

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 description¹ by writing the potential of the electrons $V(\vec{r})$ in a crystal as a sum of atomic potentials

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

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

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

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

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

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

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

¹This 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*

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

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

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

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:

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

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

$$H\psi_{\vec{k}} = \varepsilon_{\vec{k}}\psi_{\vec{k}} \quad (1.8)$$

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:

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

with

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

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

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

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

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

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

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

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

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

The real space integral

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

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

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

We then get

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

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

$$\mathbf{U}_{mi,nj}(\vec{k}) = e^{-i\vec{k} \cdot \vec{\tau}_i} \delta_{mn} \delta_{ij} \tag{1.18}$$

which obeys $\mathbf{U}^\dagger \mathbf{U} = \mathbb{I} = \mathbf{U}^{-1} \mathbf{U}$. 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, 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 \mathbf{d} orbitals into the \mathbf{t}_{2g} manifold ($\mathbf{x}\mathbf{y}$, $\mathbf{y}\mathbf{z}$, $\mathbf{z}\mathbf{x}$) and the \mathbf{e}_g manifold ($\mathbf{x}^2 - \mathbf{y}^2$, $3\mathbf{z}^2 - 1$). This means that a transition metal ion in a cubic site has instead of a single onsite energy ε_d two energies $\varepsilon_{\mathbf{t}_{2g}}$ and $\varepsilon_{\mathbf{e}_g}$ 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 $\vec{\mathbf{R}} = 0$, $\phi_n(\vec{r} - \vec{\mathbf{R}})$ is centered at $\vec{\mathbf{R}}$ and H involves potential contributions $V_{\text{atom}}(\vec{r} - \vec{\mathbf{R}}')$ centered at all $\vec{\mathbf{R}}'$). 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 multitude of integrals (1.15) is restricted to two center integrals denoted as ($\mathbf{ss}\sigma$), ($\mathbf{sp}\sigma$), ($\mathbf{pp}\sigma$), ($\mathbf{pp}\pi$), ($\mathbf{sd}\sigma$), ($\mathbf{pd}\sigma$), ($\mathbf{pd}\pi$), ($\mathbf{dd}\sigma$), ($\mathbf{dd}\pi$), ($\mathbf{dd}\delta$) 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 \mathbf{t} : $\mathbf{t}_{mn}(\vec{\mathbf{R}}) \equiv H_{mn}(\vec{\mathbf{R}})$). For the overlap matrix the usual notation is $\mathbf{s}_{mn}(\vec{\mathbf{R}}) \equiv S_{mn}(\vec{\mathbf{R}})$ with $\mathbf{s}_{mn}(0) = \delta_{mn}$ expressing the orthonormality of the atomic orbitals.

Simple examples

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

1D linear chain of atoms: The atom at the origin has two nearest neighbours at $\pm\mathbf{a}$, and the hopping amplitude is \mathbf{t}_1 . Eq. (1.13) yields

$$H_{ss}(\mathbf{k}) = \varepsilon_s + \mathbf{t}_1 \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} = \varepsilon_s + \mathbf{t}_1 (e^{i\mathbf{k}\mathbf{a}} + e^{-i\mathbf{k}\mathbf{a}}) = \varepsilon_s + 2\mathbf{t}_1 \cos(\mathbf{k}\mathbf{a}) \quad (1.21)$$

and the overlap is

$$S_{ss}(\mathbf{k}) = 1 + s_1 \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = 1 + 2s_1 \cos(\mathbf{k}\mathbf{a}) \quad (1.22)$$

Thus, the secular equation (1.11) is solved by

$$\varepsilon_{\mathbf{k}} = \frac{\varepsilon_s + 2t_1 \cos(\mathbf{k}\mathbf{a})}{1 + 2s_1 \cos(\mathbf{k}\mathbf{a})} \quad (1.23)$$

Adding the effects of hopping to second neighbours at $\pm 2\mathbf{a}$ with hopping amplitude t_2 involves doubled frequencies ($\cos(2\mathbf{k}\mathbf{a})$):

$$\varepsilon_{\mathbf{k}} = \frac{\varepsilon_s + 2t_1 \cos(\mathbf{k}\mathbf{a}) + 2t_2 \cos(2\mathbf{k}\mathbf{a})}{1 + 2s_1 \cos(\mathbf{k}\mathbf{a}) + 2s_2 \cos(2\mathbf{k}\mathbf{a})} \quad (1.24)$$

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

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

leading to the dispersion relation (we neglect the overlap)

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

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

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

1.2 Integration over the Brillouin zone

Applications of electronic structure theory imply the calculation of many different \mathbf{k} space integrals over the Brillouin zone or its irreducible part. Typical examples are the total electron number $\mathbf{n}(\varepsilon)$

$$\mathbf{n}(\varepsilon) = \frac{1}{V_G} \sum_{\mathbf{n}} \int_{V_G} d^3\mathbf{k} \theta(\varepsilon - \varepsilon_{\mathbf{n}}(\vec{\mathbf{k}})) \quad (1.28)$$

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

$$\rho(\varepsilon) = \frac{1}{V_G} \sum_{\mathbf{n}} \int_{V_G} d^3\mathbf{k} \delta(\varepsilon - \varepsilon_{\mathbf{n}}(\vec{\mathbf{k}})) \quad (1.29)$$

where V_G is the volume of the primitive cell of the reciprocal lattice, and \mathbf{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 \mathbf{k} points. 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.

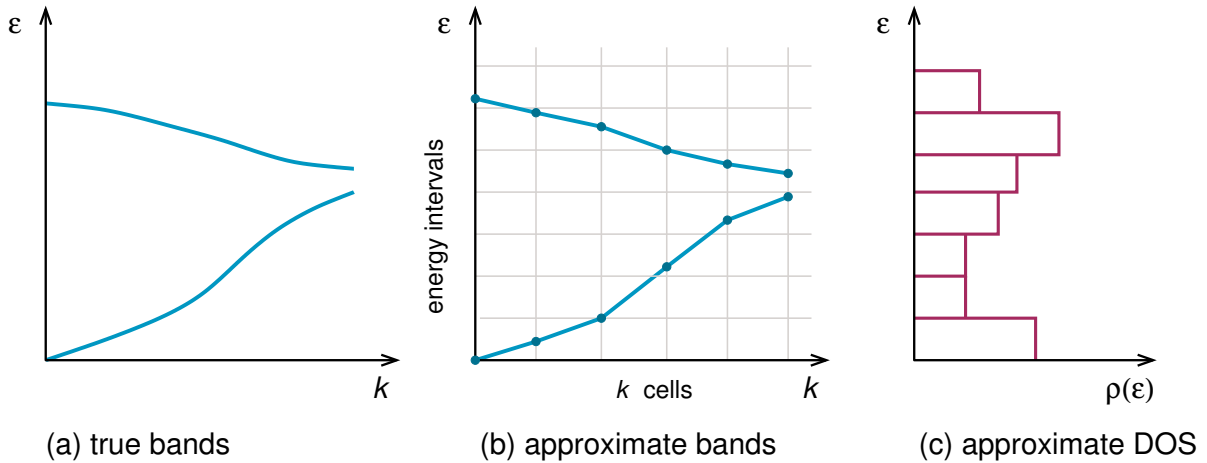


Figure 1.1: Example of simple Brillouin zone integration.

An alternative that is sometimes used is to do the summation (1.29) by approximating the delta function with a function that has a small finite width, for example a Gaussian:

$$\delta(\epsilon) \approx g(\epsilon) = \frac{2}{f} \sqrt{\frac{\ln 2}{\pi}} e^{-4 \ln 2 \frac{\epsilon^2}{f^2}} \quad (1.30)$$

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 integration². 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

²O. Jepsen, O. K. Andersen, *Solid State Commun.* **9**, 1763 (1971); G. Lehmann, M. Taut, *Phys. Stat. Sol. B* **54**, 469 (1972); P. E. Blöchl, O. Jepsen, O. K. Andersen, *Phys. Rev. B* **49**, (1994); H. Eschrig, *Optimized LCAO Method and the Electronic Structure of Extended Systems*, Akademie-Verlag Berlin 1988.

by introducing a new vertex in the middle of the longest edge of each tetrahedron.

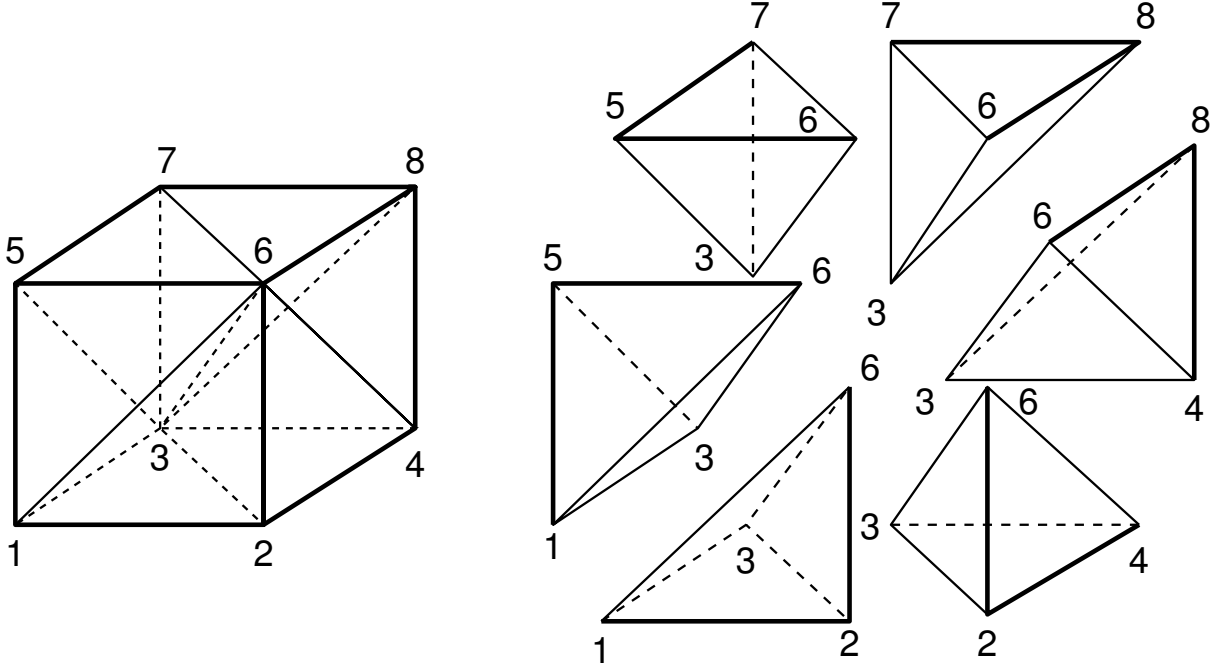


Figure 1.2: Splitting of a cubic reciprocal space sector into six tetrahedra.

For the derivation of the interpolation formulas, we refer to the literature. 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

$$V_T = \frac{1}{6} |\det(\vec{k}_2 - \vec{k}_1, \vec{k}_3 - \vec{k}_1, \vec{k}_4 - \vec{k}_1)| \quad (1.31)$$

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

$$\mathbf{n}_T(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_1 \\ \frac{V_T}{V_G} \frac{(\varepsilon - \varepsilon_1)^3}{\varepsilon_{21} \varepsilon_{31} \varepsilon_{41}} & \text{for } \varepsilon_1 < \varepsilon < \varepsilon_2 \\ \frac{V_T}{V_G} \frac{1}{\varepsilon_{31} \varepsilon_{41}} \left[\varepsilon_{21}^2 + 3\varepsilon_{21}(\varepsilon - \varepsilon_2) + 3(\varepsilon - \varepsilon_2)^2 - \frac{\varepsilon_{31} + \varepsilon_{42}}{\varepsilon_{32} \varepsilon_{42}} (\varepsilon - \varepsilon_2)^3 \right] & \text{for } \varepsilon_2 < \varepsilon < \varepsilon_3 \\ \frac{V_T}{V_G} \left(1 - \frac{(\varepsilon_4 - \varepsilon)^3}{\varepsilon_{41} \varepsilon_{42} \varepsilon_{43}} \right) & \text{for } \varepsilon_3 < \varepsilon < \varepsilon_4 \\ \frac{V_T}{V_G} & \text{for } \varepsilon_4 < \varepsilon \end{cases} \quad (1.32)$$

The contribution of the tetrahedron to the density of states $\rho(\varepsilon)$ is simply the energy derivative of $\mathbf{n}_T(\varepsilon)$:

$$\rho_T(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_1 \\ \frac{V_T}{V_G} \frac{3(\varepsilon - \varepsilon_1)^2}{\varepsilon_{21} \varepsilon_{31} \varepsilon_{41}} & \text{for } \varepsilon_1 < \varepsilon < \varepsilon_2 \\ \frac{V_T}{V_G} \frac{1}{\varepsilon_{31} \varepsilon_{41}} \left[3\varepsilon_{21} + 6(\varepsilon - \varepsilon_2) - 3 \frac{(\varepsilon_{31} + \varepsilon_{42})(\varepsilon - \varepsilon_2)^2}{\varepsilon_{32} \varepsilon_{42}} \right] & \text{for } \varepsilon_2 < \varepsilon < \varepsilon_3 \\ \frac{V_T}{V_G} \frac{3(\varepsilon_4 - \varepsilon)^2}{\varepsilon_{41} \varepsilon_{42} \varepsilon_{43}} & \text{for } \varepsilon_3 < \varepsilon < \varepsilon_4 \\ 0 & \text{for } \varepsilon_4 < \varepsilon \end{cases} \quad (1.33)$$