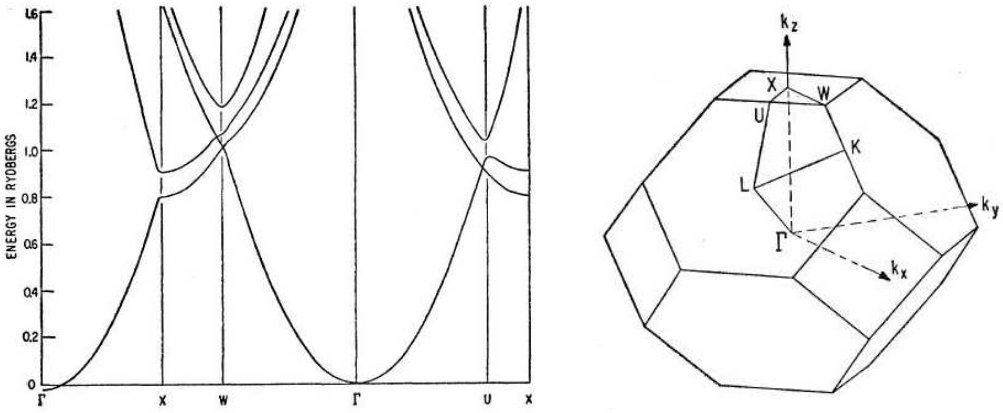
$$E_{\mathbf{k}} = \frac{\hbar^2(\mathbf{k}-\mathbf{K})^2}{2m} + \underbrace{<\mathbf{K}|\mathcal{V}|\mathbf{K}>}_{\mathcal{V}_0=0} + \underbrace{\sum_{\mathbf{K}'\neq\mathbf{K}} \frac{|<\mathbf{K}|\mathcal{V}|\mathbf{K}+\mathbf{K}'>|^2}{E^{(0)}_{\mathbf{k}-\mathbf{K}} - E^{(0)}_{\mathbf{k}-\mathbf{K}'}}}_{\text{small perturbation}\approx 0} \tag{3.70}$$

We now set in lowest order $E_k = E^{(0)}_{k\pm K}$ away from a degeneracy. At a degeneracy we have to consider the matrix elements corresponding to the reciprocal lattice vectors that label the two degenerate energies of the unperturbed problem. Let us consider the crossing of the curves $E^{(0)}_k E^{(0)}_{k+K}$ indicated by the green mark in the figure. At the degeneracy we must solve the matrix eigenvalue problem in this reduced 2×2 subspace. The eigenvalue equation is

$$E^{(0)}_k C_k + V_K C_{k-K} = E_k C_k \tag{3.71a}$$
$$E^{(0)}_k C_{k-K} + V_{-K} C_k = E_k C_{k-K} \tag{3.71b}$$

The secular equation ist

$$\det\left\{\begin{array}{cc} E^{(0)}_k - E & V_{-K} \\ V_K & E^{(0)}_k - E \end{array}\right\} = \left(E^{(0)}_k - E\right)^2 - |V_K|^2 = 0 \tag{3.72}$$



Band structure calculation for fcc aluminum by W. A. Harrison, Phys. Rev. **118**, 1182 (1960) together with the first Brillouin zone of the fcc lattice.

with the solutions

$$E_{1,2} = E^{(0)}_k \pm |V_k| \tag{3.73}$$

Obviously at the degeneracy of the unperturbed problem there appears a *gap* of width $|V_k|$. One speaks of *level repulsion* or a *lifted degeneracy*. We have indicated in the figure the resulting one-dimensional band structure. In the other figure we shown the 3-dimensional band structure of fcc aluminum as calculated by W. A. Harrison, Phys. Rev. **118**, 1182 (1960). Also shown is the 1st Brillouin zone of a fcc crystal with the characteristic points which are the endpoints of the paths along which the band structure is drawn.

3.2.5 Orthogonalized plane waves

When people started to do band structure calculations they were puzzled by the fact that the self-consistent Hartree-Fock potential never was weak, but in spite of that many metals show a nearly-free-electron band structure like aluminum in our figure. This corresponds to the fact that the electronic transport properties of metals like aluminum or copper can be described very well in terms of a free-electron or nearly-free electron model (see the chapter on electron transport in metals). The solution of the puzzle is that around every atomic nucleus in a metal (you convince yourself of that by looking at the periodic table) there are tightly bound electron orbitals, the so-called *core-electron* orbitals. The remaining *valence electrons* form the band structure. They are, in fact, holding the solid together. Of course the valence wave functions must be orthogonal to the core electrons to the core electrons.
Let us denote the core electron wave functions by $\psi_\alpha(\mathbf{r}) =< \mathbf{r}|\alpha >$ and plane waves by $< \mathbf{k}|\mathbf{k} >= \frac{1}{\sqrt{V_{\rm WS}}} e^{i\mathbf{kr}}$. We define a projector onto the core electrons

$$\mathcal{P} = \sum_\alpha |\alpha >< \alpha| \tag{3.74}$$

Then $\mathbf{Q} = \mathbb{1} - \mathcal{P}$ projects rectangular (i.e. orthogonal) to the core electrons, i.e.

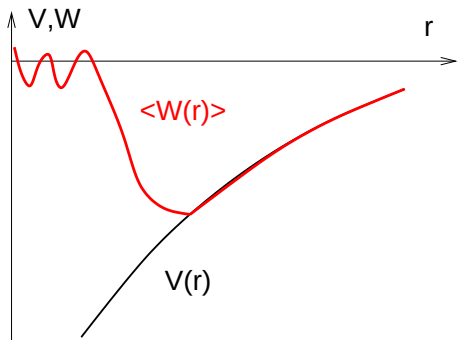
$$\mathbf{Q}|\alpha_0 >= \big(\mathbb{1} - \sum_\alpha |\alpha >< \alpha|\big)|\alpha_0 >= |\alpha_0 > -|\alpha_0 >= 0 \tag{3.75}$$

An *orthogonalized plane wave (OPW)* is defined as

$$|\mathbf{k} >_{\rm OPW} = \mathbf{Q}|\mathbf{k} > \tag{3.76}$$

explicitly:

$$< \mathbf{r}|\mathbf{k} >_{\rm OPW} =< \mathbf{r}|\big(\mathbb{1} - \sum_\alpha |\alpha >< \alpha|\big)|\mathbf{k} >= \frac{1}{\sqrt{V_{\rm WS}}} e^{i\mathbf{kr}} - \sum_\alpha \psi_\alpha(\mathbf{r}) \int \mathrm{d}^3\mathbf{r}' \psi_\alpha(\mathbf{r}') \frac{1}{\sqrt{V_{\rm WS}}} e^{i\mathbf{kr}'} \tag{3.77}$$



If we expand the valence-electron Bloch wave functions with respect to the OPW's they are *automatically* orthogonal to the core functions.

$$|\psi_\mathbf{k} > = \sum_\mathbf{K} a_{\mathbf{k}-\mathbf{K}} |\mathbf{k} - \mathbf{K} >_{\rm OPW} \tag{3.78a}$$

$$\Rightarrow \quad \mathcal{H}|\psi_\mathbf{k} = \big(\mathcal{H}_{\rm kin} + \mathcal{V}\big)\big(\mathbb{1} - \mathcal{P}\big) \sum_\mathbf{K} a_{\mathbf{k}-\mathbf{K}} |\mathbf{k} - \mathbf{K} > \tag{3.78b}$$

We define now a pseude wave function

$$|\varphi_\mathbf{k} >= \sum_\mathbf{K} a_{\mathbf{k}-\mathbf{K}} |\mathbf{k} - \mathbf{K} > \tag{3.79}$$

and we have

$$|\psi_\mathbf{k} >= \big(\mathbb{1} - \mathcal{P}\big)|\varphi_\mathbf{k} > \tag{3.80}$$

Inserting this into the Schrödinger equation for $|\psi_\mathbf{k} >$ and transfer the term $\mathcal{P}E_\mathbf{k}|\varphi_\mathbf{k} >$ to the left side we obtain

$$\Big[\mathcal{H}_{\rm kin} + \underbrace{\mathcal{V} - \mathbf{p}(E_\mathbf{k} - \mathcal{H})}_{\mathcal{W}}\Big]|\varphi_\mathbf{k} >= E_\mathbf{k}|\varphi_\mathbf{k} > \tag{3.81}$$

pseudopotential (operator!)

The matrix elements of the pseudopotential operator have the form

$$< \mathbf{k}-\mathbf{K}-\mathbf{Q}|\mathcal{W}|\mathbf{k}-\mathbf{K} >= \mathcal{V}_{\mathbf{Q}} - \sum_{\alpha} < \mathbf{k}-\mathbf{K}-\mathbf{Q}|\alpha > \big(E_\alpha - E_{\mathbf{k}}\big) < \alpha|\mathbf{k}-\mathbf{K} > \tag{3.82}$$

3.2.6 Wannier functions and the tight-binding model

We have shown that the Bloch function $\psi_{\mathbf{k}}(\mathbf{r})$ is periodic in reciprocal space ($\mathbf{k}$ space) i.e. invariant with respect to a reciprocal-lattice translation. We therefore can expand them into a Fourier series

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}_n} e^{i\mathbf{k}\mathbf{R}_n} a(\mathbf{R}_n, \mathbf{r})\,, \tag{3.83}$$

where the $a(\mathbf{R}_n, \mathbf{r})$ are given by

$$\begin{aligned} a(\mathbf{R}_n, \mathbf{r}) &= \underbrace{\frac{1}{V_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \mathrm{d}^2\mathbf{k}\, e^{-i\mathbf{k}\mathbf{R}_n \psi_{\mathbf{k}}(\mathbf{r})}}_{\sum_{\mathbf{k}}} \\ &= \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{r}-\mathbf{R}_n)} u_{\mathbf{k}}(\mathbf{r}) \\ &= a(\mathbf{r}-\mathbf{R}_n) \end{aligned} \tag{3.84}$$

The Wannier functions are wave functions centered around each lattice site.

- They become more and more equal to *atomic* wave functions as the lattice is expanded!

This is so if the lattice constant a becomes greater than the effective Bohr diameter (double Bohr radius) of the core electron wave function $\psi_\alpha(\mathbf{r})$.
We now write the Schrödinger equation in terms of Wannier functions:

$$\big(\mathcal{H}_{\mathrm{kin}} + \mathcal{V}(\mathbf{r}) - E^m_{\mathbf{k}}\big)\psi^m_{\mathbf{k}}(\mathbf{r}) = \sum_n e^{i\mathbf{k}\mathbf{R}_n}\big(\mathcal{H}_{\mathrm{kin}} + \mathcal{V}(\mathbf{r}) - E^m_{\mathbf{k}}\big) a_m(\mathbf{r}-\mathbf{R}_n) = 0 \tag{3.85}$$

We remind ourselves that $\mathcal{V}(\mathbf{r}) = \mathcal{V}(\mathbf{r}+\mathbf{R}_{n'})$ ($\mathbf{R}_{n'}$ being any lattice vector) is the periodic potential which arises from the presence of the lattice of atomic nuclei.
m is the so-called *band index*, which labels the different energy bands arising from the fact, that in addition to the translation symmetry there is also the point symmetry of the crystal. m labels the irreducible representations of the point symmetry group of the crystal (i.e the operations which leave a particular lattice point unchanged).
The atomic wave functions $\psi_\alpha(\mathbf{r}-\mathbf{R}_n)$ obey the Schrödinger equation

$$\big(\mathcal{H}_{\mathrm{kin}} + \mathcal{V}^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_n)\big)\psi_\alpha(\mathbf{r}-\mathbf{R}_n) = E^\alpha_{\mathrm{at}}\psi_\alpha(\mathbf{r}-\mathbf{R}_n)\,, \tag{3.86}$$

where $\mathcal{V}^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_n)$ is the self-consistent atomic Hartree-Fock (or LDA) potential.
We now identify m with α and $a_m(\mathbf{r}-\mathbf{R}_n)$ with $\psi_\alpha(\mathbf{r}-\mathbf{R}_n)$.

In (3.85) we replace

$$\mathcal{H}_{\mathrm{kin}} a_m(\mathbf{r}-\mathbf{R}_n) \approx \mathcal{H}_{\mathrm{kin}}\psi_\alpha(\mathbf{r}-\mathbf{R}_n)$$

by

$$\Big[E^\alpha_{\mathrm{at}} - \mathcal{V}^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_n)\Big]\psi_\alpha(\mathbf{r}-\mathbf{R}_n)$$

and obtain

$$\sum_n e^{i\mathbf{k}\mathbf{R}_n}\Big[E^{\mathrm{at}}_\alpha - \mathcal{V}^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_n) + \mathcal{V}(\mathbf{r}) - E^\alpha_{\mathbf{k}}\Big]\psi_\alpha(\mathbf{r}-\mathbf{R}_n) = 0 \tag{3.87}$$

We now consider a specific lattice site $\mathbf{R} = 0$ and multiply from the left with $\psi^*_\alpha(\mathbf{r})$ and perform a $\mathbf{r}$ integration. This gives an expression for the band structure $E^\alpha_\mathbf{k}$ corresponding to a particular atomic level

$$E^\alpha_\mathbf{k} = E^\alpha_{\rm at} - \sum_n e^{i\mathbf{k}\mathbf{R}_n} \underbrace{\int \mathrm{d}\mathbf{r} \Big[\mathcal{V}^{\rm at}(\mathbf{r}-\mathbf{R}_n) - \mathcal{V}(\mathbf{r})\Big] \psi^*_\alpha(\mathbf{r})\psi_\alpha(\mathbf{r}-\mathbf{R}_n)}_{t_{\alpha,n}} \tag{3.88}$$

This is the expression for the band structure of a crystal in the *tight-binding approximation*. In simplified cases it is instructive to consider only one atomic orbital $\alpha \equiv 0$. As the "overlap integrals" involving the products $\psi^*_\alpha(\mathbf{r})\psi_\alpha(\mathbf{r}-\mathbf{R}_n)$ vanish exponentially with increasing $|\mathbf{R}_n|$ it is sufficient to consider only the next nearest neighbors of the given lattice site $\mathbf{R} = 0$. We then obtain the well-known model expression for the tight-binding band structure

$$E_\mathbf{k} = E_0 \; - \sum_{\substack{n = \text{next} \\ \text{neighbors}}} e^{i\mathbf{k}\mathbf{R}_n} t_{0,n} \tag{3.89}$$

In the case of a simple-cubic lattice we get the explicit formula

$$E_\mathbf{k} = E_0 - 2t\Big[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\Big]\,. \tag{3.90}$$

Considering our schematic picture of the nearly-free electron band stucture on page 9 we see that this does not look very different. In particular near $\mathbf{k} = 0$ we obtain

$$E_\mathbf{k} = E_0 - t\big(6 + k^2a^2\big) \tag{3.91}$$

from which we can derive an *effective mass*

$$\frac{1}{m^*} = \frac{2ta^2}{\hbar^2}\,. \tag{3.92}$$

3.2.7 Other band structure methods

- *Kohn-Korringa-Rostocker (KKR) method*
  - Around all atoms a sphere ("muffin-tin sphere") is drawn. Inside the sphere the potential is the self-consistent atomic potential. Outside the potential is constant;
  - the Hamiltonian outside of the spheres is a free-electron one. The corresponding waves are scattered by the muffin-tin spheres. The latter are parametrized by partial-wave phase shifts, which enter into the wave scattering matrix (*T-matrix*).
  - The corresponding Lipmann-Schwinger equations of the scattering problem become matrix equations for the T-matrix elements.
- *Augmented plane wave (APW) method*
  - This method is similar to the OPW method: the plane waves are "decorated" with the atomic orbitals in order to minimize the number of APW expansion coefficients. One distinguishes between the nonlinear APW and the linearized (LAPW) method. The latter is available as a downloadable code (WIEN code).
  - *Linearized muffin-tin orbitals (LMTO)*
  - In this methods the muffin-tin orbitals are taken as basis set for the band structure calculation. LMTO codes are as well commercially available.

All these methods rely on the density-functional formalism with the local-density approximation (LDA) or the more refined it generalized gradient approximation (GGA). This method works only well if the wave functions of the valence electrons are mobile enough to screen the Coulomb potential effectively, so that the net electronic correlations are weak. This is not the case for materials with *strongly correlated electrons*. Such materials include *high-T_c superconducting* oxide materials or metals with unfilled f shell with very high effective masses (*"heavy fermion materials"*). For such materials the LDA or GGA breaks down. Instead one works with the *dynamical mean-field theory*, in which the correlated-electron problem is treated as an effective impurity problem inside a crystalline matrix.

3.2.8 Density of states

The full information on the Eigenvalue spectrum of a crystalline solid is its energy band structure $E^m_{\mathbf{k}}$. However, very often only the *energy distribution* is of importance or available (from spectroscopic experiments). In non-crystalline solids this is the only information on the electronic structure, as there is no lattice symmentry i.e. no Bloch theorem and no irreducible representations of point groups.
The energy distribution is called *density of states* and is defined by

$$\boxed{N(E) = \frac{2}{V}\sum_m \sum_{\mathbf{k}} \delta\big(E - E^m_{\mathbf{k}}\big)} \tag{3.93}$$

$N(E)$ is the density of states per unit energy interval and per unit volume. One can also define a quantity per electron instead per volume, which is sometime called "level density"

$$\boxed{g(E) = \frac{1}{n}N(E) = \frac{2}{N}\sum_m \sum_{\mathbf{k}} \delta\big(E - E^m_{\mathbf{k}}\big)} \tag{3.94}$$

Both quantities are being used in the literature.
We want to calculate $N(E)$ for a free electron gas inside a box of volume V with periodic boundary conditions. Using the recipe

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3}\int \mathrm{d}^3\mathbf{k}$$

we obtain

$$\begin{aligned} N(E) &= \frac{1}{4\pi^3}\int \mathrm{d}^3\mathbf{k}\ \delta(E - E_{\mathbf{k}}) = \frac{1}{\pi^2}\int_0^\infty \mathrm{d}k\ k^2\,\delta(E - \underbrace{\frac{\hbar^2k^2}{2m}}_{x}) \\ &= \tfrac{m}{\hbar^2\pi^2}\int_0^\infty \mathrm{d}x\ \sqrt{\tfrac{2m}{\hbar^2}x}\ \ \delta(E-x) \\ &= \begin{cases} \frac{m}{\hbar^3\pi^2}\sqrt{2mE} & E > 0 \\ 0 & E < 0 \end{cases} \end{aligned} \tag{3.95}$$

3.3 Electonic structure of disordered solids and liquids

3.3.1 Green's functions

In the field of disordered materials the Green's function concept is indispensabe.
We start with the one-electron Schrödinger equation

$$\mathcal{H}\,\psi(\mathbf{r},t) = i\hbar\,\frac{\partial}{\partial t}\,\psi(\mathbf{r},t) \tag{3.96}$$

As one wants to make use extendedly of models with Hamiltonians $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$, where $\mathcal{V}$ describes the disorder, one wants to treat the part $\mathcal{V}\psi$ like an unknown source term, i.e. one treats the Schrödinger equation like an inhomogeneous differential equation. Special solutions of inhomogeneous differential equations are given in terms of the Green's function, which obeys the inhomogeneous equation with a δ function inhomogeneity:

$$\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H}_0 \mp i\epsilon\right)G^{(0)}_{\pm}(\mathbf{r},\mathbf{r}',t,t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{3.97}$$

The term $\mp i\epsilon$ has been inserted, because in its absence the term inside the bracket would be singular.
One can also define the *full Greens' function* as

$$\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H} \mp i\epsilon\right)G_{\pm}(\mathbf{r},\mathbf{r}',t,t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{3.98}$$

G_+ is called *advanced* Green's function, G_- *retarded* Green's function,

We now assume that $\mathcal{H}$ is stationary, so that we obtain the Eigenvalue problem

$$\mathcal{H}|\psi_n >= E_n|\psi_n \tag{3.99}$$

and we have

$$\psi(\mathbf{r},t) = e^{-\frac{i}{\hbar}E_n t}\ \underbrace{\psi_n(\mathbf{r})}_{<\mathbf{r}|\psi_n>} \tag{3.100}$$

One can show (Exercises!) that (3.98) is solved by

$$G_\pm(\mathbf{r},\mathbf{r}',t,t') = \pm\frac{i}{\hbar}\sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')e^{-(i/\hbar)[E_n\pm i\epsilon](t-t')}\theta\big(\mp(t-t')\big) \tag{3.101}$$

As the Green's function depends only on the time difference $\tau = t-t'$ we can perform a Fourier transform with respect to τ:

$$G_\pm(\mathbf{r},\mathbf{r}',\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau\ e^{i\omega\tau}\ G_\pm(\mathbf{r},\mathbf{r}',\tau) = \sum_n \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{\underbrace{\hbar\omega \mp i\epsilon}_{z_\pm} - E_n} \tag{3.102}$$

We define now the *resolvent operator* (or "Green operator") as

$$\mathcal{G}(z) = \big[z\mathbb{1} - \mathcal{H}\big]^{-1} \equiv \frac{1}{z-\mathcal{H}} \tag{3.103}$$

from which we obtain

$$G_\pm(\mathbf{r},\mathbf{r}',\omega) =< \mathbf{r}|\frac{1}{z_\pm - \mathcal{H}}|\mathbf{r}' >=< \mathbf{r}|\mathcal{G}(z_\pm)|\mathbf{r}' > \tag{3.104}$$

One can, of course also consider matrix elements of $\mathcal{G}(z)$ in an arbitrary basis $|\alpha >$

$$G_{\alpha\beta}(z) =< \alpha|\mathcal{G}(z)|\beta > \ . \tag{3.105}$$

In particular we shall make use of the plane wave basis normalized with the sample volume V and periodic boundary conditions

$$< \mathbf{r}|\mathbf{k} >= \frac{1}{\sqrt{V}}e^{i\mathbf{kr}}\,; \qquad < \mathbf{k}|\mathbf{r} >= \frac{1}{\sqrt{V}}e^{-i\mathbf{kr}}\,. \tag{3.106}$$

Relation to the density of states Let us consider the difference of the trace of the resolvent taken with z just above and below the real axis:

$$\begin{aligned}
\mathrm{Tr}\big\{\mathcal{G}(z_+) - \mathcal{G}(z_-)\big\} &= \sum_n \left[\frac{1}{\underbrace{\hbar\omega}_{E} - i\epsilon - E_n} - \frac{1}{\underbrace{\hbar\omega}_{E} + i\epsilon - E_n}\right] \\
&= 2i\,\mathrm{Im}\Big\{\mathrm{Tr}\big\{\mathcal{G}(z_+)\big\}\Big\} = -2i\,\mathrm{Im}\Big\{\mathrm{Tr}\big\{\mathcal{G}(z_-)\big\}\Big\} \\
&= \sum_n \frac{2i\epsilon}{(E-E_n)^2+\epsilon^2} \ \stackrel{\epsilon\to 0}{\longrightarrow}\ 2\pi i\sum_n \delta(E-E_n)
\end{aligned} \tag{3.107}$$

In the limit $\epsilon \to 0$ we obtain

$$g(E) = \frac{1}{n}N(E) = \frac{1}{\pi N}\mathrm{Im}\Big\{\mathrm{Tr}\big\{\mathcal{G}(z_+)\big\}\Big\} = -\frac{1}{\pi N}\mathrm{Im}\Big\{\mathrm{Tr}\big\{\mathcal{G}(z_-)\big\}\Big\} \tag{3.108}$$

3.3.2 Perturbation expansion/disordered metals

We now consider a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \tag{3.109}$$

From the operator identity $\frac{1}{A+B} = \frac{1}{A}(1 - \frac{B}{A+B})$ we obtain

$$\mathcal{G}(z) = \frac{1}{z-\mathcal{H}_0}\left(1 + \mathcal{V}\frac{1}{z-\mathcal{H}}\right) = \mathcal{G}_0(z)\Big(1 + \mathcal{V}\mathcal{G}(z)\Big)\,, \tag{3.110}$$

which one can iterate to obtain

$$\begin{aligned}\mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0\mathcal{V}\mathcal{G}_0 + \mathcal{G}_0\mathcal{V}\mathcal{G}_0\mathcal{G}_0\mathcal{V}\mathcal{G}_0 + \dots \\ &= \mathcal{G}_0 + \mathcal{G}_0\frac{\mathcal{V}}{1-\mathcal{V}\mathcal{G}_0}\mathcal{G}_0 \\ &\equiv \mathcal{G}_0 + \mathcal{G}_0\mathcal{T}\mathcal{G}_0 \ , \end{aligned} \tag{3.111}$$

where we have defined the *scattering matrix* or *T-matrix* $\mathcal{T}$.

We now consider a *disordered metal* composed of atoms centered at $\mathbf{r}_n$ in an irregular way, so that the $\{\mathbf{r}_n\}$ do *not* form a lattice. The structural information is contained in the probability distribution $P(\mathbf{r}_1, \dots \mathbf{r}_{N_a})$, (where N_a is the number of atoms) and in particular the radial pair distribution function $g(|\mathbf{r}_i - \mathbf{r}_j|)$ and its Fourier transform $S(q) = 1 + \rho \int \mathrm{d}^3\mathbf{r} e^{i\mathbf{q}\mathbf{r}}[g(r) - 1]$ (see paragraph 2.1.1). The electron-atom potential is assumed to have the form

$$\mathcal{V}(\mathbf{r}) = \sum_{n=1}^{N_a} v(|\mathbf{r} - \mathbf{r}_n|) \tag{3.112}$$

from which follows

$$< \mathbf{k} + \mathbf{q}|\mathcal{V}|\mathbf{k} >= \frac{1}{V}\sum_{n=1}^{N_a} e^{i\mathbf{q}\mathbf{r}_n} v(q) \tag{3.113}$$

where $v(\mathbf{q}) = v(q)$ is the Fourier transform of $v(\mathbf{r}) = v(r)$. The electronic Hamiltonian is then composed as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \tag{3.114}$$

where $\mathcal{H}_0$ is assumed to be a *free-electron Hamiltonian*

$$\mathcal{H}_0|\mathbf{k} >= E^{(0)}_{\mathbf{k}}|\mathbf{k} >= (\frac{\hbar^2 k^2}{2m} + C)|\mathbf{k} > \tag{3.115}$$

where C is an arbitrary constant.
We further denote an average over the distribution $P\{\mathbf{r}_n\}$ by $\langle \dots \rangle$.
Before we proceed further we interest ourselves in the average $\langle \mathcal{V} \rangle$ of the potential. This is just a number and we shift our energy scale (i.e. the parameter C such that this number is set to zero:

$$\langle \mathcal{V} \rangle = 0 \tag{3.116}$$

In order to be able to calculate the density of states of the disordered metal we become interested in the *configuationally averaged resolvent*

$$\mathsf{G}(z) = \langle \mathcal{G}(z) \rangle = \left\langle \frac{1}{z - \mathcal{H}_0 - \mathcal{V}} \right\rangle \equiv \frac{1}{z - \mathcal{H}_0 - \Sigma(z)} \tag{3.117}$$

Here we have introduced an unknown operator $\Sigma(z)$ which looks like an effective potential of a ficticions system which is not disordered but, instead, depends on a complex parameter z. This (yet unknown) operator is called *self-energy operator*. We now insert the perturbation expansion (3.111) into (3.117) and solve for $\Sigma(z)$:

$$\begin{aligned}\Sigma(z) &= z - \mathcal{H}_0 - \frac{1}{\langle \mathcal{G}(z) \rangle} \\ &= \frac{1}{\mathcal{G}_0} - \frac{1}{\mathcal{G}_0 + \mathcal{G}_0 \underbrace{\langle \mathcal{V} \rangle}_{0} \mathcal{G}_0 + \mathcal{G}_0 \langle \mathcal{V}\mathcal{G}_0\mathcal{V} + \mathcal{G}_0\mathcal{V} \rangle \mathcal{G}_0 + \dots} \\ &= \frac{1}{\mathcal{G}_0}\left(1 - \frac{1}{1 + \langle \mathcal{V}\mathcal{G}_0\mathcal{V} \rangle \mathcal{G}_0 + \cdots}\right) \end{aligned} \tag{3.118}$$

To second order in $\mathcal{V}$ we get

$$\Sigma(z) = \frac{1}{\mathcal{G}_0(z)}\left\langle \mathcal{V}\mathcal{G}_0(z)\mathcal{V} \right\rangle \mathcal{G}_0(z) \, . \tag{3.119}$$

We now use the $|\mathbf{k}>$ basis. The density of states is given by

$$N(E) = \frac{1}{\pi V} \sum_{\mathbf{k}} \underbrace{< \mathbf{k}|\mathsf{G}(z_+)|\mathbf{k} >}_{G(k,z)} \tag{3.120}$$

$G(k,z)$ is at the same time the Fourier transform of the averaged Green's function

$$\langle G(\mathbf{r},\mathbf{r}',z)\rangle = G(\mathbf{r}-\mathbf{r}',z) \tag{3.121}$$

with respect to the variable $\mathbf{r}-\mathbf{r}'$. The relation (3.121) holds because the averaged material is assumed to be homegeneous. This is tantamount to stating that both $\mathsf{G}(z)$ as well as $\Sigma(z)$ are diagonal in the $|\mathbf{k}>$ representation.
We now can write down the diagonal element of the self-energy operator, which is called the *self-energy function* to second order in $\mathcal{V}$:

$$\begin{aligned}
\Sigma(k,z) &= < \mathbf{k}|\Sigma(z)|\mathbf{k} >= \sum_{\mathbf{q}} \frac{1}{G_0(k,z)} \Big\langle < \mathbf{k}|V|\mathbf{k}|+\mathbf{q} > G_0(|\mathbf{k}+\mathbf{q}|,z) < \mathbf{k}+\mathbf{q}|V|\mathbf{k} > \Big\rangle G_0(k,z) \\
&= \frac{N}{V^2} \sum_{\mathbf{q}} \underbrace{\frac{1}{N} \Big\langle \sum_{\ell m} e^{i\mathbf{q}(\mathbf{r}_\ell - \mathbf{r}_m)} \Big\rangle}_{S(q)} \big|v(q)\big|^2 G_0(|\mathbf{k}+\mathbf{q}|,z) = \Sigma'(k,E) + i\Sigma''(k,E)
\end{aligned} \tag{3.122}$$

This approximation is known as the *Born approximation for disorder* in the literature.
Let us discuss our result:
The real part of $\Sigma(\mathbf{k},z)$ produces a *shift* ("renormalization") of the "band structure":

$$E_{\mathbf{k}} \equiv E_{\mathbf{k}}^{(0)} + \Sigma'(k,E) \tag{3.123}$$

The density of states now takes the form

$$N(E) = \frac{1}{\pi V} \sum_{\mathbf{k}} \frac{\Sigma''(k,E)}{[E_{\mathbf{k}}]^2 + [\Sigma''(k,E)]^2} \tag{3.124}$$

The imaginary part of $\Sigma(\mathbf{k},z)$ introduces a new element into the density of states of our amorphous metal: The function $E_{\mathbf{k}}$ is no more sharply defined but is "washed out" by the disorder-induced imaginary part of $\Sigma(k,E)$. This is so, because neither a lattice $\mathbf{k}$ vector nor the free-electron $\mathbf{k}$ vector can serve as a "good quantum number" for labeling the electronic states. However, tha latter serves as "aproximate quantum number" but one has to deal with the fact that in this "approximate" basis the $E_{\mathbf{k}}$ resonances are washed out by disorder.

3.3.3 Lattice disorder: The coherent-potential approximation (CPA)

We study now a tight-binding Hamiltonian, which can be formally written as

$$\mathcal{H}_{\rm tb} = \sum_{i=1}^{N_a} |i> E_i < i| + \sum_{i\neq j} |i> t_{ij} < j| \tag{3.125}$$

where E_i are the diagonal elements and t_{ij} the off-diagonal elements. $< \mathbf{r}|i >= a(\mathbf{r}-\mathbf{r}_i) \approx \psi_{\rm at}(\mathbf{r}-\mathbf{r}_i)$ are orbitals associated with the site i. We now consider a *simple cubic* lattice and assume that the local energies ("local potentials") fluctuate from site to site, say with a Gaussian distribution

$$P(E_i) = \frac{1}{\sqrt{2\pi}\sigma} e^{\frac{1}{2\sigma^2}(E_i - E_0)^2} \tag{3.126}$$

or, alternatively, with a binary-alloy distribution

$$P(E_i) = c_A \delta(E_i - E_A) + c_B \delta(E_i - E_B) \tag{3.127}$$

with $c_A + c_B = 1$. The off-diagonal elements are assumed to be constant and the reference energy E_0 is assumed to be zero (in the alloy case $E_0 = c_A E_A + c_B E_B = 0$).The Hamiltonian now takes the form

$$\mathcal{H}_{\rm dis} = \sum_i |i> E_i < i| + t \sum_{i \neq j} |i>< j| \tag{3.128}$$

We now define an *effective medium*, in which the Green's function is equal to the averaged Greens function and the on-site energies are set equal to a complex number $\Sigma(z)$, so that we obtain an effective frequency-dependent Hamiltonian of the effective medium

$$\mathcal{H}_{\rm eff}(z) = \sum_i |i> \Sigma(z) < i| + t \sum_{i \neq j} |i>< j| \tag{3.129}$$

We now "dig a hole" into the effective medium near a specific site i_0, where we replaxe the uniform self energy by the fluctuating energy E_i. This introduces a "Perturbation" into the effective medium at site i_0

$$\mathcal{H}_{\rm hole} = \mathcal{H}_{\rm eff}(z) + \underbrace{|i_0> \Big(E_{i_0} - \Sigma(z) \Big) < i_0|}_{\mathcal{V}_{i_0}} \tag{3.130}$$

We now want to have (*CPA postulate*)

$$\begin{aligned} \mathcal{G}_{\rm eff}(z) &= \frac{1}{z - \mathcal{H}_{\rm eff}(z)} \\ &= \left\langle \frac{1}{z - \mathcal{H}_{\rm hole}(z)} \right\rangle \\ &= \mathcal{G}_{\rm eff} + \left\langle \mathcal{G}_{\rm eff} + \Big(\mathcal{V}_{i_0} \mathcal{G}_{\rm eff} + \mathcal{V}_{i_0} \mathcal{G}_{\rm eff} \mathcal{V}_{i_0} \mathcal{G}_{\rm eff} + \dots \Big) \right\rangle \\ &= \mathcal{G}_{\rm eff} + \mathcal{G}_{\rm eff} \Big\langle \underbrace{\frac{\mathcal{V}_{i_0}}{\mathbb{1} - \mathcal{V}_{i_0} \mathcal{G}_{\rm eff}}}_{\text{T-matrix}} \Big\rangle \mathcal{G}_{\rm eff} \end{aligned} \tag{3.131}$$

Since the T-matrix series contains only diagonal $< i_0| \dots |i_0 >$ matrix elements the T-matrix becomes diagonal $< i_0|T|i_0 > \equiv t_{i_0}$ so that the CPA postulate becomes

$$\boxed{< t_{i_0} > = \left\langle \frac{\mathcal{V}_{i_0}}{1 - \mathcal{V}_{i_0} \underbrace{< i_0|\mathcal{G}_{\rm eff}(z)|i_0 >}_{G_0(z)}} \right\rangle = \left\langle \frac{E_i - \Sigma(z)}{1 - \big[E_i - \Sigma(z)\big] G_o(z)} \right\rangle = 0} \tag{3.132}$$

We can re-write this equation as follows

$$\begin{aligned} \left\langle \frac{\Sigma(z)}{1 - \big[E_i - \Sigma(z)\big] G_0(z)} \right\rangle &= \left\langle \frac{E_i}{1 - \big[E_i - \Sigma(z)\big] G_0(z)} \right\rangle \\ = \Sigma(z) \left(1 + \underbrace{\left\langle \frac{\big[E_i - \Sigma(z)\big] G_0(z)}{1 - \big[E_i - \Sigma(z)\big] G_0(z)} \right\rangle}_{=0} \right) &= \Sigma(z) \end{aligned} \tag{3.133}$$

We now consider the case of *small* fluctuations of E_i, so that we can expand the denominator with respect to $\big[E_i - \Sigma(z)\big]$. Taking into account $\langle E_i \rangle = 0$ we obtain to lowest nonvanishing order

$$\Sigma(z) = \langle (E_i)^2 \rangle G_0(z) \tag{3.134}$$

which is just the SCBA result.
We still have the task to evaluate the effective-medium Green's function. We have

$$G_0(z) = < i_0| \frac{1}{z - \mathcal{H}_{\rm eff}(z)} |i_0 > \tag{3.135}$$

Taking the diagonal element with respect to a lattice site is equivalent to a sum over the first Brillouin zone:

$$G_0(z) = \sum_{\mathbf{k}\in \mathrm{BZ}} \frac{1}{z - \Sigma(z) - E_{\mathbf{k}}} = G_{\mathrm{lattice}}(z - \Sigma(z)) \tag{3.136}$$

where $E_{\mathbf{k}}$ is the simple-cubic tight-binding band structure (3.89) and G_{lattice} is the diagonal lattice tight-binding Green's function.