Computational Methods in Solid State Theory

SS 2016

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1. Single particle methods

1.1 The tight binding method

There are two ways of dealing with the periodic arrays of atoms in crystals; in one picture which is suitable for simple metals and covalent semiconductors, Bloch electron wave functions are considered to be waves that are little affected by the positions of the atoms: this works whenever the crystal potential is a smooth function and the atomic positions are not critical for the understanding. A different picture, suitable for insulators, but also for covalent semiconductors, considers electrons to move through the crystal slowly (or not at all) and to therefore belong to an atom for some time before moving on. The electrons are "tightly bound" to the atom and only move on for energetic reasons.

We start to introduce this description[1] by writing the potential of the electrons $V(\vec{r})$ in a crystal as a sum of atomic potentials

$$V(\vec{r}) = \sum_{\vec{R}} V_{\text{atom}}(\vec{r} - \vec{R}) \tag{1.1}$$

where the sum runs over the lattice vectors; first we treat the case of one atom per unit cell. This potential is periodic by construction because for a lattice vector $\vec{R}_0$

$$V(\vec{r}+\vec{R}_0) = \sum_{\vec{R}} V_{\text{atom}}(\vec{r}+\vec{R}_0-\vec{R}) \overset{\vec{R}'=\vec{R}-\vec{R}_0}{=} \sum_{\vec{R}'} V_{\text{atom}}(\vec{r}-\vec{R}') = V(\vec{r}) \tag{1.2}$$

Setting $\frac{\hbar^2}{2m} = 1$, the crystal Hamiltonian is

$$H = -\nabla^2 + V(\vec{r})\,. \tag{1.3}$$

We now try to relate the electron wave function to the atomic orbitals satisfying

$$H_{\text{atom}}\phi_n \equiv \big(-\nabla^2 + V_{\text{atom}}(\vec{r})\big)\phi_n = \varepsilon_n\phi_n\,. \tag{1.4}$$

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[1] This closely follows a tight binding note by Warren Pickett.

With a simple linear combination $\Phi_n(\vec{r}) = \sum_{\vec{R}} \phi_n(\vec{r} - \vec{R})$ one has difficulties fulfilling the Bloch theorem but the *ansatz*

$$B_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_n(\vec{r} - \vec{R}) \tag{1.5}$$

fulfils the Bloch condition for the wave vector $\vec{k}$:

$$\begin{aligned} \sqrt{N}\, B_{n\vec{k}}(\vec{r} + \vec{R}_0) &= \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_n(\vec{r} + \vec{R}_0 - \vec{R}) \\ &\overset{\vec{R}'=\vec{R}-\vec{R}_0}{=} \sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}'+\vec{R}_0)} \phi_n(\vec{r} - \vec{R}') = e^{i\vec{k}\cdot\vec{R}_0} \sqrt{N} B_{n\vec{k}}(\vec{r}) \end{aligned} \tag{1.6}$$

Here, it is enough to consider $\vec{k}$ vectors from the first Brillouin zone. The Bloch sum itself is not an eigenfunction for the crystal, but we can now try to expand the electron wave function in these Bloch sums:

$$\psi_{\vec{k}}(\vec{r}) = \sum_n b_n(\vec{k}) B_{n\vec{k}}(\vec{r})\,. \tag{1.7}$$

The functions $\psi_{\vec{k}}(\vec{r})$ should now solve the Schrödinger equation

$$H\psi_{\vec{k}} = \varepsilon_{\vec{k}} \psi_{\vec{k}} \tag{1.8}$$

with the $\varepsilon_{\vec{k}}$ representing the energy bands of the crystal. In order to find the conditions for the solution, we now calculate matrix elements by multiplying from the left with Bloch sums $B^*_{m\vec{k}}$ and integrating over the crystal:

$$\sum_n H_{mn}(\vec{k}) b_n(\vec{k}) = \varepsilon_{\vec{k}} \sum_n S_{mn}(\vec{k}) b_n(\vec{k}) \tag{1.9}$$

with

$$\begin{aligned} H_{mn}(\vec{k}) &= \int d^3r\, B^*_{m\vec{k}}(\vec{r}) H B_{n\vec{k}}(\vec{r}) \\ S_{mn}(\vec{k}) &= \int d^3r\, B^*_{m\vec{k}}(\vec{r}) B_{n\vec{k}}(\vec{r}) \end{aligned} \tag{1.10}$$

which are called *Hamiltonian matrix* and *overlap matrix*. Written without indices the secular equation is

$$\big(H(\vec{k}) - \varepsilon_{\vec{k}} S(\vec{k})\big) b(\vec{k}) = 0 \tag{1.11}$$

Now we can work out what the matrixes are by substituting the Bloch sums:

$$H_{mn}(\vec{k}) = \frac{1}{N}\sum_{\vec{R}_1,\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2-\vec{R}_1)} \int d^3r\, \underbrace{\phi_m^*(\vec{r}-\vec{R}_1)H\phi_n(\vec{r}-\vec{R}_2)}_{H_{mn}(\vec{R}_2-\vec{R}_1)} \tag{1.12}$$

The cell periodicity of the Hamiltonian means that we can change the summation to $\vec{R} = \vec{R}_2 - \vec{R}_1$ so that $\sum_{\vec{R}_1}$ just gives a factor N and we find

$$H_{mn}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} H_{mn}(\vec{R}) \tag{1.13}$$

$H_{mn}(\vec{k})$ and $H_{mn}(\vec{R})$ are lattice Fourier transforms of each other. Analogously one finds

$$S_{mn}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} S_{mn}(\vec{R}) \tag{1.14}$$

The real space integral

$$H_{mn}(\vec{R}) = \int d^3r\, \phi_m^*(\vec{r})H\phi_n(\vec{r}-\vec{R}) \tag{1.15}$$

indicates the amount of coupling between orbital ϕ_m at the origin and ϕ_n at the site $\vec{R}$; it is the *hopping amplitude* of an electron in orbital ϕ_n at site $\vec{R}$ to the orbital ϕ_m at the origin. The discussion can be limited to small $|\vec{R}|$ (few neighbours) as the integral will otherwise be negligible. The discussion for $S_{mn}(\vec{R})$, the overlap of $\phi_m(\vec{r})$ and $\phi_n(\vec{r}-\vec{R})$ runs very similarly.

Going beyond the elemental crystal, there can be various atoms at positions $\vec{\tau}_i$ (with respect to the origin $\vec{R}$ of the cell); then the atomic basis orbitals are $\phi_m(\vec{r}-\vec{R}-\vec{\tau}_i)$. The basis Bloch sums become

$$B_{mi\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{\tau}_i)}\phi_n(\vec{r}-\vec{R}-\vec{\tau}_i) \tag{1.16}$$

We then get

$$
\begin{aligned}
H_{mi,nj}(\vec{k}) &= \frac{1}{N}\sum_{\vec{R}_1,\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2+\vec{\tau}_j-\vec{R}_1-\vec{\tau}_i)} \int d^3r\, \phi_m^*(\vec{r}-\vec{R}_1-\vec{\tau}_i))H\phi_n(\vec{r}-\vec{R}_2-\vec{\tau}_j)) \\
&= \frac{1}{N} e^{-i\vec{k}\cdot\vec{\tau}_i} \sum_{\vec{R}_1,\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2-\vec{R}_1)} H_{mi,nj}(\vec{R}_2-\vec{R}_1+\vec{\tau}_j-\vec{\tau}_i) e^{i\vec{k}\cdot\vec{\tau}_j} \\
&= e^{-i\vec{k}\cdot\vec{\tau}_i}\left(\sum_{\vec{R}} H_{mi,nj}(\vec{R}) e^{i\vec{k}\cdot\vec{R}}\right) e^{i\vec{k}\cdot\vec{\tau}_j} = e^{-i\vec{k}\cdot\vec{\tau}_i} H^0_{mi,nj}(\vec{k}) e^{i\vec{k}\cdot\vec{\tau}_j}
\end{aligned}
\tag{1.17}
$$

where the notation $H_{mi,nj}(\vec{R}) = H_{mi,nj}(\vec{R}+\vec{\tau}_j-\vec{\tau}_i)$ was used. This can be viewed as the matrix $H^0(\vec{k})$ transformed by the unitary transformation

$$
U_{mi,nj}(\vec{k}) = e^{-i\vec{k}\cdot\vec{\tau}_j}\delta_{mn}\delta_{ij} \tag{1.18}
$$

which obeys $U^{+}U = \mathbb{1} = U^{-1}U$. A unitary transformation of a Hermitian matrix does not affect its eigenvalues, it only transforms the eigenvectors. Thus, unless there is specific reason to include the phase factors in Eq. 1.17 (*i.e.* eigenvectors are needed for some further calculation like matrix elements, for example), they can be disregarded.

Now the terms entering the Hamiltonian can be determined. We start with the single site terms with $\vec{R} = 0$ when both orbitals are at the same site. We split the crystal Hamiltonian into the atomic Hamiltonian for the atom at the origin plus the potential for all the other atoms:

$$
\begin{aligned}
H = & -\nabla^2 + V_{\text{atom}}(\vec{r}) + \sum_{\vec{R}\neq 0} V_{\text{atom}}(\vec{r}-\vec{R}) \\
= & -\nabla^2 + V_{\text{atom}}^{\text{spherical}}(\vec{r}) + V_{\text{atom}}^{\text{nonspherical}}(\vec{r}) + \sum_{\vec{R}\neq 0} V_{\text{atom}}(\vec{r}-\vec{R}) \\
= & \, H_{\text{atom}}^{\text{spherical}}(\vec{r}) + \Delta V(\vec{r})
\end{aligned}
\tag{1.19}
$$

The integral results primarily from the spherical atomic Hamiltonian, with orthogonal atomic orbitals

$$
H_{mn}(0) = \int d^3r\, \phi_m^*(\vec{r}) H_{\text{atom}}(\vec{r}) \phi_n(\vec{r}) = \varepsilon_n \delta_{mn} \tag{1.20}
$$

which gives atomic eigenvalues ε_n.

The quantity $\Delta V(\vec{r})$ has the symmetry of the atom in the crystal which is not spherical but discrete (mirror planes, rotation or screw axes). This *crystal field*, *i.e.* the nonspherical potential due to the crystal, will split some eigenvalues that would be degenerate in a spherical potential. An example is the splitting in a cubic crystal field of the five d orbitals into the t_{2g} manifold (xy, yz, zx) and the e_g manifold $(x^2 - y^2, 3z^2 - 1)$. This means that a transition metal ion in a cubic site has instead of a single onsite energy ε_d two energies $\varepsilon_{t_{2g}}$ and ε_{e_g} which can split further if the octahedral environment of the transition metal ion is distorted.

If we now consider the general integrals (1.15) they contain three center integrals ($\phi_m(\vec{r})$ is centered at $\vec{R} = 0$, $\phi_n(\vec{r} - \vec{R})$ is centered at $\vec{R}$ and H involves potential contributions $V_{\text{atom}}(\vec{r} - \vec{R}')$ centered at all $\vec{R}'$). Following the important paper J. C. Slater, G. F. Koster, Phys. Rev. **94**, 1498 (1954), the two center approximation is widely used. This means that the the multitude of integrals (1.15) is restricted to two center integrals denoted as $(ss\sigma)$, $(sp\sigma)$, $(pp\sigma)$, $(pp\pi)$, $(sd\sigma)$, $(pd\sigma)$, $(pd\pi)$, $(dd\sigma)$, $(dd\pi)$, $(dd\delta)$ and so on. Arguments are i) three-center integrals are less important than two-center integrals in principle, and ii) the purpose of the tight binding method is often to represent the bandstructure of a material (calculated with more elaborate methods) with as few parameters as possible, and in the course of a fitting process some effect of the three-center integrals can be absorbed into the two-center parameters. Following this logic, the Hamiltonian matrix elements or hopping integrals are often called *tight binding parameters* (and denoted with the letter t: $t_{mn}(\vec{R}) \equiv H_{mn}(\vec{R})$). For the overlap matrix the usual notation is $s_{mn}(\vec{R}) \equiv S_{mn}(\vec{R})$ with $s_{mn}(0) = \delta_{mn}$ expressing the orthonormality of the atomic orbitals.

Simple examples

We only consider the case of one s-like function on each atom; the tight binding matrix is then (1×1) and directly gives an expression for the energy bands $\varepsilon_{\vec{k}}$.

1D linear chain of atoms: The atom at the origin has two nearest neighbours at $\pm a$, and the hopping amplitude is t_1. Eq. (1.13) yields

$$H_{ss}(k) = \varepsilon_s + t_1 \sum_R e^{ikR} = \varepsilon_s + t_1(e^{ika} + e^{-ika}) = \varepsilon_s + 2t_1 \cos(ka) \quad (1.21)$$

and the overlap is

$$S_{ss}(k) = 1 + s_1 \sum_{R} e^{ikR} = \; = 1 + 2s_1 \cos(ka) \tag{1.22}$$

Thus, the secular equation (1.11) is solved by

$$\varepsilon_k = \frac{\varepsilon_s + 2t_1 \cos(ka)}{1 + 2s_1 \cos(ka)} \tag{1.23}$$

Adding the effects of hopping to second neighbours at ±$2a$ with hopping amplitude t_2 involves doubled frequencies ($\cos(2ka)$):

$$\varepsilon_k = \frac{\varepsilon_s + 2t_1 \cos(ka) + 2t_2 \cos(2ka)}{1 + 2s_1 \cos(ka) + 2s_2 \cos(2ka)} \tag{1.24}$$

2D square lattice of atoms: The nearest neighbour sum runs over the sites $\vec{R} = (a, 0)$, $(0, a)$, $(-a, 0)$, $(0, -a)$, and the lattice sum becomes

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \sum_{p=\pm 1} e^{ik_x ap} + \sum_{q=\pm 1} e^{ik_y aq} = 2\cos(k_x a) + 2\cos(k_y a) \tag{1.25}$$

leading to the dispersion relation (we neglect the overlap)

$$\varepsilon_{\vec{k}} = \varepsilon_s + 2t_1 \cos(k_x a) + 2t_1 \cos(k_y a) \tag{1.26}$$

To include second neighbours at points $\vec{R} = (a, a)$, $(-a, a)$, $(a, -a)$, $(-a, -a)$ with amplitude t_2, we use $e^{v+w} = e^v e^w$ and get

$$\varepsilon_{\vec{k}} = \varepsilon_s + 2t_1 \cos(k_x a) + 2t_1 \cos(k_y a) + 4t_2 \cos(k_x a) \cos(k_y a) \tag{1.27}$$

1.2 Integration over the Brillouin zone

Applications of electronic structure theory imply the calculation of many different **k** space integrals over the Brillouin zone or its irreducible part.

$$I(\varepsilon) = \frac{1}{V_G} \sum_n \int_{\Omega_{BZ}} d\vec{k}\; f(\vec{k}) \Theta(\varepsilon - \epsilon_{n,\vec{k}}) \tag{1.28}$$

Typical examples are the total electron number $n(\varepsilon)$

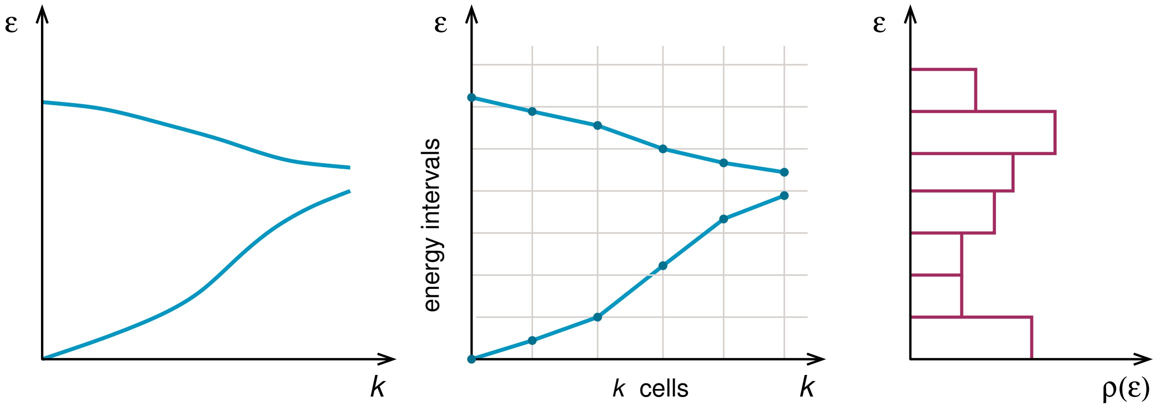
$$n(\varepsilon) = \frac{1}{V_G} \sum_n \int_{V_G} d^3k\, \Theta\big(\varepsilon - \varepsilon_n(\vec{k})\big) \tag{1.29}$$

and its energy derivative, the density of states $\rho(\varepsilon)$

$$\rho(\varepsilon) = \frac{1}{V_G} \sum_n \int_{V_G} d^3k \, \delta\big(\varepsilon - \varepsilon_n(\vec{k})\big) \tag{1.30}$$

where V_G is the volume of the primitive cell of the reciprocal lattice, and n is the band index.

One possibility of doing such integrals is by simply introducing a fine mesh in the reciprocal lattice and adding up the contributions from all **k** points (histogram method). Due to the nature of the step and delta functions, the results for the two integrals given above are not going to be satisfactory with this most simple method. This method is illustrated in Fig. 1.1.



(a) true bands (b) approximate bands (c) approximate DOS

Figure 1.1: Example of simple Brillouin zone integration.

An alternative that is sometimes used is to do the summation (1.30) by approximating the delta function with a function that has a small finite width, for example a Gaussian:

$$\delta(\varepsilon) \approx g(\varepsilon) = \frac{2}{f}\sqrt{\frac{\ln 2}{\pi}} e^{-4\ln 2 \frac{\varepsilon^2}{f^2}} \tag{1.31}$$

with full width at half maximum given by f.

Linear tetrahedron method

A far better method for Brillouin zone integration is the linear tetrahedron method. The idea is to do the integration by splitting the volume into tetrahedra, to evaluate the integrand at the corners of the tetrahedra and to use linear interpolation over the tetrahedra for the integration[2]. An example of how the reciprocal space can be broken up into tetrahedra is given in Fig. 1.2. Each tetrahedron can then be split into two tetrahedra by introducing a new vertex in the middle of the longest edge of each tetrahedron.

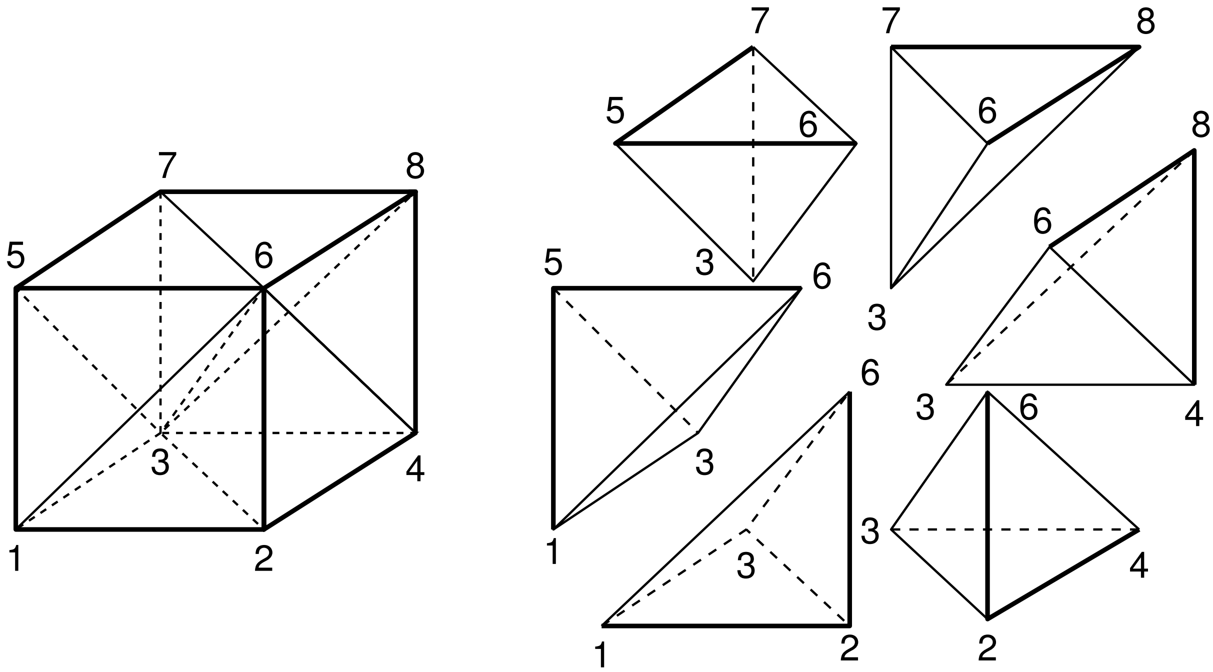


Figure 1.2: Splitting of a cubic reciprocal space sector into six tetrahedra.

Derivation of the linear tetrahedron method

Let the irreducible Brillouin zone be split into n_{T_i} tetrahedra[3]. We can recast integral Eq. (1.28) as

$$
\begin{aligned}
I(E_F) &= \frac{1}{V_{BZ}} \sum_n \int_{\Omega_{BZ}} d\vec{k}\, f(\vec{k})\Theta(E_F - \epsilon_{n,\vec{k}}) \\
&= \frac{1}{V_{BZ}} \sum_n \sum_{i=1}^{n_{T_i}} \int_{T_i} d\vec{k}\, f(\vec{k})\Theta(E_F - \epsilon_{n,\vec{k}}) \\
&= \sum_{i=1}^{n_{T_i}} \frac{1}{V_{BZ}} \sum_n \int_{T_i} d\vec{k}\, f(\vec{k})\Theta(E_F - \epsilon_{n,\vec{k}}) = \sum_{i=1}^{n_{T_i}} I_{T_i},
\end{aligned}
$$

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[2] O. Jepsen, O. K. Andersen, *The electronic structure of h.c.p. ytterbium*, Solid State Commun. **9**, 1763 (1971); P. E. Blöchl, O. Jepsen, O. K. Andersen, *Improved tetrahedron method for Brillouin-zone integrations*, Phys. Rev. B **49**, 16223 (1994); H. Eschrig, *Optimized LCAO Method and the Electronic Structure of Extended Systems*, Akademie-Verlag Berlin 1988.

[3] Thanks to Francesc Salvat-Pujol for the following derivation of the interpolation formulas.

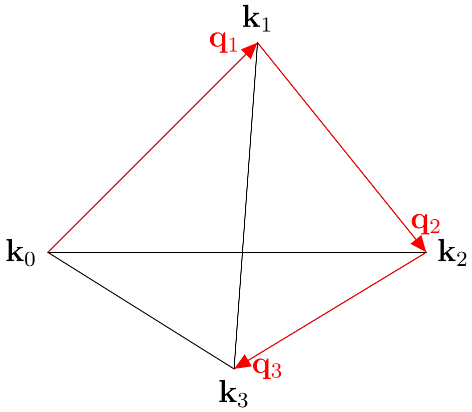

Figure 1.3: Tetrahedron vertex labeling and definition of $\vec{q}_1$, $\vec{q}_2$, $\vec{q}_3$.

where we have defined

$$I_{T_i} = \frac{1}{V_{BZ}} \sum_n \int_{T_i} d\vec{k}\, f(\vec{k}) \Theta(E_F - \epsilon_{n,\vec{k}}) \tag{1.32}$$

as the integral over the i-th tetrahedron. We also take the upper limit of integration to be $\varepsilon = E_F$ but the method of course works for any BZ integral $I(\varepsilon)$. We shall now restrict ourselves to computing integrals of the form Eq. (1.32); the full integral will be a sum of such terms.

We proceed analogously to Chen [4], Reser[5] and to Appendix A of Lehmann and Taut[6] to derive expressions for the linear tetrahedron method. We assume that the integrand in the relevant part of the BZ has been tabulated on a tetrahedral mesh (a cubic mesh will do, since each cube can be decomposed into 6 tetrahedra). We shall now derive the integration formula for each tetrahedron.

Let us consider a tetrahedron with vertices $\vec{k}_0$, $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$, see Fig. 1.3. We require that the tetrahedron-vertex labels are assigned such that

$$E_0 \leqslant E_1 \leqslant E_2 \leqslant E_3, \qquad E_i = E(\vec{k}_i). \tag{1.33}$$

Without loss of generality we take $\vec{k}_0$ at the origin of reciprocal space. The first step consists in changing to a system of oblique coordinates where the integration volume is easier to deal with, *e. g.*, a cube as opposed to a

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[4] A.-B. Chen, *Simple Brillouin-zone scheme for the spectral properties of solids*, Phys. Rev. B **16**, 3291 (1977).

[5] B. I. Reser, *On the Brillouin Zone Integration*, Phys. Stat. Sol. B **116**, 31 (1983)

[6] G. Lehmann, M. Taut, *On the Numerical Calculation of the Density of States and Related Properties*, Phys. Stat. Sol. B **54**, 469 (1972)

tetrahedron. We define the following vectors,

$$\begin{aligned}
\vec{q}_1 &= \vec{k}_1 - \vec{k}_0 \\
\vec{q}_2 &= \vec{k}_2 - \vec{k}_1 \\
\vec{q}_3 &= \vec{k}_3 - \vec{k}_2,
\end{aligned} \tag{1.34}$$

represented in red in Fig. 1.3. Any point $\vec{k}$ in the volume delimited by the tetrahedron can be expressed as a linear combination of these vectors:

$$\vec{k} = k_x\vec{e}_x + k_y\vec{e}_y + k_z\vec{e}_z = \alpha\vec{q}_1 + \alpha\beta\vec{q}_2 + \alpha\beta\gamma\vec{q}_3, \qquad \alpha, \beta, \gamma \in [0, 1]. \tag{1.35}$$

Indeed, for $\gamma = 0$, varying α and β from 0 to 1 we sweep the back side of the tetrahedron, $\vec{k}_0\vec{k}_1\vec{k}_2$. Varying γ from 0 to 1 we can move from the back side of the tetrahedron, $\vec{k}_0\vec{k}_1\vec{k}_2$, to the front side, $\vec{k}_0\vec{k}_1\vec{k}_3$. Note that α appears also in the second term, and $\alpha\beta$ appear in the third term, effectively limiting the integration volume to the tetrahedron. Thus, an integral over $\vec{k}$ in the tetrahedron volume is trivially recast as an integral over a unit cube in the (α, β, γ) system of coordinates:

$$I_{T_i} = \frac{1}{V_{\mathrm{BZ}}} \sum_n \int_0^1 d\alpha \int_0^1 d\beta \int_0^1 d\gamma\; f(\alpha, \beta, \gamma)\Theta(E_F - \epsilon_{n,\vec{k}}) \left| \frac{d(k_x, k_y, k_z)}{d(\alpha, \beta, \gamma)} \right|, \tag{1.36}$$

where the last term is the Jacobian of the coordinate transformation $(k_x, k_y, k_z) \to (\alpha, \beta, \gamma)$. To evaluate the Jacobian, we first express $\vec{k}$ explicitly. From Eq. (1.35) we have:

$$\begin{aligned}
\vec{k} = &\quad (\alpha q_{1x} + \alpha\beta q_{2x} + \alpha\beta\gamma q_{3x})\vec{e}_x \\
&+ (\alpha q_{1y} + \alpha\beta q_{2y} + \alpha\beta\gamma q_{3y})\vec{e}_y \\
&+ (\alpha q_{1z} + \alpha\beta q_{2z} + \alpha\beta\gamma q_{3z})\vec{e}_z.
\end{aligned} \tag{1.37}$$

The Jacobian is

$$\left| \frac{d(k_x, k_y, k_z)}{d(\alpha, \beta, \gamma)} \right| = \begin{vmatrix} \frac{\partial k_x}{\partial \alpha} & \frac{\partial k_x}{\partial \beta} & \frac{\partial k_x}{\partial \gamma} \\ \frac{\partial k_y}{\partial \alpha} & \frac{\partial k_y}{\partial \beta} & \frac{\partial k_y}{\partial \gamma} \\ \frac{\partial k_z}{\partial \alpha} & \frac{\partial k_z}{\partial \beta} & \frac{\partial k_z}{\partial \gamma} \end{vmatrix}$$

$$
\begin{aligned}
&= \begin{vmatrix} q_{1x} + \beta q_{2x} + \beta\gamma q_{3x} & \alpha q_{2x} + \alpha\gamma q_{3x} & \alpha\beta q_{3x} \\ q_{1y} + \beta q_{2y} + \beta\gamma q_{3y} & \alpha q_{2y} + \alpha\gamma q_{3y} & \alpha\beta q_{3y} \\ q_{1z} + \beta q_{2z} + \beta\gamma q_{3z} & \alpha q_{2z} + \alpha\gamma q_{3z} & \alpha\beta q_{3z} \end{vmatrix} \\
&= \alpha\beta \begin{vmatrix} \alpha q_{1x} + \alpha\beta q_{2x} + \alpha\beta\gamma q_{3x} & q_{2x} + \gamma q_{3x} & q_{3x} \\ \alpha q_{1y} + \alpha\beta q_{2y} + \alpha\beta\gamma q_{3y} & q_{2y} + \gamma q_{3y} & q_{3y} \\ \alpha q_{1z} + \alpha\beta q_{2z} + \alpha\beta\gamma q_{3z} & q_{2z} + \gamma q_{3z} & q_{3z} \end{vmatrix} \\
&= \alpha\beta\epsilon_{ijk}k_i(q_{2j} + \gamma q_{3j})q_{3k} \\
&= \alpha\beta\epsilon_{ijk}k_i q_{2j} q_{3k} + \alpha\beta\gamma\epsilon_{ijk}k_i q_{3j} q_{3k} \\
&= \alpha\beta\epsilon_{ijk}k_i q_{2j} q_{3k} \\
&= \alpha\beta\epsilon_{ijk}(\alpha q_{1i} + \alpha\beta q_{2i} + \alpha\beta\gamma q_{3i})q_{2j} q_{3k} \\
&= \alpha^2\beta\epsilon_{ijk}q_{1i}q_{2j}q_{3k} \\
&= \alpha^2\beta\vec{q}_1 \cdot (\vec{q}_2 \times \vec{q}_3) \\
&= 6\alpha^2\beta V_T, \qquad (1.38)
\end{aligned}
$$

where

$$
V_T = \frac{1}{6}\vec{q}_1 \cdot (\vec{q}_2 \times \vec{q}_3) = \frac{1}{6}\vec{k}_1 \cdot (\vec{k}_2 \times \vec{k}_3) \qquad (1.39)
$$

is the volume of the tetrahedron. Thus,

$$
I_{T_i} = \frac{6V_{T_i}}{V_{BZ}} \sum_n \int_0^1 d\alpha \int_0^1 d\beta \int_0^1 d\gamma \; \alpha^2\beta f(\alpha,\beta,\gamma)\Theta(E_F - \epsilon_{n,\vec{k}}). \qquad (1.40)
$$

The next step consists in carrying out a three-dimensional interpolation of $f(\alpha,\beta,\gamma)$ in the volume of the tetrahedron, that is, in the unit cube of the (α,β,γ) coordinates. Even though we shall be only interested in linear interpolation, let us assume that the function values have been tabulated in a mesh of points $(\alpha_i, \beta_j, \gamma_m)$ in the tetrahedron:

$$
\begin{aligned}
&\alpha = \alpha_0, ..., \alpha_{n_\alpha} \\
&\beta = \beta_0, ..., \beta_{n_\beta} \\
&\gamma = \gamma_0, ..., \gamma_{n_\gamma}. \qquad (1.41)
\end{aligned}
$$

This will allow us to write down general expressions, which we will then recast for the particular case of linear interpolation. A conversion between relevant values of (α,β,γ) and (k_x, k_y, k_z) is given below.

Let us consider first an interpolation along α, that is, for a fixed β and γ. We then have

$$
f(\alpha) = \sum_{j=0}^{n_\alpha} L_j(\alpha) f(\alpha_j), \qquad (1.42)
$$

where $L_j(\alpha)$ are the Lagrange interpolation coefficients, given by [7]

$$L_j(\alpha) = \prod_{0 \leqslant m \leqslant n_\alpha, m \neq j} \frac{\alpha - \alpha_m}{\alpha_j - \alpha_m} \tag{1.43}$$

In the three-dimensional case we have

$$f(\alpha, \beta, \gamma) = \sum_{i=0}^{n_\alpha} \sum_{j=0}^{n_\beta} \sum_{k=0}^{n_\gamma} L_i(\alpha) L_j(\beta) L_k(\gamma) f(\alpha_i, \beta_j, \gamma_k). \tag{1.44}$$

For a linear three-dimensional interpolation we have $n_\alpha = n_\beta = n_\gamma = 1$, so that the linear interpolation formula reads

$$f(\alpha, \beta, \gamma) = \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{k=0}^{1} L_i(\alpha) L_j(\beta) L_m(\gamma) f(\alpha_i, \beta_j, \gamma_k), \tag{1.45}$$

where $\alpha_0 = \beta_0 = \gamma_0 = 0$ and $\alpha_1 = \beta_1 = \gamma_1 = 1$. The expressions of $L_i(\alpha)$, $L_j(\beta)$, and $L_k(\gamma)$ are

$$\begin{aligned}
L_0(\alpha) &= \frac{\alpha - \alpha_1}{\alpha_0 - \alpha_1} = 1 - \alpha, & L_1(\alpha) &= \frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0} = \alpha, \\
L_0(\beta) &= \frac{\beta - \beta_1}{\beta_0 - \beta_1} = 1 - \beta, & L_1(\beta) &= \frac{\beta - \beta_0}{\beta_1 - \beta_0} = \beta, \\
L_0(\gamma) &= \frac{\gamma - \gamma_1}{\gamma_0 - \gamma_1} = 1 - \gamma, & L_1(\gamma) &= \frac{\gamma - \gamma_0}{\gamma_1 - \gamma_0} = \gamma,
\end{aligned} \tag{1.46}$$

Table 1.1 summarizes the conversion of relevant values of (α, β, γ) to tetrahedron-vertex coordinates.

Case $E_F > E_3$

Let us first consider the case where the tetrahedron is completely contained within the Fermi surface, that is

$$\epsilon_{n,\vec{k}} < E_F \tag{1.47}$$

for all vertices of the tetrahedron, $\vec{k}_i$. Under these circumstances, the Heaviside step function in equation (1.40) is always unity, so the volume integral over the tetrahedron becomes

$$I_{T_i} = \frac{6V_T}{V_{BZ}} \int_0^1 d\alpha \int_0^1 d\beta \int_0^1 d\gamma\ \alpha^2 \beta f(\alpha, \beta, \gamma). \tag{1.48}$$

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[7] A. Ralston and P. Rabinowitz, *A First Course in Numerical Analysis*, Dover 2001.

α	β	γ	$\vec{k}$	$E(\alpha,\beta,\gamma)$	$f(\alpha,\beta,\gamma)$
0	0	0	$\vec{k}_0$	E_0	$f(\vec{k}_0)$
0	0	1	$\vec{k}_0$	E_0	$f(\vec{k}_0)$
0	1	0	$\vec{k}_0$	E_0	$f(\vec{k}_0)$
0	1	1	$\vec{k}_0$	E_0	$f(\vec{k}_0)$
1	0	0	$\vec{k}_1$	E_1	$f(\vec{k}_1)$
1	0	1	$\vec{k}_1$	E_1	$f(\vec{k}_1)$
1	1	0	$\vec{k}_2$	E_2	$f(\vec{k}_2)$
1	1	1	$\vec{k}_3$	E_3	$f(\vec{k}_3)$

Table 1.1: Conversion between the (α,β,γ) system of coordinates and known points.

For the time being we suppose there is only one band, so we drop the sum over band indices n. We can then write the integral explicitly:

$$\begin{aligned} I_{T_i} &= \frac{6V_T}{V_{BZ}} \int_0^1 d\alpha\ \alpha^2 \int_0^1 d\beta\ \beta \int_0^1 d\gamma\ \sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{m=0}^{1} L_i(\alpha)L_j(\beta)L_m(\gamma)f(\alpha_i,\beta_j,\gamma_m) \\ &= \frac{6V_T}{V_{BZ}} \sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{m=0}^{1} f(\alpha_i,\beta_j,\gamma_m) \int_0^1 d\alpha\ \alpha^2 L_i(\alpha) \int_0^1 d\beta\ \beta L_j(\beta) \int_0^1 d\gamma\ L_m(\gamma) \end{aligned} \tag{1.49}$$

Using the abbreviations

$$I_{\alpha_i} = \int_0^1 d\alpha\ \alpha^2 L_i(\alpha), \qquad I_{\beta_j} = \int_0^1 d\beta\ \beta L_j(\beta), \qquad I_{\gamma_m} = \int_0^1 d\gamma\ L_m(\gamma) \tag{1.50}$$

we have

$$\begin{aligned} I_{T_i} &= \frac{6V_T}{V_{BZ}} \sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{m=0}^{1} f(\alpha_i,\beta_j,\gamma_m) I_{\alpha_i}(\alpha) I_{\beta_i}(\beta) I_{\gamma_i}(\gamma) \\ &= \frac{6V_T}{V_{BZ}}\ [f(\alpha_0,\beta_0,\gamma_0)I_{\alpha_0}I_{\beta_0}I_{\gamma_0} + f(\alpha_0,\beta_0,\gamma_1)I_{\alpha_0}I_{\beta_0}I_{\gamma_1} + \\ &\qquad f(\alpha_0,\beta_1,\gamma_0)I_{\alpha_0}I_{\beta_1}I_{\gamma_0} + f(\alpha_0,\beta_1,\gamma_1)I_{\alpha_0}I_{\beta_1}I_{\gamma_1} + \\ &\qquad f(\alpha_1,\beta_0,\gamma_0)I_{\alpha_1}I_{\beta_0}I_{\gamma_0} + f(\alpha_1,\beta_0,\gamma_1)I_{\alpha_1}I_{\beta_0}I_{\gamma_1} + \end{aligned}$$

$$f(\alpha_1, \beta_1, \gamma_0) I_{\alpha_1} I_{\beta_1} I_{\gamma_0} + f(\alpha_1, \beta_1, \gamma_1) I_{\alpha_1} I_{\beta_1} I_{\gamma_1}] \tag{1.51}$$

The integral values are

$$\begin{aligned}
I_{\alpha_0} &= \int_0^1 d\alpha\ \alpha^2 L_0(\alpha) = \int_0^1 d\alpha\ \alpha^2 (1-\alpha) = \int_0^1 d\alpha\ (\alpha^2 - \alpha^3) = \left[\frac{\alpha^3}{3} - \frac{\alpha^4}{4}\right]_0^1 = \frac{1}{3} - \frac{1}{4} = \frac{1}{12} \\
I_{\alpha_1} &= \int_0^1 d\alpha\ \alpha^2 L_1(\alpha) = \int_0^1 d\alpha\ \alpha^3 = \frac{1}{4} \\
I_{\beta_0} &= \int_0^1 d\beta\ \beta L_0(\beta) = \int_0^1 d\beta\ \beta(1-\beta) = \int_0^1 d\beta\ (\beta - \beta^2) = \left[\frac{\beta^2}{2} - \frac{\beta^3}{3}\right]_0^1 = \frac{1}{2} - \frac{1}{3} = \frac{1}{6} \\
I_{\beta_1} &= \int_0^1 d\beta\ \beta L_1(\beta) = \int_0^1 d\beta\ \beta^2 = \frac{1}{3} \\
I_{\gamma_0} &= \int_0^1 d\gamma\ L_0(\gamma) = \int_0^1 d\gamma\ \beta(1-\gamma) = \left[\gamma - \frac{\gamma^2}{2}\right]_0^1 = 1 - \frac{1}{2} = \frac{1}{2} \\
I_{\gamma_1} &= \int_0^1 d\gamma\ L_1(\gamma) = \int_0^1 d\gamma\ \gamma = \frac{1}{2}.
\end{aligned} \tag{1.52}$$

Inserting these values in Eq. (1.51) we have

$$\begin{aligned}
I_{T_i} = \frac{6V_T}{V_{BZ}} \Bigg[& f(\vec{k}_0)\ \frac{1}{12}\ \frac{1}{6}\ \frac{1}{2} + f(\vec{k}_0)\ \frac{1}{12}\ \frac{1}{6}\ \frac{1}{2} + f(\vec{k}_0)\ \frac{1}{12}\ \frac{1}{3}\ \frac{1}{2} + f(\vec{k}_0)\ \frac{1}{12}\ \frac{1}{3}\ \frac{1}{2} \\
& + f(\vec{k}_1)\ \frac{1}{4}\ \frac{1}{6}\ \frac{1}{2} + f(\vec{k}_1)\ \frac{1}{4}\ \frac{1}{6}\ \frac{1}{2} + f(\vec{k}_2)\ \frac{1}{4}\ \frac{1}{3}\ \frac{1}{2} + f(\vec{k}_3)\ \frac{1}{4}\ \frac{1}{3}\ \frac{1}{2} \Bigg] \\
= {} & \frac{6V_T}{V_{BZ}} \frac{1}{2} \left[\frac{f(\vec{k}_0)}{12} \left(\frac{1}{6} + \frac{1}{6} + \frac{1}{3} + \frac{1}{3} \right) + \frac{f(\vec{k}_1)}{12} + \frac{f(\vec{k}_2)}{12} + \frac{f(\vec{k}_3)}{12} \right] \\
= {} & \frac{V_T}{V_{BZ}} \frac{1}{4} \left[f(\vec{k}_0) + f(\vec{k}_1) + f(\vec{k}_2) + f(\vec{k}_3) \right].
\end{aligned} \tag{1.53}$$

Thus, if the volume of the tetrahedron is fully contained within the Fermi surface, the contribution of the tetrahedron volume to the total integral is an average of the vertex values, as it should be.

Case $E_0 < E_F \leqslant E_1 \leqslant E_2 \leqslant E_3$

In this case the Fermi surface crosses the tetrahedron, with crossing points $\vec{k}_{01}$, $\vec{k}_{02}$, and $\vec{k}_{03}$ along the $\vec{k}_0\vec{k}_1$, $\vec{k}_0\vec{k}_2$, and $\vec{k}_0\vec{k}_3$ axes, respectively, see Fig. 1.4.

The Fermi surface separates the tetrahedron into two regions:

- a smaller tetrahedron $\vec{k}_0\vec{k}_{01}\vec{k}_{02}\vec{k}_{03}$ which is contained within the integration region (below the Fermi surface), and

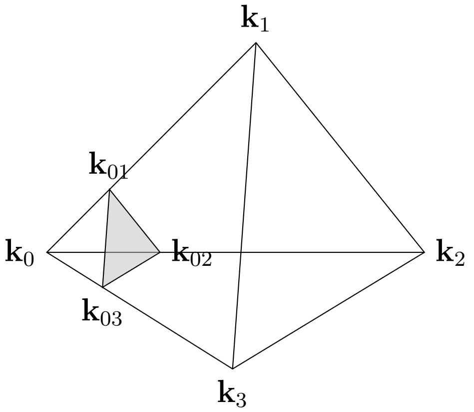

Figure 1.4: Fermi surface (gray) crossing the tetrahedron in the case $E_0 < E_F \leqslant E_1 \leqslant E_2 \leqslant E_3$.

- the rest of the tetrahedron, which lies above the Fermi surface and therefore does not contribute to the integral, due to the factor $\Theta(E_F - \epsilon_{n,\vec{k}})$.

Thus, we have to restrict our volume integral to the small tetrahedron determined by $\vec{k}_0$, $\vec{k}_{01}$, $\vec{k}_{02}$, $\vec{k}_{03}$. The coordinates of the intersection points can be found in a straightforward way:

$$\begin{aligned}\vec{k}_{01} &= \frac{E_F - E_0}{E_1 - E_0}\vec{k}_1 \equiv \Delta_{10}\vec{k}_1\\ \vec{k}_{02} &= \frac{E_F - E_0}{E_2 - E_0}\vec{k}_2 \equiv \Delta_{20}\vec{k}_2\\ \vec{k}_{03} &= \frac{E_F - E_0}{E_3 - E_0}\vec{k}_3 \equiv \Delta_{30}\vec{k}_3, \end{aligned} \tag{1.54}$$

where

$$\Delta_{ij} = \frac{E_F - E_j}{E_i - E_j}. \tag{1.55}$$

The values of $f(\vec{k})$ at the intersection points read

$$\begin{aligned} f(\vec{k}_{01}) &= f(\vec{k}_0) + \Delta_{10}[f(\vec{k}_1) - f(\vec{k}_0)] \\ f(\vec{k}_{02}) &= f(\vec{k}_0) + \Delta_{20}[f(\vec{k}_2) - f(\vec{k}_0)] \\ f(\vec{k}_{03}) &= f(\vec{k}_0) + \Delta_{30}[f(\vec{k}_3) - f(\vec{k}_0)]. \end{aligned} \tag{1.56}$$

The volume of the small tetrahedron reads

$$V = \frac{1}{6}\vec{k}_{01} \cdot (\vec{k}_{02} \times \vec{k}_{03}) = \frac{1}{6}\Delta_{10}\Delta_{20}\Delta_{30}\vec{k}_1 \cdot (\vec{k}_2 \times \vec{k}_3) = \Delta_{10}\Delta_{20}\Delta_{30}V_{T_i} \tag{1.57}$$

Using Eq. (1.53) for the small tetrahedron contained within the Fermi surface, we have

$$\begin{aligned}
\mathrm{I}_{\mathrm{T}_i} &= \frac{V_{\mathrm{T}_i}}{4V_{\mathrm{BZ}}}\Delta_{10}\Delta_{20}\Delta_{30}[f(\vec{k}_0) + f(\vec{k}_{01}) + f(\vec{k}_{02}) + f(\vec{k}_{03})] \\
&\underset{(1.57)}{=} \frac{V_{\mathrm{T}_i}}{4V_{\mathrm{BZ}}}\Delta_{10}\Delta_{20}\Delta_{30}\{4f(\vec{k}_0) + \Delta_{10}[f(\vec{k}_1) - f(\vec{k}_0)] \\
&\qquad + \Delta_{20}[f(\vec{k}_2) - f(\vec{k}_0)] + \Delta_{30}[f(\vec{k}_3) - f(\vec{k}_0)]\}
\end{aligned}$$

Thus, in the case $E_0 < E_F \leqslant E_1 \leqslant E_2 \leqslant E_3$ we have

$$\mathrm{I}_{\mathrm{T}_i} = \frac{V_{\mathrm{T}_i}}{4V_{\mathrm{BZ}}}\Delta_{10}\Delta_{20}\Delta_{30}[(4-\Delta_{10}-\Delta_{20}-\Delta_{30})f(\vec{k}_0) + \Delta_{10}f(\vec{k}_1) + \Delta_{20}f(\vec{k}_2) + \Delta_{30}f(\vec{k}_3)]. \tag{1.58}$$

Case $E_0 \leqslant E_1 < E_F \leqslant E_2 \leqslant E_3$

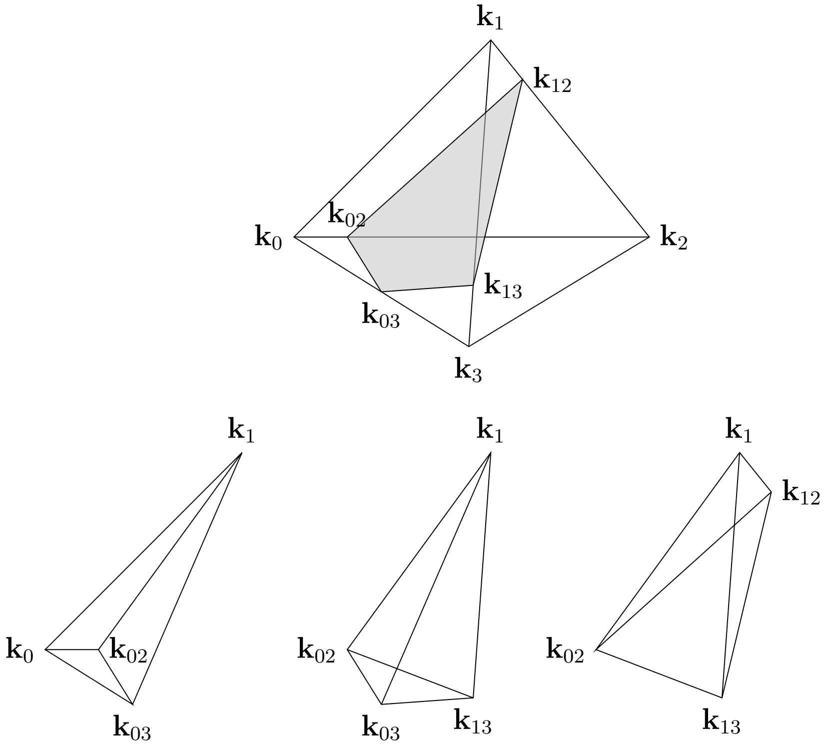

Figure 1.5: Fermi surface (gray) crossing the tetrahedron in the case $E_0 \leqslant E_1 < E_F \leqslant E_2 \leqslant E_3$, and method to split the resulting integration volume into tetrahedra.

This case is the most involved one as the integration volume needs to be split into tetrahedra (see Fig. 1.5).

Final formulas of linear tetrahedron method

Note that here we label the tetrahedron vertices from 1 to 4 as in P. Blöchl *et al.*, Phys. Rev. B **49**, 16223 (1994). For the calculation of the electron number and the density of states, the only information that is required is the volume V_T of the tetrahedra; for a tetrahedron given by the vectors $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$, $\vec{k}_4$, this can be calculated by

$$V_T = \frac{1}{6}\left|\det(\vec{k}_2 - \vec{k}_1, \vec{k}_3 - \vec{k}_1, \vec{k}_4 - \vec{k}_1)\right| \tag{1.59}$$

Then we denote the energies of a given band by $\varepsilon(\vec{k}_i) \equiv \varepsilon_i$ and energy differences by $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$; we also sort the energies at the corners of the tetrahedron as

$$\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4$$

Now the contribution of the tetrahedron to the number of states $n(\varepsilon)$ at a given energy ε is

$$n_T(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_1 \\ \frac{V_T}{V_G}\frac{(\varepsilon-\varepsilon_1)^3}{\varepsilon_{21}\varepsilon_{31}\varepsilon_{41}} & \text{for } \varepsilon_1 < \varepsilon < \varepsilon_2 \\ \frac{V_T}{V_G}\frac{1}{\varepsilon_{31}\varepsilon_{41}}\left[\varepsilon_{21}^2 + 3\varepsilon_{21}(\varepsilon - \varepsilon_2) + 3(\varepsilon - \varepsilon_2)^2 - \frac{\varepsilon_{31}+\varepsilon_{42}}{\varepsilon_{32}\varepsilon_{42}}(\varepsilon - \varepsilon_2)^3\right] & \text{for } \varepsilon_2 < \varepsilon < \varepsilon_3 \\ \frac{V_T}{V_G}\left(1 - \frac{(\varepsilon_4-\varepsilon)^3}{\varepsilon_{41}\varepsilon_{42}\varepsilon_{43}}\right) & \text{for } \varepsilon_3 < \varepsilon < \varepsilon_4 \\ \frac{V_T}{V_G} & \text{for } \varepsilon_4 < \varepsilon \end{cases} \tag{1.60}$$

V_G is the volume of the primitive cell of the reciprocal lattice. The contribution of the tetrahedron to the density of states $\rho(\varepsilon)$ is simply the energy derivative of $n_T(\varepsilon)$:

$$\rho_T(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_1 \\ \frac{V_T}{V_G}\frac{3(\varepsilon-\varepsilon_1)^2}{\varepsilon_{21}\varepsilon_{31}\varepsilon_{41}} & \text{for } \varepsilon_1 < \varepsilon < \varepsilon_2 \\ \frac{V_T}{V_G}\frac{1}{\varepsilon_{31}\varepsilon_{41}}\left[3\varepsilon_{21} + 6(\varepsilon - \varepsilon_2) - 3\frac{(\varepsilon_{31}+\varepsilon_{42})(\varepsilon-\varepsilon_2)^2}{\varepsilon_{32}\varepsilon_{42}}\right] & \text{for } \varepsilon_2 < \varepsilon < \varepsilon_3 \\ \frac{V_T}{V_G}\frac{3(\varepsilon_4-\varepsilon)^2}{\varepsilon_{41}\varepsilon_{42}\varepsilon_{43}} & \text{for } \varepsilon_3 < \varepsilon < \varepsilon_4 \\ 0 & \text{for } \varepsilon_4 < \varepsilon \end{cases} \tag{1.61}$$

1.3 Some results of crystal field theory

Crystal field theory [8] analyzes the splitting of one electron states, for example transition metal d states, in the electrical field caused by the surrounding ligands in the crystal, the so called ligand field. Ligand field theory is a more complicated approach that goes beyond crystal field theory and deduces the chemical bonding in transition metal complexes. We discuss the principal idea of crystal field theory for the example of a single d electron in an octahedral environment.

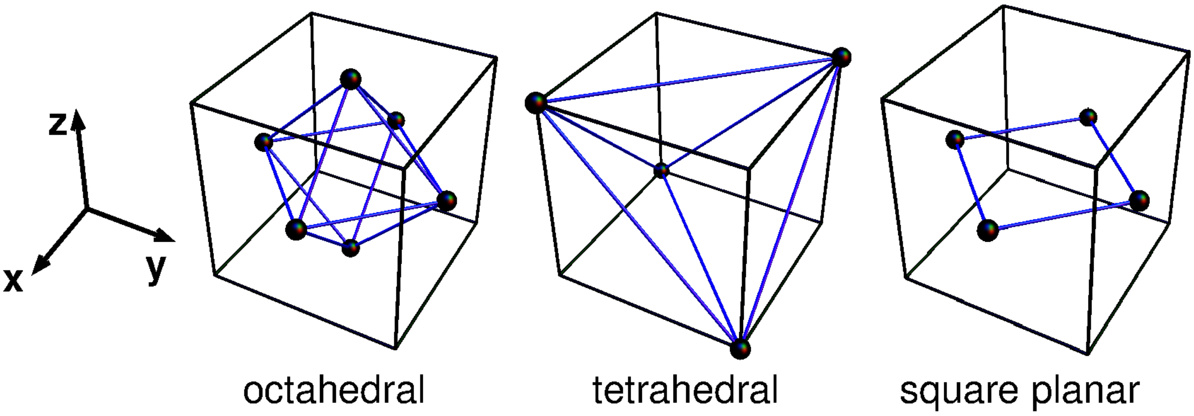

Figure 1.6: (Left) Octahedron of ligands (black spheres), inscribed into a cube. (Center) Tetrahedron of ligands. (Right) Square of ligands.

In the octahedral ligand field, the d orbitals split into two groups, based on stronger and less strong interaction with the ligands. As demonstrated in Fig. 1.7, d_{z^2} and $\mathsf{d}_{x^2-y^2}$ have lobes pointing directly towards the ligands, leading to a strong interaction, because the highest densitiy overlaps with that of the ligand. The three orbitals d_{xy}, d_{xz} and d_{yz} all have exactly the same orientation towards the ligands, pointing along the angle bisectrix; they have the highest charge density between two metal-ligand bonds. This leads to the term scheme 1.8. The crystal field splitting energy Δ is traditionally written as $\Delta_0 = 10\mathsf{Dq}$ where Dq is called ligand field splitting parameter. Perturbation theory yields

$$\mathsf{E}(\mathsf{t}_{2g}) = \varepsilon_0 - 4\mathsf{Dq}, \qquad \mathsf{E}(\mathsf{e}_g) = \varepsilon_0 + 6\mathsf{Dq}$$

where ε_0 is the shift due to the spherically symmetric part of the potential; is is called barycenter.

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[8] This chapter is based on A. R. West, *Grundlagen der Festkörperchemie*, Wiley-VCH (1992), und H. L. Schläfer, G. Gliemann, *Einführung in die Ligandenfeldtheorie.* Akademische Verlagsgesellschaft, Frankfurt (1967).

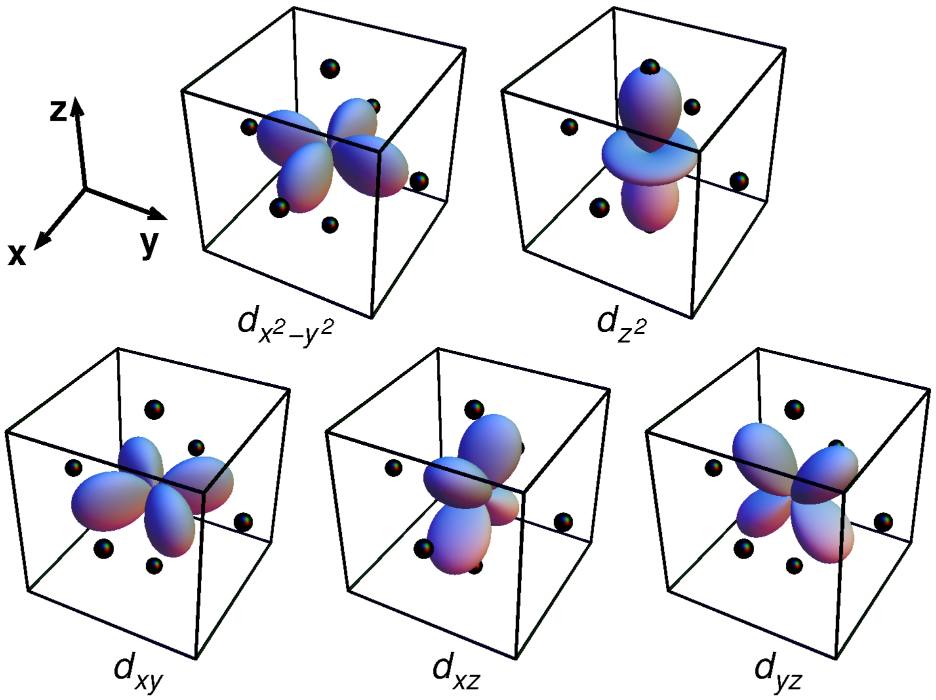

Figure 1.7: Orientation of d orbitals in an octahedral environment.

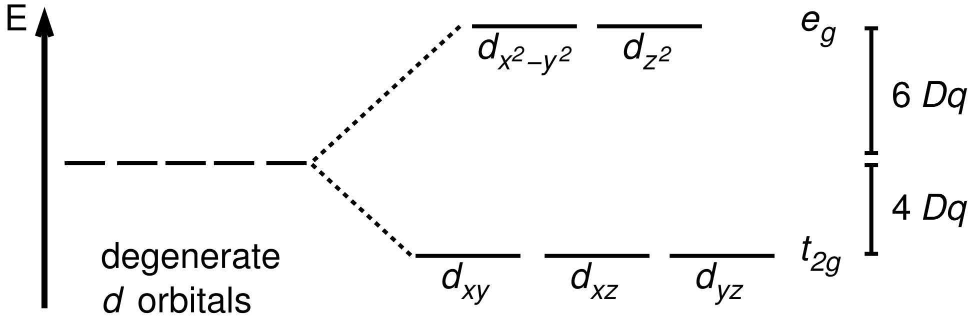

Figure 1.8: Splitting of energy levels in an octahedral ligand field.

The naming of t_{2g} and e_g is derived from the theory of molecular symmetry. Small t and e indicate one-electron states. The irreducible representations of the point group are labeled as follows:

- one dimensional representations are labeled with a and b; a when rotation around the principal axis is symmetrical, b when rotation around the principal axis is asymmetrical.
- e and t are doubly and triply degenerate representations respectively
- the subscript g (for german gerade) indicates no sign change with respect to inversion, and n indicates sign change.
- subscript numbers distinguish between the various one-, two-, three- and four dimensional representations; t_2 carries the index 2 to distinguish it from the triply degenerate p state which is named t_1.

The crystal field stabilization energy arises from the fact that some d levels become more stable compared to a spherical field. In the same way, we can understand the splitting in the tetrahedral ligand field. Here, d_{z^2} and $\mathrm{d}_{x^2-y^2}$ are always pointing along the angle bisectrix, putting the highest charge density between the bonds (see Fig. 1.9); these two states have lower energies and are labeled e. The orbitals d_{xy}, d_{xz} and d_{yz} each have higher density pointing towards ligands leading to larger interaction an thus higher energy; they are labeled t_2. The term scheme for tetrahedral field is shown in Fig. 1.10.

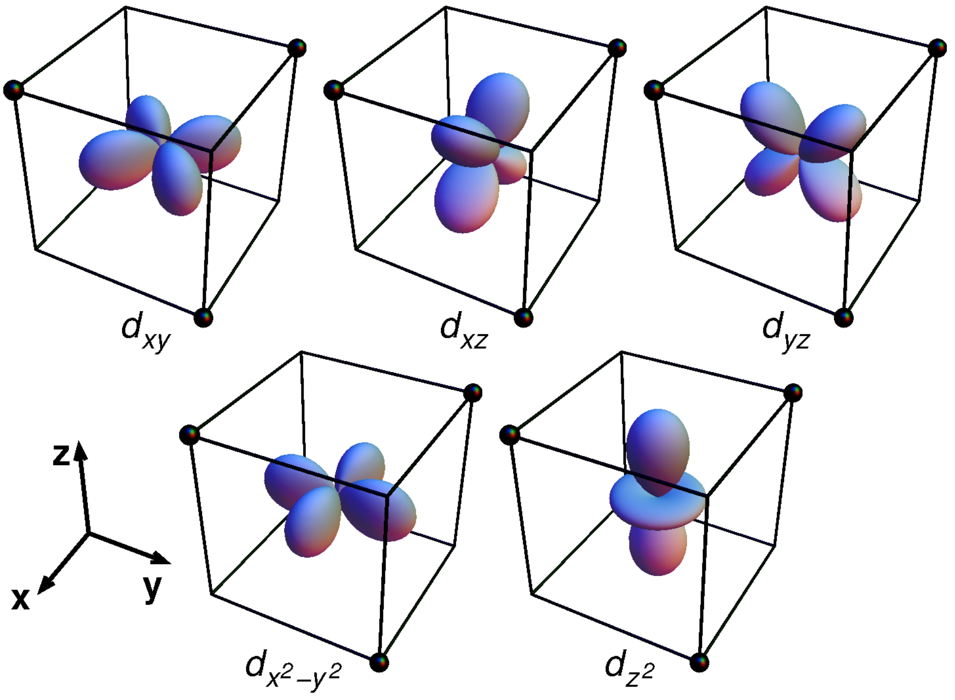

Figure 1.9: Orientation of d orbitals in a tetrahedral environment.

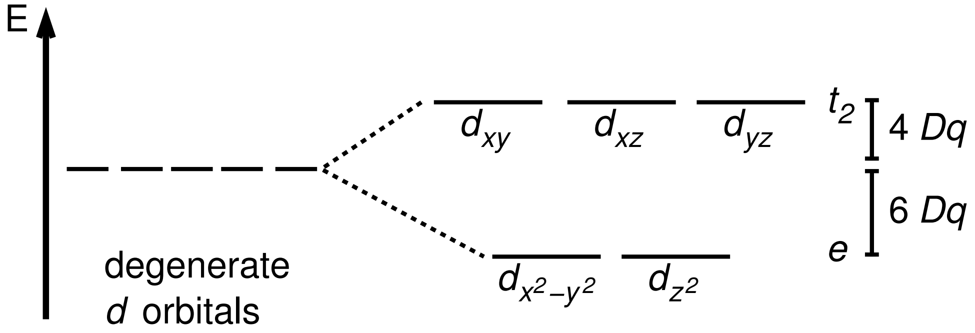

Figure 1.10: Splitting of energy levels in a tetrahedral ligand field.

Another example is the square planar ligand field which leads to the term scheme shown in Fig. 1.11. It can be considered as the extreme limit of an octahedral environment elongated along z, with ligands above and below the plane moved away from the center. A small distortion of this kind will be discussed below.

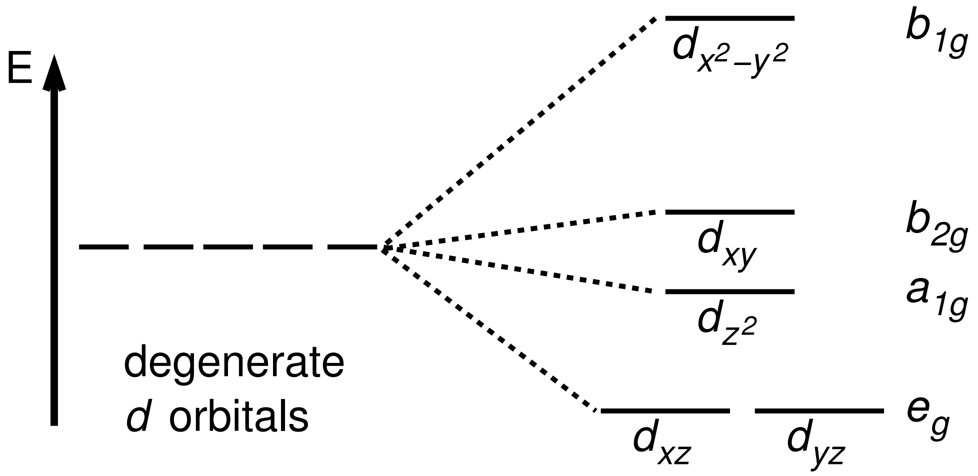

Figure 1.11: Splitting of energy levels in a square planar ligand field.

If we now consider more than one d electron in an octahedral field, we find a crystal field stabilization energy

$$\mathrm{CFSE} = n_{t_{2g}}(-4D_q) + n_{eg}(+6D_q) = -0.4\Delta_0 n_{t_{2g}} + 0.6\Delta_0 n_{eg}$$

See Fig. 1.12 for examples. Between d^3 and d^7, low spin or high spin configurations are possible depending on the crystal field splitting energy Δ_0 compared to the so called pairing energy P that consists in Coulomb repulsion U and loss of Hund's rule coupling energy J_H. There is a low spin energy gain Δ_0 for d^4, d^7 and $2\Delta_0$ for d^5, d^6.

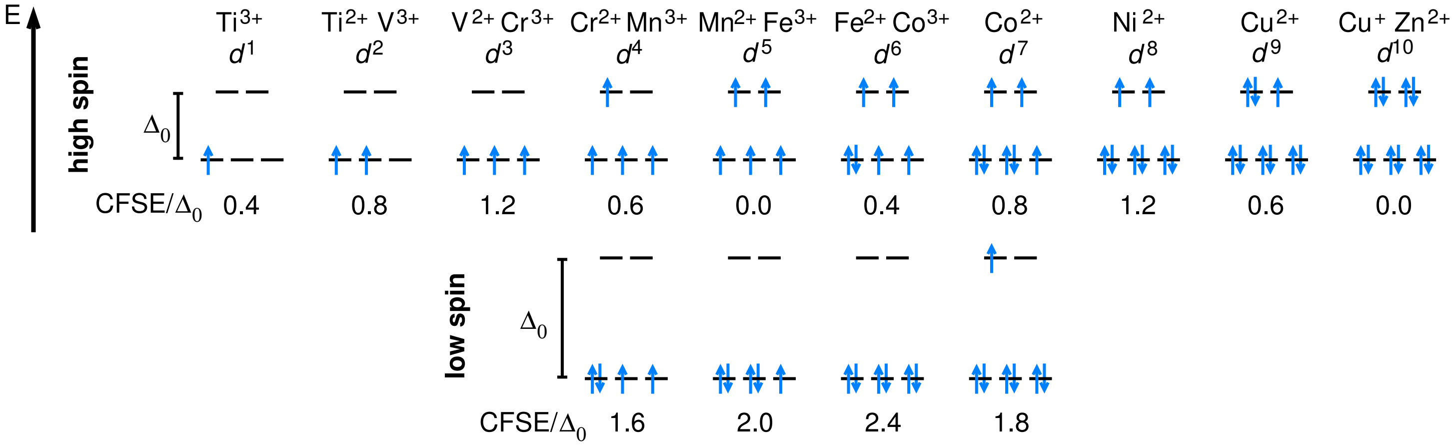

Figure 1.12: Spin configurations for transition metal ions in an octahedral field; in four cases, high and low spin configurations are possible.

Jahn Teller distortion

The Jahn Teller effect leads to a distortion of the ligand positions in case the resulting lifting of a degeneracy due to lowering of the symmetry leads to an energy gain. An important example is the Cu^{2+} ion which has a d^9 configuration. In octahedral symmetry, one of the two degenerate e_g orbitals (either d_{z^2} or $d_{x^2-y^2}$) holds one electron, the other two. Now the doubly occupied orbital leads to a stronger repulsion of the ligands than the simply occupied orbital; this would elongate the corresponding metal-ligand bonds, the four xy plane bonds in the case of doubly occupied $d_{x^2-y^2}$ or the two axial bonds in the case of doubly occupied d_{z^2}. This elongation leads to a lowering of the corresponding energy level.

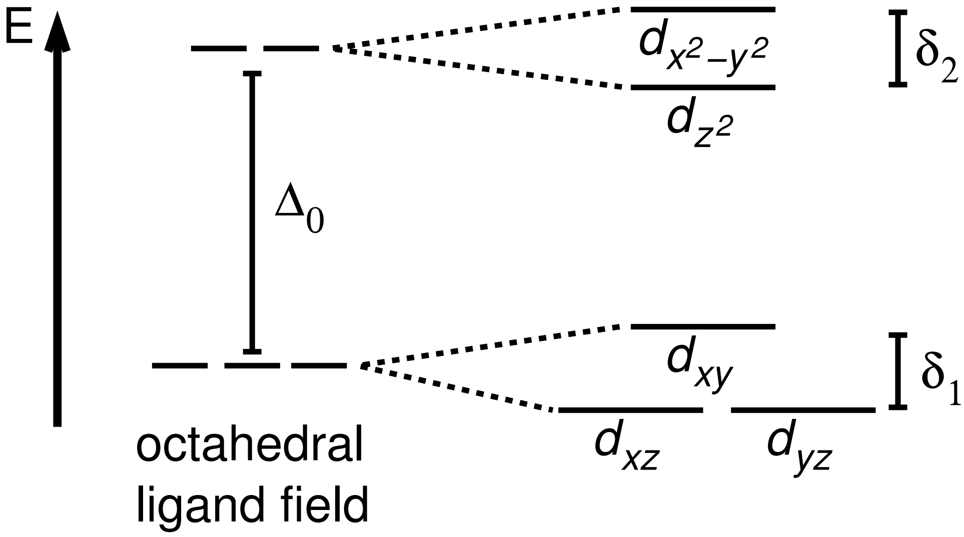

Figure 1.13: Energy level diagram of a d ion with Jahn Teller distortion. The bonds along z are longer than the other four bonds. the energy gain is $1/2\delta_2$ compared to the undistorted octahedral ligand field.